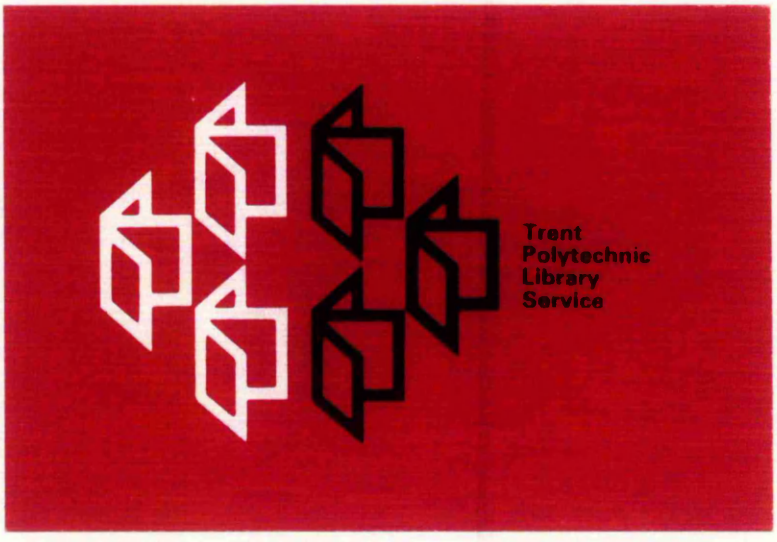

A STUDY OF

HYDROGEN-TRANSFER PHOTOCHROMISM

A THESIS

by

MICHAEL TOM ROBINSON

submitted in partial fulfilment of the requirements

for the degree of Doctor of Philosophy (Ph.D.) of

the Council for National Academic Awards.

Department of Physical Sciences,

Trent Polytechnic, Nottingham.

November 1988.

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Hydrogen-Transfer Photochromism

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ABSTRACT

2-(2',4'-dinitrobenzyl)pyridine 27 is a white crystalline compound which on exposure to 'sun-light' turns deep-blue. If this blue form is now stored in the dark overnight, the colour fades to produce the original white compound.

The aim of this work has been to synthesise compounds with structures related to 27 in order to investigate the requirements for hydrogen-transfer photochromism.

In the attempt to extend the colour range possible in this system, the 4'-nitro-group was selectively reduced to amine and converted to a range of azo-phenol and azo-amine derivatives. The colours of these products varied from tan through orange-yellow to red, but none was found to be photochromic in the solid state.

N-Salicylidene-[3-nitro-4-(α-picolyl)]aniline 142, a molecule possessing two potentially photochromic centres, was synthesised and its properties investigated.

Picolyllithium, picolylcopper and the novel reagent lithium dipicolylcuprate were synthesised and their reactions with a range of halides studied. Although in reaction with benzyl bromide there was a sharp increase in yield of 1-(2'-pyridyl)-2-phenylethane 153 in the order picolyllithium < picolylcopper < lithium dipicolylcuprate, it was found that all three reagents failed to bring about simple nucleophilic substitution of halide in reaction with 2-nitro-4-trifluoromethylchlorobenzene 146.

2-(2'-Nitro-4'-trifluoromethylbenzyl)pyridine 124 was obtained via a Grignard addition to 2-pyridinecarboxaldehyde 160, and found to be devoid of photochromic properties - unexpectedly. The reasons for this are examined.

Attempts to prepare 2,4-dinitrobenzylpyrazine 181 were unsuccessful. The anticipated absence of photochromicity in solid 3-(2',4'-dinitrobenzyl)pyridine 184 was confirmed.

The synthesis of 2,4-dinitrophenylacetaldehyde 200, surprisingly a novel compound, was achieved by reaction of 2,4-dinitrotoluene with dimethylformamidedimethylacetal. The aldehyde was condensed with a number of aromatic amines and the photochromicity and imine ⇌ enamine equilibria of the products examined.

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"Only light that is absorbed is effective in producing chemical change."

Grotthuss-Draper Law

1818

For Judith, Sheila and Christine

ACKNOWLEDGEMENTS

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1 PHOTOCHROMISM

1.1 The phenomenon of photochromism

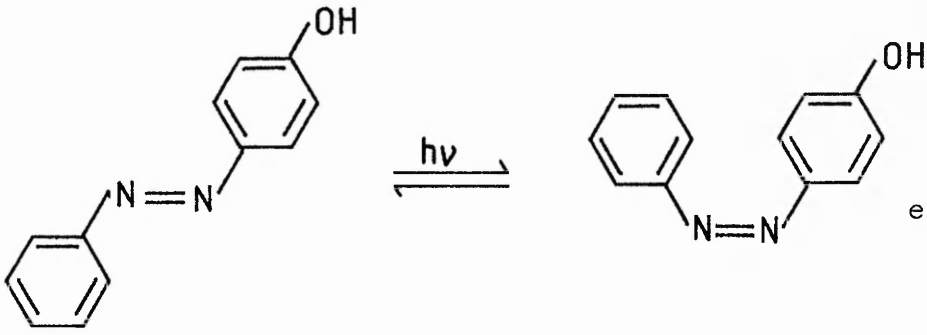
The term photochromism is made up of two parts; photo (light) and chrom (colour); hence photochromism literally means a colouration by light. In the scientific literature, it appears that the first person to observe photochromism was ter Meer[1] who showed that the potassium salt of dinitroethane changed colour when exposed to exciting radiation. Several reviews of the phenomenon have been published.[2-6]

In this thesis, photochromism is taken to mean a reversible change of a single chemical species between two (or more) differing states (A) and (B) having distinguishably different absorption spectra, such change being induced in at least one direction by the action of electromagnetic radiation. This definition can be represented by the following equation:-

$$A \underset{}{\overset{h\nu}{\rightleftharpoons}} B \qquad \text{equation 1}$$

The inducing radiation, as well as the changes in the absorption spectra, are usually in the ultraviolet, visible or infrared regions of the spectrum. The molecular transformation, for example, cis-trans isomerism, homolytic cleavage etc., responsible for the change in the absorption spectrum is immaterial for the purposes of the definition if the reversibility criterion is met. Irreversible changes fall under the more general heading of photochemistry.

The single chemical species A may for example be a molecule or an ion. The product B may be a single chemical species also, or it may represent more than one species, provided that they revert to A. Thus B may be the cis form and A the trans form of a molecule, such as



equation 2

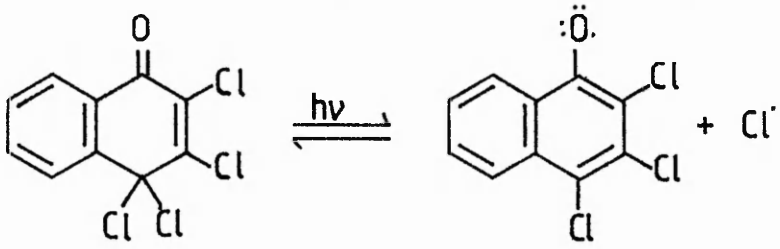
1, A 2, B

or B the cation and anion from the triarylmethane leucocyanide dye 3,

$$Ar_3C.CN \xrightleftharpoons{h\nu} Ar_3C^+ + CN^- \qquad \text{equation 3}$$

3, A 4, B

or the radicals from β-tetrachloroketodihydro naphthalene 5 (only one of which may have a significant absorption spectrum).



equation 4

5, A 6, B

B may simply represent a colour centre in an inorganic solid, for instance, see Section 2.2.

The definition of photochromism however, precludes those reversible chemical processes which operate through a cyclic series of reactions, such as

$$C \xrightarrow{h\nu} D$$

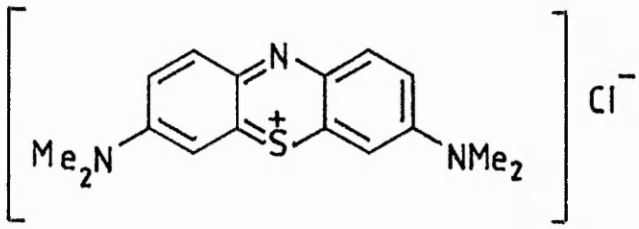
$$D + E \longrightarrow C + F$$

In this process, Compound C is converted into D by irradiation and then Compound D reacts with Compound E to regenerate Compound C and also a new chemical, Compound F. A classic example of a cyclic process is the photoreduction (bleaching) of methylene blue 7 with iron (II) ion and its subsequent oxidation (recolouration) by air (equations 5 and 6):-

$$M(aq) + Fe^{2+}(aq) \xrightarrow{h\nu} RedM^{-}(aq) + Fe^{3+}(aq) \quad \text{equation 5}$$

$$RedM^{-}(aq) + O_2(aq) \longrightarrow M(aq) + OH^{-}(aq) \quad \text{equation 6}$$

where $RedM^{-}$ represents the reduced form of methylene blue, M:-



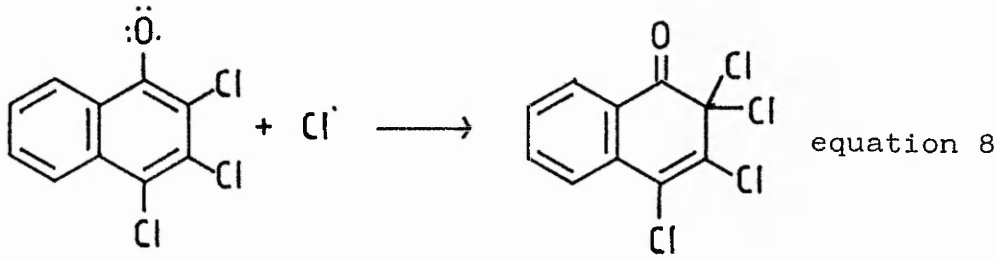
7, methylene blue

Equation 1 represents the idealised state in so far that it suggests that all of the photoproduct B reverts to A. In all the systems reported up to 1970, this ideal had not

been achieved. Invariably some of the photoproduct B decomposed irreversibly into further substances G_1, G_2. (equation 7). This irreversible

$$A \rightleftharpoons B \longrightarrow G_1,\ G_2 \qquad \text{equation 7}$$

degradation is the cause of fatigue; that is to say, it limits the number of cycles of 'colour' and 'fade' that a photochromic system may undergo. For instance, it has been demonstrated that the products of the reaction shown in equation 4 may also recombine to form 8 which is isomeric with the original ketone 5 but not photochromic (equation 8). Free radical addition polymerisation also occurs.[7]



equation 8

6 8

1.2 Historical aspects

The modern definition of photochromism clearly describes the phenomenon which was first noted in the last century and was called "phototropism". The term was initially applied by Marckwald[8] to the change in colour of crystals of 1,4-dihydro-2,3,4,4-tetrachloronaphthalen-1-one 5 when exposed to sunlight and which was reversed in the dark (colourless → amethyst → colourless, equation 4 describes). In the same year, 1899, Biltz[9-11] discussed the "phototropy" of benzaldehydephenylhydrazone and certain osazones initially reported by Wislicenus[12] in 1893.

The first substantive period of serious research in the field of photochromism occurred in the years 1900 - 1920. These early studies were concerned primarily with synthesis of materials and observations of such factors as the nature of the exciting radiation, rate of excitation, decay time and fatigue. The investigations did not, in general, concern themselves with fundamental questions such as those of the mechanism of the photochromic processes and the concomitant energy relationships. Interest in photochromism in the 1930s was limited, but the period 1940 - 1960 saw a revival of research. Many new compounds were prepared, both organic and inorganic. More careful studies were made of fatigue characteristics, rates and mechanisms of known photochromic processes, structures of reactants, products and intermediates as determined by X-ray, spin resonance and other instrumental methods of analysis. Since 1960, research in the field has shown steady growth as industrial applications of the phenomena of photochromism have been realised.

1.3 Industrial applications of photochromic materials

1.3.1 Applications depending upon sensitivity to radiation

Films

In the simplest possible method of using a photochromic material, a transient image is directly obtained, for instance, in a self-erasing film for which use it is only necessary for the time required for reversion of the coloured to the non-coloured form be long compared with the time required for the image to be formed. Alternatively, photochromic films can serve as re-usable negative materials for making ordinary silver halide prints.[13] For these image-forming applications,

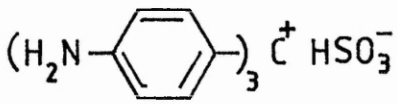
nearly all photochromic substances have been considered. The spiropyrans are especially promising because of their relatively high sensitivity to long-wavelength ultraviolet and violet light.

Prints

One obvious application is making photographic prints or proofs of limited lifetime. Another is the reproduction of printed matter such as letters, technical journals or engineering drawings in the office, library or plant. Reproduction can be made from microfilm or full-size originals with only minor modifications of existing equipment. Photochromic materials would appear to be especially valuable as media for holograms produced by Fresnel or "lensless" holography, since, for materials which are photochromic in the solid state, the monomolecular character of the photosensitive surface will allow much higher resolution to be obtained than will silver halide grains.

Measurement

Photochromic materials are practical for measuring the intensity and distribution of ultraviolet radiation. Their use as dosimeters was patented first in 1927.[14] Aqueous para-rosaniline leucobisulphite 9 was



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the preferred photochromic solution. In the usual device,

the colour intensity produced upon exposure is compared to a set of standards. More recently actinometers have been developed, utilizing fulgides,[15] for which accurate preparation of standard solutions and calibration curves are not required. Photochromic materials are potentially useful monitors in applications relating to measurement of high-energy radiation; using appropriate dye mixtures, it is possible to differentiate between the components of mixed radiations. Photons and electrons, or X-rays and neutrons, or X-rays and heavy particles can thus be distinguished.[16,17] High resolution X-ray micrography and autoradiography using photochromic dyes have been reported.[18]

Protection

Photochromic films and glasses have obvious utility as wrappers and containers for photosensitive products. The products would be protected from damaging light yet still be viewable. Photochromic materials are being studied for packaging foodstuffs and beer, and chemicals and pharmaceutical solutions such as sera and vaccines. Photochromic textiles may be used as optical filters or "protective materials" for other dyed textiles or fabrics; for example the use of photochromic linings for ordinary curtains has been considered.[19,20] Many materials, especially the spiropyrans, anils, metal dithizonates and certain inorganic pigments have been suggested for these uses. It would seem that the problem of fatigue would leave only the inorganic glasses and pigments as practical choices for protective applications.

1.3.2 Applications depending upon reversibility

Computers

In principle, any material or device that has two identifiable stable states and can be reversibly switched from one state to the other may be used as memory elements in digital computers using binary logic. Information is introduced into the memory element by one type of signal and is stored there until a different signal removes the information and restores the original state. In a practical computer, the memory element must respond to signals of extremely short duration. Through the nineteen-sixties, it seemed unlikely that chemical substances (as opposed to physical processes) of practical use would be discovered. Materials that showed a large photochromic spectral change of micro second time scale (organic dyes in solution) generally exhibited pronounced fatigue. Those that showed negligible fatigue (solid inorganics and glasses) generally exhibited small, slow spectral changes. The computer would either require frequent brain transplants or merely think very slowly!! However, the early belief in the requirement for a large visible spectral change proved to be a fallacy; it is only necessary that the change be reliably detectable by the sensing device. Whereas a large absorbance change may be required for display to humans, the human eye is not the sensor in the computer memory, and a much smaller absorbance change in the ultraviolet range might serve. Particular attention has been paid to inorganic materials such as sodalite, CaF_2, $BaTiO_3$, $SrTiO_3$ and alkali halides.

Among the organic photochromic compounds, only fulgides[21,22] and spiropyrans,[23] have shown sufficient fatigue resistance to justify continued research.

Displays

Photochromic materials have inherent characteristics valuable in certain display applications. High resolution: the molecular nature of the phenomenon implies that the optical system and not the material will limit the achievable resolution. Erasability: erroneous or outdated information can be selectively erased, or the entire viewing screen can be erased, within the limitations of the fatigue characteristics of the material. Memory: when displaying data from a line-scanning sensor where the film becomes a continuous recording, old data can be recalled. In a rather unusual application, displays have been developed in which the image is formed in fluid solutions of photochromic spiropyrans. These solutions are either free as bulk liquid[24] or contained in microscopic capsules capable of movement.[25] When the fluid or capsules are stationary, the image is legible; when mechanically set into motion, the image is disintegrated. These dynamic displays when used for advertising purposes are very effective.

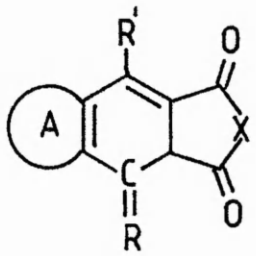
Sunglasses

The radiation reaching the surface of the earth consists of 1 - 5% ultraviolet, 41 - 45% visible and 52 - 60% infrared wavelengths.[26] The human eye is injured by sunlight both because of its intensity and because of its spectral distribution. Protection from such injury may be achieved by the

wearing of sunglasses which often have a luminous transmittance of about 50% and remove much ultraviolet and infrared radiation from the incident sunlight. Photochromic materials are especially attractive for sunglasses because of their ability to alter continuously and spontaneously their transmittance. The alterations must occur in both directions at fairly slow, psychologically acceptable rates; large transmittance changes in microseconds would be very disturbing in this application!

Of the many inorganic substances which exhibit photochromic properties only glasses doped with silver halides have proved of technological interest. Silver halide glasses consist of a borosilicate matrix with an admixture cf silver halides and some copper oxide.[27,28] To make photochromic glass, the constituents have to be heated to a temperature of 500 - 700°C. In this process there are formed precipitates containing Ag^+, X^-, Cu^+ etc., (where X = halide) which are responsible for the photochromic properties. Exposure to ultraviolet radiation causes an increase of the absorbance in the wavelength range of 350 - 900 nm. When the ultraviolet source is removed, the glasses return to their initial transparent state.

A recently filed patent[29] describes the effects of incorporating into lenses compounds of structure 10 where R is adamantylidene, X is O or NR^2, R^1 and R^2 are H, alkyl, aryl or aralkyl and A is an aromatic or heterocyclic ring system. In



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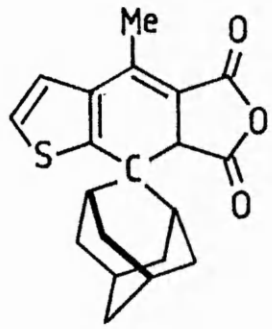


11

the particular case of plastics incorporating fulgide 11, exposure of the lens to bright light reduced its transmittance by 94.5%. The half-life for the restoration of transparency was 32 seconds.

1.3.3 Applications depending upon specific colour changes

Camouflage

If the surface of an object is photochromic and the colour changes can be controlled to match the object's surroundings, a novel camouflage technique is available. Through the nineteen sixties and seventies, the obvious military applications were investigated. Photochromic paints and coatings for aeroplanes, land vehicles and submarines were considered. One major difficulty, however, is that of uniformly irradiating large areas. A second is that of continuously controlling the change to match exactly the surroundings which could also be continuously changing, for instance, when a moving vehicle is involved. For the same reason, it would seem that the incorporation of photochromic dyes into textiles used in the manufacture of military uniforms or tents or tarpaulins is not a realistic possibility.[30]

Decoration

Many additional applications may be classed as decorative and might be of some commercial importance in the future. Photochromic paints, plaster and floor tiles for control of interior colours; photochromic curtains, upholstery and carpeting; and photochromic waxes and finishes for furniture are all possibilities.[19] Photochromic paintings in which a daytime scene turns into a night scene have been made and an expansion of this application to theatrical stage settings and effects seems feasible. The spiropyrans are readily incorporated into oil paints and into crayons and fulgides may be formulated into "magic" inks.[31] Personal decoration is also possible using photochromic clothing, wigs, face powder, lipstick and nail polish! In these applications, toxicity and carcinogenicity of the photochromic material are important considerations, and there seems to be no information available about this aspect of potentially useful experimental materials.

2 INORGANIC PHOTOCHROMISM

2.1 Defect structure of inorganic solids

With few exceptions the photochromism in inorganic solids is a structure-sensitive phenomenon and, therefore, invariably involves localised defects, impurities and dislocations. Hence it is necessary to discuss briefly the types of imperfections frequently encountered in inorganic solids before reviewing the various processes responsible for this phenomenon.

Vacant lattice sites are formed by the Frenkel or Schottky mechanisms as illustrated in Figure 1.

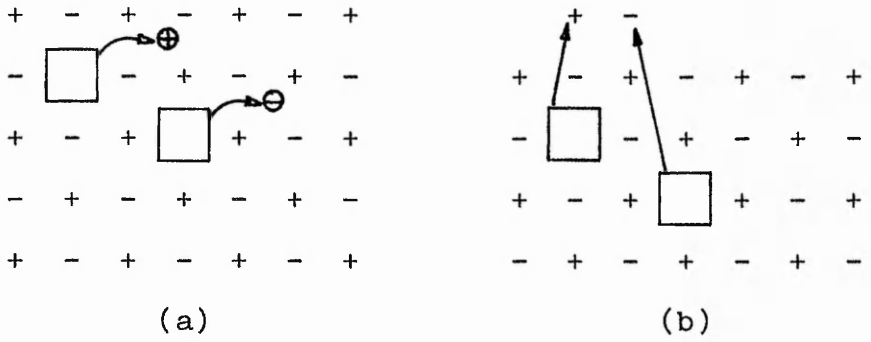


Figure 1. Defects in inorganic solids (a) Frenkel defects (b) Schottky defects.

In the Frenkel defect, the cation or the anion is displaced to an interstitial position, thereby creating the appropriate vacancies at the regular lattice sites. In the Schottky mechanism, the displaced ions are moved to an equivalent lattice site at the surface, creating the cation and anion vacancies. Defects of this kind are thermodynamic in origin and their formation involves the expenditure of energy.

In addition to the Frenkel and Schottky mechanisms, vacancies or interstitial ions can be formed by introducing foreign atoms (or ions) that can occupy sites normally available to regular lattice constituents. When the foreign ions have oxidation states different from those of the ions of the host lattice, extra ions have to be introduced interstitially to maintain the electrical neutrality of the crystal as a whole.

The defects discussed so far have been in the context of Stoichiometric Compounds. In many systems, especially in metal oxides, the same type of defects are produced by

deviations from stoichiometry. Nonstoichiometry in such crystals is commonly brought about by heating the crystals in the vapour of one of its constituent ions. When an oxide or sulphide, for example, occurs in a variable oxidation state such as in transition metal oxides, one oxidation state can function as an impurity for the other oxidation states of the same element. In these types of materials it is possible to introduce a massive concentration of defects without introducing foreign atoms as impurities. Another type of imperfection present in most inorganic solids is dislocation which occurs when there is a mismatch of the crystal lattice in one section with respect to another.

2.2 Formation of colour centres

Inorganic photochromic materials are typically either large-band-gap insulators or semiconductors, both of which are characterised by a valence band (fully occupied by electrons) separated from the conduction band (empty of electrons) by an appreciable energy gap - Figure 2. The optical excitation of these materials

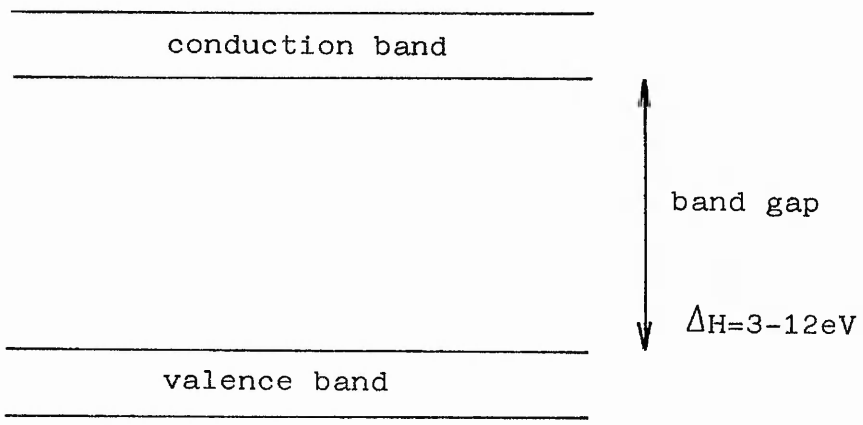


Figure 2. Schematic representation of valence band, conduction band and band gap.

with photons of energies corresponding to the band gap leads to the formation of metastable centres that absorb light in the visible region of the spectrum and give rise to the colour characteristic of the material. The system can return to its original ground state either by optical excitation within the colour-centre band or by heating the sample to elevated temperatures.

The primary process of the photochromic phenomenon is the optical excitation of the material, and there may readily be distinguished several electronic processes relevant to photochromism when quanta of the order of the band gap energy are absorbed by a solid.

These are:-

1. Creation of an electron in the conduction band and a hole in the valence band by excitation across the band gap.
2. The formation of bound electron-hole pairs, known as excitons, which can move through the crystal and transport energy.
3. Excitations involving various atomic imperfections that produce localised states within the forbidden gap.
4. Excitations involving impurities that produce additional allowed levels within the forbidden gap.
5. Transitions involving electron-hole recombinations.

These are summarised in Figure 3.

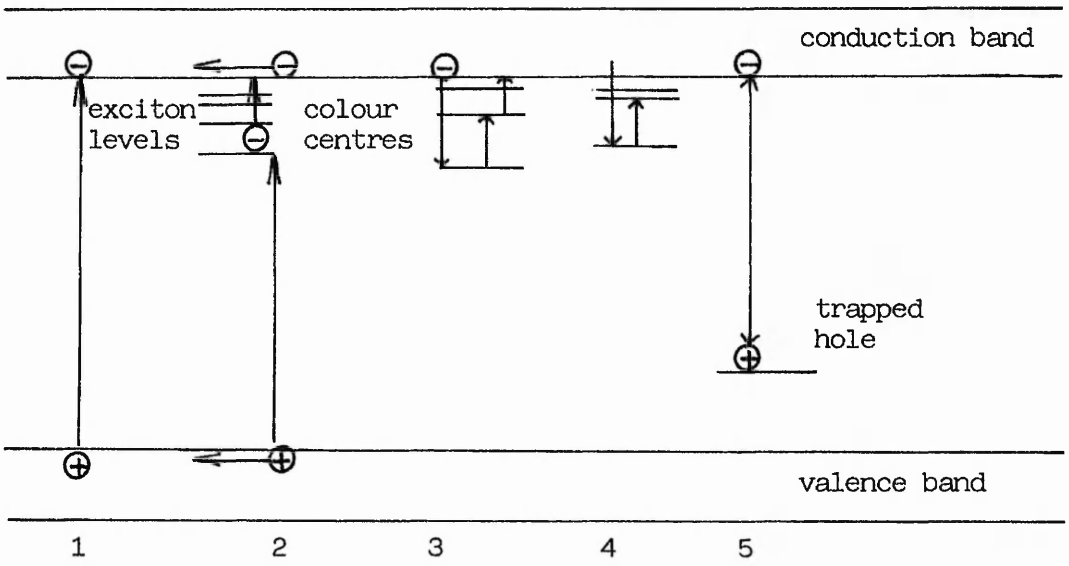


Figure 3. Schematic representation of various excitation processes in photochromic inorganic solids. 1.band-band transition 2.exciton transition 3.colour centres caused by defects 4.colour centres caused by impurity 5.electron-hole recombination

2.3 Photochromism in halides

Alkali halides are characteristically large band-gap insulators with an energy gap in the range 6-12 eV, and hence they are completely transparent in the visible region. Photochromism occurs in many alkali halide crystals on irradiation with ultraviolet light, where excitons play a dominant role in the phenomenon. Doping with impurities such as Ce^{4+} or OH^{1-} ions can significantly increase the density of colouration.[32] Photochromic effects have also been reported in alkaline earth halides, in particular, CaF_2. Staebler and Kiss[33] have coloured La,Ce,Gd and Tb-doped CaF_2 by irradiation with ionising radiation. When these samples were irradiated optically, new absorption bands,

characteristic of the rare earth ions were produced. The reverse process may be initiated optically or thermally. These materials have been used for thick hologram storage.[34] Taylor[35] has observed photochromic effects in CeO_2-doped CaF_2. Absorption bands at 378 and 577 nm are induced by absorbing short-wavelength ultraviolet radiation from a low-pressure mercury lamp and are bleached by light at 380 nm.

2.4 Photochromism in oxides

Many metal oxide systems have been reported to be photochromic, and in general, these have been interpreted on the basis of electron trapping in defects within the crystal. The potential for development of solid-state imaging devices was greatly increased when it was observed that high density colouration can be produced at room temperature in thin films of transition metal oxides, such as MoO_3 and WO_3, when a strong electric field is applied across the film.[36] For example, a sandwich structure made by vacuum evaporation of a WO_3 film on NESA glass

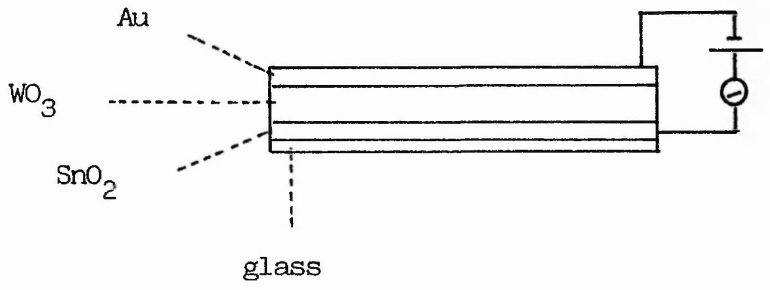


Figure 4. Schematic representation showing electrochromism

(a special glass incorporating tin (IV) oxide) followed by evaporation of a thin transparent gold film on top of it, becomes deeply coloured when a 2V direct-current electric field is applied across the structure - Figure 4. Colouration occurs at a critical field strength, and the intensity of colouration is proportional to the applied field and length of exposure. When coupled with a photoconductive film, a thin film of these materials forms a solid-state imaging device - Figure 5. When an optical image is projected on

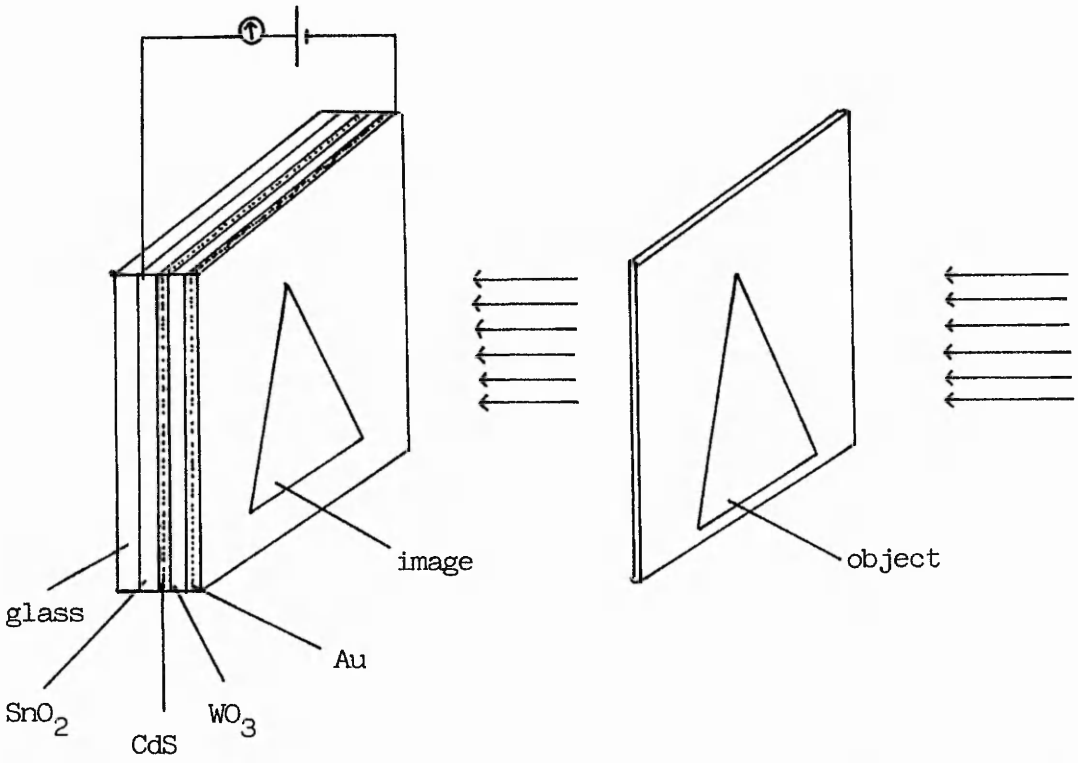


Figure 5. Diagram of an electrophotographic arrangement.[36]

the photoconducting layer, local variation of the conductivity causes a corresponding distribution of potential across the electro chromic film. If the voltage across the

electrochromic layer in the dark is maintained below the critical voltage necessary for colouration, exposure to light of the energy corresponding to the response frequency of the photoconducting layer will cause the exposed region to exceed the critical voltage; image formation then results in the electrochromic film. The colour centres formed by the passage of electrons through the oxide layer are essentially similar to those formed during optical irradiation.

So far research in inorganic photochromic phenomena has been restricted to a few relatively simple systems, such as the alkali metal halides. Relatively little work has been carried out on more complex materials, such as sodalite.[37,38] Clearly in this area there is much scope for further study.

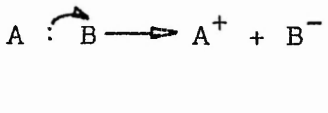
3 ORGANIC PHOTOCHROMISM

One of the ways of classifying photochromic processes is on the basis of their mechanisms of which the most common are heterolytic cleavage, homolytic cleavage, cis-trans isomerism and tautomerism. A knowledge of the kinetics of these mechanisms allows the suitability of the various compounds for differing applications to be determined and can give insight into the nature of processes which involve photochromic equilibria, for instance in living systems (e.g. in the chemistry of vision).

3.1.1 Heterolytic cleavage

Heterolytic cleavage is one of the most extensively studied forms of photochromism. The excitation energy of a photo-activated molecule may be utilised in the heterolytic cleavage of a covalent bond in an organic molecule leaving charged moieties that exist as isolated ions 12 or which may still

be connected by other chemical bonds 13. In those special cases



12

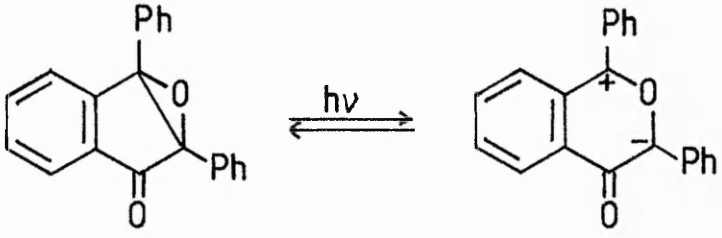
13

where the charged moieties are able to recombine to generate the original molecule, there is the possibility of the system exhibiting photochromism. The photochromism of those compounds listed below is generally attributed to this type of cleavage, and

Heterolytic cleavage —
- Spiropyrans
- Triarylmethane dyes
- Cationic polymethine dyes
- Indenone oxides
- Nitrones

Scheme 1

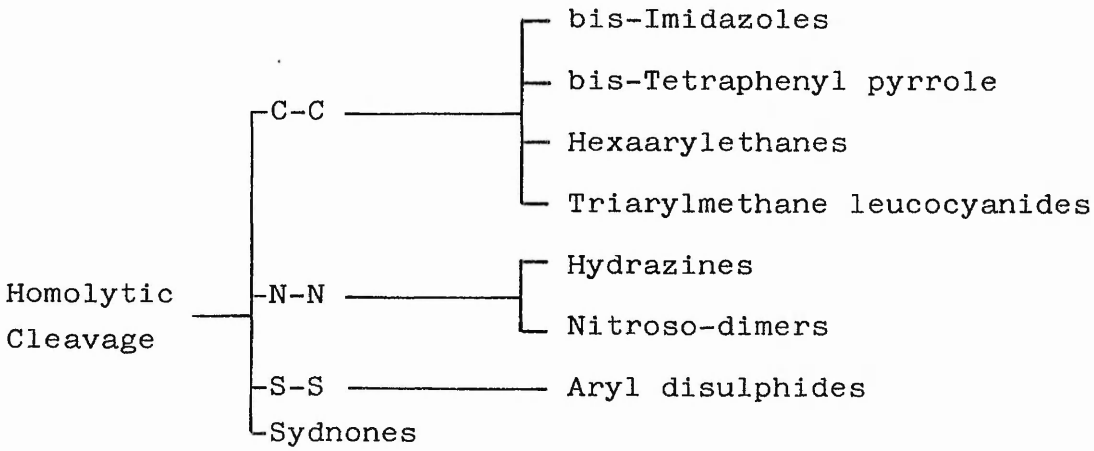
may be illustrated by 2,3-diphenyl indenone oxide 14 which, when irradiated in the solid state produces the doubly-charged species 15. The spiropyrans are reviewed in Section 3.3.



14 (white) 15 (red)

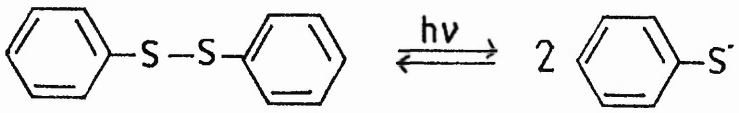
3.1.2 Homolytic cleavage

Alternatively, homolytic cleavage may occur on the absorption of radiation producing species with different absorption spectra from the original molecule, this process again being reversible. This phenomenon is illustrated by compounds listed in Scheme 2.



Scheme 2

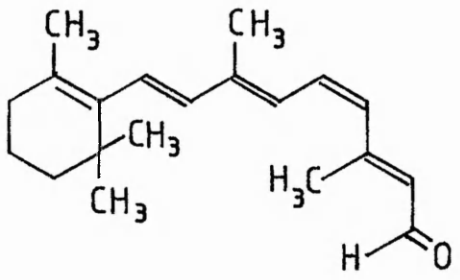
A specific example of such a process is the reversible dissociation of diphenyl disulphide 16.



16 (white) 17 (pale yellow)

3.1.3 cis-trans Isomerism

The photo-induced cis-trans isomerism of organic molecules about unsaturated linkages is a phenomenon that has been recognised for some time. Indeed, in at least two cases, this type of photochemical reaction may be said to be "part of one's daily life". The isomerisation of rhodopsin (the Schiff base of 11-mono-cis-retinal 18 with the ϵ-amino group of a lysine residue in the protein opsin) to "pre-lumirhodopsin" (all trans) is well documented as being the initial step in the detection of light by the retina[39] and the cis-trans isomerism of urocanic acid 19 in the epidermis has been suggested as a mechanism by which part of the ultraviolet radiation incident on the body may be safely dissipated.[40,41]



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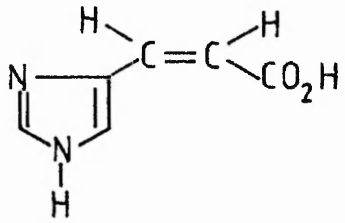

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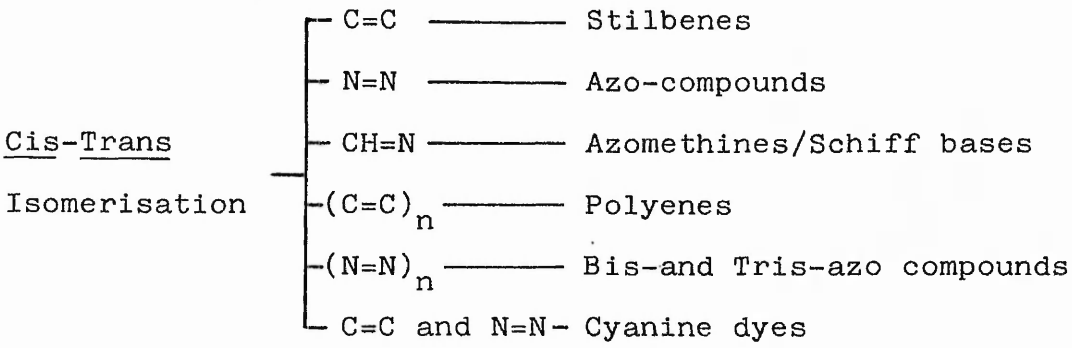
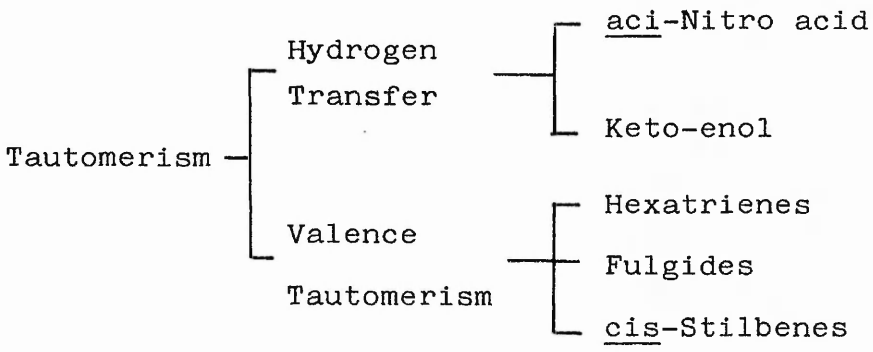
The classes of compounds undergoing photo-induced cis-trans isomerism are summarised in Scheme 3.



Scheme 3

3.1.4 Tautomerism

Tautomerism is a term which describes the reversible interconversion of isomers. Photochromic tautomerism refers to a photochemically induced shift in equilibria between isomers which have significantly different electronic absorption spectra. The two major types of photochromic tautomerism are hydrogen transfer tautomerism and valence tautomerism, Scheme 4.



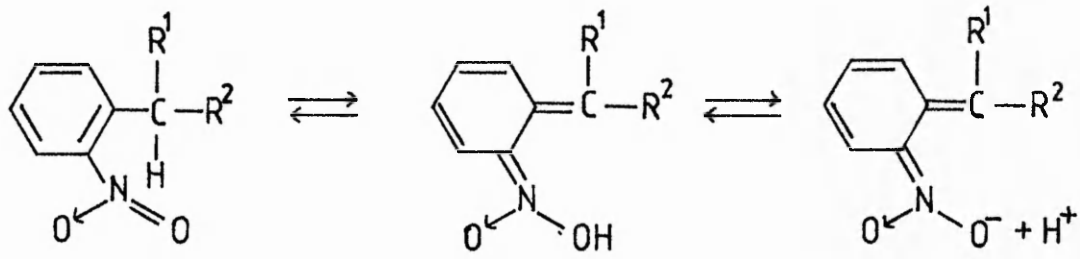
Scheme 4

It may be seen from this scheme that hydrogen transfer tautomeric mechanisms may be further subdivided under two headings, aci-nitro acid tautomerism and keto-enol tautomerism.

These are now reviewed in detail because they form the central theme of much of the new work described in this thesis. In discussing this work, especially with regard to aci-nitro acid tautomerism, it is particularly important to pay careful attention to the state [solid, solution (and solvent), glass, melt] in which samples have been irradiated, and indeed temperatures of transitions because there is little standardisation of such conditions in the literature and the phenomena observed vary greatly with the conditions obtaining.

3.2.1 aci-Nitro acid tautomerism

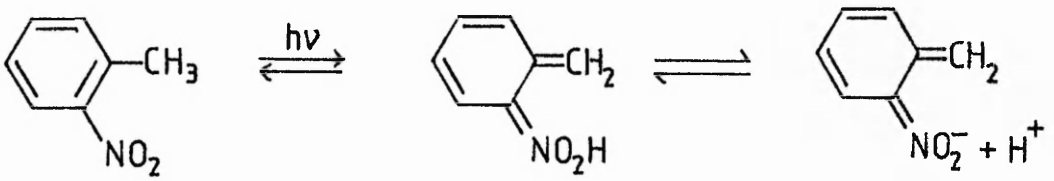
Transfer of a hydrogen atom from an alkyl group in 20 to a nitro group gives rise to the aci-nitro acid tautomer 21 which itself may ionise to generate a proton and the aci-nitro acid anion 22.



nitro-compound 20 | aci-nitro acid 21 | aci-nitro acid anion 22

o-Nitrotoluene 20, $R^1=R^2=H$, is the simplest structure known to exhibit aci-nitro acid tautomeric photochromism. Wettermark et al.[42,43] showed that a transient yellow

intermediate with a 1-second lifetime was formed in aqueous base when 23 was irradiated with 5μS pulses of ultraviolet radiation and they proposed the following equilibria to explain these observations:-



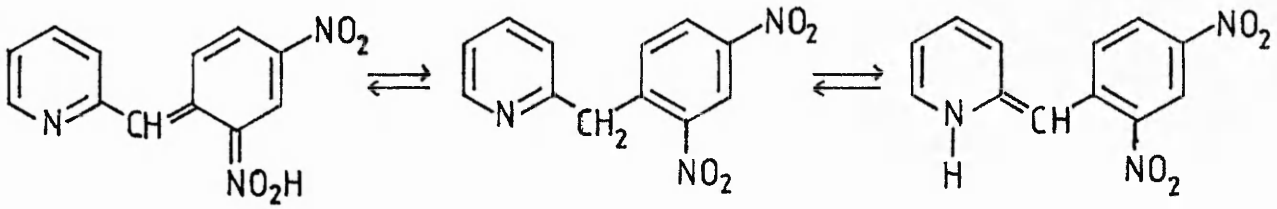
263 nm 370 nm 410 nm

23 24 25

In acid solution, where the phenomenon is also observed, the fading rate is accelerated by a factor of 10^7. Morrison and Migdalof[44] carried out a key experiment with regard to the proposed H-transfer tautomerism by showing that hydrogen-deuterium exchange occurred at the methyl group of o-nitrotoluene when it was photolyzed in D_2O, whereas p-nitrotoluene (which is not photochromic) did not show any exchange. 2,4-dinitrotoluene and 2,4,6-trinitrotoluene show similar properties.[45,46]

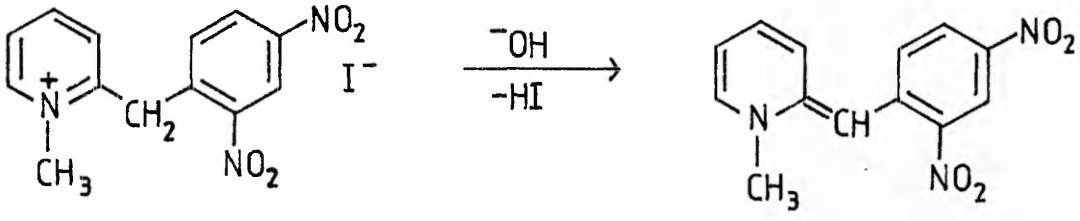
Other nitro-aromatic compounds have been shown to be photochromic. The change in colour of solid 2-(2',4'-dinitrobenzyl)pyridine (hereafter referred to as DNBP) 27, from white to deep-blue when irradiated by sunlight was first reported in 1925 by Tschitschibabin et al.[47] With the extension of the nitro-toluene moiety

to incorporate a pyridyl substituent, there arises a second possible mode for H-transfer. A hydrogen from the CH_2 bridge may now, in theory, move to the nitrogen of the pyridine ring to form the N-H quinoid structure 28 in addition to or instead of transferring to the ortho-nitro group to form the aci-nitro acid 26 as in the case of o-nitrotoluene.



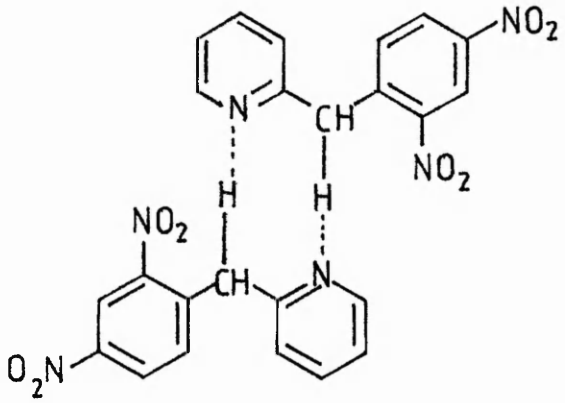
26 27, DNBP 28

Tschitschibabin proposed the former having noted that the product of treatment of the methiodide 29 with alkali was a similarly deep-blue compound to that obtained on irradiation of DNBP, in this case having the structure 30. However, it has



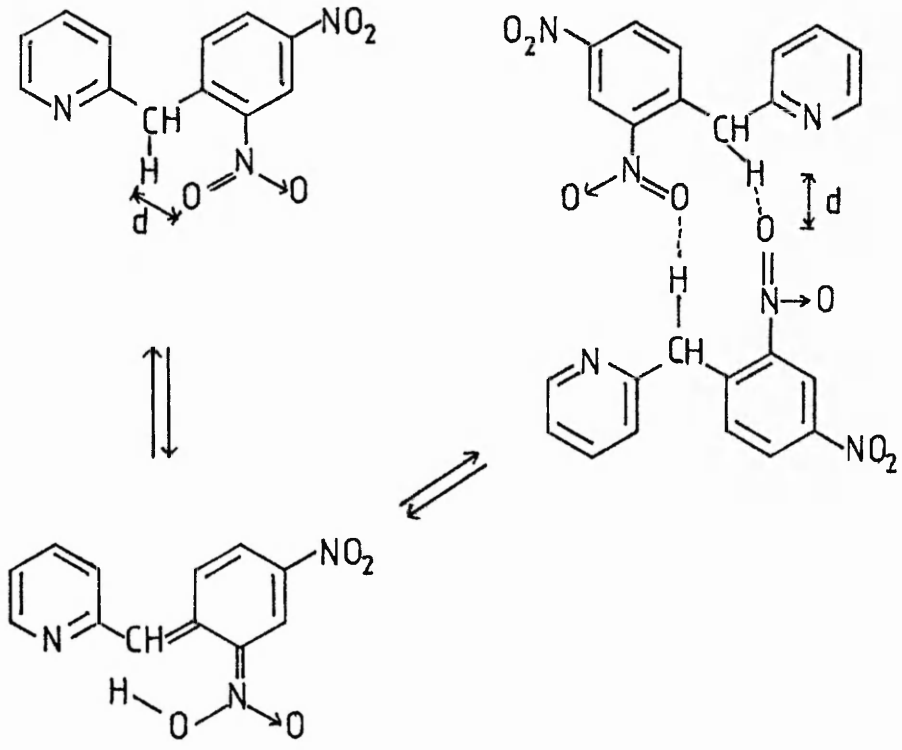
29 30

been demonstrated that in the absence of the ortho-nitro group, photochromism is also absent,[48] which suggests that the ortho-nitro group must contribute in some way to the mechanism of the photochromic change. Hardwick et al.[49] were the first to observe that the photochromism of DNBP 27 was not confined to the solid state but occurs in solution as well. Although at room temperature it is barely noticeable, at -30° in propan-2-ol the blue colour produced on irradiation is quite intense and lasts for several minutes. These authors determined the activation energy for the fading reactions of the blue crystals and the blue solution and found the value 100 $kJmol^{-1}$ for the solid to be significantly higher than for the solution (58.5 $kJmol^{-1}$). They suggested that the mechanism in solution was an intramolecular hydrogen shift (27 ⇄ 28) while that in the solid was intermolecular, 31, both resulting in a molecular transformation to the same N-H quinoid form as indicated in 28.



31, intermolecular H-transfer

They thought it equally likely that the nitro group may be involved, again in either an intramolecular 32 or intermolecular sense 33, producing the aci-nitro acid 26. The value for the

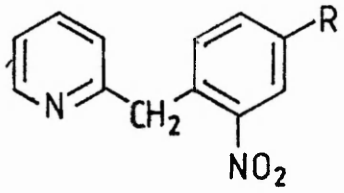


32, intra

33, inter

shortest intramolecular methylene-hydrogen to nitro-oxygen distance (d in 32) has been determined by X-ray crystallography[50] for non-irradiated crystalline DNBP and reported to be 0.24 nm, and the shortest intermolecular distance (d in 33) 0.26 nm.

The para-nitro group *per se* is not an essential structural requirement of the molecule for photochromism to occur since several compounds, observed to be photochromic in the solid state, have functional groups other than nitro in the 4'-position. Table 1 lists these compounds together with the colour of the irradiated crystalline form and λ_{max} values for their ultraviolet irradiated ethanolic solutions.[51]



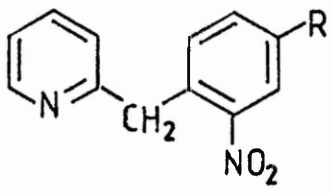
Compound	R	Colour (solid)[a]	λ_{max}/nm
34	CO_2CH_3	Dark blue-green (RT)	405, 460, 485, 575
35	$CO_2CH_2CH_3$	Pale blue-green (RT)	410, 460, 485, 585
36	$CONH_2$	Pale green (RT)	403, 450, 485, 580
37	CO_2H	Pale grey (Dry ice)	405, 450, 470, 580
38	CN[52]	Green (RT)	

Table 1

Photochromic compounds and spectral data for ethanolic solutions (-91°C) [a]white crystals before irradiation.

In an attempt to discover more about the mechanism of the photochromicity exhibited by these compounds, *inter alia*,

Weinstein, Bluhm and Sousa[53] investigated the rates of the fading reaction in ethanol solution at room temperature by flash photolysis techniques. In every case studied, the fading process was found to follow first-order kinetics. The values of the rate constant, k, for the fading reaction are listed in Table 2 and can be seen to be markedly sensitive to the electronegativity of the para-substituent. In Figure 6, log k values are shown to be linearly related to Hammett σ^- values.[54] The observed substituent effect is probably due to differences in energy of activation, since it was found previously for the fading reactions of the 4'-CN and 4'-NO_2 derivatives that the energy of activation differs while the value of the entropy of activation is the same.[52]



Compound	R	k/s^{-1}	$t_{1/2}$/ms	σ_p
39	NH_2	3700	0.187	-0.660
40	OH	329	2.11	-0.357
41	H	56.3	12.3	0
42	Cl	27.4	25.3	0.227
43	CO_2^-	26.3	26.3	0.132
36	$CONH_2$	5.94	117	
35	$CO_2C_2H_5$	2.45	283	0.522
34	CO_2CH_3	2.42	286	0.463
38	CN	1.17	592	0.628
27	NO_2	0.122	5680	0.778

Table 2

Values of k and $t_{1/2}$ for fading reactions of 2-(2'-nitro-4'-substituted benzyl)pyridines in ethanol.[53]

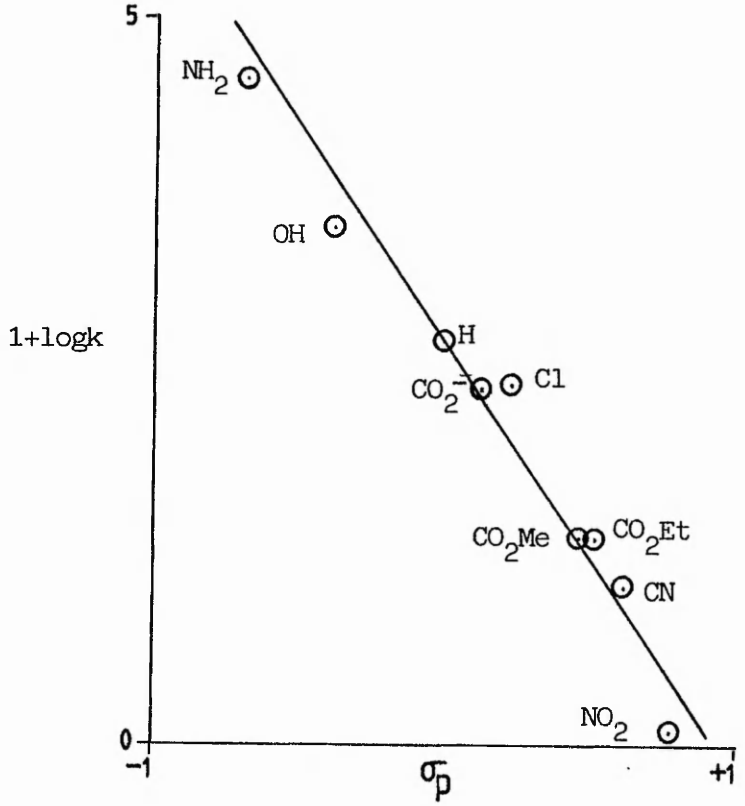
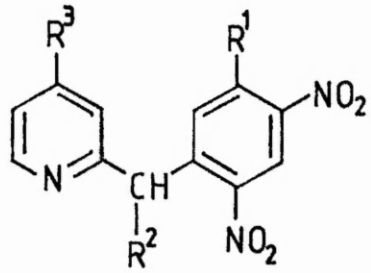


Figure 6.

Plot of logk values vs Hammett σ_p constants.[53]

Klemm et al. synthesised[55,56] further compounds based on 2-(2',4'-dinitrobenzyl)pyridine, some of which are photochromic in the solid state, some only in solution (Table 3). From their studies, Klemm et al. postulated[57] that the

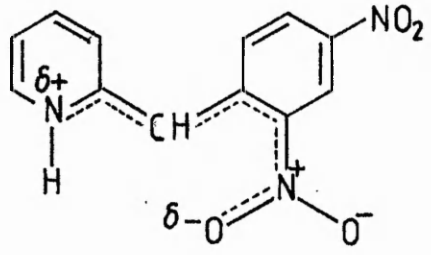


Compound	R^1	R^2	R^3	Solid	Solution	Reference
44	CH_3	H	H	+		56
45	Cl	H	H	+		56
46	SO_3^-	H	H		+	56
47	H	OH	H		+	51
48	H	Br	H	+		56
49	H	$-C_6H_4-NO_2(p)$	H	+		55
50	H	CH_3	H		+	57
51	H	H	CH_3	+		56
52	CH_3	H	CH_3	+		56
53	H	H	CO_2H		+	56

Table 3

Further compounds showing photochromicity (+) in solid or solution state.

coloured form of dinitrobenzylpyridine possessed a polymethine structure 54.



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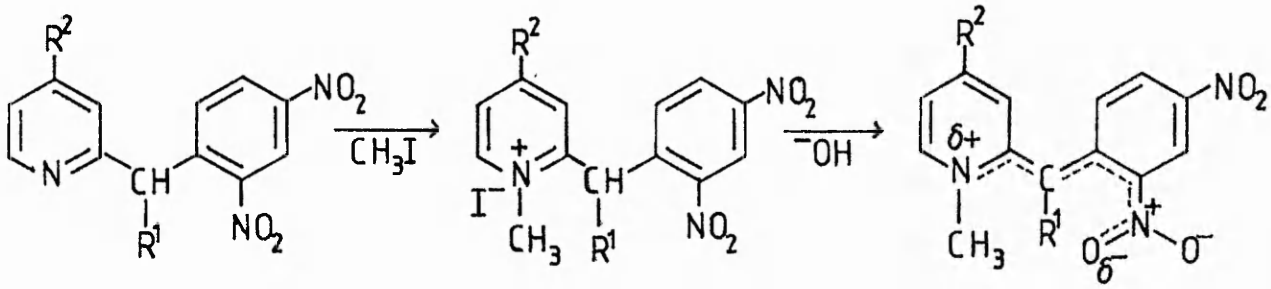
Using an approach similar to that adopted by Tschitschibabin,[47] model compounds were prepared (Scheme 5). These were found to have



55 56 57

Scheme 5

spectral properties very closely related to those of the coloured compounds formed photochemically (Table 4).

Compound	R^1	R^2	λ_{max}/nm (in ethanol) coloured form	model compound
27	H	H	547	553
50	CH_3	H	625	630
51	H	CH_3	555	555

Table 4

λ_{max} of coloured forms of DNBP derivatives in comparison with λ_{max} of model compounds.[57]

Klemm further argued that the peaks at 1640 cm^{-1} and 1460 cm^{-1} in the infrared spectra of the photochemically produced coloured compounds and also present in the model compounds ascribable to the quaternary NR_4^+ structure and the C-H deformation of $N-CH_3$ respectively, provided further evidence for the postulated polymethine structures. He also pointed out that the characteristic absorptions at 1490, 1500 cm^{-1} (NO_2 asymmetric) and 1330, 1360 cm^{-1} (NO_2 symmetric) were shifted to give values towards the lower end of the nitro-absorption band, typifying nitro-groups with partial negative charges, as suggested by these structures. Klemm et al.[58] investigated further the photochromism of dinitrobenzylpyridine by means of nanosecond laser absorption spectroscopy. Two coloured transient species were observed in the spectral ranges 390 - 410 nm and 510 - 580 nm in both polar and non-polar solvents. The first band (390 - 410 nm, lifetime $\sim 1\mu s$) was assigned as the absorption band of the aci-nitro acid form 26 and the second band

(510 - 580 nm, lifetime ~0.5 s) was assigned as the absorption band of the N-quinoid form, 28, of 2-(2',4'-dinitrobenzyl)pyridine. Takahashi et al.[59] confirmed these assignments by using the technique of time-resolved resonance Raman spectroscopy with solutions of DNBP in acetonitrile. By subtracting the spectrum obtained 5μs after the irradiating pulse from the spectrum measured 0.2μs after the pulse they obtained the spectrum of the short-lived species which proved to be identical with the spectrum of the aci-nitro acid anion. The anion is obtained by adding alkali to an ethanolic solution of DNBP.[60] The spectrum obtained 5μs after the irradiating pulse reveals striking resemblances to the spectrum of the deep-blue N-CH_3 derivative of DNBP 30. Takahashi concluded that the longer-lived transient species has the N-H quinoid structure and is the species responsible for the blue colour produced when samples of DNBP are exposed to ultraviolet radiation.

Additionally electron-spin resonance studies suggest that the colour of the irradiated forms does not arise from some stable triplet state.[49,57]

Sixl and Warta[61] investigated photochromism in crystals of dinitrobenzylpyridine by optical absorption spectroscopy. They were able to construct a complete energy level diagram for the system in the temperature range -263° to 57°C showing the pathways of the photoreactions and thermal reactions together with the corresponding energy barriers - Figure 7. They were able to draw a number of conclusions about the interconversion of the tautomer in the solid state.

The N-H quinoid 28 and aci-nitro acid photoproducts 26 are generated photochemically from photoexcited DNBP 27. Photoexcitation of the N-H quinoid form generates the aci-nitro acid and photoexcitation of the latter generates DNBP. As regards the fading reactions, the aci-nitro acid configuration decays via the N-H quinoid form to DNBP; the N-H quinoid form decays directly to DNBP. These authors also concluded that the aci-nitro acid tautomeric form is more stable than the coloured N-H quinoid form only in the narrow temperature range -70° to $-80^{\circ}C$. The latter conclusion explains why Clark and Lothian,[62] who also investigated these phenomena in the solid state but only at room temperature, were able to identify only the N-H quinoid photoproduct.

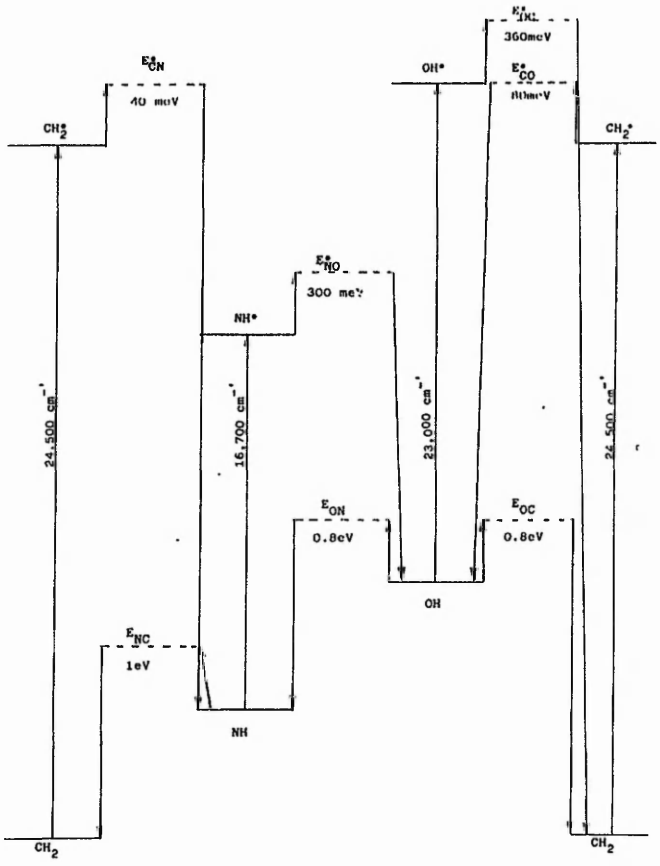


Figure 7.

Energy level system of the 2-DNBP system.[61]

CH_2 dinitrobenzylpyridine, 27 .

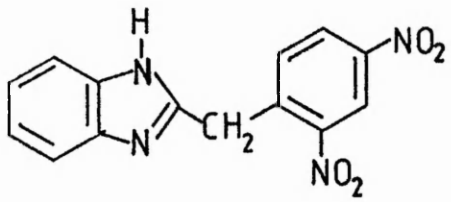
NH N-H quinoid, 28 OH aci-nitro acid, 26

CH_2*, NH*, OH* are the photoexcited states of CH_2,NH,OH.

E^*_{CN}, E^*_{NO}, E^*_{OC}, E^*_{CO} are the energy barriers for the transitions $CH_2^* \longrightarrow NH$, $NH^* \longrightarrow OH$, $OH^* \longrightarrow CH_2$, $CH_2^* \longrightarrow OH$.

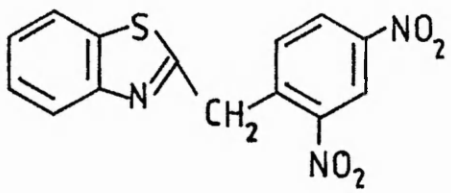
E_{NC}, E_{ON}, E_{OC} are the activation energies for the transitions $NH \longrightarrow CH_2$, $OH \longrightarrow NH$, $OH \longrightarrow CH_2$. The energy levels given in wave numbers correspond to the absorption energies of the CH_2, NH and OH photoproducts.

Interest has been shown in compounds in which the 2,4-dinitrobenzyl moiety has been attached to N-heterocyclic ring systems other than pyridine. A number of benzimidazole derivatives, including compound 58

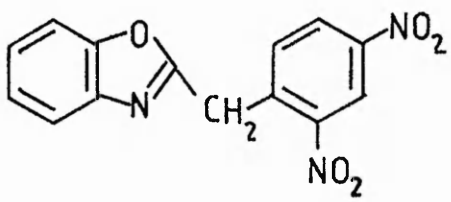


58

have been shown to be photochromic when ethanolic solutions are irradiated at -75°C.[63] The corresponding benzothiazole 59 and benzoxazole 60 are also photochromic under similar conditions.[64]



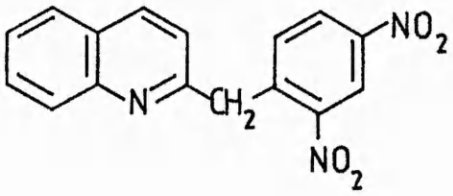
59



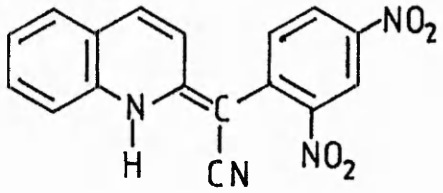
60

Surprisingly, 2-(2',4'-dinitrobenzyl)quinoline 61 is not photochromic in view of the fact that the α-cyano derivative 62, which is deep-blue in colour, exists in the

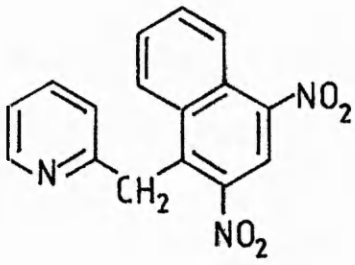
quinoid structure.[65] Ponyaev et al.[66] have also shown



61



62

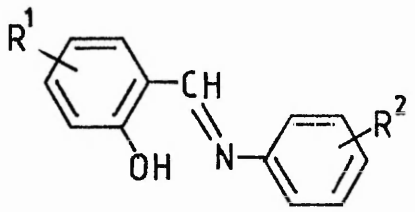


63

2-(2',4'-dinitronaphthylmethyl)pyridine 63 to be photochromic in aqueous ethanolic solutions at room temperatures. The fading rates of the photocoloured species are first order, as for DNBP 27 but with rate constants almost 2 orders of magnitude less. This is thought to be due to delocalization of the charge in a more extended chromophoric chain which leads to greater stability in the photoinduced forms.

3.2.2 Keto-enol tautomerism

The condensation products of aldehydes and primary amines are called imines or Schiff bases and many have been reported to be photochromic or thermochromic in the crystalline state. Photochromicity and thermochromicity were found to be mutually exclusive properties in the series of crystalline N-salicylideneanilines investigated by Cohen et al., Table 5.[67]

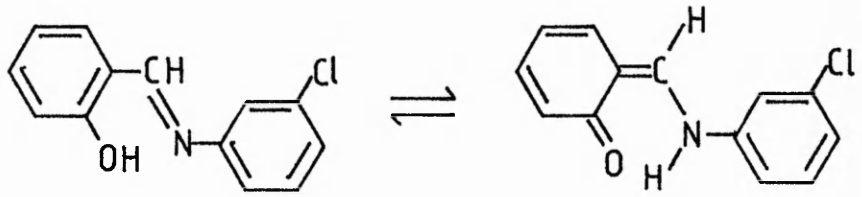


	R^1	R^2	Thermochromic	Photochromic
64	H	H	-	+
65	H	2-Cl	-	+
66	H	3-Me	-	+
67	H	3-Cl	+	-
68	H	4-Me	+	-
69	H	$4\text{-}CO_2Et$	+	-
70	4'-Me	H	-	+
71	5'-Me	H	+	-
72	5'-Cl	H	+	-

Table 5

A selection of anils showing that thermochromicity and photochromicity are mutually exclusive properties.[67]

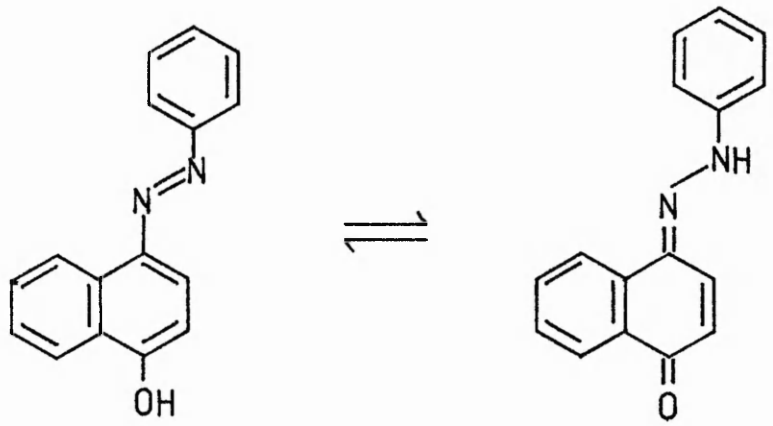
Thermochromism was attributed to a shift of the tautomeric equilibria to the cis-keto form (equation 9).



equation 9

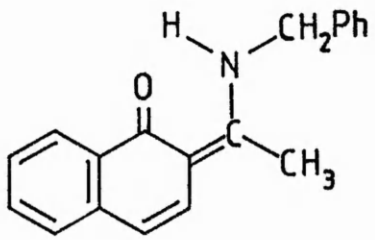
67, enol 73, cis-keto

Such equilibria have been observed with phenylazonaphthols 74 where both tautomers have been detected in the crystalline state by infrared spectra.[68,69]

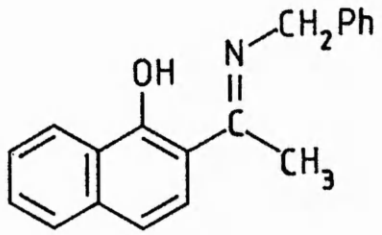


74 75

Nuclear magnetic resonance studies of compound 76 also supported the quinoid structure,[70] not the imine 77

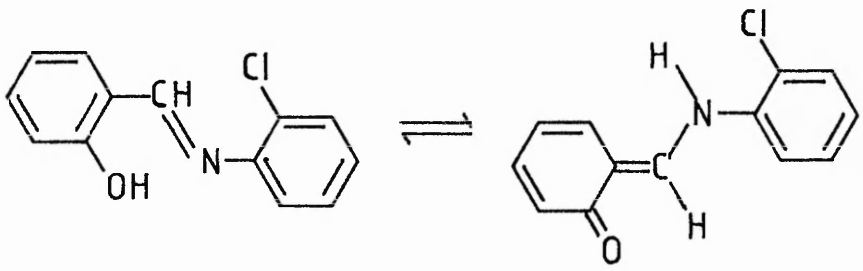


76



77

Photochromism in the N-salicylideneanilines was attributed to a shift of the tautomeric equilibria to the trans-keto configuration (equation 10).[71,72] Barbara et al.[71], employing time- and wavelength-

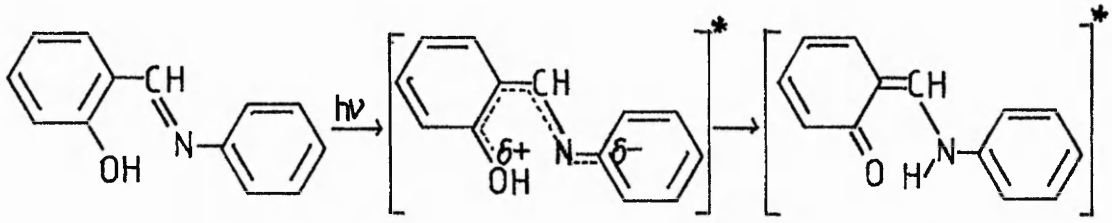


equation 10

65, enol

78, trans-keto

resolved picosecond and nanosecond emission spectroscopy showed that an excited tautomeric proton transfer occurs within 5 ps at temperatures above 4K in both protic and aprotic solvents (equation 11) but



equation 11

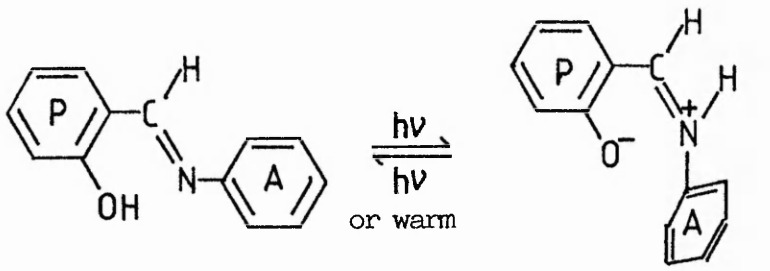
64 79 80

drew no conclusions about the mechanism by which these excited states may decay into the trans-keto configuration nor about the mechanism by which the photochromic product may be formed in the solid state.

Hadjoudis[72] obtained the first direct evidence for the nature of both the thermoinduced and photoinduced coloured species in the solid state when he employed nuclear quadrupole resonance. The ^{14}N NQR spectra for thermochromic N-(5'-chlorosalicylideneaniline) 72 showed that at room temperature an enol cis-keto equilibrium exists. The ^{14}N NQR spectra for photochromic N-salicylidene-2-chloroaniline 65 confirmed the existence, in the ultraviolet irradiated form, of an enol trans-keto equilibrium.

Lewis and Sandorfy[73] studied the infrared spectral characteristics of N-salicylideneaniline 64, its deuterium analogue N(2-deuteroxybenzylidene)-aniline, N-salicylidene-m-toluidine 66 and their photoproducts. The spectrum of a low temperature (-196°C) irradiated

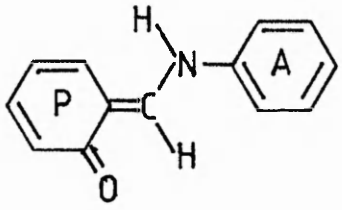
polycrystalline film of the anil 64 produced from a melt between quartz plates exhibits new absorption bands at 3380, 1646 and 1537 cm^{-1}. These bands may be bleached by re-irradiating the sample at 547 nm or by allowing the sample to warm to room temperature. The irradiation and re-irradiation of the sample may be repeated without any sign of fatigue or photodecomposition. These observations were rationalised in terms of the proposed zwitterion 81



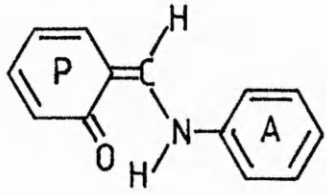
64, enol 81, zwitterion

in which the aniline ring (A) is twisted out of the plane of the phenolic ring (P). The band at 3380 cm^{-1} is attributed to the N^{+}-H stretching vibration, the sharpness and relatively high frequency of the band precluding the possibility of hydrogen bonding to the phenolate oxygen. The bands at 1646 and 1537 cm^{-1} are attributed to $C{=}\overset{+}{N}H$ stretching and N-H deformation modes.

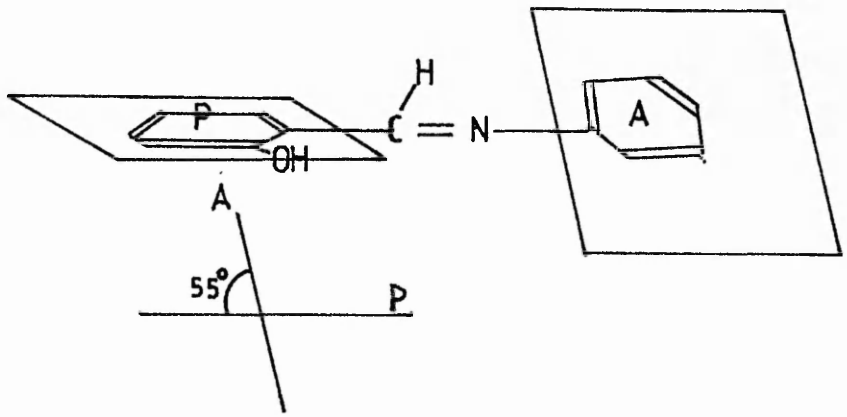
Carles et al.[74] investigated the kinetics of the fading reactions of crystalline films of a range of photochromic salicylideneanilines. They proposed for anil 64 that the isomers, X and Y, were produced simultaneously



X, 82



Y, 80



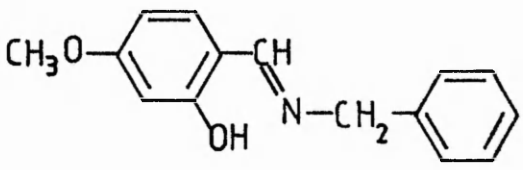
Z, 64

$$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$$

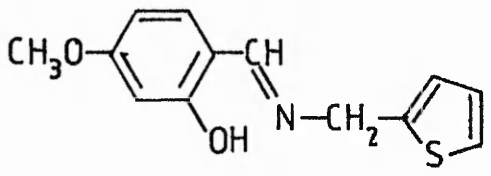
Scheme 6

during the preliminary irradiation process, and that fading occurred via two consecutive first order reactions with

different rate constants k_1 and k_2 where $k_1 < k_2$ (Scheme 6). The rate of decay of Y to Z was observed to be slow. This may be accounted for by assuming that the planes of the P and A rings in Y retain the same orientation known to exist in Z, viz. 55°, and that the N-H bond of Y is out-of-plane with respect to the P ring. Further support for these views comes from the study of a total of 87 photochromic and thermochromic anils made by Hadjoudis et al.[75] These authors concluded initially that in those anils with planar structures and intermolecular distances of the order of 0.35 nm between the planes, thermochromicity is observed, while in those in which the plane of the aniline ring (A) is rotated 40° to 55° with respect to the plane of the phenol ring (P), resulting in a relatively open structure, photochromicity is observed. However, these authors also reported[75,76] that compounds 83 and 84 are thermochromic and photochromic in the crystalline state both compounds having



83



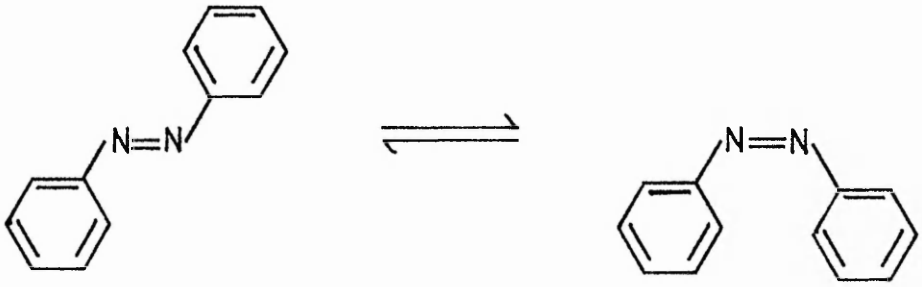
84

non-planar structures and hence predicted to be photochromic only. Hadjoudis suggests that a further factor may be the

level of electron density on the imino nitrogen and concludes that if this is high then the compound is thermochromic, if low, it is photochromic. There may be instances therefore, where the electron density is such that a 'borderline' situation is observed and both properties are expressed.

3.2.3 N=N cis-trans Isomerism

By investigating the solubility of azobenzene, Hartley[77] was able to show that there are two forms of the compound, the stable trans-form 85 (obtained by the partial reduction of nitrobenzene) and

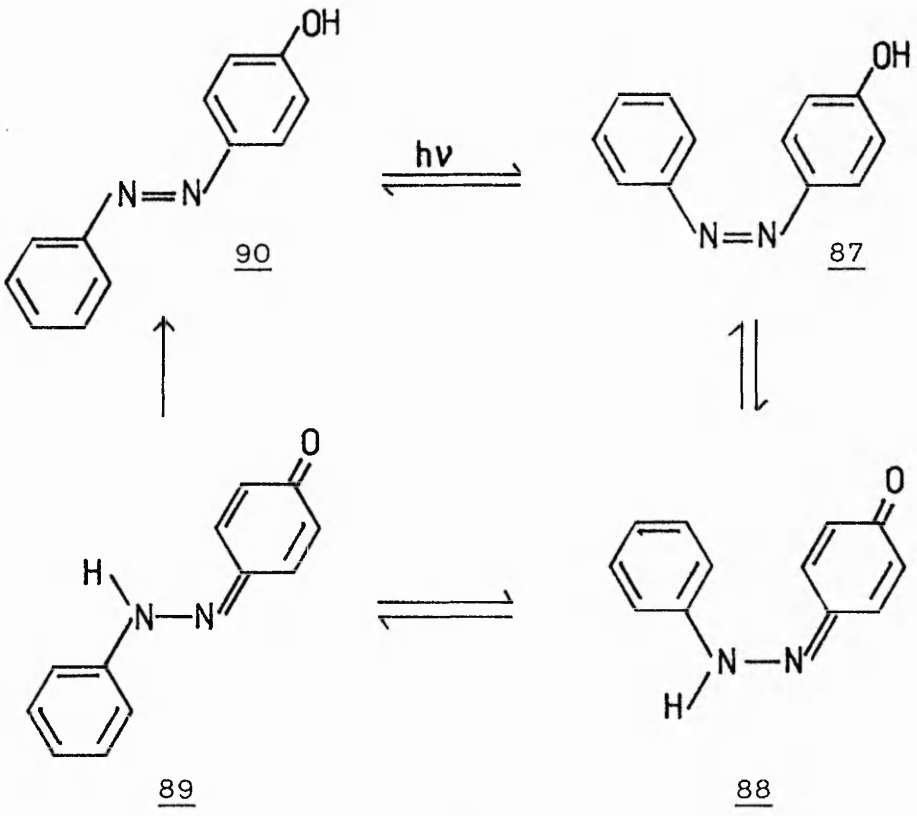


85 86

the less stable cis-form 86. The latter is obtained by irradiating the trans-isomer, and the suspected stereo-isomerism was indeed confirmed by X-ray crystallography[78] and by measurement of the dipole moments (μ) of the two forms of azobenzene; for trans-azobenzene, μ=0D, for the cis-isomer, μ=3D.[79] Azobenzene 85 and nearly all its mono-substituted derivatives have their principal absorption bands ($\pi \longrightarrow \pi^*$ transitions) in the ultra-violet region and their orange colour is caused by a weak $n \longrightarrow \pi^*$ absorption near 450 nm. On conversion to the

cis-isomer, the $\pi \longrightarrow \pi^*$ band shifts to shorter wavelengths and there is an increase in the strength of the $n \longrightarrow \pi^*$ absorption often accompanied by a shift in absorption maximum. Consequently, these compounds appear to "deepen" in colour upon trans $\longrightarrow$ cis photoisomerisation. Most of the simple azobenzenes are stable enough in the cis-form to be isolated and purified by chromatography, the energies of activation (cis $\longrightarrow$ trans) being of the order of 90 $kJmol^{-1}$.[80] Substitution of positions ortho or para to the azo-function of these dyes with strongly electron-donating groups such as dimethylamino shifts the main absorption band into the visible spectrum, sometimes causing it to overlap the $n \longrightarrow \pi^*$ band. These further substituted 4-dimethylaminoazobenzenes absorb at about 410 to 430 nm, and several have been shown to photoisomerise, the cis-isomers absorbing at 50 to 70 nm shorter wavelengths.[81]

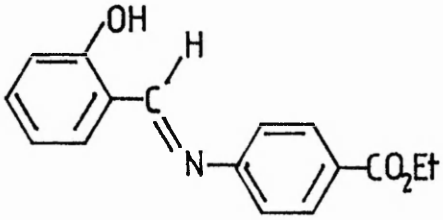
In contrast, the incorporation of the hydroxy group ortho or para to the azo-linkage reduces or even eliminates photochromism[82] since these compounds are much less stable in the cis-form. This is thought to result from the hydroxyazo dye 87 being in equilibrium (though to a small extent) with the hydrazone form 88. Once in the hydrazone form rapid rotation about the N-N single bond occurs and the dye reverts to the trans-form, as summarised in Scheme 7.



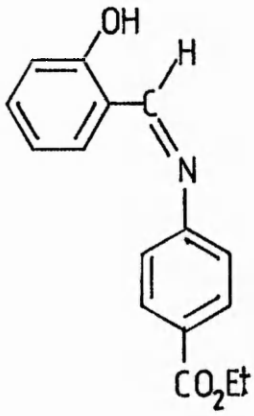
Scheme 7

3.2.4 CH=N cis-trans Isomerism

Manchot and Furlong[83] reported the isolation of two forms of N-salicylidene-p-carboethoxyaniline 91, believing them to be the E and Z isomers 91 and 92. One form - yellow needles



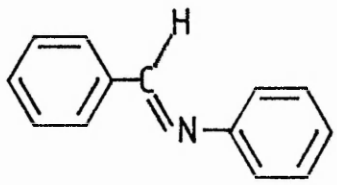
91, E



92, Z

with melting point 87-88°C when exposed to light is converted into a different form - orange needles melting at 83-84°C. Subsequent investigation by Jensen and Bang[84] showed that both the yellow and the orange forms of the imine have the same dipole moment, suggesting that the compound is merely dimorphic. What these authors failed to consider is the possibility that the two crystalline forms 91 and 92 were indeed E and Z isomers which rapidly established the same equilibrium mixture of isomers upon being dissolved in the solvents.

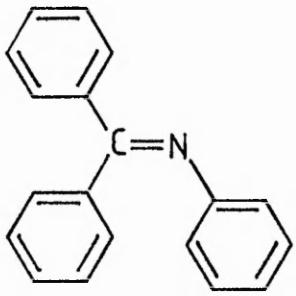
In 1957, Fischer and Frei[85] reported that benzalaniline 93



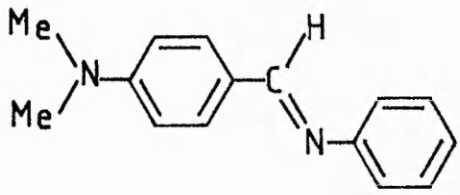
93, E

showed typical reversible photochromic changes when irradiated in methylcyclohexane-isopentane at -140°C. Absorption spectra of the irradiated solution showed a well-defined isosbestic point, the less stable Z-form absorbing at shorter wavelengths than the E-form. On warming the irradiated solution to a temperature between -70° and -40°C, the original absorption spectrum was restored,[86] and analysis of the temperature dependence of this process gave an energy of activation of 67-71 $kJmol^{-1}$. On the basis of these findings, and the

observations that N-benzohydrylidene-aniline 94 did not show any spectroscopic changes on irradiation, Fischer and Frei suggested that E-Z isomerisation was occurring. More recently,[87] nuclear magnetic resonance studies have supported the assignment of the Z-configuration to the photoisomer produced from the imine of E-configuration 95 below -70°C.



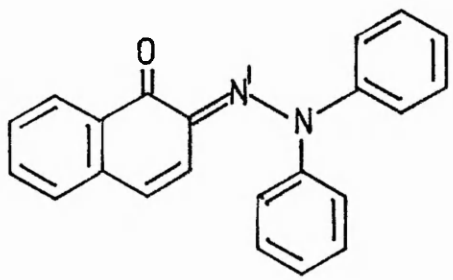
94



95

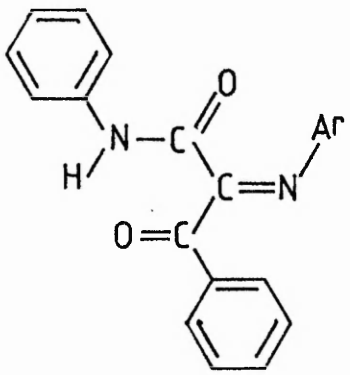
Comments have been made earlier (Section 3.2.2) concerning those imines (Schiff bases) which derive their photochromicity from enol ⇌ keto tautomerism.

1,2-Naphthoquinone-2-diphenylhydrazone 96 showed reversible photochromic changes when irradiated in methylcyclohexane-isohexane solution at -100°C.[88] Investigation of the fading reaction at 30°C indicated a half-life

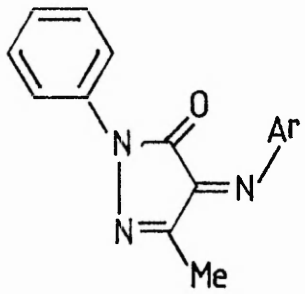


96

of 25 minutes. The question of whether photoisomerisation occurs by a torsional mechanism, involving rotation about the carbon-nitrogen double bond, or by an inversion mechanism, which involves transfer of the substituent at nitrogen N' from one side of the molecule to the other via a linear transition state which retains the carbon-nitrogen double bond intact, is difficult to resolve. It has been proposed[89] that the torsional mechanism is facilitated by electron-donating substituents and the inversion mechanism by electron-withdrawing substituents in the aryl ring attached to the imino nitrogen of the azomethine dyes 97 and 98 for which these two mechanisms of photochromicity have also been suggested.



97

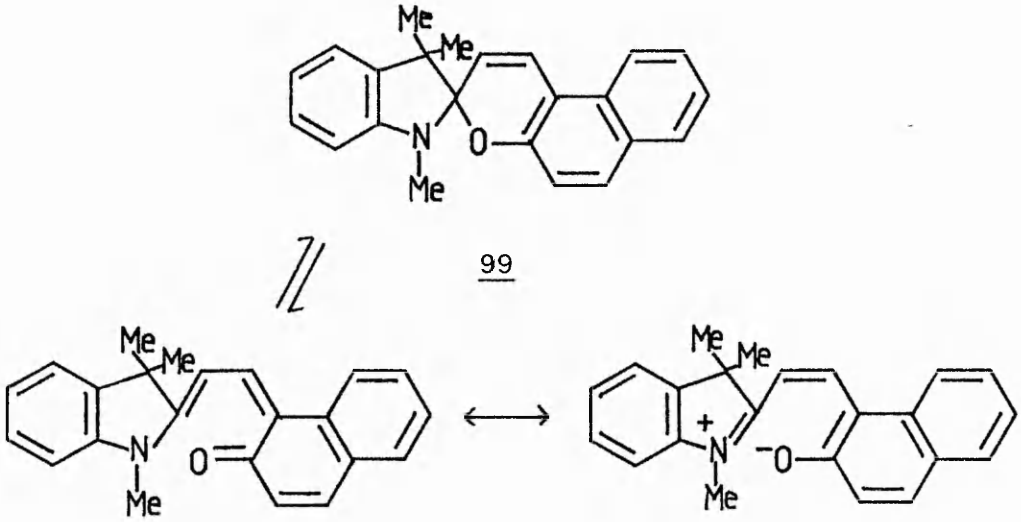


98

3.3 Spiropyrans

Photochromism in spiropyrans was first noted by Fischer and Hirshberg[90] in 1952 when they irradiated ethanolic solutions of 1,3,3-trimethylindoline-2-spiro-6'-(2',3'-β-naphthopyran) 99 at -50°C and observed a colour change from colourless to

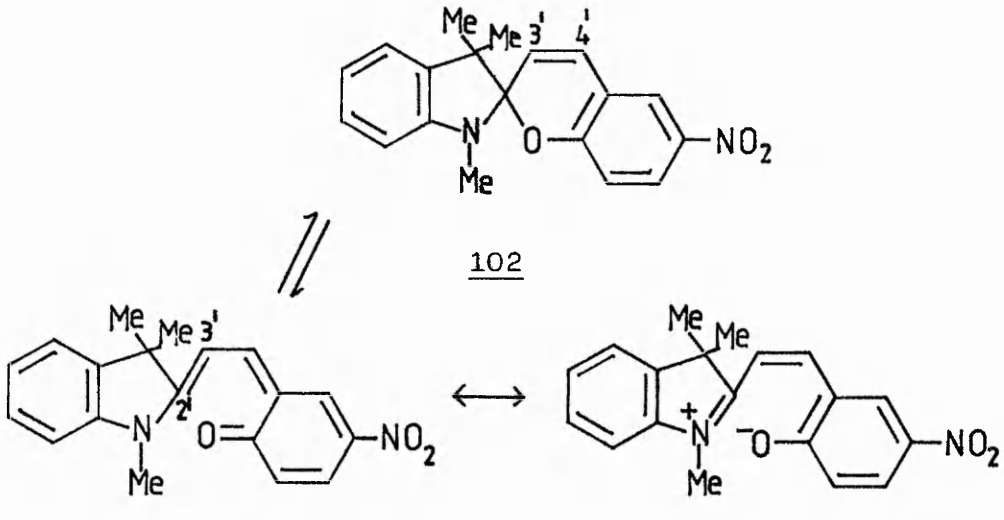
intense violet-red. The coloured species were believed



99

100 101

to be resonance hybrids of quinoid 100 and bipolar forms 101 though little supporting evidence was offered at that time. Ollis et al.[91] recorded the proton nuclear-magnetic-resonance spectrum for unirradiated 6-nitro BIPS 102. The two singlets

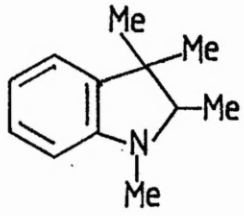


102

103 104

in this spectrum (at 1.19 and 1.30 ppm) each of a relative

intensity corresponding to three protons suggested that the two methyl groups are being deshielded to different extents, one by the oxygen atom of the pyran ring, and the other by the $C_{3'}$-$C_{4'}$ double bond. The N-methyl peak appears at 2.74 ppm, which compares well with the value of 2.70 ppm found for the indoline 105.[92] The coloured form can be

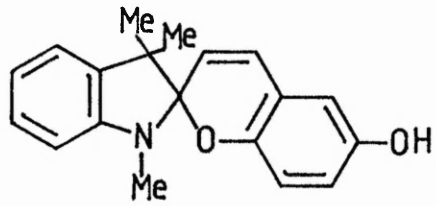


105

produced photochemically in sufficiently high concentration to permit its study directly by proton NMR. In this spectrum the gem-dimethyl groups appear as one singlet of a relative intensity corresponding to six protons, indicating that they are deshielded to the same extent - by the $C_{2'}$-$C_{3'}$ double bond - as shown in the proposed structure 103. Further, the signal for the N-methyl group in the spectrum of the coloured form occurs at 4.12 ppm, suggesting that the methyl group is attached to a nitrogen atom bearing a partial positive charge which would be the case if there were a contribution also from canonical structure 104.

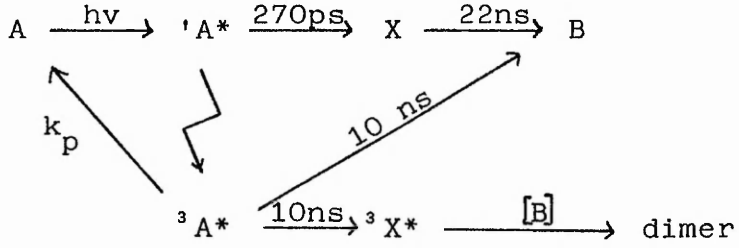
Several hundred spiropyrans have been shown to possess photochromic properties in solution in a wide range of solvents. Most solution studies have been carried out in ethanol, toluene and dioxane. (In this area, the term solution is wide ranging and includes not only dilute fluid solutions but also more rigid media such as gels, plasticised resins, films and bulk plastic solids, for example, perspex). The coloured solutions in polar solvents can in many cases be decolourised by visible light. The photocolouration - photobleaching cycles may usually be repeated many times before fatigue sets in to any extent - typically, 500 to 1000; occasionally, less than 5 or more than 30,000.

In contrast, very few spiropyrans are photochromic in the solid state. Recently, Yoshida et al.[93] have successfully prepared films of HBPS 106 by vacuum deposition onto fused quartz plates, such films developing a deep blue colour on ultraviolet irradiation.



106

Numerous studies of the photochromic equilibria in spiropyrans have been made by kinetic pulse spectroscopy, especially laser spectroscopy.[94-96] Instrumentation has been refined to permit, currently, time resolution in the picosecond range. The results of detailed kinetic studies by Lenoble and Becker[96] on nitrogen degassed hexane solutions of 6-nitro BIPS 102 are summarised in Scheme 8:-

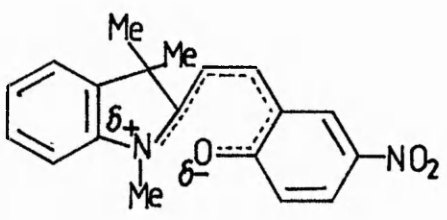


Scheme 8

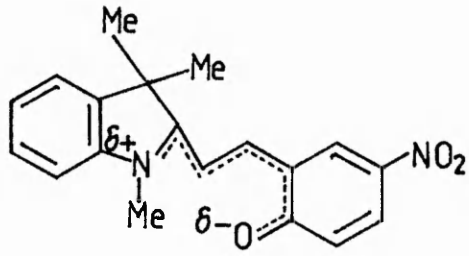
The identity of each species is as follows:-

A	6-nitro BIPS 102 uncoloured form
'A*	electronically excited singlet state of A
^{3}A*	electronically excited triplet state of A
X	merocyanine structure, cisoid form 107
^{3}X*	electronically excited triplet state of X
B	merocyanine structure, transoid form 108
k_p	rate constant for phosphorescence

Figures indicate lifetimes.



107



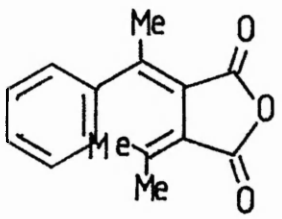
108

Kholmanskii and Dyumaev[23] have summarised the potential uses of photochromic spiropyrans. In addition to previously mentioned applications, viz. recording media, filters and photographic materials, there are some rather intriguing ones. The possibility of the photocontrol of the potential difference on the surface of a cellulose 2,4-diacetate membrane incorporating 6-nitro BIPS 102 has been investigated.[97] For this purpose, one uses the ability of the coloured form of the spiropyran on the surface of the membrane to react effectively with a proton to form a positively charged product. The surface charge on the membrane and hence the potential difference is regulated by pulses of radiation allowing one to control the passage of other ions through the membrane. The possibility of incorporating photochromic spiropyrans into biological membranes is extremely attractive, allowing the photocontrol of the transport of metal salts (KC1 and NaC1) and aminoacids through liquid membranes. The control of the electrical conductivity of solutions by light using spiropyrans is possible.[98] Because the coloured form of a spiropyran carries a greater charge distribution than the non-coloured form, the former is capable of altering the surface tension at the interface between two liquids enabling the spiropyran to function as a surfactant.[99] The application of flash photolysis techniques to solutions of spiropyrans in liquid crystal materials has enabled the study of problems relating to the hydrodynamics of liquids.[100]

It is evident that applications of photochromic spiropyrans are utilising not only the change in ultraviolet-visible absorption spectra produced on irradiation but also the difference in charge distribution between the coloured and non-coloured forms. That these properties manifest themselves in virtually any matrix - in the pure compound (in the crystalline or amorphous state), in solution and in polymers - and that these matrices may be used over a wide range of temperatures and viscosities, make it possible to employ spiropyrans in an increasing number of areas.

3.4 Fulgides

In contrast to the spiropyrans, the photochromism associated with fulgides has been known for a long time. In 1905, H. Stobbe[101] gave the name 'fulgides' (after the Latin 'fulgere', to glisten and shine) to the aryl derivatives of bis methylene succinic anhydride e.g. 109 because they are frequently obtained as beautiful reflective coloured crystals. Stobbe was unable to provide a

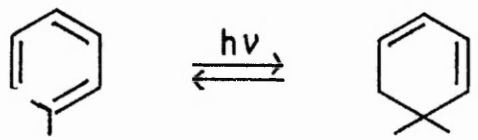


109

satisfactory explanation for the observed photochromism of fulgides but noted that the crystals underwent

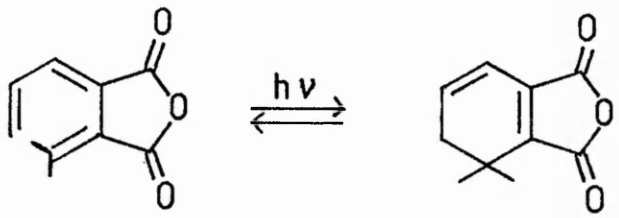
irreversible photorearrangement to give colourless anhydrides on prolonged irradiation.

For the fulgides, the basic process occurring in the photochromic change is an electrocyclic reaction of a conjugated triene 110:-



110 111

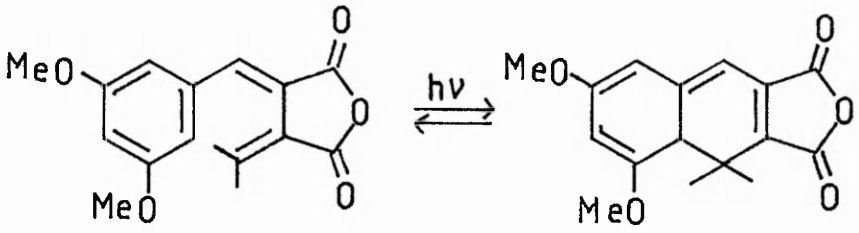
The acyclic molecule is rather flexible and can adopt many different conformations, most of which do not have the correct geometry for cyclisation. Adding a cyclic anhydride group, to give 112, makes the system more rigid and more likely to be in a conformation favourable for ring closure:-



112 113

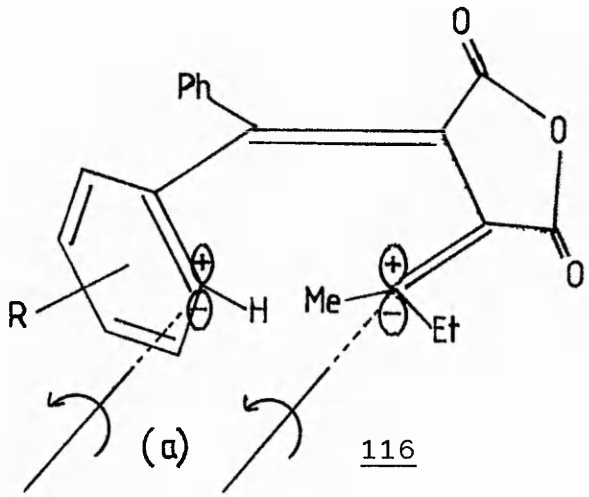
But the ring-closed form 113 is still not coloured in this simple example - it absorbs only in the ultraviolet. The introduction of an aromatic ring, in particular one which carries electron-donating substituents, extends the conjugated system and causes the ring-closed product to

be coloured 115:-



114 115

Heller et al. have carried out extensive research programmes over a period of sixteen years in order to discover the detailed mechanisms of the reactions outlined above and to "tailor" molecules with specific physical properties. In early studies,[102-104] it was established that in the phenyl substituted fulgides 116 the electrocyclic ring-closure reaction occurs in a conrotatory fashion, (a) in Scheme 9, to give coloured 1,8a-dihydronaphthalene derivatives 117. Exposure of the coloured forms to white light causes a symmetry allowed conrotatory reversal (a) while thermal bleaching involves disrotatory ring-opening (b).



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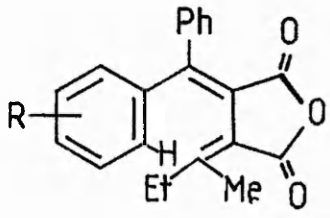

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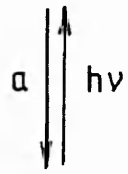
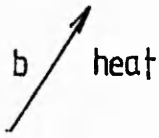
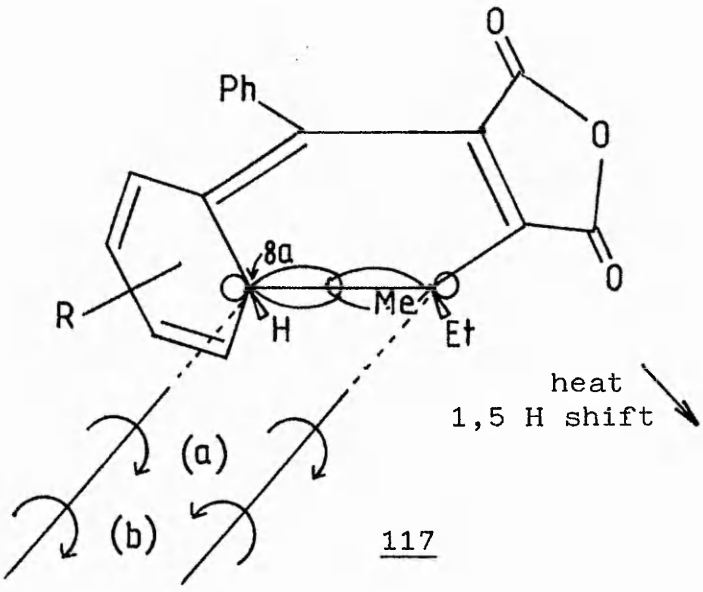
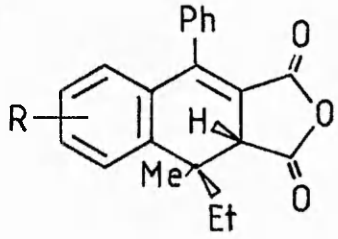






117

heat
1,5 H shift

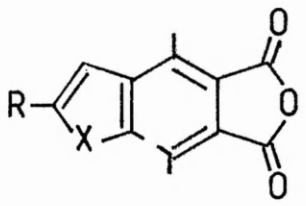


119

Scheme 9

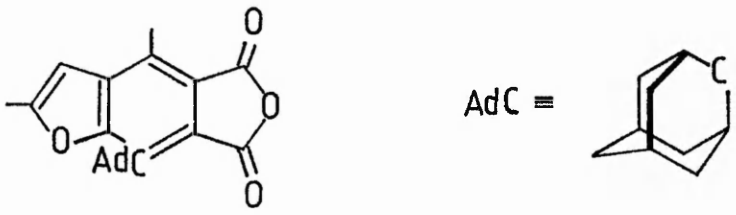
These reactions, unlike other organic photochromic processes, do not involve reactive radicals, ions or dipolar intermediates. The only significant fatigue process is a thermal 1,5-hydrogen shift 117 ⟶ 119. It follows that fatigue can be virtually eliminated by replacing the angular 8a hydrogen in the coloured form by some other group, e.g. a methyl group. Such a substitution has the added advantage that the newly introduced methyl group creates steric interactions with the alkyl groups already present inhibiting the thermal ring-opening process. Temperatures in excess of 100°C are now needed for this process to occur with these substituted compounds. These fatigue-resistant, thermally stable, photochromic organic compounds have been named by Heller as Aberchromes in recognition of the work which has been done by his group at Aberystwyth,[105] and more recently at Cardiff. Perhaps any new generation compounds will become Cardichromes!

That fulgides may be "tailor-made" to produce molecules with specified physical properties is illustrated with the following examples.[105] The benzene ring can be replaced by heterocyclic ring systems to give 120, X=O, N or S.



120

For the compound 120a, X=O, R=Me, the quantum yield for colouring at 366 nm is 0.20 and for bleaching at 494 nm at 21°C, 0.058. The conversion of the colourless into the coloured form, λ_{max}= 494 nm, is virtually quantitative owing to a combination of weak absorption and a low quantum yield for reversal of the coloured form in the 300 - 400 nm region of the spectrum. This compound is now widely used for chemical actinometry in the near ultraviolet region.[106,107] In contrast, the compound 120b, X=N-Me, R=H, with similar irradiation gives a dark-blue coloured form with λ_{max} = 633 nm, a bathochromic shift of 139 nm. Compound 120c, X=S, R=Ph, on irradiation at 366 nm is converted in high yield to a 'permanganate' purple crystalline form having λ_{max} = 520 nm. In compound 121, the introduction of the bulky inflexible adamantylidene



121

group causes a six-fold improvement in the quantum yield for bleaching (0.38) compared with the furanyl derivative mentioned above, under similar irradiating conditions. A wide variety of Aberchromes has been synthesised showing complete thermal stability, or fast thermal colouring, or

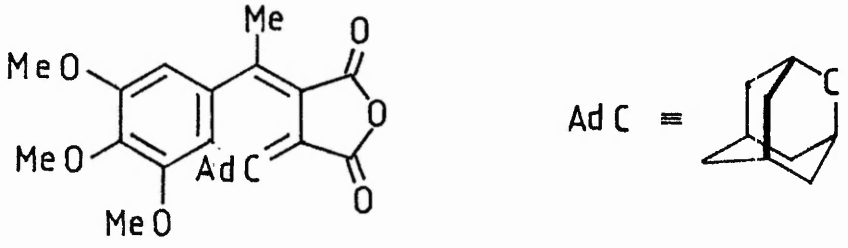
fast thermal fade, high or low quantum yields for colouring and bleaching, and showing a wide range of colour changes.

For photochromic compounds to colour quickly in unfiltered sunlight and fade rapidly in diffuse daylight, the following combination of properties is required:

(a) a high quantum efficiency for colouring in near ultraviolet light

(b) a low quantum efficiency for bleaching with visible light and

(c) a fast thermal fade at ambient temperatures but not so rapid that the combination of whitelight bleaching and thermal fade prevents colouring by the ultraviolet component of strong sunlight. To describe photochromic compounds showing this special combination of properties, Heller has introduced the term "heliochromic",[108] and one such heliochromic compound is shown in 122. The heliochromic properties of these compounds



122

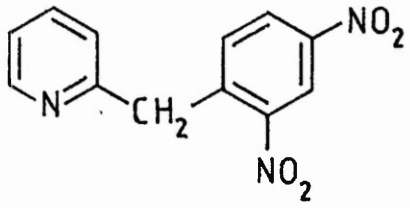
are markedly affected by substituent changes to give fatigue-resistant systems showing a wide range of colour changes from orange to deep blue with fade rates varying from under a minute to many hours under similar conditions. For commercial

applications in photoactive lenses or in security inks;[109] photochromic compounds must show a very high resistance to photodegradation and other irreversible side reactions. The investigation of these heliochromic compounds will be of academic and commercial interest for many years to come.

4 DISCUSSION

4.1 Introduction

The aim of this work has been to synthesise compounds related to 2-(2',4'-dinitrobenzyl)pyridine 27 in order to investigate the structural requirements for hydrogen-transfer photochromism, with a view to maximising the effect



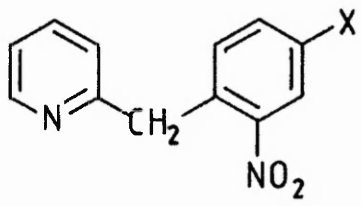
27

and extending the colour range possible in such systems. A number of pertinent structural modifications to DNBP 27 were conceived, the investigation being developed along five themes. These are outlined below and then discussed in more detail in Sections 4.2 - 4.6.

Tschitschibabin reported[47] that white crystals of DNBP 27, on exposure to sunlight, turned deep-blue. Some forty years later, it was observed[51] that if the 4'-NO_2 group of DNBP were replaced by CO_2CH_3, $CO_2CH_2CH_3$, $CONH_2$ or CN, on irradiation by ultraviolet light, these compounds turned dark blue-green, pale blue-green, pale green and green respectively. It was felt to be of interest to investigate the possibility of widening this range of colour by introducing into the 4'-position substituents which increased

the extent of the delocalised pi-electron system. This idea is further developed in Section 4.2.

As previously mentioned (p.30), it has been shown that the rate constants for the fading reactions of compounds of the type 123 are markedly sensitive to the electronegativity



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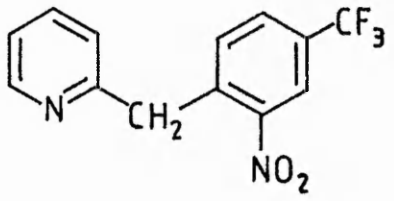


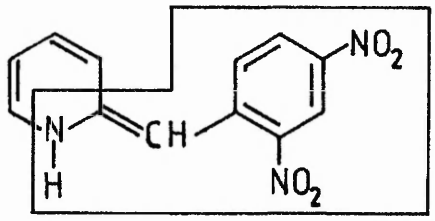
124

of the 4'-substituent, X. Further, it would appear from the work of Weinstein et al.[53] that only in those compounds where substituent X has Hammett $\sigma_p \geqslant 0.36$ is photochromism observed in the solid state at room temperature. It was therefore proposed to test this hypothesis in the electronically interesting case of compound 124, the CF_3-group having $\sigma_p = 0.54$, and this work is described in Section 4.3.

In the third and fourth areas of study, the dinitrobenzyl moiety was retained intact and the necessity for photochromism of methine tautomerism and/or ring protonation investigated. This is discussed in Sections 4.4 and 4.5.

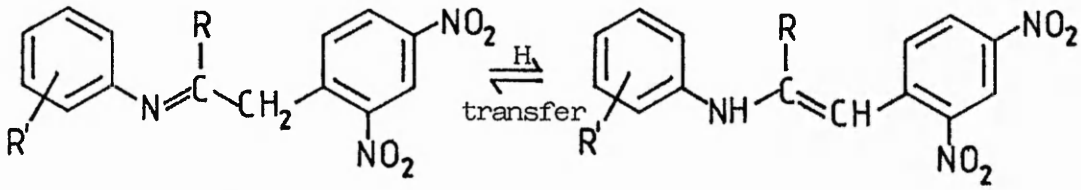
As previously described (p.36), Sixl and Warta[61] investigated photochromism in crystals of DNBP 27 by optical absorption spectroscopy, and from their observations were able to establish that the deep-blue colour of ultraviolet

irradiated DNBP 27 was due - at room temperature - to the formation of the N-H quinoid tautomer 28. Extension of this idea leads one to speculate whether simply the



28

structural features contained in the ringed part of the molecule 28 are all that is required to produce a species which is coloured and whether or not this could be achieved by straight forward imine/enamine tautomerism in a system such as 125 $\rightleftharpoons$ 126:-



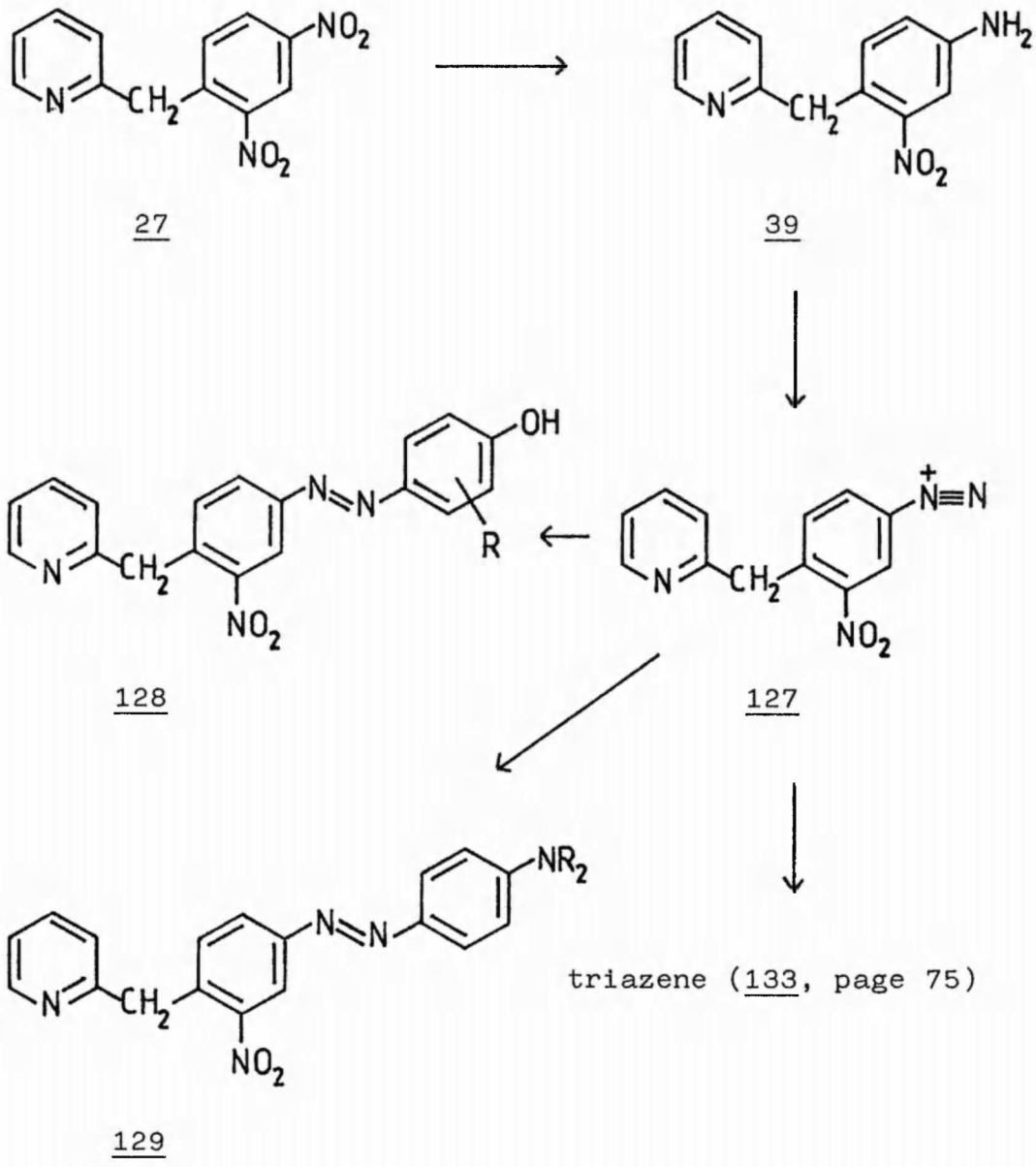
125 126

R=H,CH_3,Ph; R'=H,CH_3

This is looked at in Section 4.6.

4.2 Azo compounds and imines

As noted in the introduction, four compounds related to 2-(2',4'-dinitrobenzyl)pyridine 27 are photochromic in the solid state at room temperature, namely those compounds in which the 4'-NO_2group is replaced by CO_2CH_3, $CO_2CH_2CH_3$, $CONH_2$ and CN. These compounds in the ultraviolet irradiated form all have blue/green colours and a wider range of colours was sought. It was anticipated that this might be achieved by increasing the extent of the delocalised-electron system since it is well established that bathochromic shifts in UV-visible spectra are associated with increasing chain length in a conjugated system; for instance, in the series $C_6H_5(CH=CH)_nC_6H_5$, for n=1, λ_{max}= 306 nm, and for n=6, λ_{max}= 420 nm.[110] Thus, it was proposed to reduce 4'-NO_2 in 27 to 4'-NH_2, to diazotise the resulting amine and then to couple the diazonium ion with a range of phenols and amines producing extensively-conjugated molecules as outlined in Scheme 10.

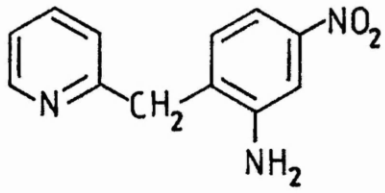


27 39 128 127 129

Scheme 10

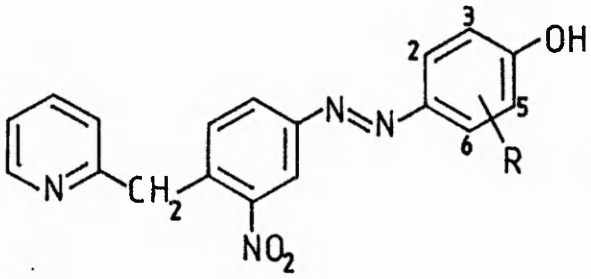
4.2.1 Preparation of the azo compounds

Accordingly, a regiospecific reducing agent was required for the first stage 27 ⟶ 39. In a trial experiment, 1,3-dinitrobenzene was reduced using $Na_2S.9H_2O/S$ to 3-nitroaniline (yield 53%, lit. 58%[111a]), but this reagent was ineffective with 2-DNBP 27, the starting material being totally recovered. The absence of reduction is possibly due to the basic character of the pyridine ring influencing the equilibrium position $S^{2-}+H_2O \rightleftharpoons HS^-+OH^-$. However, the reduction 27 ⟶ 39 was successfully achieved with $H_2S/aqNH_3$/ethanol - a Zinin reduction. Though both Nunn and Schofield[48] and R. H. Wilson[112] reduced 2-DNBP in this way to orange 2-(4'-amino-2'-nitrobenzyl)pyridine 39, neither reported the presence additionally of the yellow isomeric 2-(2'-amino-4'-nitrobenzyl)pyridine 130 (5.9%) in the reaction mixture. This, surprisingly, appears to be a novel compound. (It is not, unsurprisingly, photochromic).



130

2-(2'-Nitro-4'-aminobenzyl)pyridine 39 was then diazotised by standard techniques and the diazonium product coupled to a range of phenols and tertiary amines. In addition, the triazene 133 was obtained by a coupling reaction with the original (primary) amine 39. Spectral data for the coupled products are reported in Tables 6 - 8. (Supplementary data are reported in Appendix 1).



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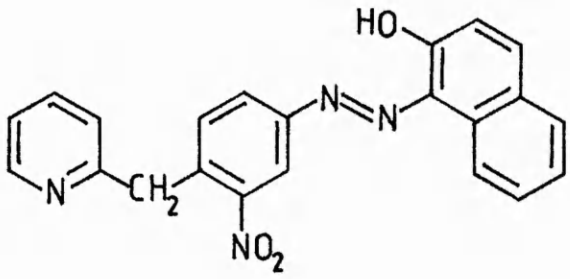
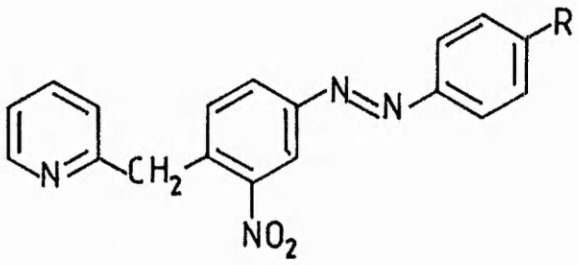


131

Compound Formula	Colour	IR/cm^{-1} (KBr)			UV-visible λ_{max}/nm (a)	
		N=N	Asym. NO_2	Sym. NO_2	Pre-	Post-
128a						
R=H	tan	1435	1530	1355	368	373
128b						
R=3-Cl	yellow-brown	1440	1527	1350	372	385
128c						
R=3,5-diCl	yellow-orange	1435	1530	1350	364	376
128d						
R=2-NO_2	orange-yellow	1435	1530	1355	345	357
128e						
R=2-Cl	brown	1438	1528	1349	378	382
128f						
R=2,6-diCl	orange	1435	1531	1349	347	350
128g						
R=3-Me	yellow	1438	1522	1342	372	382
128h						
R=2-Me	yellow-orange	1430	1520	1342	380	384
131						
	rust	1435	1530	1350	477	485

Table 6

Colours, infrared data and ultraviolet-visible spectral data for the phenol derivatives. (a) Values of λ_{max} for ethanolic solutions at -70 to -75°C, before and after UV irradiation.



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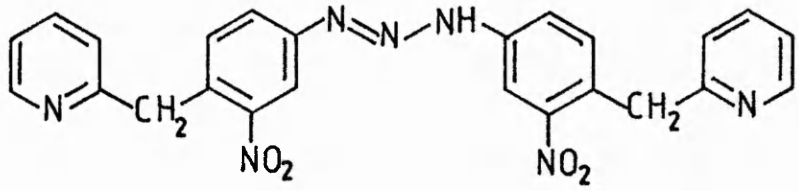


133

Compound Formula	Colour	IR/cm^{-1} (KBr)			UV-visible λ_{max}/nm (a)	
		N=N	Asym. NO_2	Sym. NO_2	Pre-	Post-
132a R=N$(CH_3)_2$	red	1431	1525	1370	436	438
132b R=N$(CH_2CH_3)_2$	red-orange	1437	1518	1350	456	459
132c R=N(O)	orange	1436	1525	1350	413	417
133	yellow-brown	1437	1530	1350	235	242

Table 7

Colours, infrared data and ultraviolet-visible spectral data for the amine derivatives. (a) Values of λ_{max} for ethanolic solutions at -70 to -75°C, before and after UV irradiation.

Compound, phenol derivative 128a

λ_{max}/nm	202	230	253	368	670 (very broad)
Absorbance	1.40	0.76	0.67	0.93	0.10
ϵ_{max}	25,000	13,600	12,000	17,000	1800

Compound, amine derivative 132a

λ_{max}/nm	211	265	436
Absorbance	0.59	0.60	0.84
ϵ_{max}	23,600	24,000	33,600

Table 8

UV-visible spectral data for ethanolic solutions (at room temperature) of phenol derivative 128a and amine derivative 132a.

4.2.2 Properties of the azo compounds 128a-h, 131, 132a-c and 133

In contrast to 2-DNBP and the four compounds mentioned in Section 4.1, which are white crystalline solids, the 9 phenol- and 4 amine-derivatives (128a-h, 131, 132a-c, 133) range in colour from red through orange-red, orange-yellow to yellow-brown and tan. However, when these novel compounds in the solid state at room temperature are exposed to ultra-violet radiation, there is no colour change detectable by eye. These compounds are not photochromic. In extending the delocalised-electron system via the 4'-position, the property of photochromism has been lost.

The absorption spectra for ethanolic solutions of these azo compounds were also recorded, at room temperature and at low temperatures (-70° to -75°C), before exposure to ultraviolet radiation and after exposure. No compound displayed thermochromism i.e. there were no shifts in λ_{max} values in the spectra obtained for unirradiated solutions at room temperature and at low temperature. There were small bathochromic shifts in λ_{max} values in the spectra recorded at low temperature before and after exposure to ultraviolet radiation. These shifts are reported in Tables 6 and 7.

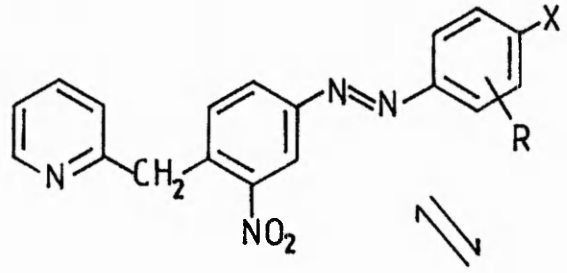
In an attempt to assign the absorptions quoted in Table 8, reference has been made to the absorption data for the simple azo-compounds given in Table 9. It would appear that the strong absorptions at longest wavelength i.e. λ_{max} = 368 nm for the phenol 128a and λ_{max} = 436 nm for the amine 132a are due to $\pi \longrightarrow \pi^*$ transitions. It was this absorption band which was monitored after the ultraviolet irradiation of cooled ethanolic solutions of the novel compounds. In all cases bathochromic shifts occurred, generally larger shifts for the phenols than for the amines, the largest being 13 nm for compound 128b. It is unlikely that these shifts were due to trans $\longrightarrow$ cis isomerism, because the evidence in Table 9 indicates that for azobenzene 134 and the simple derivative 135, trans $\longrightarrow$ cis isomerism is accompanied by hypsochromic shifts. It seems more likely that the observed bathochromic shifts for the novel compounds occur due to a slight shift in the equilibrium from parent compound 137 to aci-nitro acid tautomer 138 or from parent

Compound		$\pi \longrightarrow \pi^*$		$n \longrightarrow \pi^*$		Reference
		λ_{max}/nm	ϵ_{max}	λ_{max}/nm	ϵ_{max}	
Ph-N=N-Ph trans	134a	319	22,000	443	510	113
Ph-N=N-Ph cis	134b	280	5,260	432	1518	113
Ph-N=N-C_6H_4.NMe_2 trans	135a	410	30,400	(a)	(a)	114,115
Ph-N=N-C_6H_4.NMe_2 cis	135b	362	12,000	460	4,300	116

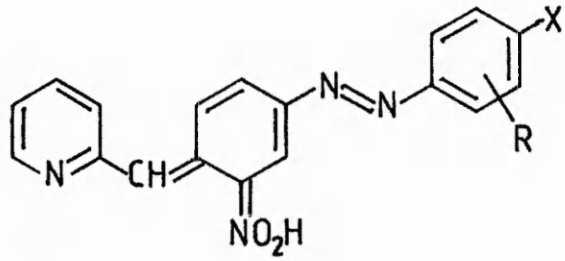
Table 9

UV-visible spectral data for some simple azo-compounds in ethanol solution. (a) Overlain by $\pi \longrightarrow \pi^*$band.

compound to N-H quinoid tautomer 139 in each of which an extension of the conjugated system occurs, thus facilitating the $\pi \longrightarrow \pi^*$ transfer. On removal of the ultraviolet source and/or on warming the cooled solutions to room temperature, the original equilibrium position is restored.



137



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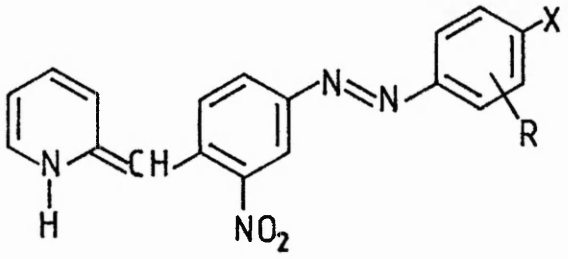
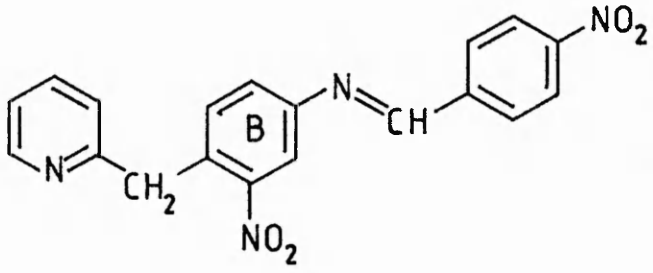


139

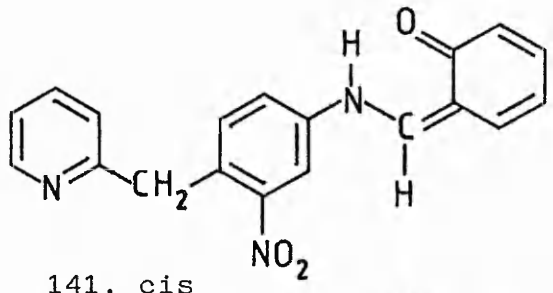
Solutions of the triazene 133 (see Table 7) similarly showed only small bathochromic shifts on ultraviolet irradiation, despite the presence of two potentially photochromic centres, each, in theory, able to give rise to both aci-nitro acid and N-H quinoid tautomers. However, in the formation of such tautomers, there is still no H-transfer mechanism through which the two ends of the molecule may form a single conjugated system.

4.2.3 Preparation and properties of the imines

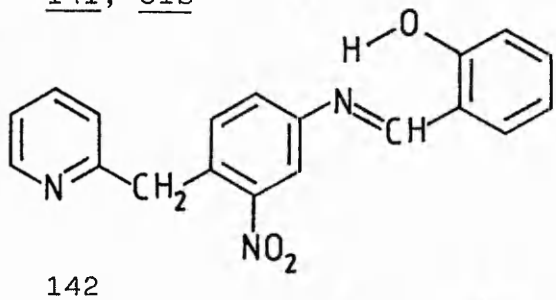
Extended delocalised-electron systems similar to those described above may also be obtained by condensing an aromatic aldehyde with 2-(4'-amino-2'-nitrobenzyl)pyridine 39. Two aldehydes were investigated. 4-Nitrobenzaldehyde was chosen in the expectation that the nitro-group would maintain the requirement of electron withdrawal from ring B (see 140). Salicylaldehyde was selected because the condensation product would in this case, in theory, give rise to a second potentially photochromic centre,[67] since H-transfer could occur both from the methylene group and from the hydroxy group, the former producing the aci-nitro acid and/or N-H quinoid tautomer, the latter producing the cis-keto 141 and/or trans-keto tautomer 143. Accordingly, compounds 140 and 142 were synthesised.



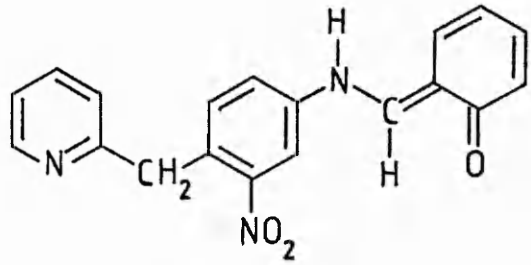
140



141, cis



142



143, trans

Samples of these imines in the form of potassium bromide discs were irradiated by ultraviolet light. The former 140 was unaffected. Over a period of 30 minutes, the colour of the disc from the salicylidene compound 142 changed from yellow to orange-yellow to orange-brown, but no changes could be detected in the infrared spectrum. The colour of the irradiated disc reverted to its original yellow when stored in the dark under dry conditions over one week. Absorption spectra for ethanolic solutions of both imines 140 and 142, at room temperature and low temperature, before and after ultraviolet irradiation were recorded and the data are shown in Table 10. As for the azo derivatives no thermochromism was displayed, and only very small bathochromic shifts were noted after irradiation in the absorption spectra, for λ_{max} of greatest wavelength (all λ_{max} values are reported in Table 11). Presumably the explanations given earlier for the small bathochromic shifts observed with the azo compounds are equally applicable here. It was indeed most disappointing that the imine 142, with its great potential for photochromic behaviour, should show none.

Compound	Colour	IR/cm^{-1} (KBr)			UV-visible	
			Asym.	Sym.	λ_{max}/nm (a)	
		CH=N	NO_2	NO_2	Pre-	Post-
142	yellow	1624	1525	1350	347	351
140	lime-green	1629	1520	1345	340	343

Table 10

Colours, infrared data and ultraviolet-visible spectral data for the two imines. (a) Values of λ_{max} for ethanolic solutions at -70 to -75°C, before and after UV irradiation.

Compound	λ_{max}/nm	209	224	264	347
142	Absorbance	0.90	0.93	0.64	0.32
	ϵ_{max}	20,300	20,900	14,400	7,200
	λ_{max}/nm	210		257	340
140	Absorbance	1.14		1.22	0.42
	ϵ_{max}	20,400		21,900	7,500

Table 11

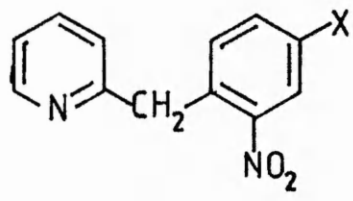
UV-visible spectral data for ethanolic solutions (at room temperature) of the two imines 142 and 140.

4.3 Trifluoromethyl derivatives

Weinstein, Bluhm and Sousa[53] noted that for a number of 2-(2'-nitro-4'-substitutedbenzyl)pyridines in ethanol the rate constant for the fading reaction is markedly sensitive to the electronegativity of the 4'-substituent (see page 30). In general, for substituents for which the Hammett σ^-_p constant is negative, the half-life is very short (e.g. for NH_2, σ^-_p = -0.660, $t_{½}$ = 0.187 ms) and for substituents for which the σ^-_p constant is positive, the half-life is relatively long (e.g. for NO_2, σ^-_p = +0.778, $t_{½}$ = 5680 ms). For those compounds noted earlier as being photochromic in the solid state at room temperature (27, 34, 35, 36 and 38), the Hammett σ^-_p values for the 4'-substituent are in each case greater than +0.36 (see page 31, Table 2). It therefore seemed of interest to test the hypothesis that "those compounds in which the 4'-substituent has σ^-_p constant greater than +0.36 are similarly photochromic".

A selection of functional groups with Hammett σ^-_p values greater than 0.36 is listed in Table 12. Examination of these five groups reveals that four are multiply-bonded i.e. contain both σ-bonds and π-bonds while the trifluoromethyl group is

Substituent	σ^-_p
SO_2CF_3	+0.93
$COCF_3$	+0.80
N=N-Ph	+0.64
CF_3	+0.53
$COCH_3$	+0.50



123

Table 12.

Hammett σ^-_p values for five functional groups.[54]

only σ-bonded. Hence, if the four multiply-bonded groups were introduced into 123 at the 4'-position they would effectively increase the conjugation of the system. With the trifluoromethyl group this is not the case. Thus by introducing a CF_3-group it should be possible to differentiate between the influence of electronegativity (i.e. simple electron withdrawal through the σ system) and mesomeric interaction on the propensity for photochromism.

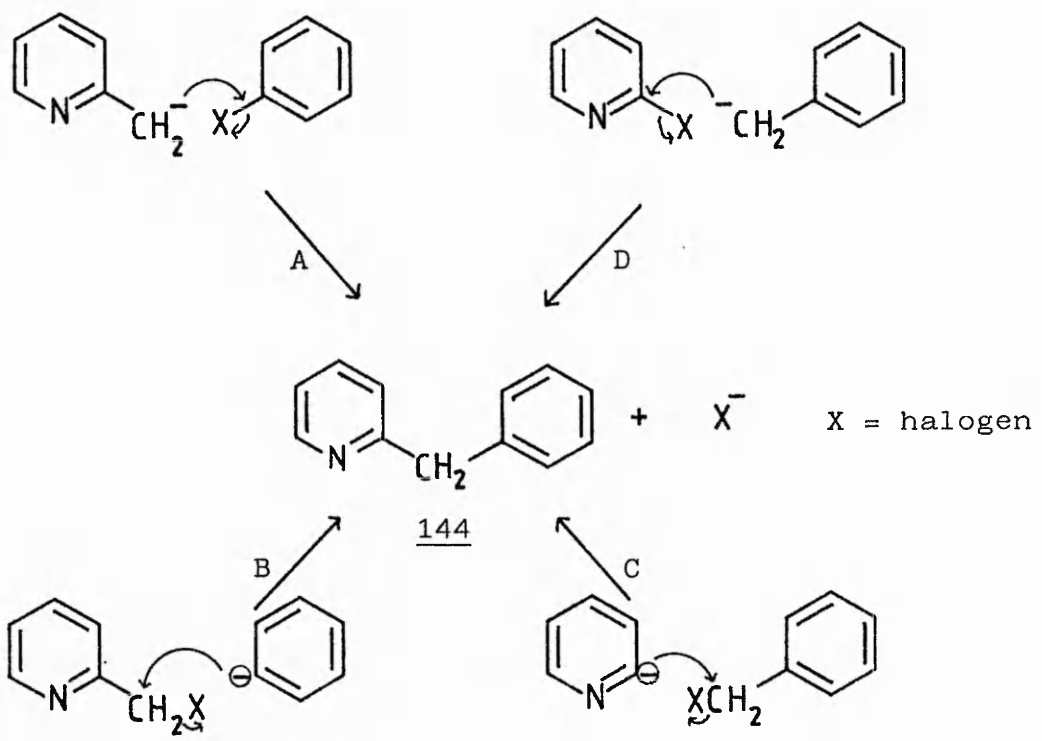
4.3.1 Syntheses of 2-(2'-nitro-4'-trifluoromethylbenzyl)pyridine 124 via organo-lithium and organo-copper intermediates

Although there are available means for introducing the CF_3-group directly into a benzene ring, for instance,

$$CF_3I + C_6H_5I \xrightarrow[DMF/150^{o}]{Cu} C_6H_5CF_3 \qquad 45\%$$

6 hours/sealed tube[118]

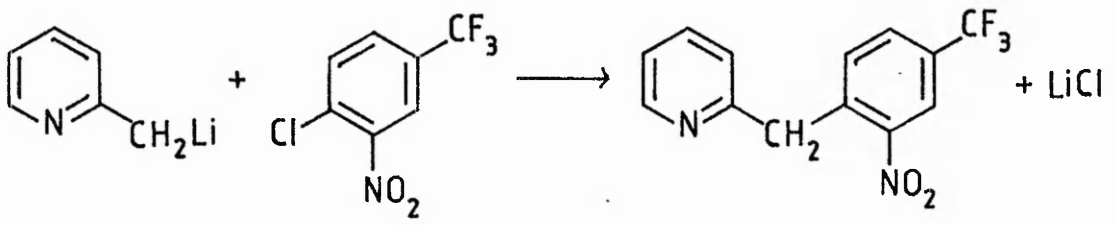
the conditions required are generally rather extreme and appeared unsuitable for the synthesis of 124. Compound 124, in principle, is amenable to synthesis by a direct nucleophilic displacement procedure from readily available starting materials. Four possible nucleophilic substitution reactions may be envisaged as shown in Scheme 11.



Scheme 11

Route A is the method of choice for three reasons. The presence of electron-withdrawing groups (NO_2 and/or CF_3) in the benzene ring will enhance the nucleofugal properties of group X; the picolyl-anion can readily be generated in high yield;[119] the starting materials are cheap. The route in detail is as follows:-

PhLi (or BuLi) + $C_5H_4N.CH_3$ ⟶ $C_5H_4N.CH_2Li$ + PhH (or BuH)



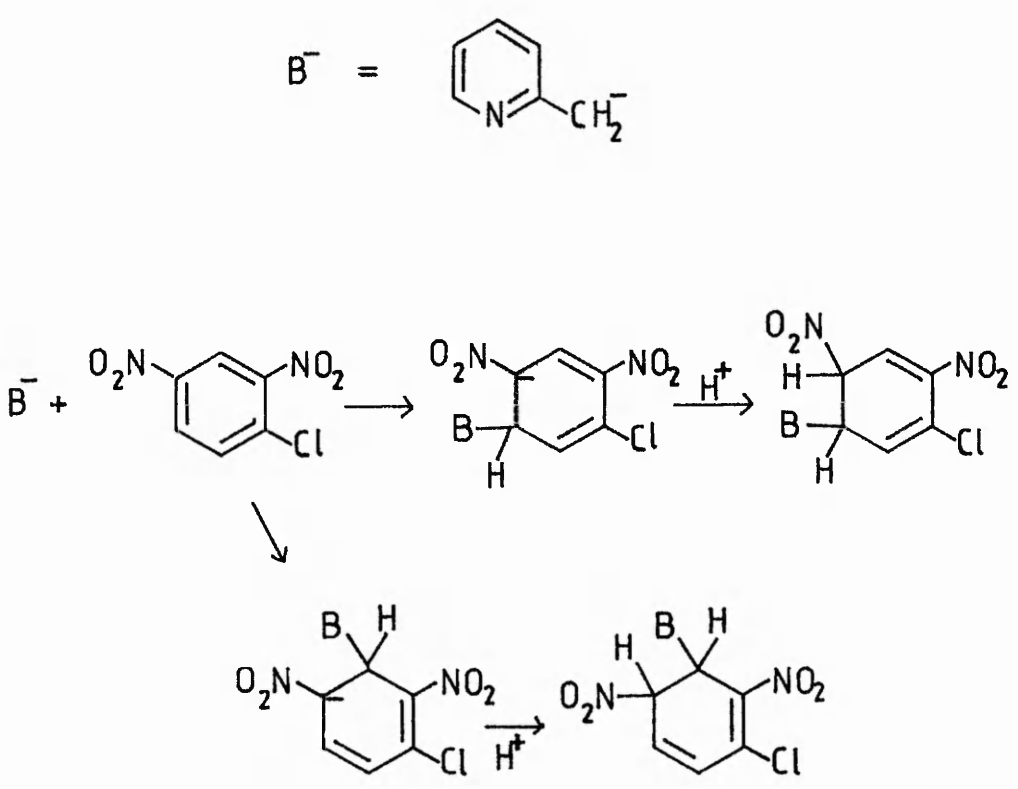
145 146 124

Scheme 12

Picolyllithium, generated from picoline and commercially available phenyllithium or butyllithium, was reacted with 4-chloro-3-nitrotrifluoromethylbenzene 146 under a variety of conditions of solvent and temperature (dimethylformamide, ether, tetrahydrofuran, -70° to +60°C). T.l.c. of product mixtures frequently indicated the presence of five or more components, including picoline and starting halide 146. In many cases, flash chromatography was used in an attempt to isolate the target molecule 124 but in no case was this achieved.

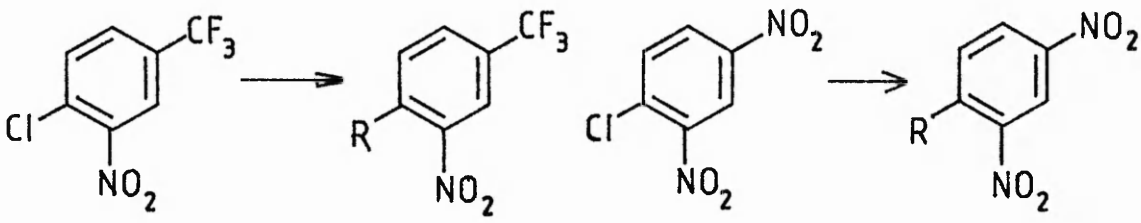
It was not clear why this apparently simple nucleophilic substitution reaction was failing, and it was decided to repeat the sequence using 2,4-dinitrochlorobenzene 149 in place of the CF_3-derivative, this having two advantages. Firstly, the nucleofugal properties of the leaving-group would be enhanced by the presence of a second NO_2-group in place of the CF_3-group. Secondly, the product, 2-DNBP 27, a known compound, if present, would be readily identifiable. In trial reactions, DNBP was indeed detected by t.l.c. in trace amounts together with three new components and starting materials.

The presence of 4 components in the product mixture, including DNBP, showed that reactions were occurring other than the straight displacement of halide. If these side reactions, as seemed likely, were due to the highly basic nature of the picolyl-anion, the species bringing about, for instance, adduct formation of a type described by Buncel[120] and illustrated in Scheme 13, then a less basic reagent was required. It also seemed unlikely that the absence of a clean



Scheme 13

reaction was due to the halide. This latter possibility can almost certainly be discounted since in trial reactions between sodium ethoxide and halides 146 and 149 yields of the expected products 147 and 150 were 85% and 90%; similarly for ammonia in reaction with these halides, the yields of amino-derivatives 148 and 151 were 47% and 61%. These results do however confirm that the CF_3-group is less able to assist



146 147, R = OEt 149 150, R = OEt

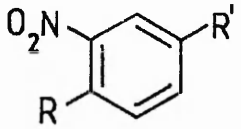
148, R = NH_2 151, R = NH_2

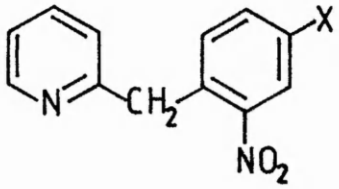
the loss of halide ion than the nitro-substituent. Further, and more importantly, with the rather less basic nucleophiles, EtO^-,NH_3, only nucleophilic substitution of halide occurs. Thus the combined evidence from the reactions between picolyllithium and halides 146 and 149 and from the trial experiments suggests that the picolyl-anion is too basic in character for this reagent to be successful and hence an alternative strategy had to be sought.

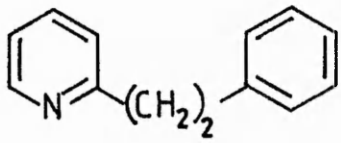
G. H. Posner has commented[121] that, in contrast to lithium and magnesium organo-compounds, copper compounds are less basic and more likely to undergo only straight substitution reactions. Picolylcopper appears not to have been used in this context, and it was decided to investigate its reaction, if any, with dinitrochlorobenzene. Picolylcopper was generated by adding picolyllithium to copper (I) chloride dispersed in tetrahydrofuran and subsequently reacted with 2,4-dinitrochlorobenzene over a range of temperatures. On only one occasion, at -15°C, was a trace of DNBP 27 indicated by t.l.c. In the light of these trials it was thought

expeditious to confirm that picolylcopper had indeed been generated in the above reaction sequence. Hence a quantitative analysis of picolylcopper was carried out (see page 143). This confirmed that the copper derivative was produced in good yield, but that deterioration of this reagent occurred quite quickly. Clearer evidence that picolylcopper was able to take part in nucleophilic substitution reactions came from its reaction with benzyl bromide, producing 1-(2'-pyridyl)-2-phenylethane 153 in 66% yield.

It has been well established that diorganocuprates are more reactive than mono-organocopper species[122] and it was therefore decided to investigate the possibility of synthesising lithium dipicolylcopper, a novel reagent, and to study its reactions with a range of substrates. Accordingly, this new reagent was prepared by the action of picolyllithium on copper (I) iodide (2:1 mole ratio) in tetrahydrofuran, and then reacted with a number of halogen-containing compounds in order to determine the optimum conditions of solvent and temperature to produce synthetically useful yields of pyridyl derivatives. A summary of the results of these reactions and of the analogous reactions investigated in this part of the study is shown in Table 13. A number of conclusions may be drawn from this work. Halogen in the side-chain is much more readily displaced than halogen in the benzene nucleus even when the nucleus is activated towards substitution by the presence of electron-withdrawing substituents. Further, the reactions between the copper-derivatives and benzyl bromide produce no side-products. It







152a-d 123 153

	Reactant		Product		Yield (%) of Product with:		
	R	R'			PicLi	PicCu	$LiPic_2Cu$
152a	Cl	NO_2	123	$X=NO_2$	trace	8	7
152b	Cl	CF_3	123	$X=CF_3$	trace	trace	trace
152c	F	CF_3	123	$X=CF_3$	trace	trace	trace
152d	F	NO_2	123	$X=NO_2$	trace	5%	0
	$PhCH_2Br$		153		42	76	90

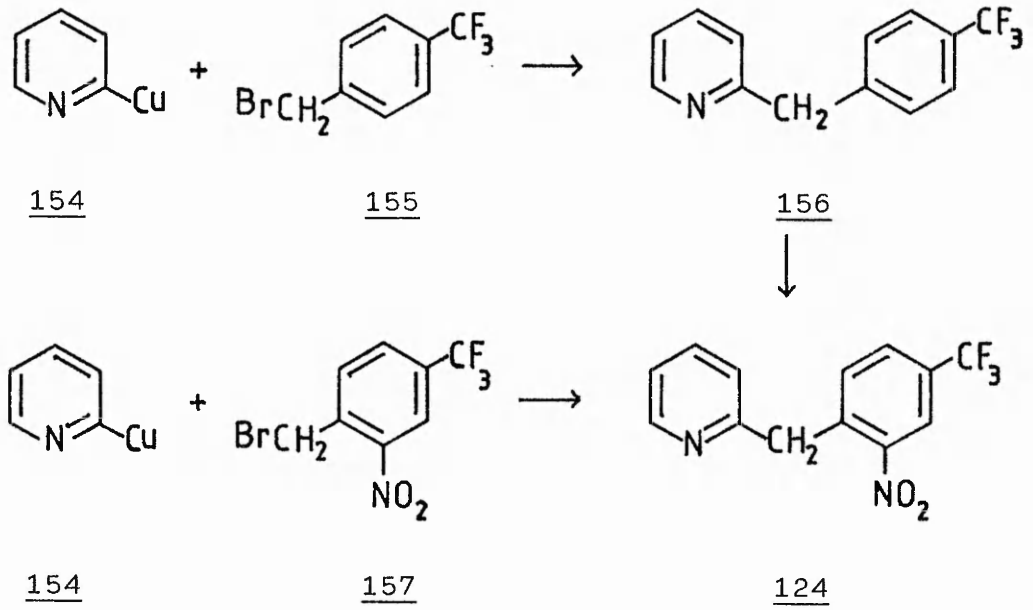
Table 13

% Yields of reactions between a range of halides and the three picolyl-metal derivatives.

appears also that the less basic picolylcopper intermediates are more effective in displacing halogen from the activated benzene nucleus than picolyllithium.

The final conclusion, reluctantly, is that the target molecule 124 cannot be prepared by the "simple nucleophilic substitution reaction" - route A - envisaged at the outset.

Perhaps encouragement may be drawn from the results obtained thus far for investigating the reactions between pyridylcopper and benzyl bromides such as those shown in Scheme 14. These ideas were never tested because,



154 155 156

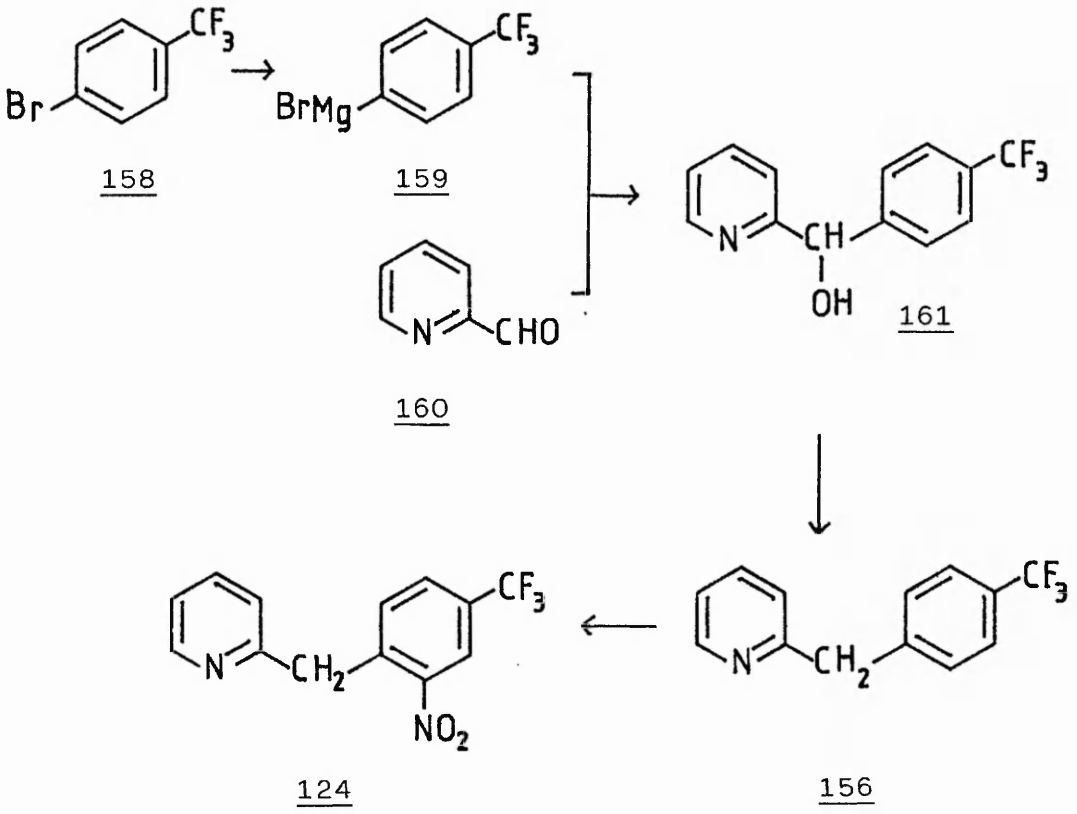
154 157 124

Scheme 14

concurrently with the above work, information derived from further searches of the literature suggested an alternative strategy via Grignard reagents.

4.3.2 Syntheses via Grignard reagents

The new pathway to 2-(2'-nitro-4'-trifluoromethylbenzyl) pyridine 124, outlined in Scheme 15, adopts the nucleophilic addition reaction of a Grignard reagent in contrast to the

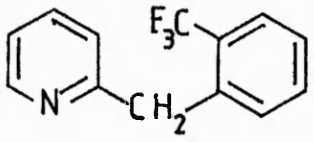


Scheme 15

nucleophilic substitution approach of route A. Reaction of the Grignard 159 and pyridine-2-carboxaldehyde 160 produced the carbinol 161 which was reduced via the halide (zinc/acetic acid). Nitration of 156 with a mixture of fuming nitric acid and concentrated sulphuric acid successfully

gave - at last - the target molecule 124, an orange-yellow liquid, in overall yield, based on 4-trifluoromethylbromobenzene 158, of 35%.

The same sequence, starting with the isomer 2-trifluoromethylbromobenzene, should give 162. It was anticipated that conditions could be found to dinitrate this to form 163, a molecule with clear potential for



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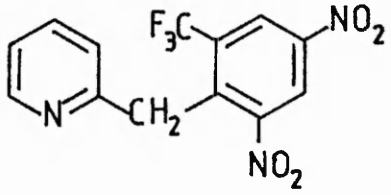

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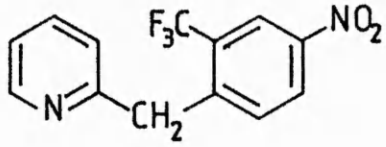


164

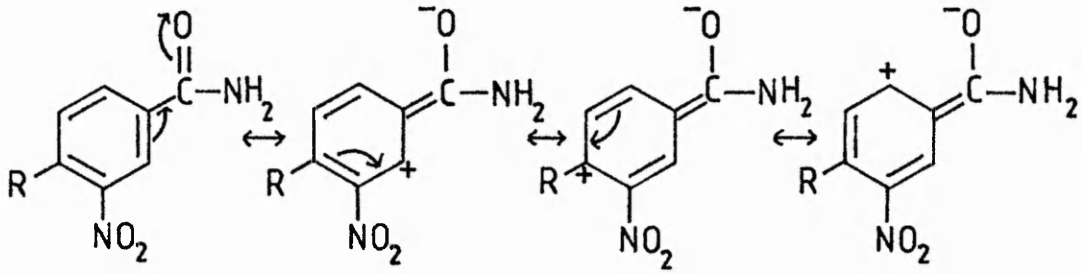
photochromicity, having nitro-groups in both the 2- and 4-positions of the benzene ring. Compound 163 should reveal something of the influence of the relatively bulky electron-withdrawing CF_3-group adjacent to the methylene bridge on photochromic behaviour. Compound 162 was obtained in 22% overall yield using the Grignard route, but attempts to nitrate 162 with fuming nitric acid produced only the mono-nitro-derivative 164. (Shortage of time precluded further investigation of the nitration reaction).

4.3.3 Properties of the nitrotrifluoromethylbenzylpyridine isomers 124 and 164

Ultraviolet irradiation of 2-(2'-nitro-4'-trifluoromethylbenzyl)pyridine 124 held as a solid by immersion in an ice/water mixture failed to cause any colour change observable by the naked eye. Similar irradiation of a thin film of the liquid 124 produced no change in the infrared spectrum. Absorption spectra were recorded for ethanolic solutions of 124 at room temperature and at low temperatures, before exposure to ultraviolet radiation and after exposure. In all cases there were absorptions at λ_{max} $211^{\pm}1$ nm and $255^{\pm}1$ nm with ε_{max} 19,600 and 7,680 respectively. No new peaks appeared in the spectra on irradiation. Compound 124 does not possess photochromic properties under the conditions investigated. The isomer, 2-(4'-nitro-2'-trifluoromethylbenzyl)pyridine 164, examined in a similar way also showed no photochromic properties.

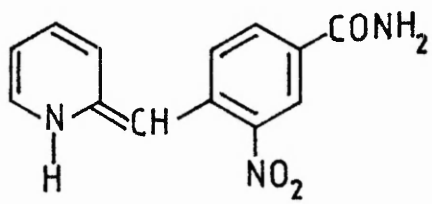
The absence of photochromism in 124 was unexpected (and disappointing). As stated at the outset, it is known that 5 compounds of the form 2-(2'-nitro-4'-substituent-benzyl)-pyridine are photochromic in the solid state at room temperature, and for each of these, the 4'-substituent has a value for the Hammett σ_p constant which is greater than +0.36 viz. $CONH_2$, 0.36; CO_2CH_3, 0.46; $CO_2CH_2CH_3$, 0.52; CN, 0.63; NO_2, 0.78. For the trifluoromethyl-group, σ_p = +0.53, and hence if the initial hypothesis were correct then it would have been anticipated that compound 124 should be photochromic. In the event, this proved not to be the case. A tentative

conclusion from this study must therefore be that the mechanism by which electronic charge is withdrawn by the 4'-substituent may be an all-important factor. The five "active" substituents possess π-bonds and are capable of mesomeric interaction with the π-electrons of the benzene ring leading to a number of resonance structures, shown for the substituent $CONH_2$, 165 to 168,



165 166 167 168

and thus helping to stabilise the tautomers 169 and 170:-



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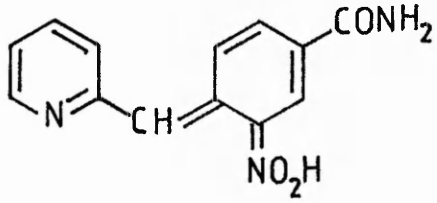


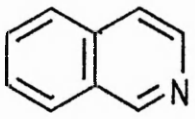
170

Although fluorine has the highest electronegativity value of all the elements, causing the CF_3-substituent to exert a very strong -I effect, the absence of activity would imply that this mechanism of electron withdrawal from the benzene ring is not relevant to the photochromic process.

That the isomer 164 is not photochromic is less unexpected because no photochromic benzylpyridine derivative without a 2'-nitro-group has to date been reported in the literature.

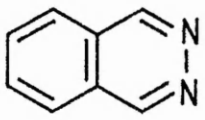
4.4 Pyrazine derivatives

Following Tschitschibabin's discovery that 2-(2',4'-dinitrobenzyl)pyridine 27 is photochromic in the solid state, a number of compounds have been synthesised in which the dinitrobenzyl moiety is attached to a N-heterocycle, for instance, quinoline and benzimidazole (see page 39). Consideration was given by this author to looking at the properties of compounds produced by attaching the 2,4-dinitrobenzyl group to heterocyclic systems such as those shown below 171 to 176. In particular, the photo-



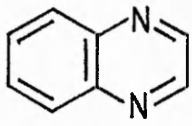
171

isoquinoline



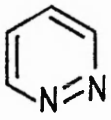
172

phthalazine



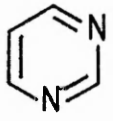
173

quinoxaline



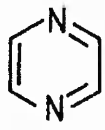
174

pyridazine



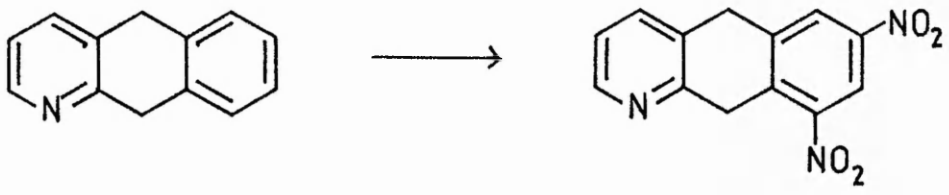
175

pyrimidine



176

pyrazine

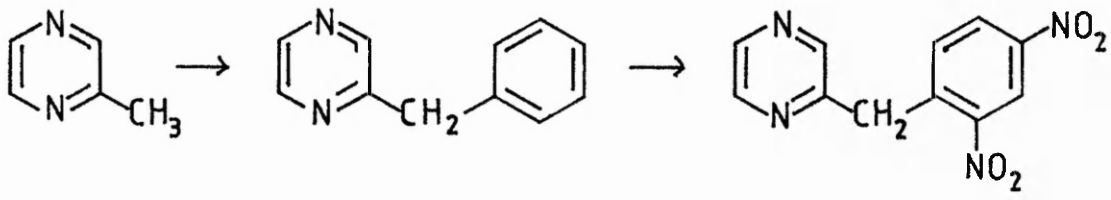


177 178

5,10-dihydrobenzo[g]quinoline

chromicity (or not) of 178 could shed light on the importance of molecular geometry to the photochromic process and would be of interest. The increased rigidity of 178 over DNBP 27 may decrease the ease of any hydrogen-transfer from the α-methylene bridge and thus affect formation of the N-H quinoid tautomeric form.

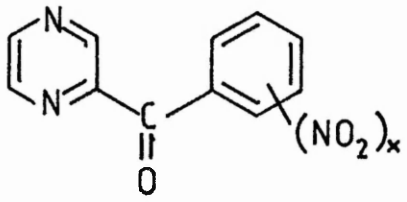
In the event, constraints of time allowed only preliminary investigations into the synthesis of 2,4-dinitrobenzylpyrazine 181. The route adopted is shown in Scheme 16. Methylpyrazine 179 was reacted with sodium amide



179 180 181

Scheme 16

and bromobenzene in liquid ammonia producing benzylpyrazine 180 in 51% yield (lit. 52.5%).[123] Attempts to nitrate benzylpyrazine with fuming nitric acid/concentrated sulphuric acid invariably produced 6-component mixtures. On two occasions, partial resolution of these by flash chromatography gave 2-component mixtures for which ^{13}C NMR spectra and infrared spectra were recorded. There was evidence in these spectra to suggest that both oxidation and nitration had occurred. A likely constituent of the mixture is 182, the pyrazine methylene being susceptible to oxidation and nitration occurring in the more reactive ring. Nitration of

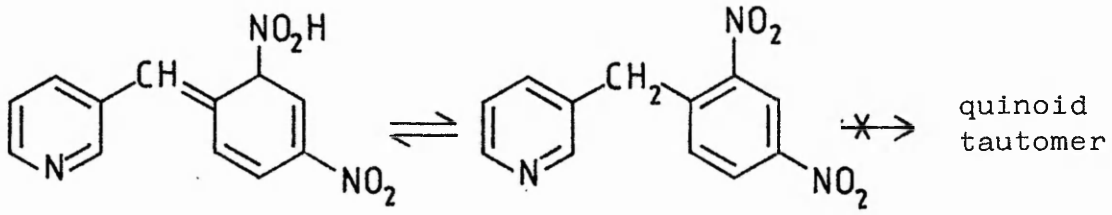


182

benzylpyrazine with nitric acid in acetic anhydride[125] was no more successful, producing a 7-component reaction mixture, including starting material. No further attempts were made to obtain 2,4-dinitrobenzylpyrazine 181.

4.5 3-Pyridine derivatives

When H-transfer processes are induced in 2-(2',4'-dinitrobenzyl)pyridine 27 by ultraviolet radiation, two species are produced, the aci-nitro acid 26 and the N-H quinoid 28, both of which are extensively conjugated, this lending a degree of stability in each case. However, if H-transfer is to occur in 3-(2',4'-dinitrobenzyl)pyridine 184, only one species, the aci-nitro acid form 183 can be produced, there being no 'reasonable' N-H quinoid form. In the absence of an N-H quinoid tautomer, the species which,



183 184

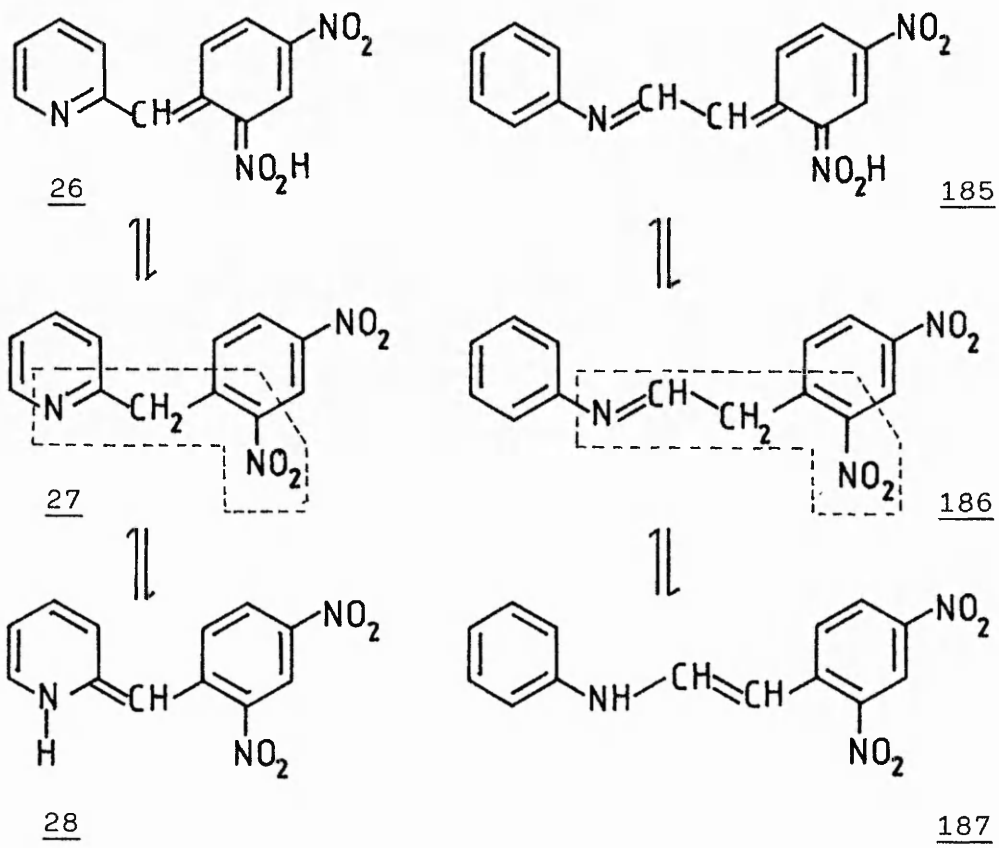
according to Sixl and Warta[61] accounts for the deep-blue colour of irradiated crystalline 2-DNBP 27, it seems unlikely that 3-DNBP 184 will display photochromic properties. Surprisingly this does not appear to have been checked in the literature. Hence the synthesis of 3-(2',4'-dinitrobenzyl)-pyridine 184 was undertaken. Nitration of 3-benzylpyridine under the conditions described for nitrating 2-benzylpyridine (see page 151) gave 3-(2',4'-dinitrobenzyl)pyridine in 44% yield as a pale yellow liquid.

Ultraviolet irradiation of this liquid and of the solid produced by cooling the sample in a dry ice/acetone mixture produced no visible change in the compound. Similarly, absorption spectra of ethanolic solutions of 3-DNBP 184, at room temperature and at -70° to -75°C, were unaffected by exposure of the solutions to the ultraviolet source. Hence this would appear to confirm Sixl and Warta's conclusion that it is indeed the formation of the N-H quinoid tautomer that is solely responsible for causing a shift in the absorption of radiation of the 2-substituted pyridines into the visible region of the spectrum.

4.6 Imines-enamines

Over a period of some 60 years, it had been established that the photochromism associated with 2-(2',4'-dinitrobenzyl)pyridine 27 was due to one or other or both of two contributing H-transfer processes according to state (solid or solution) and temperature - namely formation of aci-nitro acid or N-H quinoid species. This indeed appeared also to be the case with 2-(2',4'-dinitrobenzyl)-benzimidazole 58, 2-(2',4'-dinitrobenzyl)benzothiazole 59, 2-(2',4'-dinitrobenzyl)benzoxazole 60 among other dinitrobenzyl-aromatic compounds. In all these examples, the nitrogen atom present with the potential for N-H quinoid formation has always been in an aromatic environment. It seemed of interest to investigate whether hydrogen-transfer may also occur from the CH_2 of the dinitrobenzyl moiety to a nitrogen atom at the same bond distance from CH_2 as in

DNBP 27 but no longer part of an aromatic ring, in short, to synthesise the imine 186, Scheme 17. It may be seen from 27 and 186 that, superficially, the bond linkage $N{=}C{-}CH_2{-}C{=}C{-}NO_2$ is common to both structures. Thus for structure 186, H-transfer may, in theory, occur to produce



Scheme 17

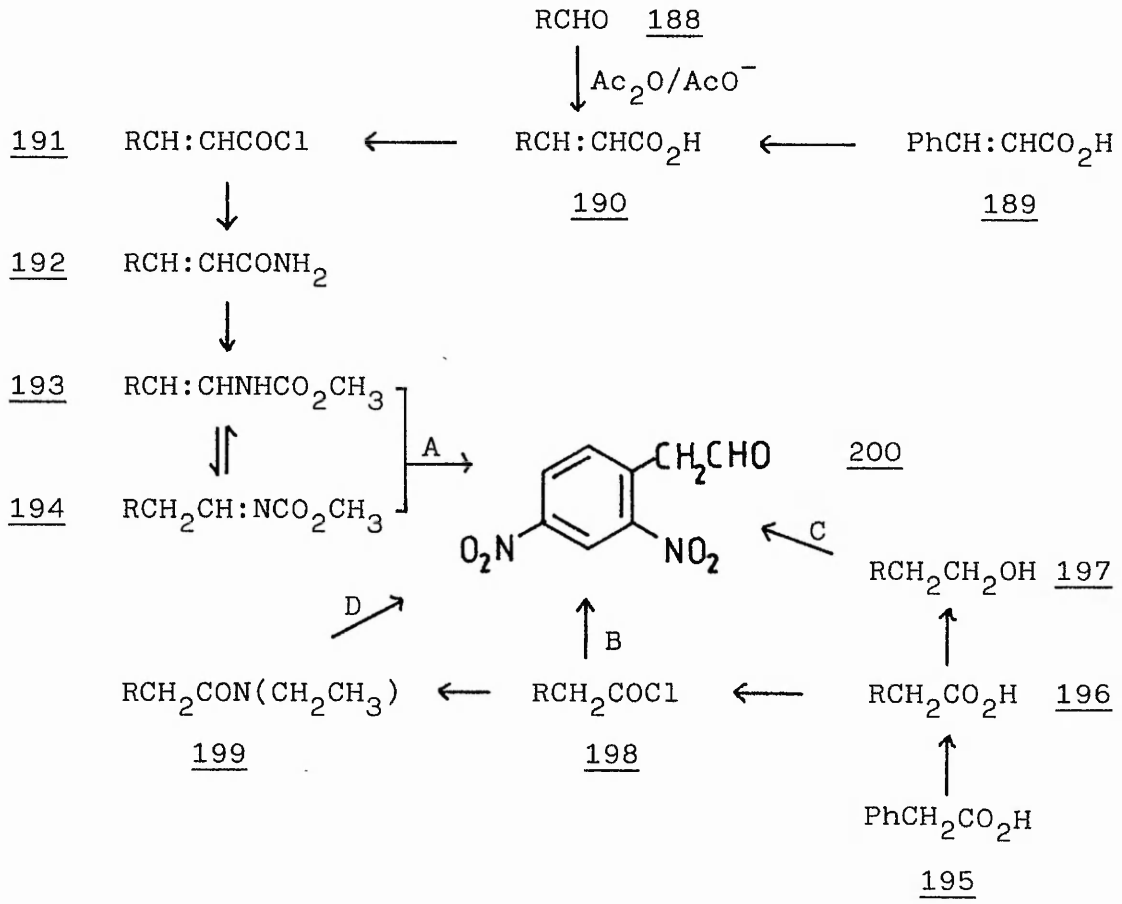
either the aci-nitro acid 185 or the enamine 187. It must however be borne in mind when comparing structures 28 and 187 that although they are superficially similar the latter contains a less extensively conjugated system, and the basic

characters of the respective N-atoms are almost certainly different, and these may be critical factors.

The most obvious route to 186 seemed to be a condensation reaction between 2,4-dinitrophenylacetaldehyde 200 and aniline. Surprisingly, the former compound had not previously been reported in the literature.

4.6.1 Synthesis of 2,4-dinitrophenylacetaldehyde

The synthesis of 2,4-dinitrophenylacetaldehyde proved unexpectedly difficult and a number of schemes were devised. Four of the envisaged pathways are shown in Scheme 18 and a further five in Scheme 20. Route A had been used by Weerman[126-128] to synthesise 2-nitrophenylacetaldehyde and



Scheme 18

hence was thought appropriate for the synthesis of the dinitro-derivative. Rather than carry out a Perkin condensation reaction on the somewhat expensive 2,4-dinitrobenzaldehyde, attempts were made to nitrate cinnamic acid. The reagents and conditions used are set out in Table 14. After reaction, the mixtures were poured onto ice and extracted with ether. If,

Entry	Reagent	Conditions
1	fuming HNO_3	60 min., reflux
2	fuming HNO_3	45 min., reflux
3	fuming HNO_3	30 min., reflux
4	fuming HNO_3	5 min., reflux
5	Conc. HNO_3, Conc. H_2SO_4	1 hr., $0^oC \longrightarrow 4\text{-}O_2NC_6H_4CHO$
6	Conc. HNO_3, Ac_2O	1 hr., 0^oC
7	KNO_3, Conc. H_2SO_4	1 hr., 50^oC
8	KNO_3, Conc. H_2SO_4	1 hr., 20^oC
9	KNO_3, Conc. H_2SO_4	1 hr., 0^oC

Table 14

Reagents and conditions used in attempts to nitrate cinnamic acid.

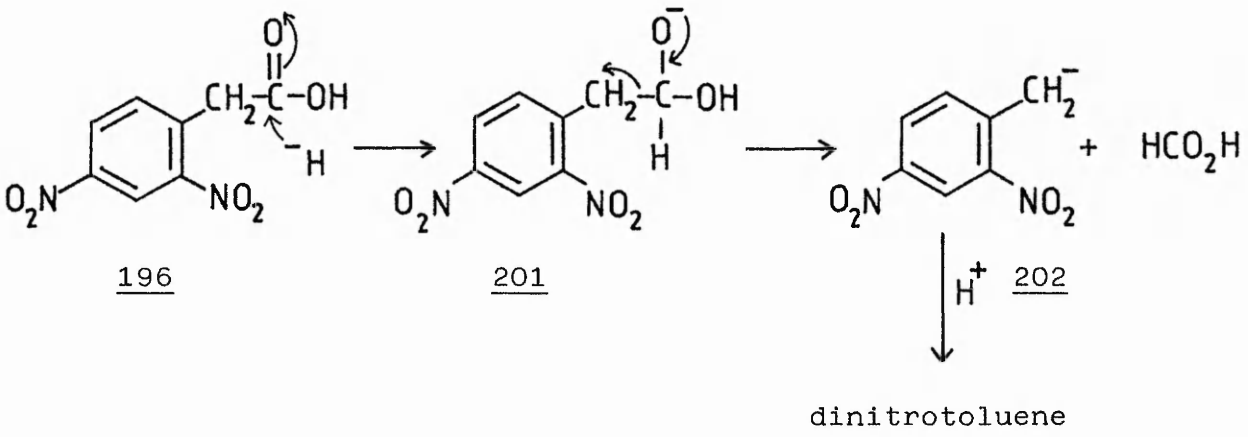
in the ^1H NMR spectra of the crude products, there were no signals indicating the presence of the side chain ethylenic protons, the products were discarded. On one occasion, entry 5 in Table 14, a product was purified, and characterised as 4-nitrobenzaldehyde (15%). Thus nitration of the ring had been accompanied by oxidation of the side chain. On no occasion was 2,4-dinitrocinnamic acid obtained. Thus pathway A in Scheme 18 was doomed at step 1.

Of the remaining routes outlined in Scheme 18, pathway B seemed to be the most direct. The first step, dinitration of phenylacetic acid 195 was accomplished easily (and frequently) with yields of 60 - 64%, and the conversion of acid 196 to acyl chloride 198 was achieved by heating the acid under reflux with excess thionyl chloride. The reduction of acyl chloride 198 to aldehyde 200 was attempted with sodium borohydride/$CdCl_2$.1.5DMF, a reagent which Johnstone and Telford[129] had used successfully in reducing a range of acid chlorides to aldehydes including 4-nitrobenzoyl chloride and phenylacetyl chloride. The reaction was attempted four times on scales ranging from 6.6 to 42 mmol of acyl chloride 198 but no aldehydic material was ever isolated. The presence of the nitro-groups in the benzene ring increases the acidity of the methylene protons which in turn, presumably, decreases the susceptibility of the acyl chloride group to reduction.

Brown and McFarlin[130] had used lithium tri-tertiary-butoxyaluminohydride (LTBA) in diglyme at -78°C to reduce 4-nitrobenzoyl chloride to 4-nitrobenzaldehyde in 80% yield. The net result of using LTBA to reduce the acid chloride 198 was a 7-component reaction mixture from which no aldehyde could be isolated. Pearl[131] used the same reagent in tetrahydrofuran at room temperature, but under these conditions dinitrophenylacetyl chloride was not reduced to the aldehyde. Thus route B of Scheme 18 was abandoned.

Consideration was now given to pathway C. In trial experiments, using sodium borohydride in the presence of anhydrous aluminium chloride,[132] phenylacetic acid was reduced to 2-phenylethanol in 60% yield and 4-nitrobenzoic acid to

4-nitrobenzyl alcohol in 70% yield. With 2,4-dinitrophenylacetic acid as starting material, however, only a trace of 2-(2',4'-dinitrophenyl)ethanol 197 was obtained, together with a 10% (isolated) yield of 2,4-dinitrotoluene. The origin of this product is obscure. Presumably, the distribution of charge at the methylene group is affected by the electron-withdrawing nitro-groups, such that, at some stage of the reduction, intermediate 202 is produced, which, when protonated, generates 2,4-dinitrotoluene.



Scheme 19

In further trials, this time with borane-methylsulphide,[133] both phenylacetic acid and 4-nitrobenzoic acid were reduced to the corresponding primary alcohol in yields in excess of 98%. This time similar yields were obtained with 2,4-dinitrophenylacetic acid also, not only on the 10 mmol scale (the quantity used in the initial trial) but also when the reaction was scaled up by a factor of 6.

Now a reliable route to 2-(2',4'-dinitrophenyl)ethanol 197 had been established, there remained only the minor problem of oxidation of the primary alcohol to the aldehyde 200. Some 37 experiments later, the 'minor problem' remained unsolved.

Pyridinium chlorochromate (PCC)[134] was a favourite reagent with senior members of the laboratory and the first to be tested in this situation. Benzyl alcohol and phenethyl alcohol were oxidised by PCC to the corresponding aldehyde in yields of 89% in each case (but 2-phenoxyethanol yielded 50% of the ester, $PhOCH_2CO_2CH_2CH_2OPh$, indicating that the precaution of buffering the reaction mixture may be required to prevent over-oxidation of the alcohol to the acid). However, in 7 attempts to oxidise 2-(2',4'-dinitrophenyl)ethanol 197 no dinitrophenylacetaldehyde was ever isolated. On a 1 or 2g scale, with equimolar quantities of reagents or 50% excess of PCC, in air or under nitrogen, buffered or not, with reaction times of 30 minutes or 120 minutes, no dinitrophenylacetaldehyde was obtained. Consistently, t.l.c. indicated a 4-component reaction mixture. Using flash chromatography, it proved only ever possible to isolate the component with the greatest R_f value. This product was shown by infrared and proton NMR spectral analysis to be 2,4-dinitrobenzaldehyde (about 12%).

The seven further oxidising agents tested in an attempt to oxidise the primary alcohol 197 to dinitrophenylacetaldehyde 200 are listed in Table 15. In no case was the required aldehyde isolated. In a number of these attempts,

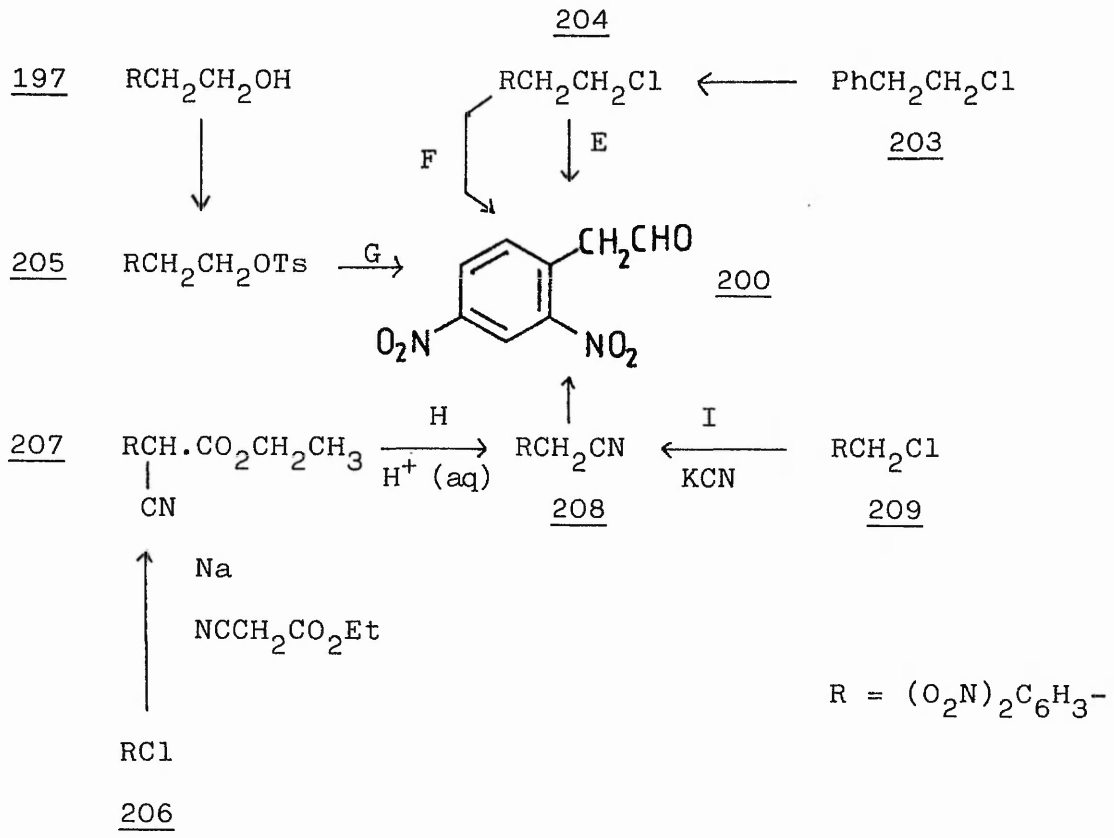
Author	Reagent	Reference
Cainelli	chromic acid on resin	135
Singh	quinolinium chlorochromate	136
Corey	pyridinium dichromate	137
Fétizon	silver carbonate	138
Doyle	bromine/nickel benzoate	139
Pfitzner	dicyclohexylcarbodiimide/dimethyl sulphoxide	140
Mancuso	oxalyl chloride/dimethyl sulphoxide	141

Table 15

List of reagents used in the attempt to oxidise 2-(2',4'-dinitrophenyl)ethanol to 2,4-dinitrophenylacetaldehyde.

there was occasionally observed on the t.l.c. slide a mauve-coloured spot with R_f=0.40 (silica, ethyl acetate/light petroleum 1:1). 2,4-Dinitrophenylacetaldehyde, when eventually synthesised, was observed to give a similarly mauve-coloured spot with identical R_f value. It would seem that the target aldehyde was produced in trace amounts in some of the reactions outlined above.

Concurrently with the above work, investigations of other synthetic pathways to the required aldehyde 200 were being carried out, as outlined in Scheme 20.



Scheme 20

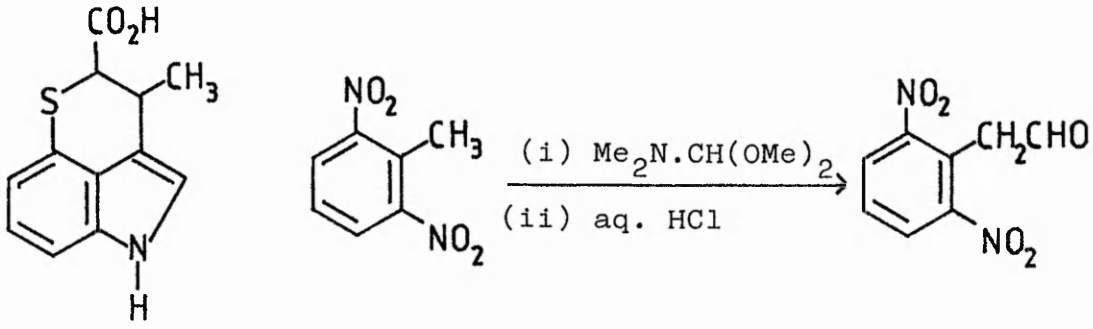
In the Sommelet reaction, a halide is treated with hexamethylenetetramine (HMTA) and the resulting salt hydrolysed in the presence of excess HMTA, usually with aqueous acetic acid, to the aldehyde. In a trial reaction 4-nitrobenzyl chloride gave 4-nitrobenzaldehyde in 30% yield (lit. 63%[111b]) but phenethyl chloride 203 did not react with HMTA. Thus route E was considered unlikely to be successful.

In the Kornblum reaction,[142] oxidation of the tosyl derivative of an alcohol to the corresponding aldehyde can be brought about using dimethyl sulphoxide. This was not successful when tried with 2-(2',4'-dinitrophenyl)ethanol however. In a modified Kornblum reaction,[143] the halide, not the alcohol, is oxidised with dimethyl sulphoxide in the presence of sodium bicarbonate and sodium iodide. In a trial reaction with phenethyl chloride, no aldehydic material was obtained. Thus routes G and F were abandoned.

The number of options was dwindling! The nitrile 208 had been synthesised by both of the routes H and I, Scheme 20. In the final step, it was proposed to attempt the reduction of the nitrile 208, via the imine, either by Stephen's method [144,145] (using tin (II) chloride/hydrogen chloride) or by using triethylsilane, as reported by Fry and Ott.[146] However, these reactions were never tried owing to the developments described in the next paragraph. For the same reason, the route to the target aldehyde 200 via the amide 199, D Scheme 18, remained untested.

Because the synthesis of 2,4-dinitrophenylacetaldehyde 200 was proving so unexpectedly difficult, an exhaustive investigation of the literature was undertaken. This revealed, in a paper[147] reporting the synthesis of an antibiotic indole 210, a method for converting 2,6-dinitrotoluene 211 to

2,6-dinitrophenylacetaldehyde 212, Scheme 21.



210 211 212

Scheme 21

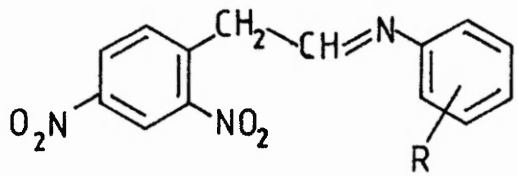
Therefore it was decided to see whether synthesis of the aldehyde 200 could be achieved in an analogous manner starting with 2,4-dinitrotoluene. The latter was treated with dimethylformamidedimethylacetal in dimethylformamide and the intermediate condensation product hydrolysed by hydrochloric acid. Extraction with ether and purification by flash chromatography yielded (at last!) 2,4-dinitrophenylacetaldehyde (1.14g, 15%) as an orange-brown solid.

The aldehyde was characterised by infrared, ^{1}H and ^{13}C NMR spectroscopy and the microanalysis of stable derivatives (see page 137). In the interpretation of the mass spectrum, it is of interest to note a comment made by Harley - Mason et al.,[148] viz., "Some of the reactions occurring upon electron impact seem to bear a definite analogy to photochemical reactions which may be induced in nitro-compounds." In

dinitrobenzylpyridine 27, ultraviolet irradiation causes H-transfer, forming the aci-nitro acid, and in the mass spectrum for DNBP 27, a signal at m/e 242 may be interpreted as the species produced by loss of OH from the aci-nitro tautomer. In the same way, the mass spectrum for the aldehyde 200 can be interpreted on the assumption that H-transfer occurs on electron impact similarly to form the aci-nitro acid. After this has occurred, loss of CO produces an ion with m/e 182 (6%) followed by loss of OH to produce an ion with m/e 165 (64%), the second largest peak in the spectrum. The whole scheme is shown in Appendix 3.

4.6.2 Preparation and properties of the imines-enamines

The aldehyde 200 was condensed with aniline and with the three toluidines by mixing warm ethanolic solutions of both components. The imines 213 to 216 crystallised very readily and on each occasion only one product was indicated



213, R=H

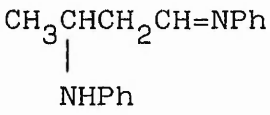
214, R=2-CH_3

215, R=3-CH_3

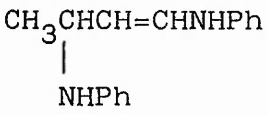
216, R=4-CH_3

by t.l.c. which contrasts sharply with the condensation reactions between acetaldehyde and aniline and between phenylacetaldehyde and aniline. In the former reaction, the initially formed "simple imine", $CH_3CH{=}NPh$ readily

undergoes aldol-type condensation reactions producing dimers,[149-151] e.g. 217 and 218, trimers and polymers.[152] Other aldehydes, including phenylacetaldehyde, give

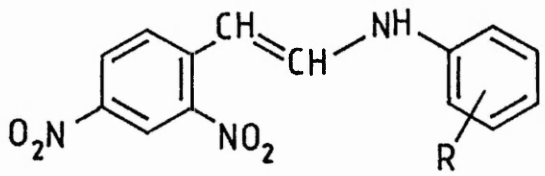


217



218

similar dimers.[149-154] It is fortunate in the present work that the aldol-type dimerisation is inhibited almost certainly because the nitro-groups in the benzene ring stabilise the enamine tautomer 219.



219

The four imines 213 to 216 were obtained as very dark-red crystalline solids. When they were exposed to ultraviolet radiation, there was no colour change detectable by eye. Samples of the imines 213 to 216 in the form of potassium bromide discs were irradiated by ultraviolet light, but no changes could be detected in the infrared spectra. The absorption spectra for ethanolic solutions of these imines were recorded at room temperature and at low temperatures (-70° to -75°C), before exposure to ultraviolet radiation

and after exposure. No compound displayed thermochromism, as confirmed by the data in Table 16 for the parent imine 213. There were slight bathochromic shifts in λ_{max} values circa 209 nm - see Table 17. The most significant feature in these data is the total disappearance after irradiation of the absorption at 470 - 481 nm. This absorption signal did not reappear when the sample was allowed to warm to room temperature or on standing in the dark for a period of weeks. Thus it would seem that these compounds are not photochromic. In 'removing' the N-atom from an aromatic environment and 'placing' it in an 'aliphatic-type' environment, the property of photochromism has been lost.

The permanent disappearance of the absorption signal at λ_{max} = 470 - 481 nm must arise through decomposition reactions of the imine, presumably involving solvolysis also. An attempt was made to analyse the kinetics of the irradiation reaction of the parent imine 213, in which the colour of the ethanolic solution was bleached. Samples of solutions of the imine were irradiated at room temperature for periods of time varying from 0 to 10 minutes. For each sample, after the appropriate period of exposure to ultraviolet light, the UV-visible spectrum was obtained. When superimposed, these spectra indicated two isosbestic points (at λ = 317 nm and λ = 369 nm), suggesting an equilibrium mixture was being produced. The absorbance values for the peak at $\lambda = 477 \pm 2$ nm were monitored; the results are recorded in Appendix 4. However, graphical analyses of these results (Appendices 5,6) to determine the order of the reaction were inconclusive owing to the large degree of scatter in the experimental plots,

Compound 213

	λ_{max}/nm		
Room temperature	207±0.5	261±2	480±1
-70°C to -75°C	208.5±0.5	259±3	479±2

Table 16

UV-visible spectral data for the parent imine 213 in ethanol solution at room temperature and low temperature.

	213, parent	214, 2-CH_3	215, 3-CH_3	216, 4-CH_3
	208.5±0.5	209.0±0.5	211.0±0.5	209.0±0.5
A	259 ±3	258 ±3	257 ±3	253 ±3
	479 ±2	470 ±2	481 ±2	481 ±2
	214.5±0.5	215 ±0.5	217 ±1	218.0±0.5
B	254 ±3	258 ±3	253 ±3	250 ±3
	-	-	-	-
	210.0±0.5	212.5±0.5	212.0±0.5	213.0±0.5
C	247 ±2	250 ±2	249 ±2	247 ±2
	-	-	-	-

Table 17

UV-visible spectral data for ethanolic solutions of the four imines 213 to 216

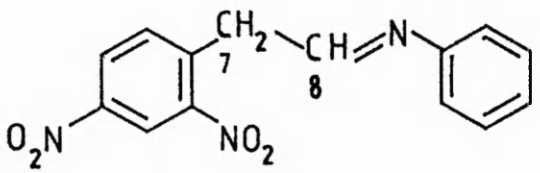
A - temperature -70° to -75°C, unirradiated

B - temperature -70° to -75°C, irradiated for 5 minutes

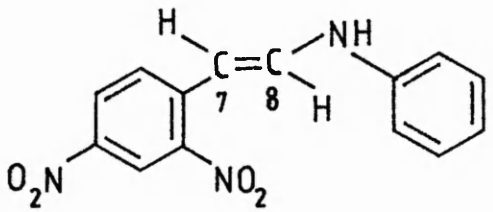
C - sample B having been allowed to warm to room temperature.

probably because it was not possible to maintain adequate temperature control of the samples during the period of irradiation.

The original intention had been to synthesise the imine 213, with a view to investigating the possibility of ultraviolet-induced H-transfer to produce the enamine 220.



213, imine



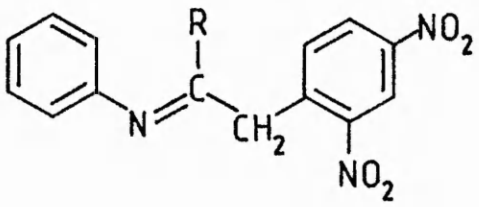
220, enamine

However, the balance of the spectral evidence accumulated, relating to the structure of this compound in solution suggests that the enamine is the more stable form. The evidence for the solid state is ambiguous. ^{1}H and ^{13}C nuclear magnetic resonance spectra were obtained for solutions of 213 in dimethyl sulphoxide. In the ^{1}H spectrum, there occur a singlet at δ = 10.05 (integrating for one hydrogen, relative to all other signals in the spectrum, and D_2O exchangeable) indicating N-H, and doublets centred on δ = 8.31 and 6.49 (each integrating for one hydrogen) with coupling constant J = 13.1 Hz, indicative of trans geometry in the enamine tautomer. Similarly, in the ^{13}C spectrum, signals at ~ 139 and at 94.21 ppm correspond with C_7 and C_8 of the enamine. These data suggest that the

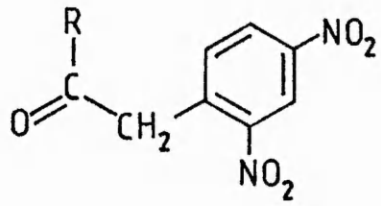
compound in solution in dimethyl sulphoxide exists entirely in the enamine form. There are no signals suggestive of the imine tautomer. In the infrared spectrum (KBr disc), a medium strength signal at 3330 cm^{-1} indicates the N-H stretching of an enamine although the signals at 1640 and 1630 cm^{-1} could be due to either C=C or C=N stretching. In the mass spectrum, there occur significant peaks at m/e = 165 (12%) and m/e = 104 (100%). These may readily be accounted for in terms of the imine tautomer fragmenting, the former peak by H-transfer (as occurred in the spectrum of 2,4-dinitrophenylacetaldehyde, see page 111) and loss of a PhNC fragment, and the latter by scission of the C_7-C_8 bond. The full analysis is reported in Appendix 7.

4.6.3 Ketimines

Imines derived by the condensation of ketones with amines are referred to as ketimines, e.g. 221, R=CH_3,Ph. When it looked as though the preparation of the aldehyde 200



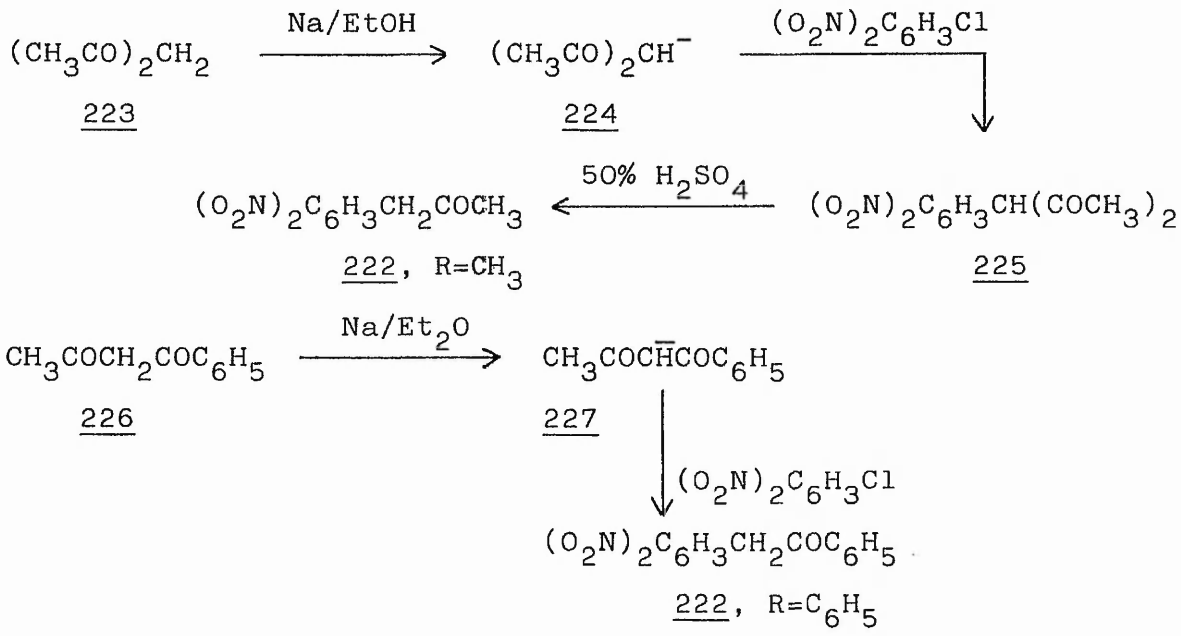
221 a,R=CH_3; b,R=Ph



222 a,R=CH_3; b,R=Ph

might prove unsuccessful, two ketones 222 R=CH_3,Ph were synthesised in the expectation of condensing each of them with aniline to form the corresponding ketimines 221,

R=CH_3 and C_6H_5. The ketones 222, R=CH_3 and C_6H_5, were obtained by similar routes,[166,167] starting with acetylacetone and benzoylacetone respectively, as outlined in Scheme 22.



Scheme 22

The condensation reactions between ketones 222, R= CH_3, C_6H_5, and aniline were attempted in a range of solvents [155] (benzene, toluene, xylene), with equimolar quantities of reagents and also with a large excess of aniline,[156] without catalyst and with catalysts (toluene sulphonic acid, zinc chloride),[157] but on no occasion was a ketimine isolated. In most cases, t.l.c. of the reaction mixture indicated only the starting materials. Occasionally, a third component was indicated but it never proved possible to isolate it. The absence of reaction may be attributable to two causes. Firstly, the

presence of the nitro-groups may, by mesomerically withdrawing electron-charge from the methylene group, cause the equilibrium between ketone and enol to lie in favour of the enol. Secondly, there is likely to be steric hindrance due to the presence of the bulky dinitrophenyl-group obstructing the approach of the similarly bulky aniline molecule.

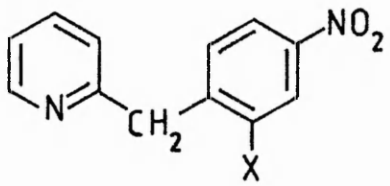
4.7 Summary

In Section 4, the author has described his investigations into a number of factors which may have a bearing on the photochromism of 2-(2',4'-dinitrobenzyl)pyridine, 27. The principal conclusions to be drawn from this work are as follows:-

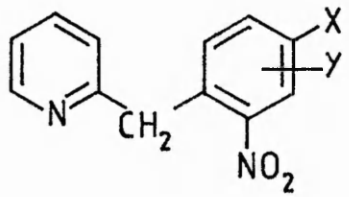
1. Increasing the extent of the delocalised-electron system associated with DNBP 27 (via an azo-linkage or by imine-formation at $C_{4'}$) produced coloured compounds which are not photochromic.
2. Introducing a second potentially photochromic centre, by imine-formation at $C_{4'}$ with salicylaldehyde, failed to produce a photochromic compound.
3. Introducing the CF_3-group into the $C_{4'}$-position did not produce a photochromic product. The isomer 164 obtained by interchanging the CF_3- and NO_2- groups was similarly devoid of photochromic properties.
4. 3-(2',4'-Dinitrobenzyl)pyridine is not photochromic.
5. The superficially analogous compound 213 in which the dinitrobenzyl-group was attached via a methine bridge to nitrogen was non-photochromic.

Finally, there emerges the general point that the presence of two nitro-groups in a benzene ring seems to impart a distinctive chemistry.

Ultraviolet irradiation of DNBP 27 in the solid state at room temperature causes the colour change from white to deep-blue, due, according to Sixl and Warta,[61] to the formation of the N-H quinoid 28. But precisely what part in this process do the two nitro-groups play? The presence of the 2'-nitro-group appears to be essential, in that no benzylpyridine derivative without a nitro-group in the 2'-position has been reported in the literature to be photochromic. The 4'-nitro-group, however, is not an essential feature, since if it is replaced by $CONH_2$, CO_2CH_3, $CO_2CH_2CH_3$ or CN, the compounds so produced are photochromic. These groups are all strongly electron-withdrawing, but the current work has established that replacement of 4'-nitro by 4'-CF_3 produces a compound which is not photochromic. It is suggested that these differences in behaviour are due to the different modes of electron-withdrawal - mesomeric interaction with groups like $CONH_2$ but only electron-withdrawal via the sigma-framework in the case of the CF_3-group. It would therefore be of interest to determine if photochromic properties were associated with the isomers 228,a-d.



228



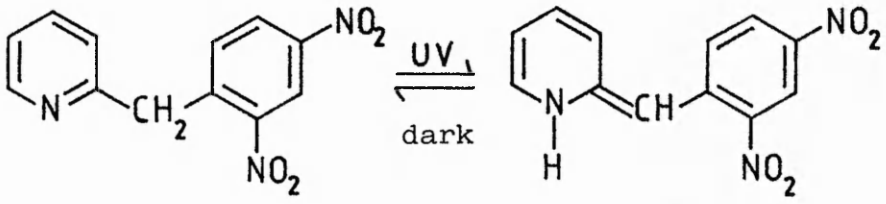
229

a-d, X = $CONH_2$, CO_2CH_3, $CO_2CH_2CH_3$, CN

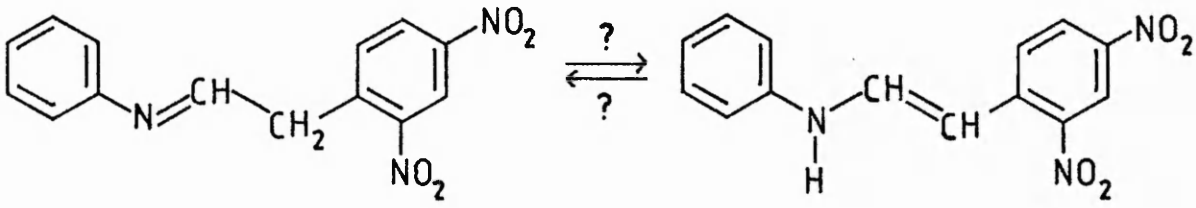
It was hoped that compounds of the type 229, X= $N{=}N{-}C_6H_4{-}OH$, Y=H or X= $N{=}N{-}C_6H_4{-}N(CH_3)_2$, Y=H, would be photochromic — but they were not. Whether this is to do with weak electron-withdrawing power or the bulkiness of the X-substituent is not clear. The presence of such large groups may influence the geometry of the CH_2-group in the molecule in the solid state, thus possibly increasing the inter-atomic distance between the N-atom of the pyridine ring and the nearer H-atom of the methylene-group. Such a change, if it occurs, is likely to inhibit H-transfer from the methylene bridge to the N-atom. Klemm reported[56] that compound 229, X=NO_2, Y=5'-CH_3, is photochromic in the solid state at room temperature, indicating that an additional substituent in the benzene ring does not necessarily preclude photochromism provided a nitro-group is retained in the 4'-position. It may, therefore, be possible to synthesise compounds 229, X=NO_2, Y= $N{=}N{-}C_6H_4OH$ or $N{=}N{-}C_6H_4{-}N(CH_3)_2$ in which the presence of the two nitro-groups should ensure the retention of photochromic behaviour in the compound and the extended conjugation should lead to a compound which is itself coloured prior to irradiation. Similarly, it would be of interest to introduce into the 4'-position other groups capable of strongly withdrawing electrons via a mesomeric mechanism e.g. SO_2CF_3 (σ_p=0.93), $COCF_3$ (0.80), $COCH_3$ (0.50). A fourth functional group in this category is $N{=}N{-}C_6H_5$ (σ_p=0.64). Unfortunately, when tried in the present investigation, compound 229, X= $N{=}N{-}C_6H_5$, Y=H, was not amenable to synthesis by the

simple condensation reaction between the amine, 229, X=NH_2, Y=H, and nitrosobenzene (C_6H_5.NO).

The anticipated comparison of the effect of ultraviolet irradiation of the two superficially similar compounds 27 and 213, as illustrated in Scheme 23, proved impossible to make because the product of the condensation reaction between 2,4-dinitrophenylacetaldehyde 200 and aniline was not the expected imine 213 but the enamine 219.



27 28



213 219

Scheme 23

Many of the synthetic routes used in this work have involved compounds containing the dinitrophenyl moiety. On a number of occasions, where reactions involved the dinitro-compound, the synthetic conversion failed (Table 18, entries 1b, 2b, 3b). In 4b, the two nitro-groups activated the

methyl-group sufficiently to cause the latter to react with dimethylformamidedimethylacetal, leading to the successful isolation of the novel 2,4-dinitrophenylacetaldehyde 200, whereas reaction of the parent compound failed completely. Likewise, in 5b, the presence of two nitro-groups allowed the formation of the enamine (but not the imine) whereas reaction of phenylacetaldehyde itself failed to give either product. Thus, the electron-withdrawing nitro-groups seem to impart a distinctive nature.

		Yield/%
1a	$C_6H_5CH_2COCl \longrightarrow C_6H_5CH_2CHO$	58[a]
b	di-NO_2	0
	reagent: $NaBH_4/CdCl_2.1.5DMF$	
2a	$C_6H_5CH_2CO_2H \longrightarrow C_6H_5CH_2CH_2OH$	60
b	di-NO_2	trace[b]
	reagent: $NaBH_4/AlCl_3$	
3a	$C_6H_5CH_2CH_2OH \longrightarrow C_6H_5CH_2CHO$	89
b	di-NO_2	trace
	reagent: pyridinium chlorochromate[c]	
4a	$C_6H_5CH_3 \longrightarrow C_6H_5CH_2CHO$	0
b	di-NO_2	15
	reagent: DMFDMA[d]	
5a	$C_6H_5CH_2CHO \longrightarrow C_6H_5CH_2CH{=}NC_6H_5$	0[e]
b	di-NO_2	57[f]
	reagent: $C_6H_5NH_2$	

Table 18

Comparative yields in certain reactions of parent compound and di-nitro-derivative. (a) Reference 129 (b) 10% yield dinitrotoluene (c) inter alia (d) dimethylformamidedimethylacetal (e) many products excluding this imine (f) one product only.

EXPERIMENTAL SECTION

General

Infra-red spectra were recorded using a Perkin Elmer 683 grating spectrophotometer calibrated with polystyrene film. Ultra-violet absorption spectra were determined using a Perkin Elmer 402 u.v.-visible spectrophotometer. Proton magnetic resonance spectroscopy was performed using a Hitachi Perkin Elmer R24B 60 MHz spectrometer or Brüker AM360 with tetramethylsilane as the internal standard. Carbon-13 n.m.r. spectra were recorded on a JOEL JNM FX60Q 60 MHz Fourier Transform spectrometer. Low resolution mass spectrometry was carried out by the Department of Chemistry, Leicester Polytechnic. Elemental analyses were determined by the analytical section of Nottingham University. Melting points were measured in degrees centigrade using open capilliaries in an electrically heated Gallenkamp melting point apparatus and are uncorrected. Flash chromatography was carried out using Merck Kieselgel 60 (230-400 mesh). All solvents for chromatography were redistilled. Ether and toluene were dried over sodium wire, tetrahydrofuran over calcium hydride. Other solvents were dried using 5A molecular sieves. Light petroleum used had b.p. 60 - 80^{o}C unless otherwise stated.

Preparation of 2-(2',4'-dinitrobenzyl)pyridine 27.

2-Benzylpyridine (13.0g, 0.77 mol) was added to concentrated sulphuric acid (40 cm^3, 0.72 mol) maintaining the temperature below 5°C. Fuming nitric acid (10 cm^3, 0.23 mol) was then added over a period of 10 minutes. The reaction mixture was heated on a steam bath for 30 minutes and poured onto crushed ice (250g). The resultant mixture was added to excess ammonia (160 cm^3, d 0.88)/crushed ice (250g) and the yellow solid thus obtained was filtered off. Recrystallization (methanol) of this material after treatment with celite and decolourising charcoal gave colourless crystals of 27 (8.0g, 40%),m.p. 91-92° (lit.[47] m.p. 93°).

Preparation of 2-(4'-amino-2'-nitrobenzyl)pyridine 39 and 2-(2'-amino-4'-nitrobenzyl)pyridine 130.

Compound 27 (40g, 0.15 mol) was reduced by the method of Nunn and Schofield.[48] After reduction, the sulphur by-product (not reported by Nunn and Schofield) was filtered off and the filtrate evaporated to dryness. Purification by flash-chromatography (eluent ethyl acetate/toluene 1:1) gave compound 39 (17.3g, 49%),m.p. 118° (lit.m.p.[112] 118.5°) and compound 130 (2.1g, 5.9%) as yellow needles, m.p. 107°. (Found: C,63.0; H,5.2; N,18.5. $C_{12}H_{11}N_3O_2$ requires C,62.9; H,4.8; N,18.3). $\delta_H(CDCl_3)$: 8.52 (1H,dd,α-pyridine), 7.80 - 7.03 (6H,m,aromatics), 4.90 (2H,s,NH_2), 4.08, (2H,s,CH_2). ν_{max}(KBr): 3400 (NH_2), 3200 (NH_2), 1510 (NO_2), 1340 cm^{-1} (NO_2). $\delta_C(CDCl_3)$: 159.08 (C_2), 148.88 (C_6), 147.91 (C_{11}), 146.94 (C_9), 137.20 (C_4), 131.29 (C_8), 130.64 (C_{13}), 122.98 (C_3), 121.87 (C_5), 112.85 (C_{12}), 110.05 (C_{10}), 41.75 (C_7).

Preparation of Hydroxyazobenzenes 128a-h, 131

These compounds were synthesised using the method described by Vogel[111c] for the preparation of 1-phenylazonaphth-2-ol. The procedure was carried out using 0.011-0.013 mol of compound 39 and an equimolar quantity of the appropriate phenol.

3-nitro-4-(α-picolyl)benzeneazo-4'-phenol 128a (from phenol).

3-nitro-4-(α-picolyl)benzeneazo-3'-chloro-4'-phenol 128b (from 2-chlorophenol).

3-nitro-4-(α-picolyl)benzeneazo-3',5'-dichloro-4'-phenol 128c (from 2,6-dichlorophenol).

3-nitro-4-(α-picolyl)benzeneazo-2'-nitro-4'-phenol 128d (from 3-nitrophenol).

3-nitro-4-(α-picolyl)benzeneazo-2'-chloro-4'-phenol 128e (from 3-chlorophenol).

3-nitro-4-(α-picolyl)benzeneazo-2',6'-dichloro-4'-phenol 128f (from 3,5-dichlorophenol).

3-nitro-4-(α-picolyl)benzeneazo-3'-methyl-4'-phenol 128g (from 2-methylphenol).

3-nitro-4-(α-picolyl)benzeneazo-2'-methyl-4'-phenol 128h (from 3-methylphenol).

3-nitro-4-(α-picolyl)benzeneazo-1'-naphth-2'-ol 131 (from naphth-2-ol).

Azo-compound (Formula)	% Yield	m.p. (from ethanol)	Found % (required) C	H	N	δ_H(CDCl$_3$/DMSO) CH_2 aromatic
128a	82	206-207	64.6	4.2	16.8	4.54(s)
($C_{18}H_{14}N_4O_3$)			64.6	4.2	16.8	8.5-6.8
128b	73	217-218	58.6	3.7	15.6	4.52(s)
($C_{18}H_{13}N_4O_3Cl$)			58.6	3.6	15.2	8.4-7.0
128c	70	225-226	53.4	3.1	14.0	4.55(s)
($C_{18}H_{12}N_4O_3Cl_2$)			53.6	3.0	13.9	8.5-7.2
128d	52	202-203	56.6	3.4	18.8	4.55(s)
($C_{18}H_{13}N_5O_5$)			57.0	3.5	18.5	8.5-7.1
128e	95	218-219	58.3	3.6	15.0	4.57(s)
($C_{18}H_{13}N_4O_3Cl$)			58.6	3.6	15.2	8.5-6.8
128f	92	232	53.6	3.1	14.2	4.59(s)
($C_{18}H_{12}N_4O_3Cl_2$)			53.6	3.0	13.9	8.4-6.9
128g	97	200	65.6	4.5	15.9	4.54(s)
($C_{19}H_{16}N_4O_3$)			65.5	4.6	16.1	8.5-6.9
						2.24(s)CH_3
128h	95	234	65.7	4.6	16.0	4.53(s)
($C_{19}H_{16}N_4O_3$)			65.5	4.6	16.1	8.5-6.8
						2.63(s)CH_3
131	95	168-169	68.3	4.0	14.9	4.46(s)
($C_{22}H_{16}N_4O_3$)			68.7	4.2	14.6	8.6-6.6

Preparation of aminoazobenzenes 132a-c.

These compounds were synthesised using the method described by Vogel[111d] for the preparation of methyl red. The procedure was carried out using 0.010-0.011 mol of compound 39 and 0.015-0.016 mol of the appropriate amine.

3-nitro-4-(α-picolyl)benzeneazo-4'-dimethylaminobenzene 132a (from dimethylaniline).

3-nitro-4-(α-picolyl)benzeneazo-4'-diethylaminobenzene 132b (from diethylaniline).

3-nitro-4-(α-picolyl)benzeneazo-4'-N-morpholinobenzene 132c (from N-phenylmorpholine).

Preparation of 1,3-bis[3-nitro-4-(α-picolyl)] triazene 133.

Compound 133 was synthesised from compound 39 using the method described by Vogel[111e] for the preparation of diazoaminobenzene (0.02 mol scale).

Azo-compound (Formula)	% Yield	m.p.	Found % (required) C	H	N	$\delta_H(CDCl_3)$ CH_2 aromatic
132a	95	118	66.4	5.5	19.3	4.49
$(C_{20}H_{19}N_5O_2)$		(a)	66.5	5.3	19.4	8.6-6.6
						2.98(s)CH_3
132b	94	83-84	67.4	6.2	17.5	4.45
$(C_{22}H_{23}N_5O_2)$		(b)	67.8	6.0	18.0	8.5-6.5
						3.35(q)CH_2
						1.15(t)CH_3
132c	95	135	65.5	5.5	17.3	4.47
$(C_{22}H_{21}N_5O_3)$		(a)	65.5	5.3	17.4	8.5-6.8
						3.80(t)CH_2-O
						3.25(t)CH_2-N
133 (d)	88	157-158	62.0	4.4	20.3	4.50
$(C_{24}H_{19}N_7O_4)$		(c)	61.4	4.1	20.9	8.6-7.0
						11.3 (broad s) NH
						D_2O exchangeable

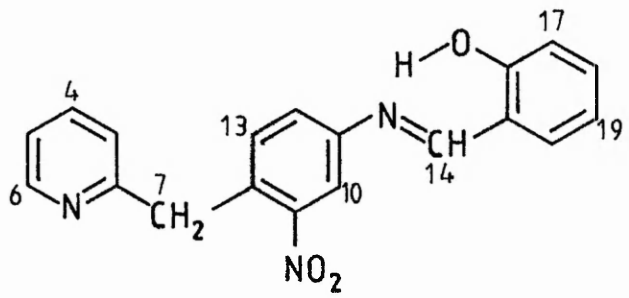
(a) ethyl acetate

(b) ethyl acetate/light petroleum 1:1(c) toluene

(d) mass spectrum analysed in Appendix 2.

Preparation of N-salicylidene-[3-nitro-4-(α-picolyl)] aniline 142.

2-(4'-amino-2'-nitrobenzyl)pyridine 39 (1.00g, 4.4 mmol) and salicylaldehyde (0.54g, 4.4 mmol) in ethanol (10 cm^3) were warmed on a steam bath for 15 minutes. The yellow solid obtained on cooling and filtration of the reaction mixture was recrystallised from ethanol to give yellow crystals of 142 (1.24g, 86%),m.p. 112°. (Found: C,68.4; H,4.6; N,12.7. $C_{19}H_{15}N_3O_3$ requires C,68.5; H,4.5; N,12.6). ν_{max}(KBr): 3430 (OH), 1624 (CH=N), 1525 (NO_2), 1350 cm^{-1} (NO_2).

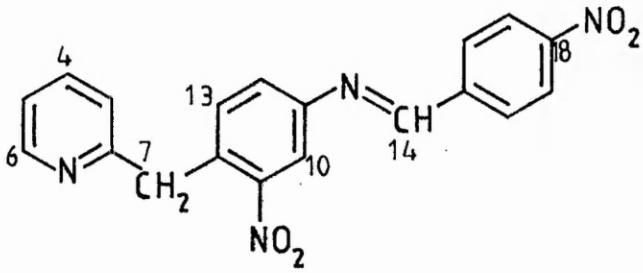


142

δ_H(CDCl3)				δ_C(CDCl3)			
3	7.20 (d)	13	7.50 (d)	2	158.40	12	126.09
4	7.61 (dt)	14	8.64 (s)	3	123.29	13	132.27
5	7.13 (t)	17	7.20 (d)	4	136.61	14	164.50
6	8.50 (d)	18	7.42 (m)	5	121.64	15	118.78
7	4.50 (s)	19	6.96 (t)	6	149.47	16	161.20
10	7.88 (d)	20	7.40 (dt)	7	40.90	17	117.42
12	7.47 (d)	OH	12.64 (s)	8	134.01	18	134.04
				9	149.81	19	119.37
				10	117.03	20	132.75
				11	148.05		

Preparation of N-(4'-nitrobenzylidene)-[3-nitro-4-(α-picolyl)] aniline 140.

2-(4'-amino-2'-nitrobenzyl)pyridine 39 (0.76g, 3.3 mmol) and 4-nitrobenzaldehyde (0.50g, 3.3 mmol) in ethanol (10 cm^3) were warmed on a steam bath for 15 minutes. The lime-green solid obtained on cooling and filtration of the reaction mixture was recrystallised from ethanol to give lime-green crystals of 140 (1.08g, 91%), m.p. 155°. (Found: C,62.8; H,3.9; N,15.5. $C_{19}H_{14}N_4O_4$ requires C,63.0; H,3.9; N,15.5). ν_{max}(KBr): 1629 (CH=N), 1520 (NO_2), 1345 cm^{-1} (NO_2).



140

δ_H(CDCl3)				δ_C(CDCl3)			
3	7.22 (d)	10	7.86 (d)	2	158.41	11	150.19
4	7.62 (dt)	12	7.44 (d)	3	123.32	12	125.88
5	7.14 (t)	13	7.50 (d)	4	136.63	13	132.42
6	8.52 (d)	14	8.60 (s)	5	121.65	14	159.24
7	4.51 (s)	16	8.10 (d)	6	149.47	15	140.77
		17	8.34 (d)	7	40.96	16	129.71
				8	133.93	17	124.06
				9	149.73	18	149.43
				10	116.87		

Preparation of 2,4-dinitrophenylacetic acid 196.

This acid was prepared using the method described by Vogel[111f] on a 0.18 mol scale.

Preparation of 2,4-dinitrophenylacetyl chloride 198.

The acid 196 (10.0g, 0.044 mol) and thionyl chloride (16.0g, 0.13 mol) were maintained at 95-100°C for one hour. Excess thionyl chloride was removed at the pump and the crude product acid chloride purified by crystallisation from carbon disulphide to give yellow crystals of 198 (7.0g, 65%),m.p. 59° (lit.[158] m.p. 64-65°). $\delta_H(CDCl_3)$: 9.2 (1H,d,3-H), 8.6-8.4 (1H,dd,5-H), 7.8 (1H,d,6-H), 4.67 (2H,s,CH_2). ν_{max}(KBr): 1800 (C=O), 1540 (NO_2), 1350 cm^{-1} (NO_2).

Preparation of N,N-diethyl-2,4-dinitrophenylacetamide 199.

The acyl chloride 198 (2.44g, 0.01 mol), diethylamine (0.75g, 0.01 mol) and triethylamine (1.01g, 0.01 mol) in dichloromethane (45 cm^3) were heated under reflux for 35 minutes. The mixture was cooled, poured into cold water and separated. The organic layer was washed with water (3 x 45 cm^3), dried (magnesium sulphate) and the solvent removed to yield a brown solid. The solid was purified by flash chromatography (eluent ethyl acetate/light petroleum 1:1) and recrystallised (ethyl acetate) to yield a pale yellow solid 199, (1.1g, 39%),m.p. 96.5-97° (lit.[158] m.p. 96°). $\delta_H(CDCl_3)$: 8.90 (1H,d,J=3Hz,3H), 8.40 (1H,dd,J=3Hz,J'=9Hz, 5-H), 7.55 (1H,d,J'=9Hz,6-H), 4.18 (2H,s,CH_2), 3.35

(4H,m,CH_2), 1.20 (6H,m,CH_3). ν_{max}($CDCl_3$): 1645 (C=O), 1537 (NO_2), 1350 cm^{-1} (NO_2).

Attempted reduction of 2,4-dinitrophenylacetyl chloride 198 to 2,4-dinitrophenylacetaldehyde 200.

(1) Using sodium borohydride.[129]

Sodium borohydride (0.25g, 6.6 mmol) was dissolved in acetonitrile (33 cm^3) and N,N-dimethylpropylene urea (2 cm^3), and then stirred for 5 minutes with $CdCl_2$.1.5DMF (1.22g, 4.2 mmol) at -5 to 0°C. (The latter reagent was obtained by recrystallising $CdCl_2$.2.5H_2O from dry DMF). To the slightly opaque solution was added the acyl chloride 198 (1.63g, 6.6 mmol) in acetonitrile (10 cm^3) rapidly with stirring and the stirring continued for 5 minutes. Dilute hydrochloric acid (25 cm^3, 4M) was added slowly to the mixture which was then extracted with ether (3 x 50 cm^3). The ether solution was washed with water (6 x 100 cm^3), dried (magnesium sulphate) and the solvent removed to yield 0.77g of a soft brown solid. T.l.c. indicated the presence of at least 5 products. The test for the presence of an aldehyde in the mixture with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (purpald)[159] proved inconclusive and a subsequent attempt to purify the reaction product by precipitation of the sodium bisulphite adduct was unsuccessful. The above reaction was repeated using (a) 25 mmol of acyl chloride 198 (b) 42 mmol of acyl chloride 198 (c) 16 mmol acyl chloride 198 at -10 to -5°C. No aldehyde was ever isolated.

(2) Using lithium tri-t-butoxyaluminohydride.[130]

A solution of lithium tri-t-butoxyaluminohydride (5.08g, 20 mmol) in diglyme (30 cm^3) was added over a period of one hour to the acyl chloride 198 (4.89g, 20 mmol) in diglyme (20 cm^3) maintained at -78°C under nitrogen. The mixture was allowed to come to room temperature (1 hour) and poured onto crushed ice. The mixture was filtered and the solid obtained pressed dry and extracted with ethanol (6 x 50 cm^3). Evaporation of the solvent yielded 3.41g of a dark orange-red gum. T.l.c. indicated the presence of at least 7 products. The test for an aldehyde with purpald[159] again proved inconclusive. Flash chromatography (eluent ethyl acetate/light petroleum 1:1) was unsuccessful in effectively separating these products and no spectroscopic evidence was obtained for the presence of any aldehydic material.

The reduction was attempted again, with the same reducing agent, according to the method described by Pearl,[131] using 14.3 mmol of the chloride 198 and yielded 0.2g of a rust brown solid. T.l.c. indicated the presence of 4 products. No aldehydic material appeared to be present.

Attempted preparation of 2,4-dinitrocinnamic acid 190.

Concentrated nitric acid (12 cm^3, 0.18 mol) was added over a period of 25 minutes to a solution of cinnamic acid (2.5g, 17 mmol) in concentrated sulphuric acid (11 cm^3, 0.20 mol) cooled in ice. The reaction mixture was stirred for 1 hour, poured onto ice (100g) and extracted with ether (2 x 125 cm^3).

The ether solution was washed with saturated sodium bicarbonate (2 x 100 cm^3), dried (magnesium sulphate) and the solvent removed to yield red-orange crystals. Flash chromatography (eluent ethyl acetate/light petroleum 1:1) gave homogeneous material which was recrystallised from ethyl acetate and identified as 4-nitrobenzaldehyde, (0.39g, 15%),m.p. 104° (lit.[111g] m.p. 106°). $\delta_H(CDCl_3)$: 10.25 (1H,s,CHO), 8.47 (2H,d,J=9Hz, CH-C-NO_2), 8.12 (2H,d,J=9Hz,CH-C-CHO). ν_{max}(KBr): 2910 (CHO), 2830 (CHO), 1705 (CO), 1532 (NO_2), 1351 cm^{-1} (NO_2).

Attempted reduction of 2,4-dinitrophenylacetic acid 196 to 2-(2',4'-dinitrophenyl)ethanol 197 using sodium borohydride in the presence of aluminium chloride.[132]

The acid 196 (4.51g, 20 mmol) in diglyme (50 cm^3) was added to a solution of sodium borohydride (0.72g, 19 mmol) in diglyme (50 cm^3) followed by anhydrous aluminium chloride (0.83g, 6.2 mmol) keeping the temperature of the reaction mixture below 40°C. The mixture was held at 35°- 40°C for 1 hour. The excess hydride was destroyed with hydrochloric acid (10 cm^3, 2M) and the mixture basified with sodium carbonate (25 cm^3, 10%) and extracted with ether (3 x 100 cm^3). Removal of solvent yielded a brown solid (1.68g). Flash chromatography (eluent ethyl acetate/light petroleum 1:1) gave homogeneous material which was recrystallised from ethyl acetate and identified as 2,4-dinitrotoluene, (0.35g, 10%),m.p. 67.5° (lit.[111h] m.p. 71°). $\delta_H(CDCl_3)$: 8.82 (1H,d,3-H), 8.40 (1H,dd,5-H), 7.68 (1H,d,6-H), 2.75 (3H,s,CH_3). ν_{max}(KBr): 1528 (NO_2), 1350 cm^{-1} (NO_2).

Preparation of 2-(2',4'-dinitrophenyl)ethanol 197.

Borane methyl sulphide[133] (6.0 cm^3, 10M, 0.06 mol) was added over 10 - 15 minutes to the acid 196 (9.04g, 0.04 mol) in dry diglyme (100 cm^3) and the mixture stirred for 45 hours at room temperature. The excess borane methyl sulphide was destroyed by the addition of methanol (100 cm^3). Volatile components of the mixture were removed by evaporation. Ethyl acetate (200 cm^3) was then added and the mixture washed several times with water to remove diglyme. The solution was dried over magnesium sulphate, filtered and concentrated to yield the alcohol 197 (8.48g, 100%) as light brown crystals, m.p. 66.5° (lit.[160] m.p. 69°). δ_H(DMSO): 8.54 (1H,d,J=3Hz,3-H), 8.34 (1H,dd,J=3Hz,J'=9Hz,5-H), 7.70 (1H,d,J'=9Hz,6-H), 4.80 (1H,t,OH),3.64 (2H,m,OCH_2), 3.07 (2H,t,CH_2-CH_2-OH). ν_{max}(KBr): 3270 (OH), 1540 (NO_2), 1355 (NO_2), 1050 cm^{-1} (1^oC-OH).

Attempted preparation of 2,4-dinitrophenylacetaldehyde 200.

The alcohol 197 (1.36g, 6.4 mmol) was reacted with pyridinium chlorochromate (2.08g, 9.6 mmol) as described by Corey and Suggs[134] yielding 1.23g of rust brown gum. T.l.c. indicated a 4-component mixture including starting material. By flash chromatography (eluent ethyl acetate/light petroleum 1:1) there was obtained 2,4-dinitrobenzaldehyde (0.15g, 12%) but no other aldehydic material. $\delta_H(CDCl_3)$: 10.60 (1H,s,CHO), 9.10 (1H,d,3-H), 8.70 (1H,dd,5-H), 8.22 (1H,d,6-H). $\nu_{max}(CDCl_3)$: 2920 (CHO), 2840 (CHO), 1710 (C=O), 1535 (NO_2), 1340 cm^{-1} (NO_2). Semicarbazone, yellow solid from ethanol/water (1:1),m.p. 265-266°, (lit.[161] m.p. 265°).

Preparation of 2-(4'-nitrophenyl)ethylchloride 230

The title compound 230 was synthesised using Limanov's procedure.[162] From 2-phenylethylchloride (5.00g, 36 mmol) was obtained 230 (6.54g, 98%), pale yellow crystals (ethyl acetate) m.p. 47.5° (lit.[162] 49°). $\delta_H(CDCl_3)$: 8.10 (2H,d,J=9Hz,CH-C-NO_2), 7.38 (2H,d,J=9Hz,C<u>H</u>-C-CH_2), 3.80 (2H,t,J=6Hz,CH_2-Cl), 3.15 (2H,t,J=6Hz,C<u>H</u>$_2$-CH_2Cl). $\nu_{max}(CDCl_3)$: 1520 (NO_2), 1348 cm^{-1} (NO_2).

Preparation of 2,4-dinitrobenzylchloride 209.

The title compound 209 was synthesised using the method of Barba and Shukla,[163] on a 50 mmol scale (benzyl chloride). Thus 209 (9.10g, 84%) was obtained as pale yellow crystals (ethyl acetate) m.p. 32° (lit.[164] m.p. 34°). $\delta_H(CDCl_3)$: 8.81 (1H,d,J=3Hz,3-H), 8.55 (1H,dd,J=3Hz,J'=9Hz,5-H), 8.05 (1H,d,J'=9Hz,6-H), 5.08 (2H,s,CH_2).

Preparation of 2,4-dinitrophenylacetonitrile 208.

2,4-Dinitrophenylacetonitrile 208 was synthesised using the conditions described by Vogel[111i] for the preparation of benzyl cyanide. The title compound 208, obtained from 2,4-dinitrobenzylchloride (4.33g, 20 mmol) was recrystallised from tetrachloromethane (1.38g, 33%),m.p. 87° (lit.[165] m.p. 89°). $\delta_H(CDCl_3)$: 8.70 (1H,d,3-H), 8.33 (1H,dd,5-H), 7.63 (1H,d,6-H), 2.75 (2H,s,CH_2). ν_{max}(KBr): 2230 (CN), 1527 (NO_2), 1348 cm^{-1} (NO_2).

Preparation of ethyl 2,4-dinitrophenylcyanoacetate 207.

Ethyl 2,4-dinitrophenylcyanoacetate 207 was synthesised using the method described by Fairbourne and Fawson[165] and was obtained as colourless needles (ethanol/light petroleum 1:1) (7.50g, 55%), m.p. 66° (lit.[165] m.p. 66°). $\delta_H(CDCl_3)$: 8.81 (1H,d,J=3Hz,3-H), 8.42 (1H,dd,J=3Hz,J'=9Hz,5-H), 7.89 (1H,d,J'=9Hz,6-H), 5.69 (1H,s,CH), 4.26 (2H,q,CH_2), 1.30 (3H,t,CH_3). ν_{max}(KBr): 2250 (CN), 1755 (CO), 1540 (NO_2), 1345 cm^{-1} (NO_2).

Preparation of 2,4-dinitrophenylacetaldehyde 200.

The title compound 200 was synthesised by the method described by Kozikowski et al.[147] for the preparation of 2,6-dinitrophenylacetaldehyde. The procedure was carried out using 2,4-dinitrotoluene (6.40g, 35 mmol). The crude product (3.83g) was chromatographed (eluent ethyl acetate/light petroleum 1:1) to yield 2,4-dinitrophenylacetaldehyde (1.14g, 15%) as an orange-brown solid. $\delta_H(CDCl_3)$: 9.91 (1H,s,CHO), 8.98 (1H,d,J=3Hz,3-H), 8.52 (1H,dd,J=3Hz,J'=8Hz,5-H), 7.65 (1H,d,J'=8Hz,6-H), 4.37 (2H,s,CH_2). $\nu_{max}(CDCl_3)$: 2920 (CHO), 2840 (CHO), 1727 (CO), 1534 (NO_2), 1345 cm^{-1} (NO_2). $\delta_C(CDCl_3)$: 194.66 (CHO), 149.21 (C_2), 147.72 (C_4), 135.19 (C_1), 134.86 (C_6), 127.59 (C_5), 120.64 (C_3), 48.31 (CH_2). MS: 182 (M^+-CO), 165 (182-OH), 119 (165-NO_2), 63 ($C_5H_3^+$).

Preparation of imines 213-216.

A solution in ethanol (10 cm^3) of the aldehyde 200, (0.71 - 1.62 mmol) and the appropriate amine (0.78 - 1.78 mmol) was heated on a steam bath for 15 minutes. The reaction mixture was cooled in ice and then filtered to yield the imine as a dark red crystalline solid which was recrystallised from ethanol.

1-(phenylimino)-2-(2',4'-dinitrophenyl)ethane 213 (from aniline).

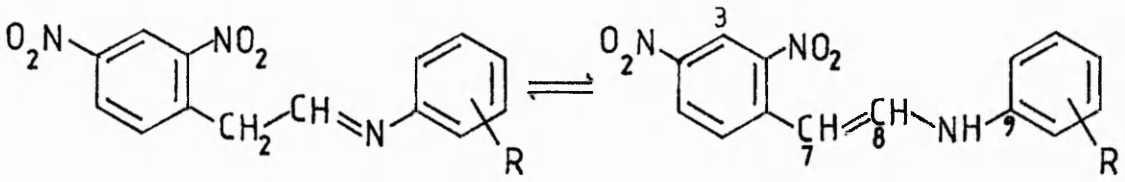
1-(2'-methylphenylimino)-2-(2',4'-dinitrophenyl)ethane 214 from 2-methylaniline).

1-(3'-methylphenylimino)-2-(2',4'-dinitrophenyl)ethane 215 (from 3-methylaniline).

1- (4'-methylphenylimino)-2-(2',4'-dinitrophenyl)ethane 216 (from 4-methylaniline).

Imino-compound (Formula)	% Yield	m.p. °C (from ethanol)	Found % (required) C	H	N
213	57	233	58.7	3.8	14.6
$(C_{14}H_{11}N_3O_4)$			58.9	3.9	14.7
214	71	173	60.0	4.4	14.0
$(C_{15}H_{13}N_3O_4)$			60.2	4.4	14.0
215	86	209	59.9	4.4	14.3
$(C_{15}H_{13}N_3O_4)$			60.2	4.4	14.0
216	97	215	59.8	4.4	13.8
$(C_{15}H_{13}N_3O_4)$			60.2	4.4	14.0

Compound 213. δ_H(DMSO): 10.05 (1H,s,NH), 8.59 (1H,d,J=2.4Hz,3-H), 8.31 (1H,d,J'=13.1Hz,CH-NH), 8.23 (1H,d,J''=9.3Hz,6-H), 8.11 (1H,dd,J=2.4Hz,J''=9.3Hz,H-5), 7.33 - 6.93 (5H,m,C_6H_5), 6.49 (1H,d,J'=13.1Hz,CH=CH-NH).



Compound 213. δ_C(DMSO):

140.87	C_2	124.17	C_5
139.40	C_1	123.38	C_6
139.27	C_4	120.18	C_3
139.05	C_7	119.79	C_{12}
138.94	C_9	113.64	C_{10}
127.70	C_{11}	94.21	C_8

δ_C(DMSO):

Compound 214		Compound 215		Compound 216	
141.87	C_2	143.24	C_1	142.91	C_1
141.35	C_4	141.55	C_2	141.74	C_2
140.37	C_9	141.16	C_4	141.29	C_4
131.81	C_1	139.53	C_7[a,b]	140.18	C_7
130.83	C_7	129.40	C_{13}	138.82	C_9
127.91	C_{11}	126.29	C_5	131.81	C_{12}
127.39	C_5	124.47	C_6	129.99	C_{11}
126.88	C_6	123.30	C_{12}	126.10	C_5
125.84	C_{13}	121.94	C_3	124.41	C_6
123.63	C_{10}	116.23	C_{10}	121.87	C_3
121.87	C_3	112.85	C_{14}	115.71	C_{10}
118.04	C_{12}	96.55	C_8	96.03	C_8
116.86	C_{14}	21.49	CH_3	20.58	CH_3
97.27	C_8				
17.73	CH_3				

(a) C_9 calculated ~140

(b) C_{11} calculated ~139

ν_{max}(KBr): (cm^{-1})

Compound 213	Compound 214	Compound 215	Compound 216	
3330	3360	3340	3330	N-H
1640	1638	1636	1638	(CH=CH)
1630	1629		1634	N=CH
1587	1565	1577	1580	NO_2
1322	1328		1323	NO_2
1308	1308	1305	1307	

Preparation of 3-(2',4'-dinitrophenyl)pentan-2,4-dione 225.

The dione 225 was synthesised using the method of Joshi and Gambhir.[166] The procedure was carried out using 2,4-dinitrochlorobenzene (10.0g, 0.05 mol) and yielded the title compound 225 (8.01g, 60%) as colourless needles (acetic acid) m.p. 121° (lit.[166] 121°). $\delta_H(CDl_3)$: 16.4 (1H,s,O----H,D_2O exchangeable), 8.90 (1H,d,J=3Hz,3-H), 8.63 (1H,dd,J=3Hz,J'=9Hz,5-H), 7.77 (1H,d,J'=9Hz,6-H), 1.90 (6H,s,CH_3). $\delta_C(CDCl_3)$: 189.66 (C-OH), 150.77 (C_2), 148.11 (C_4), 137.52 (C_1), 135.58 (C_6), 127.07 (C_5), 119.92 (C_3), 108.82 (Ph-C=), 23.96 (CH_3). ν_{max}(KBr): 3120 (O---- H), 1530 (NO_2), 1355 cm^{-1} (NO_2).

Preparation of 2,4-dinitrophenylacetone 222a.

The ketone 222a was synthesised as described by Joshi and Gambhir,[166] starting with the diketone 225 (7.00g, 26 mmol). T.l.c. indicated the presence of 5 components. By flash chromatography (eluent ethyl acetate/light petroleum 3:1) the title compound 222 was obtained as a pale yellow solid (1.46g, 25%),m.p. 74° (lit.[166] 75°). $\delta_H(CDCl_3)$: 8.98 (1H,d,J=2.4Hz,3-H), 8.45 (1H,dd,J=2.4Hz,J'=8.4Hz,5-H), 7.54 (1H,d,J'=8.4Hz,6-H), 4.29 (2H,s,CH_2), 2.38 (3H,s,CH_3). $\delta_C(CDCl_3)$: 201.41 (CO), 149.34 (C_2), 147.72 (C_4), 136.94 (C_1), 134.73 (C_6), 127.26 (C_5), 120.64 (C_3), 48.31 (CH_2), 30.00 (CH_3). ν_{max}(KBr): 1708 (CO), 1520 (NO_2), 1345 cm^{-1} (NO_2).

Attempted preparation of 1-(2',4'-dinitrophenyl)-2-(phenylimino)propane 221a.

The ketone 222a (1.00g, 4.5 mmol) and aniline (1.86g, 20 mmol) in xylene (50cm^3) were heated under reflux in a Dean and Stark apparatus for 24 hours. T.l.c. indicated the presence of 5 components in the reaction mixture, including the starting materials. Attempts to separate these components using flash chromatography (eluent ethyl acetate/light petroleum 1:1) were unsuccessful.

Preparation of 2,4-dinitrophenylbenzoylmethane 222b.

The title compound 222b was synthesised using the method of Gambhir and Joshi[167] on a 50 mmol scale (2,4-dinitrochlorobenzene) as colourless needles (2.92g, 27%), m.p. 134° (lit.[167] 137°). $\delta_H(CDCl_3,DMSO)$: 8.98 (1H,d,J=2.5Hz,3-H), 8.65 (1H,dd,J=2.5Hz,J'=9Hz,5-H), 7.95 (1H,d,J'=9Hz,6-H), 8.30 - 7.60 (5H,m,C_6H_5), 5.08 (2H,s,CH_2). $\delta_C(CDCl_3,DMSO)$: 194.40 (CO), 149.08 (C_2), 147.07 (C_4), 137.91 (C_9), 136.16 (C_1), 135.51 (C_6), 133.56 (C_{12}), 128.69 (C_{10}), 128.11 (C_{11}), 127.26 (C_5), 119.86 (C_3), 43.76 (CH_2). $\nu_{max}(CDCl_3)$: 1690 (CO), 1535 (NO_2), 1345 cm^{-1} (NO_2).

Preparation and quantitative analysis of picolylcopper 231.

2-Picolyllithium was prepared in flask A (see Figure 8) from 2-picoline (2.47 cm^3, 25 mmol) as described by Beumel, Smith and Rybalka.[119] Flask B was charged with copper (I) chloride (2.48g, 25 mmol) in tetrahydrofuran (20 cm^3) and cooled to -15°C. The picolyllithium was transferred from flask A to flask B under positive nitrogen

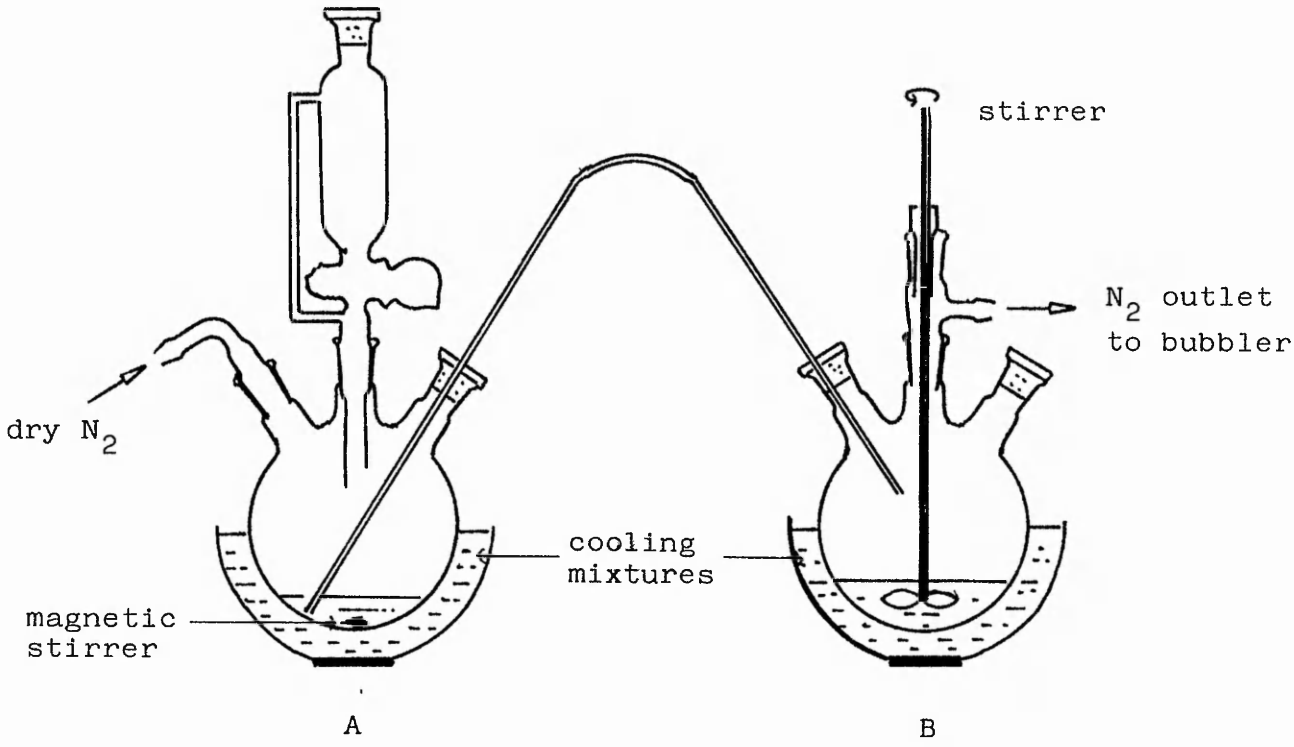


Figure 8

Apparatus used for the preparation of picolylcopper and lithium dipicolylcuprate.

pressure via the needle system and the reaction mixture (flask B) was stirred. Aliquots of this (5 cm^3) were extracted by syringe after 10, 30 and 60 minutes and discharged separately into 3 flasks containing aqueous ammonium thiocyanate (20 cm^3, 0.2M, excess), precipitating copper (I) thiocyanate ($Cu_2(CNS)_2$). Each flask was shaken with saturated aqueous sulphur dioxide (10 cm^3) and the precipitate was allowed to stand overnight before filtering through a weighed Gooch sintered-glass crucible. The pale green precipitate was washed with water (100 cm^3), aqueous ammonium thiocyanate (1 cm^3, 10%), saturated aqueous sulphur dioxide (1 cm^3) and ethanol. The precipitate was dried to constant weight at 110 - 120°C.

Results of analysis [a]

Reaction time/minutes	10	30	60
Yield $Cu_2(CNS)_2$/g	0.305	0.118	0.137
% Yield picolylcopper	95	37	43

(a calculation given in Appendix 8).

Qualitative analysis of copper (I) thiocyanate 232.

ν_{max}(KBr): 2167 cm^{-1} (SC≡N).

The copper (I) thiocyanate was readily soluble in concentrated aqueous ammonia, producing a deep-blue solution ($Cu^+ \longrightarrow Cu(NH_3)_2^+(aq) \longrightarrow Cu(NH_3)_4^{2+}(aq)$). This solution, on careful neutralisation with dilute hydrochloric acid generated a green-yellow solution ($CuCl_4^{2-}(aq)$) which on the

addition of one crystal of iron (III) nitrate produced a blood-red colouration ($Fe(H_2O)_5(CNS)^{2+}(aq)$).

Preparation of 1-(2'-pyridyl)-2-phenylethane 153.

(1) Using picolylcopper 231.

To picolylcopper (25 mmol), prepared as described above (page143), was added benzyl bromide (3.0 cm^3, 25 mmol) in tetrahydrofuran (20 cm^3) over 15 minutes and the mixture stirred for a further 30 minutes and while coming to room temperature. The mixture was acidified with hydrochloric acid (50 cm^3, 4M) and extracted with ether (3 x 50 cm^3). The aqueous layer was basified with aqueous ammonia (100 cm^3, 4M) with cooling and extracted with ether (3 x 100 cm^3). The ether layer was dried (magnesium sulphate) and the solvent removed. The residual liquid was distilled to yield 1-(2'-pyridyl)-2-phenylethane 153 (3.04g, 66%) as a colourless liquid. Picrate, m.p. 126°C (lit.[168] 126-127°). $\delta_H(CDCl_3)$: 8.50 (1H,d,α-pyridine), 7.60 - 6.90 (8H,m, aromatics), 3.03 (4H,s,$-CH_2-CH_2-$).

(2) Using lithium dipicolylcuprate 233.

Picolyllithium (50 mmol), prepared as described earlier (page 143), was transferred from flask A via the needle system to flask B which contained copper (I) iodide (4.75g, 25 mmol) in tetrahydrofuran (20 cm^3) cooled in an ice/salt mixture. The reaction mixture was stirred for 5 minutes to generate

lithium dipicolylcuprate 233. Benzyl bromide (2.0 cm^3, 15 mmol) in tetrahydrofuran (10 cm^3) was added over 15 minutes and the mixture stirred for a further 15 minutes and while coming to room temperature. From this mixture, 1-(2'-pyridyl)-2-phenylethane 153 (2.55g, 93%) was isolated as described above. Picrate, m.p. 127°C (lit.[168] 126-127°).

Preparation of 2-trifluoromethylphenyl-2'-pyridylmethanol 234. The title compound 234 was synthesised using the method described by Moser and Bradsher[169] for the preparation of 2-pyridyl-2-tolylcarbinol, starting with 2-trifluoromethylbromobenzene (11.9g, 53 mmol). Purification by distillation yielded 234 as a viscous yellow oil (8.35g, 66%)b.p. 125°(1 mm) which crystallised on standing, m.p. 63°C. (Found: C,61.9; H,4.1; N,5.5. $C_{13}H_{10}F_3NO$ requires C,61.7; H,4.0; N,5.5). $\delta_H(CDCl_3)$: 8.60 (1H,d,α-pyridine), 7.80 - 6.95 (7H,m,aromatics), 6.20 (1H,s,C<u>H</u>OH), 5.60 (1H,s,OH,D_2O exchangeable). ν_{max}(film): 3380 (broad,OH), 1310, 1160, 1120 cm^{-1} (CF_3). $\delta_C(CDCl_3)$: 159.99 (C_2), 147.65 (C_6), 142.26 (C_8), 137.13 (C_4), 133.63 (CF_3), 132.39 (C_{12}), 129.99 (C_{11}), 127.85 (C_{13}), 125.58 (C_{10}), 125.19 (C_9), 122.72 (C_3), 121.68 (C_5), 69.41 (CHOH,C_7). Picrate, m.p. 153 - 153.5°C. (Found: C,47.3; H,2.9; N,11.8. $C_{19}H_{13}F_3N_4O_8$ requires C,47.3; H,2.7; N,11.6).

Preparation of 2-(2'-trifluoromethylbenzyl)pyridine 162.

2-(2'-Trifluoromethylbenzyl)pyridine 162 was synthesised using the method described by Moser and Bradsher[169] for the preparation of 2-(2'-methylbenzyl)pyridine. The procedure was carried out using compound 234 (4.00g, 16 mmol). Purification by distillation yielded 162 as a pale yellow liquid (2.62g, 70%) b.p. 98° (0.1 mm). (Found: C,65.7; H,4.6; N,5.8. $C_{13}H_{10}F_3N$ requires C,65.8; H,4.3; N,5.9). $\delta_H(CDCl_3)$: 8.50 (1H,d,α-pyridine), 7.70 - 6.90 (7H,m,aromatics), 4.32 (2H,s,CH_2). ν_{max}(film): 1310, 1160, 1110 cm^{-1} (CF_3). $\delta_C(CDCl_3)$: 159.86 (C_2), 149.34 (C_6), 137.84 (C_8), 136.48 (C_4), 133.69 (CF_3), 132.07 (C_{12}), 131.81 (C_{13}), 126.55 (C_{10}), 126.16 (C_{11}), 125.77 (C_9), 123.24 (C_3), 121.35 (C_5), 40.77 (CH_2). Picrate, m.p. 128.5-129°C (Found: C,48.9; H,2.9; N,12.0. $C_{19}H_{13}F_3N_4O_7$ requires C,48.9; H,2.8; N,12.0).

Attempted preparation of 2-(2'-trifluoromethyl-4',6'-dinitrobenzyl)pyridine 163.

Fuming nitric acid (12 cm^3, 0.28 mol) was added over a period of 5 minutes to compound 162 (2.00g, 8.4 mmol) with cooling. The reaction mixture was boiled under reflux for 45 minutes then cooled and added to ice (25g). The resultant mixture was basified with aqueous ammonia (25 cm^3, 15M) and the pale yellow solid thus obtained was filtered off. Recrystallisation (methanol) of this material after treatment with celite and decolourising charcoal gave colourless crystals of 2-(2'-trifluoromethyl-4'-nitrobenzyl)pyridine 164 (1.12g, 47%),m.p. 120°C. MS: 282 (M^+, 6%), 236 (M^+-NO_2, 10%),

213 (M^+-CF_3, 100%), 167 ($M^+-CF_3-NO_2$, 82%). Picrate, m.p. 120.5 - 121°C. (Found: C,44.6; H,2.3; N,14.1. $C_{19}H_{12}F_3N_5O_9$ requires C,44.6; H,2.4; N,13.7).

Preparation of 4-trifluoromethylphenyl-2'-pyridylmethanol 161. The title compound 161 was synthesised by the method described by Moser and Bradsher[169] for the preparation of 2-pyridyl-2-tolylcarbinol, starting with 4-trifluoromethylbromobenzene (11.9g, 53 mmol). Purification by flash chromotography (eluent ethyl acetate/light petroleum 1:1) yielded the title compound 161 as a yellow solid (8.55g, 68%)m.p. 65.0 - 65.5°. (Found: C,61.8; H,4.1; N,5.5 $C_{13}H_{10}F_3NO$ requires C,61.7; H,4.0; N,5.5). $\delta_H(CDCl_3)$: 8.45 (1H,d,α-pyridine), 7.90 - 7.00 (7H,m,aromatics), 5.82 (1H,s,CH OH), 5.55 (1H,s,OH,D_2O exchangeable). $\nu_{max}(CDCl_3)$: 3360 (broad,OH), 1325, 1165, 1125 cm^{-1} (CF_3). $\delta_C(CDCl_3)$: 160.05 (C_2), 147.97 (C_6), 147.07 (C_8), 137.13 (C_4), 133.11 (CF_3), 127.20 (C_9), 125.58 (C_{10}), 122.78 (C_3), 121.29 (C_5), 115.06 (C_{11}), 74.39 (CHOH,C_7).

Preparation of 2-(4'-trifluoromethylbenzyl)pyridine 156. 2-(4'-Trifluoromethylbenzyl)pyridine 156 was synthesised using the procedure of Moser and Bradsher[169] for the preparation of 2-(2'-methylbenzyl)pyridine, starting with compound 161 (5.00g, 20 mmol). Purification by distillation yielded the title compound 156 as a colourless liquid (3.20g, 68%) b.p. 125°C (0.1 mm). (Found: C,65.4; H,4.7; N,5.9. $C_{13}H_{10}F_3N$ requires C,65.8; H,4.3; N,5.9). $\delta_H(CDCl_3)$: 8.45

(1H,d,α-pyridine), 7.55 - 6.80 (7H,m,aromatics), 4.10 (2H,s,CH_2). ν_{max}(film): 1325, 1165, 1120 cm^{-1} (CF_3). δ_C($CDCl_3$): 159.86 (C_2), 149.60 (C_6), 143.69 (C_8), 136.74 (C_4), 133.37 (CF_3), 129.40 (C_9), 125.64 (C_{10}), 123.17 (C_3), 121.61 (C_5), 115.25 (C_{11}), 44.48 (CH_2). Picrate, m.p. 116 - 116.5°C. (Found: C,48.9; H,2.9; 12.1. $C_{19}H_{13}F_3N_4O_7$ requires C,48.9; H,2.8; N,12.0).

Preparation of 2-(2'-nitro-4'-trifluoromethylbenzyl) pyridine 124.

2-(4'-Trifluoromethylbenzyl)pyridine (1.0g, 4.2 mmol) was added to concentrated sulphuric acid (4 cm^3, 72 mmol) maintaining the temperature below 5°C. Fuming nitric acid (2 cm^3, 46 mmol) was then added over a period of 5 minutes. The reaction mixture was boiled under reflux for 30 minutes and, after cooling, poured onto crushed ice (25g). The resultant mixture was added to excess ammonia (15 cm^3, d 0.88)/crushed ice (25g) and the product was extracted with ethyl acetate (3 x 25 cm^3). The organic layer was dried (magnesium sulphate) and the solvent removed. Purification of the product by flash chromatography (eluent ethyl acetate/light petroleum 1:1) yielded the title compound 124 as an orange-yellow liquid (0.90g, 76%),m.p. 13.0 - 13.5°C. (Found: C,55.4; H,3.5; N,9.9. $C_{13}H_9F_3N_2O_2$ requires C,55.3; H,3.2; N,9.9). δ_H($CDCl_3$): 8.49 (1H,d,H_6), 8.24 (1H,d,J=1.5Hz,H_{10}), 7.80 (1H,dd,J=1.5Hz,J'=8.0Hz,H_{12}), 7.64 (1H,dd,H_4), 7.61 (1H,d,J'=8.0Hz,H_{13}), 7.24 (1H,d,H_3),

7.15 (1H,dd,H_5), 4.55 (2H,s,CH_2). ν_{max}(film): 1535 (NO_2), 1355 (NO_2), 1325, 1180, 1130 cm^{-1} (CF_3). δ_C($CDCl_3$): 157.52 (C_2), 149.53 (C_6), 138.78 (C_9), 136.81 (C_4), 134.02 (C_{12}), 132.07 (CF_3), 131.68 (C_8), 129.40 (C_{13}), 129.21 (C_{10}), 123.50 (C_3), 121.94 (C_5), 113.95 (C_{11}), 40.97 (CH_2). MS: 265 (M^+-OH, 10%), 236 (M^+-NO_2, 100%), 167 (M^+-NO_2-CF_3, 58%). Picrate, m.p. 152 - 152.5°C. (Found: C,44.7; H,2.5; N,13.8. $C_{19}H_{12}F_3N_5O_9$ requires C,44.6; H,2.4; N,13.7).

Preparation of 3-(2',4'-dinitrobenzyl)pyridine 184.

3-Benzylpyridine (1.30g, 7.7 mmol) was added to concentrated sulphuric acid (4.0 cm^3, 72 mmol) maintaining the temperature below 5°C. Fuming nitric acid (1.0 cm^3, 23 mmol) was then added over a period of 10 minutes. The reaction mixture was heated on a steam bath for 30 minutes, then cooled and poured onto crushed ice (25g). The resultant mixture was added to excess ammonia (16 cm^3,d 0.88)/crushed ice (25g) and the product was extracted with ethyl acetate (3 x 25 cm^3). The organic layer was dried (magnesium sulphate) and the solvent removed. Purification of the product by flash chromatography (eluent ethyl acetate/light petroleum 9:1) yielded the title compound 184 as a pale yellow liquid (0.88g, 44%). Picrate, m.p. 150°C. (Found: C,44.2; H,2.5; N,16.8. $C_{18}H_{12}N_6O_{11}$ requires C,44.3; H,2.5; N,17.2). For compound 184, δ_H($CDCl_3$): 8.70 (1H,d,α-pyridine), 8.37 - 7.04 (6H,m,aromatics), 4.36 (1H,s,CH_2). ν_{max}(film): 1525, 1350 cm^{-1}

(NO_2). δ_C($CDCl_3$): 150.05 (C_2), 148.69 (C_6), 146.87 (C_9), 141.29 (C_{11}), 136.42 (C_4), 133.56 (C_{13}), 132.65 (C_3), 128.62 (C_8), 127.20 (C_{10}), 123.82 (C_5), 120.57 (C_{12}), 35.84 (C_7).

Preparation of benzylpyrazine 180.

The title compound 180 was synthesised using the method described by Behun and Levine.[123] The procedure was carried out using 0.10 mol methylpyrazine and yielded the title compound 180 (4.37g, 51%) as a pale yellow liquid b.p. 125°C (1.7 mm) (lit.[123] 106°C, 1.3 mm). Picrate, m.p. 129 - 130°C. (Found: C,50.9; H,3.2; N,17.2. $C_{17}H_{13}N_5O_7$ requires C,51.1; H,3.3; N,17.5).

Attempted preparation of 2,4-dinitrobenzylpyrazine 181.

Benzylpyrazine (2.00g, 12 mmol) was added to concentrated sulphuric acid (6.0 cm^3, 0.11 mol) maintaining the temperature below 5°C. Fuming nitric acid (1.5 cm^3, 35 mmol) was then added over a period of 10 minutes. The reaction mixture was heated on a steam bath for 30 minutes, then cooled and poured onto crushed ice (50g). The yellow-brown gum produced was filtered off. T.l.c. indicated a 6-component mixture including starting material. Repeated attempts to resolve this mixture by flash chromatography were unsuccessful.

Ultraviolet-visible spectra

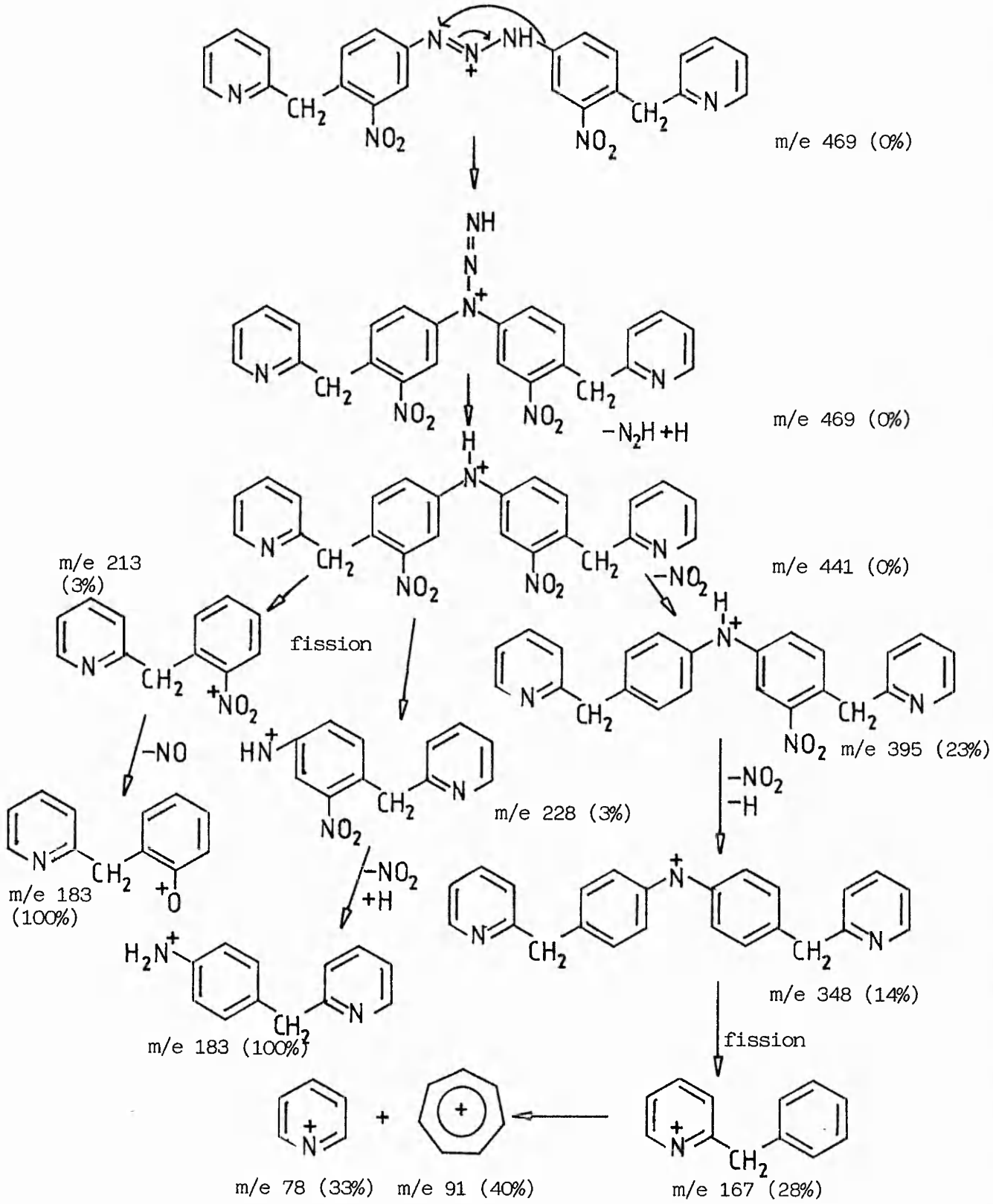
Ultraviolet-visible spectra as reported in the text for solutions at room temperature were obtained according to standard procedures. A suitable attachment for obtaining spectra of irradiated and unirradiated solutions held at low temperatures was not available; hence these spectra were determined as follows. Standard solutions were prepared and then cooled in a crystallising dish held in a dry ice/acetone mixture or ethyl acetate/liquid nitrogen mixture and, where appropriate, irradiated with an unfiltered 300 watt ultraviolet source placed 10" above the solution. After set periods of exposure, samples of solutions were transferred quickly to silica cells, the transparent faces of which had been thinly coated with glycerine to prevent condensation of atmospheric moisture. Spectra were recorded immediately. Samples were then allowed to warm to room temperature and the spectra re-run.

Appendix 1

Data relating to concentration of solution in ethanol, absorbance, λ_{max} and absorption maxima for the azo compounds described in Section 4.2.1.

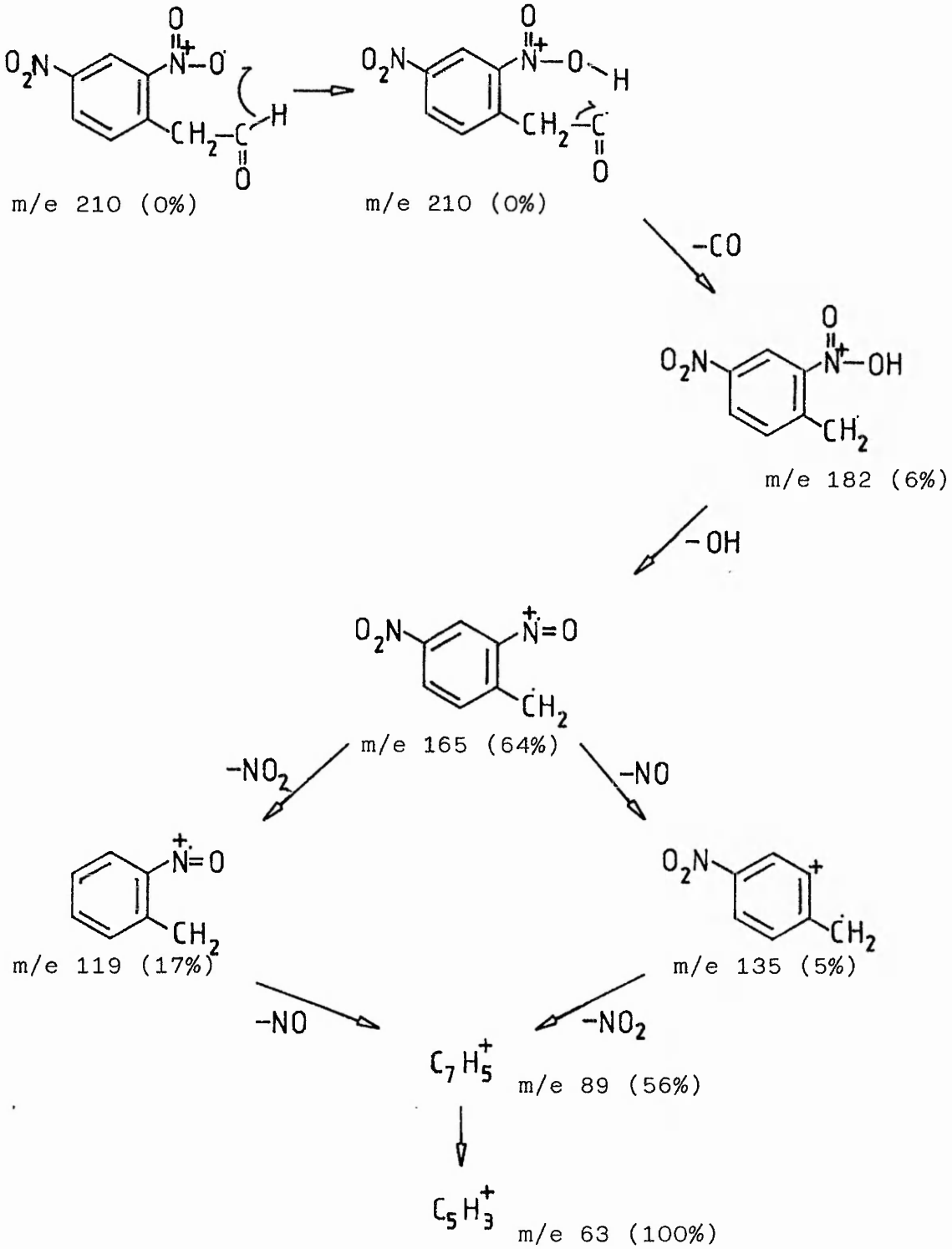
Compound	Concentration /moldm^{-3} x 10^{-5}	Absorbance	λ_{max}/nm	ε_{max}
128a	5.60	0.93	$368^{\pm}1$	17,000
128b	4.25	1.07	$372^{\pm}2$	25,200
128c	2.22	0.84	$364^{\pm}2$	37,800
128d	3.55	0.56	$345^{\pm}1$	15,800
128e	5.86	1.30	$378^{\pm}3$	22,200
128f	5.16	0.82	$347^{\pm}2$	15,900
128g	5.00	1.20	$372^{\pm}2$	24,000
128h	4.88	1.16	$380^{\pm}1$	23,800
131	6.56	0.73	$477^{\pm}2$	11,100
132a	2.49	0.84	$436^{\pm}2$	33,700
132b	1.36	0.49	$456^{\pm}2$	36,000
132c	2.48	0.70	$413^{\pm}2$	28,200
132d	2.68	0.74	$235^{\pm}1$	27,600

Appendix 2



Analysis of the Mass Spectrum of 1,3-bis [3-nitro-4-(α-picolyl)] triazene 133 (abundance %) based on the work done by R. A. W. Johnstone et al.[170]

Appendix 3



Analysis of the Mass Spectrum of 2,4-dinitrophenylacetaldehyde 200

(abundance %)

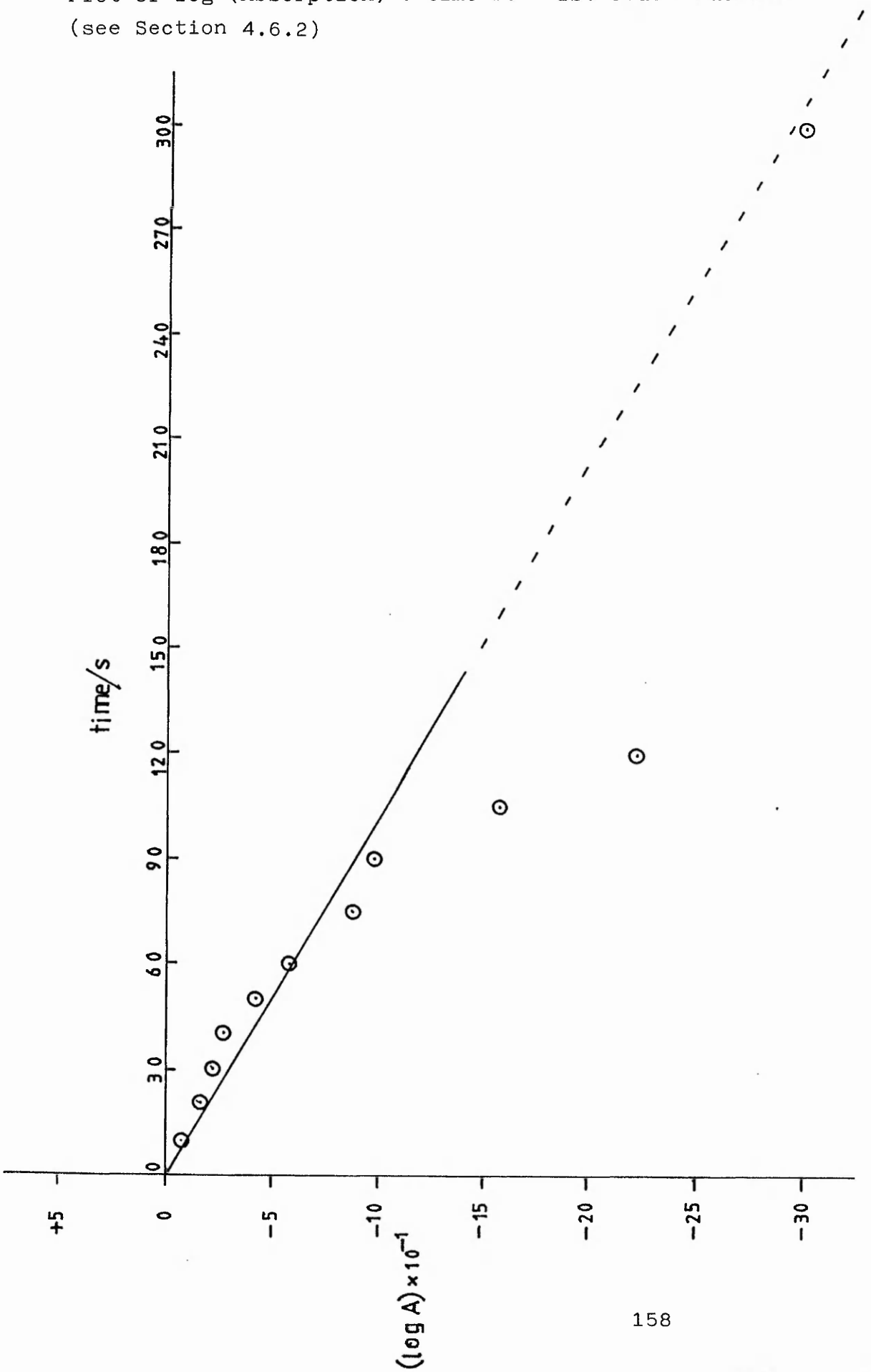
Appendix 4

Absorbance values (A_t) for ethanolic solutions of the parent imine 213 (at room temperature) exposed to ultraviolet radiation for periods of time (t,seconds) (see page113).

time/s	A_t	$A=(A_t-A_{\infty})$	(log A) x 10^1	$^1/A$
0	1.085	1.059	0.2490	0.9443
10	0.860	0.834	-0.7803	1.199
20	0.726	0.700	-1.549	1.429
30	0.618	0.592	-2.277	1.689
40	0.586	0.560	-2.518	1.786
50	0.407	0.381	-4.191	2.625
60	0.285	0.259	-5.867	3.861
75	0.160	0.134	-8.729	7.463
90	0.130	0.104	-9.830	9.615
105	0.053	0.027	-15.69	37.04
120	0.032	0.006	-22.22	166.7
300	0.027	0.001	-30.00	1000
600	0.026	0		

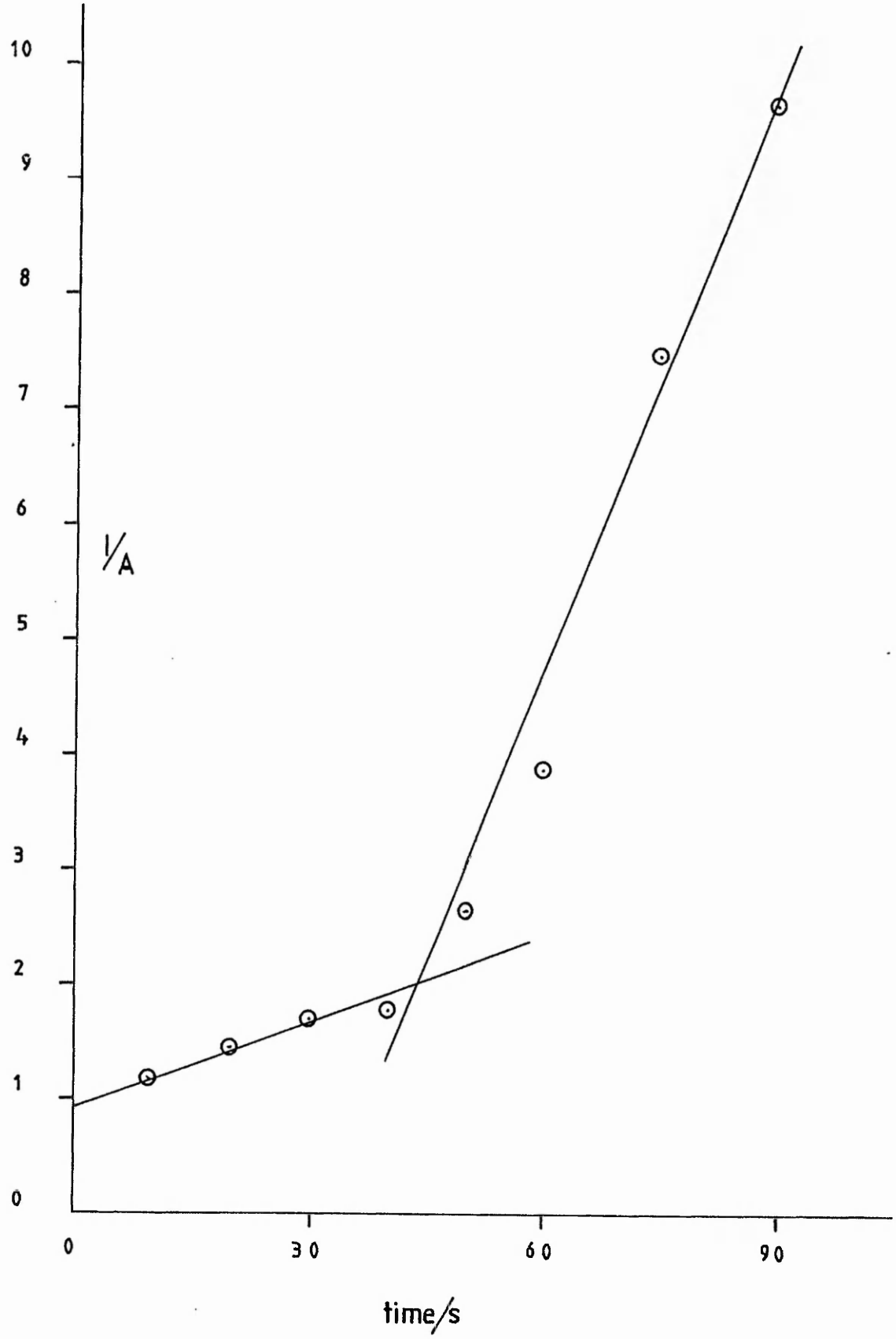
Appendix 5

Plot of log (Absorption) v time re - 1st order kinetics
(see Section 4.6.2)

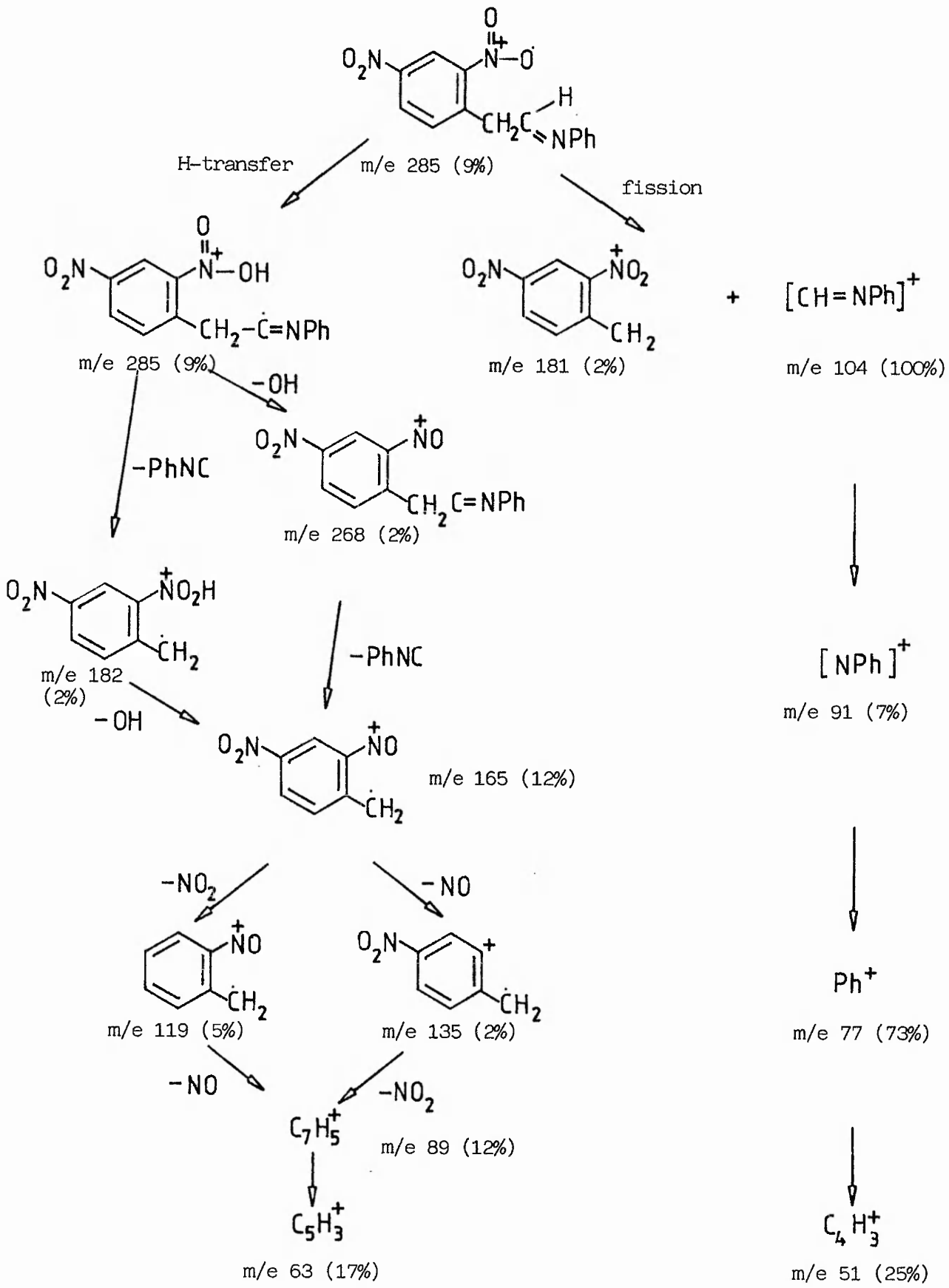


Appendix 6

Plot of 1/Absorption v time re - 2nd order kinetics
(see Section 4.6.2)



Appendix 7



Analysis of the Mass Spectrum of 1-(phenylimino)-2-(2',4'-dinitrophenyl)ethane 213

(abundance %)

Appendix 8

Calculation of % yield of picolylcopper (see page 145).

picoline → picolyllithium → picolylcopper → copper (I) thiocyanate

1/40 mol 1/40 mol 1/40 mol 1/80 mol $Cu_2(CNS)_2$

RMM 243

Volume of final reaction mixture = 47.5 cm^3

Thus a 5 cm^3 aliquot of reaction mixture produces a theoretical yield of

$$Cu_2(CNS)_2 = \frac{5}{47.5} \times \frac{1}{80} \times 243g$$

$$= 0.320g$$

$$\text{\% Yield of picolylcopper (for the 10 minute aliquot)} = \frac{0.305}{0.320} \times 100 = 95\%$$

The largest errors occur in determining (i) the total volume of the reaction mixture (ii) the volume of the aliquot extracted. Overall % error in the yield $\sim$5%.

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