Medicinal Nitro-compounds. Part I. Photo-rearrangement of *N*-Aryl-2-nitrobenzamides [1]

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2-Nitrobenzanilide (4a) rearranges to 2-(2-hydroxyphenylazo)benzoic acid (5a) on exposure to light. Azoxybenzene-2-carboxylic acid (6a) is an intermediate in this transformation and also rearranges to the acid (5a) in high yield. Other *N*-aryl-2-nitrobenzamides (4b—f) afford the analogous azo-compounds (5b—f), but when the *N*-aryl system carries electron-attracting substituents (4g—j) the compounds are photostable. Irradiation of 2-nitrobenzo-*m*-toluidide (12) yields a mixture of two isomeric azocarboxylic acids. The scope of the rearrangement has been explored: *N*-(1-naphthyl)-2-nitrobenzenesulphonamide (18) affords the analogous azobenzenesulphonic acid (19) but *N*-alkyl- or *N*-aralkyl-2-nitrobenzamides, *N*-substituted 4-nitrobenzamides, and *NN'*-diphenyl-2-nitrobenzamidine (16) do not yield azo- or azoxy-compounds.

NITRO-COMPOUNDS are widely used to elicit a variety of physiological and biochemical responses although the toxicological hazards associated with their use in human and veterinary medicine are causing concern.[2] Those medicinal nitro-compounds bearing a substituent *ortho* to the nitro-group offer an intriguing area for study, since related nitroarenes often undergo intramolecular cyclisation, or redox reactions; these neighbouring-group participation reactions have been initiated by ion-impact,[3,4] thermal, and photochemical processes, and by acids and bases.[5] Many of the interactions proceed under mild conditions, and in high yield:[6] possibly, similar transformations could proceed under physiological conditions. We have begun an examination on the chemical and biochemical properties of medicinal nitro-compounds for evidence of such interactions of biological significance.

2-Methyl-3-*o*-tolylquinazolin-4(3*H*)-one (methaqualone) (1) is one of the most potent of a series of quinazolone derivatives with hypnotic activity.[7] Surprisingly, it is metabolised *via* the quinazolone oxide (2) to 2-nitrobenzo-*o*-toluidide (3), which is the principal human

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[1] Preliminary communication, B. C. Gunn and M. F. G. Stevens, *J.C.S. Chem. Comm.*, 1972, 835.

[2] J. Venulet and R. L. Van Etten, in ' The Chemistry of the Nitro and Nitroso Groups,' Part 2, ed. H. Feuer, Interscience, New York, 1970, pp. 201—287.

[3] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, **88**, 4974.

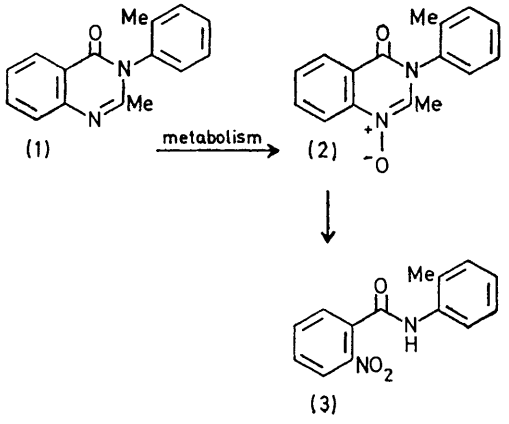
[4] G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc.* (*B*), 1971, 1273.

[5] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 398.

[6] P. N. Preston and G. Tennant, *Chem. Rev.*, 1972, **72**, 627.

[7] A. H. Amin, D. R. Mehta and S. S. Samarth, ' Progress in Drug Research,' ed. E. Jucker, Birkhäuser Verlag, vol. 14, p. 216.

urinary metabolite.[8] We have examined the photoreactions of this metabolite and some related 2- and 4-nitrobenzamides because of the biological interest in this type of compound.[9]



A maroon colour develops when dry crystals of 2-nitrobenzanilide (4a) are exposed to laboratory light for several months, and (rapidly) when a solution in 95% ethanol is irradiated with an unfiltered 100 W medium-pressure arc. In the solution reaction the yield of coloured product ($\lambda_{max.}$ 326 nm) reaches a maximum after about 24 h. The product was isolated by exploiting its acidic character and its property of being tenaciously adsorbed on an alumina column. Typical yields are *ca.* 10—15%, but the efficiency of the process could be improved by circulating the reaction mixture through an alumina column by means of a peristaltic pump, the eluted starting material being continuously returned to the reactor. In this way competitive light absorption by the photoproduct was reduced, and the yield was improved (to 25%). The photoproduct from the solution photolysis was identical with that formed from the light-exposed crystals, and had i.r., n.m.r., and mass spectra consistent with the *o*-hydroxyazobenzene structure (5a); in agreement, on catalytic reduction it afforded only anthranilic acid and *o*-aminophenol. Furthermore, its m.p. and u.v. spectrum (Table) were in accord with values quoted for a red compound formed by alkaline hydrolysis of the oxadiazocine (7), to which structure (5a) has also been assigned.[10]

This photoisomerisation appears to be a general property of *N*-aryl-2-nitrobenzamides. The chloroanilides (4b and c), the methaqualone metabolite (3), and its *p*-tolyl isomer (4e) were even more photosensitive than 2-nitrobenzanilide, and turned red within a few hours when exposed to laboratory light. The photoproducts were assigned structures (5b—e) respectively on account of their spectral similarities (Table) to the *o*-hydroxyazobenzene (5a). The 2-nitrobenzoyl derivative of 1-naphthylamine (4f) also afforded a photoisomer (5f) identical with the azo-dye formed by coupling diazotised anthranilic acid and 2-naphthol.

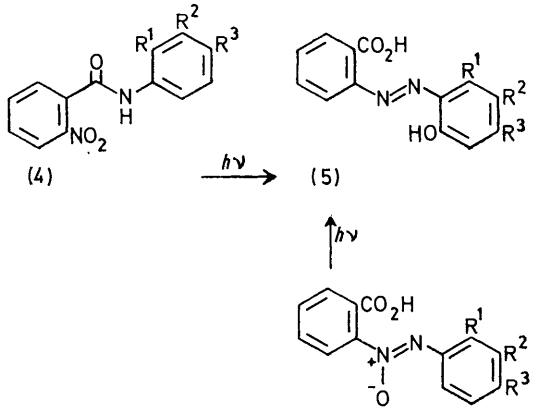
[8] T. Murata and I. Yamamoto, *Chem. and Pharm. Bull. (Japan)*, 1970, **18**, 133, 143.

Electronic absorption spectra ($\lambda_{max.}$/nm; log ε in parentheses) of azo- and azoxy-compounds in 95% ethanol

Compound				
(5a)		248(4·02)	325(4·16)	386(3·89)
(5a) *		247(4·03)	328(4·19)	386(3·90)
2-Hydroxyazobenzene *†			326(4·27)	387(3·99)
(5b)		252(4·01)	329(4·15)	380(4·05)
(5c)		251(4·05)	328(4·16)	380(4·07)
(5d)		246(3·85)	341(4·20)	394‡(3·82)
(5e)		252(3·99)	327(4·19)	402(3·81)
(6a)	229(4·06)		309(4·04)	
(6b)	231(4·07)		316(4·16)	
(6c)	232(4·04)		315(4·12)	
2-(Phenylazo)-benzoic acid	225(4·18)		319(4·20)	
2-(2-Cyanophenylazo)benzonitrile	240(4·13)	246(4·15)	329(4·30)	
(21) or (22)	240 ‡§		335 §	

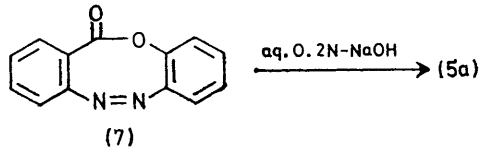
* Ref. 10. † In benzene. ‡ Inflection. § Insufficient material to calculate log ε.

In contrast anilides bearing electron-attracting substituents (4g—j) were stable in the crystal phase over 2 years, and were not subjected to solution photolysis.



	R¹	R²	R³
a;	H	H	H
b;	Cl	H	H
c;	H	H	Cl
d;	Me	H	H
e;	H	H	Me
f;	—CH:CH·CH:CH—		H
g;	NO_2	H	H
h;	H	H	NO_2
i;	CN	H	H
j;	H	H	CN

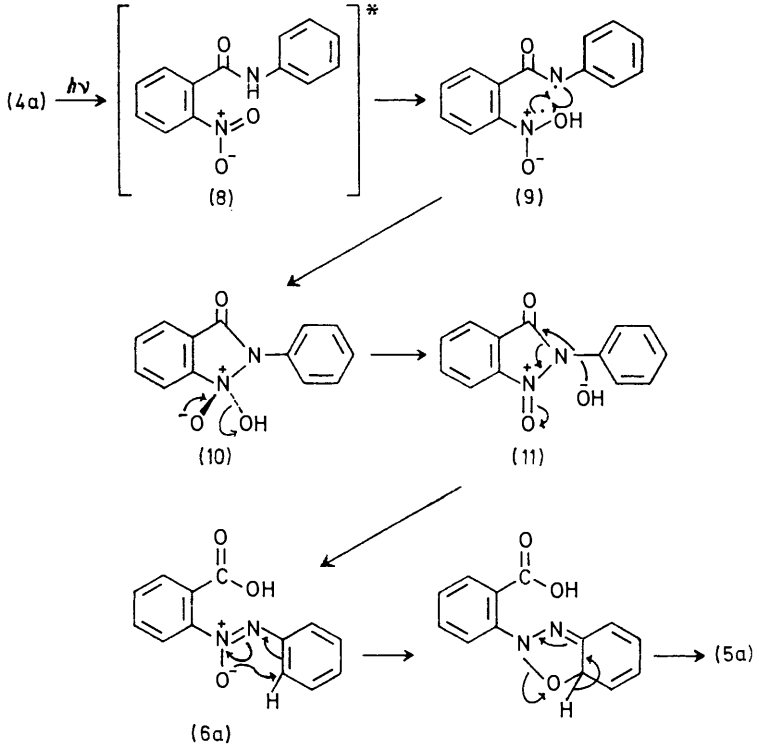
In assigning a mechanism to this rearrangement, we have been helped by the work of Badger and Buttery,[11]



who showed that azoxybenzenes undergo a photorearrangement to *o*-hydroxyazobenzenes, and that the

[9] W. D. Roll, *J. Pharm. Sci.*, 1968, **57**, 1671; 1970, **59**, 1838.
[10] T. Miura, M. Kato, and T. Tamano, *Tetrahedron Letters*, 1968, 2743.
[11] G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 1954, 2243.

oxygen atom always migrates to the aryl group more distant from the N–O function; a revised mechanism for this rearrangement has recently been put forward.[12] T.l.c. of the reaction mixture from 2-nitrobenzanilide showed the presence of two minor (unidentified) coloured products, together with starting material, the red photoproduct (5a) and a yellow spot subsequently identified as azoxybenzene-2-carboxylic acid (6a); this spot turned red on exposure to light, and a sample of the azoxybenzene independently prepared and irradiated in 95% ethanol afforded the same red azo-compound (5a) quantitatively. Similarly, the chloro-azoxybenzenes (6b and c) were detected in the reaction



SCHEME 1

mixtures from the anilides (4b and c), and samples of these yellow azoxy-compounds also rearranged photochemically to the appropriate *o*-hydroxyazobenzenes (5b and c). Clearly, azoxybenzenes feature as intermediates in the rearrangement of *N*-aryl-2-nitrobenzamides.

Azoxy- and azo-compounds are known to be formed readily from nitroarenes, but these reactions often require a basic medium. The formation of coupled products can usually be interpreted in terms of a bimolecular reaction involving reduction intermediates;[13-16] in most cases where these transformations are photochemically initiated, bimolecular reactions are implied by the nature of the products.[17-20] The rearrangement (4) ⟶ (5) on the other hand seems to be a monomolecular process, and our suggested mechanism [for 2-nitrobenzanilide (4a) as an example] is outlined in Scheme 1.

The multiplicity of the excited state responsible for intramolecular H-abstraction in *ortho*-nitro reactions is the subject of controversy.[21] The observation that intermolecular photoreductions of nitroarenes can often be initiated by triplet sensitizers and inhibited by oxygen has been advanced to support the involvement of a *triplet* excited species in these cases.[22-25] As the photoreduction product, 2-aminobenzanilide, was not detected in the photolysate of (4a) (and it was independently shown to be stable under the reaction conditions) we tentatively propose that a *singlet* excited species (8) is responsible for the H-abstraction step. The diradical (9) thus formed could then collapse to the indazolone *N*-oxide (10). The tetrahedral arrange-

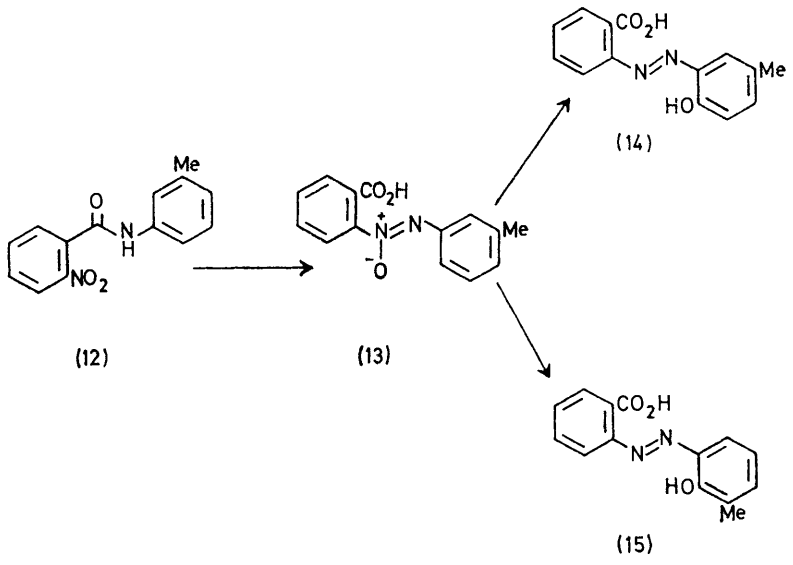
[12] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.
[13] G. M. Robinson, *J. Chem. Soc.*, 1917, **111**, 109.
[14] B. Homolka, *Ber.*, 1884, **17**, 1902.
[15] H. Dickhauser and F. Kröhnke, *Chem. Ber.*, 1970, **103**, 320.
[16] C. Simons and L. G. Ratner, *J. Chem. Soc.*, 1944, 421.
[17] A. Patchornik, B. Amit, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1970, **92**, 6333.
[18] J. A. Barltrop, P. J. Plant, and P. Schofield, *Chem. Comm.*, 1966, 822.
[19] D. Döpp, *Chem. Ber.*, 1971, **104**, 1035.
[20] Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1583.
[21] H. A. Morrison in ' The Chemistry of the Nitro and Nitroso Groups,' Part I, ed. H. Feuer, Interscience, New York, 1969, pp. 181—185.
[22] J. A. Barltrop and N. J. Bunce, *J. Chem. Soc.* (*C*), 1968, 1467.
[23] S. Hashimoto and K. Kano, *Tetrahedron Letters*, 1970, 3509.
[24] S. Hashimoto and K. Kano, *Bull. Chem. Soc. Japan*, 1972, **45**, 549.
[25] S. Hashimoto, K. Kano, and K. Ueda, *Bull. Chem. Soc. Japan*, 1971, **44**, 1102.

ment of substituents about N-1 of the indazolone prohibits attainment of a favourable cyclic transition state for nucleophilic attack of hydroxyl at the carbonyl group, but this step may well be accomplished *via* the intimate ion pair (11). Cleavage of the hetero-ring then leads to the azoxybenzene (6a), which in turn rearranges to the *o*-hydroxyazobenzene (5a).[12]

A $\pi\pi^*$ singlet excited state of the azoxybenzene has been implicated in rearrangements related to the photorearrangement (6) ⟶ (5), since excitation to the triplet state by benzophenone leads to deoxygenation and the formation of azo-compounds.[12,26,27] Since the 95% ethanol used in the photoreactions was not degassed, and presumably contained dissolved oxygen, the irradiation conditions were (fortuitously) favourable for intramolecular cyclisation and the formation of *o*-hydroxyazo-compounds, but were not conducive to amine formation and azoxybenzene deoxygenation.

Irradiation of the methaqualone metabolite (3) afforded, in addition to the red *o*-hydroxyazo-compound (5d), traces of four unidentified coloured products, one of which was presumably the azoxybenzene (6d); significantly 2-aminobenzo-*o*-toluidide was not one of the products. Other workers have characterised the many by-products formed in the photoreactions of azoxybenzenes.[28-30]

Irradiation of 2-nitrobenzo-*m*-toluidide (12) presents an interesting situation. If the reactions proceeds through the expected azoxy-intermediate (13), further rearrangement should yield two isomeric *o*-hydroxyazobenzenes. This prediction was realised. Two major coloured products were isolated in approximately equal amounts; one was identical with the product formed by coupling diazotised anthranilic acid with *p*-cresol, and was assigned structure (14); the other was presumably the isomer (15). Tanikaga [27] has examined the photorearrangement of some *meta*-substituted azoxybenzenes. In all cases approximately equal amounts of two isomeric *o*-hydroxyazo-compounds were formed. This author made further observations consistent with our own results. He claimed that rearrangement of azoxybenzenes to *o*-hydroxyazobenzenes is fastest in polar protic solvents (*cf.* the slow discolouration of acetone or benzene solutions of *N*-aryl-2-nitrobenzamides and the rapid change in ethanol); highest yields of *o*-hydroxyazobenzenes were obtained with either unsubstituted or methyl-substituted azoxybenzenes, whereas azoxybenzenes with nitro-substituents were unreactive (*cf.* the rapid discolouration of the tolyl amides and the photostability of the nitro-analogues).



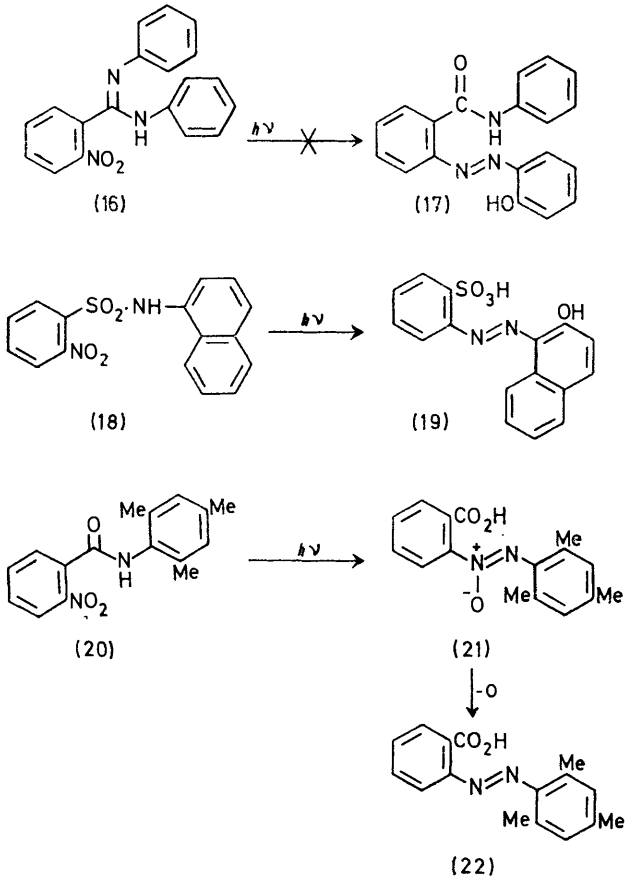
That the rearrangement (4) ⟶ (5) is purely photochemical was evident from the stability of 2-nitrobenzanilide (4a) to conditions which have been used to promote intramolecular cyclisation in *ortho*-substituted nitroarenes.[5,6] The anilide was stable when maintained above its m.p. either alone, or in admixture with toluene-*p*-sulphonic acid; it was stable in boiling acetic acid, pyridine, and piperidine; it was recovered unchanged from ethanolic sodium carbonate solution; in boiling hydrochloric acid or sodium hydroxide it underwent hydrolysis to the component acid and amine.

There was no indication of M — OH species in the mass spectra of the anilides (4a—c). Loss of 17 mass units consequent upon an intramolecular H-abstraction process is often a feature of the spectra of nitro-compounds bearing a hydrogen atom in the *ortho*-position, particularly when the hydrogen is benzylic in character.[3,4] Instead, the base peak in the spectra of the anilides we

[26] R. Tanikaga, *Bull. Chem. Soc. Japan*, 1968, **41**, 1664.
[27] R. Tanikaga, *Bull. Chem. Soc. Japan*, 1968, **41**, 2151.
[28] M. Iwata and S. Emoto, *Bull. Chem. Soc. Japan*, 1970, **43**, 946.
[29] S. Hashimoto, K. Kano, and J. Sunamoto, *Kogyo Kagaku Zasshi*, 1968, **71**, 864.
[30] S. Hashimoto, J. Sunamoto, and H. Fujii, *Kogyo Kagaku Zasshi*, 1967, **70**, 699.

attribute to the *o*-nitrophenylacylium ion (*m/e* 150) formed by central cleavage of the C–N bond.

Unfortunately the photoisomerisation is not applicable to the synthesis of mixed aromatic–aliphatic azoxy- or azo-compounds, because 2-nitrobenzamide itself, and its *N*-methyl, ethyl, isopropyl, benzyl, and phenethyl derivatives are photostable, as are 4-nitrobenzamide and its *N*-methyl and *N*-phenyl analogues. However, in an attempt to widen the scope and synthetic utility of the rearrangement we briefly examined the effect of light on the amidine (16) and sulphonamide (18). The amidine was stable to laboratory light over 3 years, but irradiation in 95% ethanol gave a dark solution containing several products (t.l.c.) in addition to substantial amounts of starting material; none of these products had the spectroscopic and chromatographic properties expected of the *o*-hydroxyazo-derivative (17). The sulphonamide (18), in contrast, rapidly turned red in both crystal and solution phases, and the anticipated



sulphonic acid (19), identical with the product formed by coupling diazotised sulphanilic acid with 2-naphthol, was identified (t.l.c.) as one of the many photoproducts. This latter reaction recalls the base-catalysed rearrangement of 2-nitrobenzsulphenanilides to azosulphenates [31] and its photochemical counterpart.[32]

[31] C. Brown, *Chem. Comm.*, 1969, 100.
[32] R. S. Goudie and P. N. Preston, *J. Chem. Soc.* (*C*), 1971, 3081.
[33] G. E. Lewis and J. A. Reiss, *Austral. J. Chem.*, 1966, **19**, 1887.

It has been reported that azoxybenzenes with no free *ortho*-position in the ring more distant from the N–O function are photostable in ethanol solution.[33] Accordingly, we expected that irradiation of the trimethyl anilide (20) would lead to an accumulation of the azoxy-derivative (21). The anilide (20) was stable in the solid state to laboratory light over 2 years: photoreaction in 95% ethanol was slow, but after 100 h a small amount of a red acidic product was separated from unchanged starting material. The properties of the product indicate that it is either the azoxybenzene (21) or the deoxygenated analogue (22).

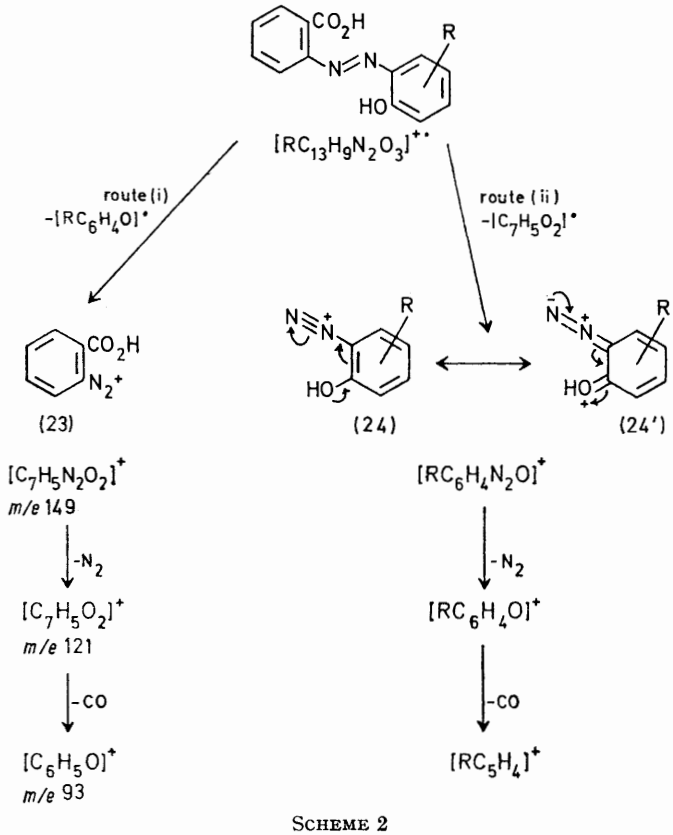
The mass spectral fragmentations of the hydroxyazo-compounds prepared in the present work correspond closely to those reported for other azo-compounds.[34] The dominating process is cleavage of the C–N bonds to give the diazonium ions (23) and (24), which further fragment by loss of nitrogen to give the respective aryl cations (Scheme 2). In all cases the ions at *m/e* 149 and 121 formed by cleavage as in route (i) were less abundant than those formed by route (ii). The differing abundances presumably reflect the influence of the hydroxy-group, which, by conjugation with the diazonium group [(24) ⟷ (24′)] confers double-bond character (and hence stability) on the bond linking the diazonium group with the hydroxyaryl system. The spectrum of the azoxybenzene (6a) showed features in common with the spectra of the hydroxyazo-compounds with the notable addition of a small, but characteristic $M - 16$ peak corresponding to loss of the oxygen atom.[35,36] The mass spectrum of the photoproduct from the trimethylanilide (20) showed an apparent molecular ion at *m/e* 268 ($C_{16}H_{16}N_2O_2$) indicative of the azo-structure (22). In this case the peaks at *m/e* 149 and 121 were of very low abundance, and the spectrum was dominated by the appearance of the 1,3,5-trimethylphenyl cation (or its rearrangement ion) at *m/e* 119. However, we cannot exclude the possibility that the compound is the azoxy-compound (21), the molecular ion at *m/e* 284 being absent.

The electronic absorption spectrum of this photoproduct showed a long-wavelength absorption at 335 nm comparable to those found in the spectra of 2-(phenylazo)benzoic acid (319 nm) and 2-(2-cyanophenylazo)benzonitrile (329 nm) and again points to the azo-structure (22): on the other hand, the spectrum also resembles those of the azoxy-derivatives (6a—c) (Table). We were unable to resolve the problem by a synthesis of the azobenzene (22) since diazotised anthranilic acid does not react with mesitylene under conventional coupling conditions.

Finally, we note two possible applications of the photorearrangement (4) ⟶ (5). The reaction provides access to a series of 2-(2-hydroxyphenylazo)benzoic acid derivatives which have industrial uses as chelating

[34] J. H. Bowie, G. E. Lewis, and R. G. Cooks, *J. Chem. Soc.* (*B*), 1967, 621.
[35] T. A. Bryce and J. R. Maxwell, *Chem. Comm.*, 1965, 206.
[36] J. H. Bowie, R. G. Cooks, and G. E. Lewis, *Austral. J. Chem.*, 1967, **20**, 1601.

agents,[37] and which, because of the orienting effects of the hydroxy-, chloro-, or methyl substituents as appropriate, would be difficult to prepare by diazonium coupling reactions. Also, as methaqualone (1) is an ingredient of the currently widely-abused hypnotic



SCHEME 2

The compositions of the ions have been confirmed by high resolution mass measurements

drug Mandrax®, a method of detecting the metabolite (3) in body fluids could have forensic interest. A spot of the nitrotoluidide (3) on a t.l.c. plate can be located simply by exposing the plate to light: a red colour characteristic of the hydroxyazo-compound (5d) develops. The sensitivity of the detection is superior to that achieved by conventional spray reagents for nitro-compounds.[38]

EXPERIMENTAL

Photoreactions were conducted in 95% ethanol in an Hanovia Photochemical Reactor with an unfiltered 100 W medium-pressure arc. I.r. spectra were recorded for KBr discs and n.m.r. spectra for solutions in [$^2H_6$]dimethyl sulphoxide. T.l.c. separations were accomplished on silica gel (0·25 mm) with chloroform–acetone–methanol–concentrated aqueous ammonia (60 : 10 : 25 : 0·5) as developing solvent.

Synthesis of Nitrobenzamides.—2-Nitrobenzamide (95%), m.p. 174—175°, was prepared by stirring a solution of 2-nitrobenzoyl chloride in benzene with an excess of cold concentrated aqueous ammonia and ice. Similarly prepared from 2-nitrobenzoyl chloride, the appropriate amine (1 mol. equiv.) and excess of aqueous 2N-sodium hydroxide at 20° were the following *N*-substituted 2-nitrobenzamides: *N*-methyl-, m.p. 107—108°; *N*-ethyl-, m.p. 92—93°; *N*-isopropyl-, m.p. 138—139°; *N*-benzyl-, m.p. 126—127°; *N*-phenethyl-, m.p. 117—119°; *N*-phenyl-, m.p. 154—155°; *N*-*o*-chlorophenyl-, m.p. 190—191°; *N*-*p*-chlorophenyl-, m.p. 183—184°; *N*-*o*-tolyl-, m.p. 175—176°; *N*-*m*-tolyl-, m.p. 169—170°; *N*-*p*-tolyl-, m.p. 146—147°; *N*-1-naphthyl-, m.p. 201—203°; *N*-*o*-nitrophenyl-, m.p. 167—168°; *N*-*p*-nitrophenyl-, m.p. 211—212°; *N*-*o*-cyanophenyl-, m.p. 205—206°; *N*-*p*-cyanophenyl-, m.p. 221—222°; *N*-mesityl-, m.p. 211—212°.

Alternatively, reaction between a solution of 2-nitrobenzoyl chloride in benzene and solid amines could be accomplished in refluxing pyridine (10 min).

4-Nitrobenzamide (m.p. 201—202°) and its *N*-methyl (m.p. 218—219°) and *N*-phenyl (m.p. 215—216°) analogues were similarly prepared by adaptation of the foregoing procedures. All compounds were crystallised from ethanol or aqueous ethanol, and had m.p.s consistent with published values.

2-(2-*Hydroxyphenylazo*)*benzoic acid* (5a).—(i) Irradiation of a solution of 2-nitrobenzanilide (5·0 g) in ethanol (1 l) gave a black-currant-coloured solution which was concentrated to 100 ml after 24 h. Chromatography on a neutral alumina column led to the recovery of starting material (80%), which was eluted from the column with ethanol, leaving a red immobile band at the top. The red photo-product was desorbed from the extruded column with aqueous 2N-sodium hydroxide (25 ml) and reprecipitated with 10N-hydrochloric acid to give 2-(2-hydroxyphenylazo)benzoic acid (15%), which crystallised from benzene as red plates, m.p. 200—201° (lit.,[10] 212·5—213°) (Found: C, 64·7; H, 4·2; N, 11·4. Calc. for $C_{13}H_{10}N_2O_3$: C, 64·5; H, 4·1; N, 11·6%), $\nu_{max.}$ 3200—2300 (bonded OH) and 1680 cm^{-1} (C=O). T.l.c. of the reaction mixture showed, in addition to starting material and the red photo-product (5a), traces of azoxybenzene-2-carboxylic acid (6a) and two unidentified minor coloured products.

Hydrogenation of 2-(2-hydroxyphenylazo)benzoic acid over 10% palladium–charcoal (uptake 2 mol. equiv.) gave only anthranilic acid and *o*-aminophenol.

(ii) Irradiation of azoxybenzene-2-carboxylic acid (6a) [39] in ethanol afforded a red solution after 4 h. T.l.c. confirmed that rearrangement to 2-(2-hydroxyphenylazo)-benzoic acid was quantitative. A sample of the azobenzoic acid isolated after 24 h was identical with the foregoing sample.

2′-*Chloroazoxybenzene*-2-*carboxylic Acid* (6b).—A mixture of 2-(2-chlorophenyl)-3-cyanoindazole 1-oxide (1·7 g; prepared [40] from *o*-nitrobenzylidene-2-chloroaniline) and potassium dichromate (0·75 g) was refluxed in acetic acid (20 ml) for 3 h, cooled, poured into water (100 ml), and acidified with 4N-hydrochloric acid. The precipitated *azoxybenzene* (1·5 g) crystallised from benzene as cream flakes, m.p. 125—126° (Found: C, 56·3; H, 3·1; N, 10·0. $C_{13}H_9ClN_2O_3$ requires C, 56·4; H, 3·3; N, 10·1%). The solid rapidly turned red on exposure to laboratory light.

4′-*Chloroazoxybenzene*-2-*carboxylic Acid* (6c).—Oxidation of 2-(4-chlorophenyl)-3-cyanoindazole 1-oxide [40] with potassium dichromate in boiling acetic acid according to the

[37] H. Diehl and J. Ellingboe, *Analyt. Chem.*, 1960, **32**, 1120.
[38] B. C. Gunn and M. F. G. Stevens, *J. Pharm. Pharmacol.*, 1972, **24**, 141P.
[39] A. Reissert and F. Lemmer, *Ber.*, 1926, **59**, 351.
[40] K. Akashi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1941, **20**, 798.

foregoing procedure afforded this *azoxybenzene* (70%), which crystallised from benzene as yellow flakes which rapidly turn red in light, m.p. 129—131° (Found: C, 56·1; H, 3·5; N, 10·4%).

2-(2-*Chloro*-6-*hydroxyphenylazo*)*benzoic Acid* (5b).—(i) Photorearrangement of *N*-*o*-chlorophenyl-2-nitrobenzamide in ethanol as previously described afforded the *chloroazobenzoic acid* (12%), which crystallised from benzene as red needles, m.p. 210—211° (Found: C, 56·2; H, 3·1; N, 10·3. $C_{13}H_9ClN_2O_3$ requires C, 56·4; H, 3·3; N, 10·1%), $\nu_{max.}$ 3400—2300 (bonded OH) and 1690 cm^{-1} (C=O). T.l.c. showed the presence of substantial amounts of starting material, 2′-chloroazoxybenzene-2-carboxylic acid, and other unidentified coloured products.

(ii) Irradiation of 2′-chloroazoxybenzene-2-carboxylic acid (6b) in ethanol for 24 h afforded a red solid when solvent was removed. The solid, m.p. 210—211° (90%), was identical (i.r.) with the sample prepared before.

2-(4-*Chloro*-2-*hydroxyphenylazo*)*benzoic Acid* (5c).—Irradiation of *N*-*p*-chlorophenyl-2-nitrobenzamide or 4′-chloroazoxybenzene-2-carboxylic acid for 24 h yielded this *chloroazobenzoic acid* in 15 and 100% yields, respectively. The product crystallised from benzene as red needles, m.p. 200—202° (Found: C, 56·2; H, 3·4; N, 10·1. $C_{13}H_9ClN_2O_3$ requires C, 56·4; H, 3·3; N, 10·1%), $\nu_{max.}$ 3600—2500 (bonded OH) and 1680 cm^{-1} (C=O).

2-(2-*Hydroxy*-6-*methylphenylazo*)*benzoic Acid* (5d).—Prepared by irradiation of 2-nitrobenzo-*o*-toluidide, the *azobenzoic acid* (15%) crystallised from benzene as maroon rosettes, m.p. 198—200° (Found: C, 65·9; H, 4·9; N, 11·3. $C_{14}H_{12}N_2O_3$ requires C, 65·6; H, 4·7; N, 10·9%), $\nu_{max.}$ 3600—2500 (bonded OH) and 1700 cm^{-1} (C=O), τ 7·32 (s, CH_3).

2-(2-*Hydroxy*-4-*methylphenylazo*)*benzoic acid* (5e) was prepared (10%) from irradiation of 2-nitrobenzo-*p*-toluidide, and crystallised from benzene as orange-red needles, m.p. 175—177° (Found: C, 65·8; H, 4·9; N, 11·0. $C_{14}H_{12}N_2O_3$ requires C, 65·6; H, 4·7; N, 10·9%), $\nu_{max.}$ 3600—2500 (bonded OH) and 1690 cm^{-1} (C=O).

2-(2-*Hydroxy*-5-*methylphenylazo*)*benzoic Acid* (14).—(i) A solution of diazotised anthranilic acid was coupled with *p*-cresol (1 mol. equiv.) in an excess of aqueous 2N-sodium hydroxide. The precipitated azo-compound (80%) crystallised from benzene as red needles, m.p. 192—194° (lit.,[37] 193°), $\nu_{max.}$ 3200—2800 (bonded OH) and 1690 cm^{-1} (C=O), τ 7·5 (s, CH_3).

(ii) The maroon solution produced when 2-nitrobenzo-*m*-toluidide was irradiated for 24 h was concentrated and chromatographed on an alumina column. The immobile red band was desorbed with aqueous alkali, and a crude red solid (20%) was precipitated with acid. T.l.c. revealed the presence of two red compounds in approximately equal amounts. One was identical with the foregoing azo-compound: the other had similar spectroscopic and chromatographic properties and was presumably the isomer (15).

2-(2-*Hydroxy*-1-*naphthylazo*)*benzoic Acid* (5f).—This azo-dye formed either by coupling diazotised anthranilic acid with 2-naphthol in alkaline medium (75%) or by irradiation of *N*-(1-naphthyl)-2-nitrobenzamide (12%), crystallised from ethanol as red needles, m.p. 268—270° (lit.,[37] 273·5—274·5°). T.l.c. showed the presence of at least five other coloured products.

Photoreaction of N-(1-*Naphthyl*)-2-*nitrobenzenesulphonamide*.—The sulphonamide [41] rapidly turned red in the crystal phase on exposure to laboratory light. Irradiation in ethanol (24 h) afforded a red solution which contained four coloured components. The major photoproduct had chromatographic characteristics identical on a range of adsorbents, and with different solvent systems, with a sample of 2-(2-hydroxy-1-naphthylazo)benzenesulphonic acid prepared independently by coupling diazotised sulphanilic acid and 2-naphthol in alkaline medium.

Photoreaction of N-*Mesityl*-2-*nitrobenzamide*.—Irradiation of the mesitylamide (1·0 g) in ethanol (1 l) for 100 h gave a yellow solution which was chromatographed on alumina. The immobile orange-red band was desorbed with aqueous 2N-sodium hydroxide and a red solid (60 mg; m.p. 120—121°) was precipitated with acid. Its spectroscopic properties are recorded in the Table.

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[41] J. H. Freeman and E. C. Wagner, *J. Org. Chem.*, 1951, **16**, 815.