Photochemical Transformations. Part XXVIII.† Aryl Azides as Potential Photosensitive Protecting Groups

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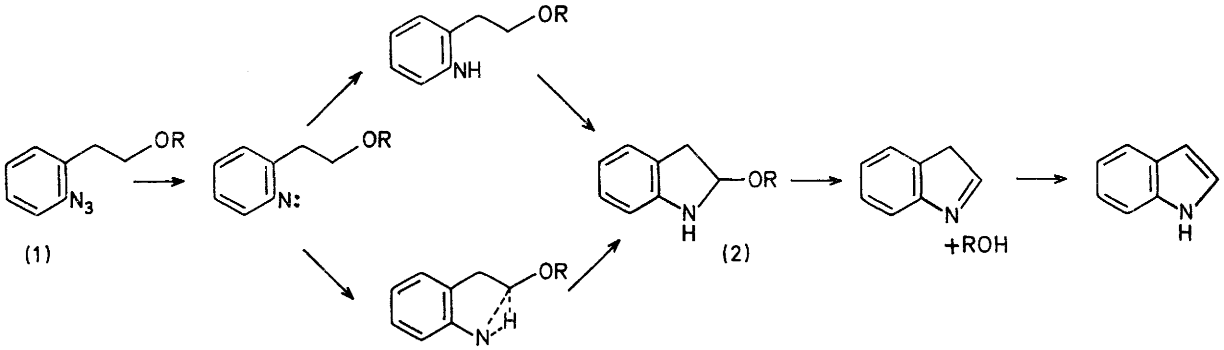
The potential of certain aromatic azides as photosensitive protecting groups has been explored. With alkyl or acyl derivatives of β-(*o*-azidophenyl)ethyl alcohol photolysis yields indole and the corresponding alcohol or acid. Whereas *o*-azidobenzyl benzoate is photolysed in protic solvents to give polymers and little of the free acid, derivatives of 5-azido-4-hydroxymethyl-1-methoxynaphthalene are more efficiently photolysed with release of the protected group.

A PREREQUISITE for photosensitive protecting groups is a chromophore which is sensitive to light of readily accessible wavelengths but relatively stable to most of the wide variety of chemical reagents commonly encountered in the ground state manifold. In many respects the azide system fits these requirements, yet despite previous photochemical studies on azides[1] the potential of azide-containing systems as photosensitive protecting groups has not hitherto been assessed. Consequently the following study was initiated. As a preliminary choice, derivatives of β-(*o*-azidophenyl)ethyl alcohol (1; R = H) were investigated. Aromatic azides were chosen since they are more stable to chemical reagents than aliphatic azides, cannot form imines,[2] and absorb light at longer wavelengths.[3] In principle photolysis should produce a nitrene intermediate which



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* Part XXVII, *Annalen*, 1970, **737**, 108.

[1] W. Lwowski, *Angew. Chem. Internat. Edn.*, 1967, **6**, 897; A. Reisner and R. Marley, *Trans. Faraday Soc.*, 1968, **64**, 1806; R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes and Arynes,' Nelson and Co., London, 1969, pp. 28 and 87.

[2] *Cf.* G. L'Abbé, *Chem. Rev.*, 1969, **69**, 345; R. M. Moriarty and M. Rahman, *Tetrahedron*, 1965, **21**, 2877.

[3] Yu. N. Sheinker, *Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, 1043.

can abstract hydrogen adjacent to the alcohol function, generating, eventually, the aminol derivative (2) which can readily decompose to indole releasing the protected group (Scheme). A related, thermally induced nitrene insertion into the C–H bond of an *o*-alkylated phenyl azide has been reported.[4]

Initially the methyl ether (1; R = Me) was synthesised. Nitration of methyl phenethyl ether with fuming nitric acid in acetic anhydride gave, predominantly, the *ortho*-isomer,[5] which readily afforded the required azide after reduction with tin(II) chloride, diazotisation, and reaction with sodium azide.[6]

Photolysis of a solution of the azide (1; R = Me) in benzene (Pyrex filter; medium-pressure mercury lamp) afforded indole, in 43% yield, with release of methanol, which was not estimated. This reaction, which represents the first instance of the photoinduced insertion of an aryl nitrene into an alkyl side chain, established the feasibility of the Scheme and it was then extended to the benzoate ester (1; R = Bz). The latter was made by benzoyl chloride–pyridine acylation of the alcohol (1; R = H), itself prepared from β-(*o*-nitrophenyl)ethyl alcohol by the procedure already described.

TABLE 1

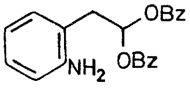
Photolysis of β-(*o*-azidophenyl)ethyl benzoate (1; R = Bz)

Run	Solvent	Conditions [a]	Time (hr.)	Products
1	Tetrahydrofuran	A	0·5	Benzoic acid 12%; (4) 16%
2	Benzene	A	3·7	Benzoic acid 5%; (4) 35%
3	Benzene	B	9·5	Benzoic acid 7%; indole 8%, (4) 13%; (5) 11%; (3) 5%
4	Ether	B	12·0	Benzoic acid 9%; indole 2%; (4) 2%; (5) 5%
5	Benzene	C	*ca.* 0·2	Benzoic acid 6%; (4) 19%
6	Penta-1,3-diene	B	9·0	Benzoic acid 8%; (6) 8%
7	Penta-1,3-diene–benzene (1 : 2)	A	3·5	Benzoic acid 11%; (4) 16%
8	Penta-1,3-diene–tetrahydrofuran (2 : 3)	B	12·0	Benzoic acid 21%; indole 4%; (6) 4%

[a] A, 50 W Hanovia low-pressure mercury lamp type 766/63 in silica vessel; B, Philips 125 W medium-pressure lamp type MBW/V in Pyrex vessel; C, 15 W germicidal lamp with a flowing film reactor.

The benzoate ester was irradiated under a variety of conditions, summarised in Table 1. In contrast to the methyl ether, it gave little of the expected products, indole and benzoic acid. In all cases the major product was a brown polar benzoate of unknown structure but probably polymeric in nature. It is known that indole itself readily polymerises in the presence of acid,[7] and this probably accounts for some of the polar material. Amongst the other products formed were 2-(*o*-aminophenyl)-1,1-bisbenzoyloxyethane (3), probably generated by addition of benzoic acid to the anticipated intermediate (2; R = Bz), derived from intramolecular carbon–hydrogen insertion. The azo-compound (4) and β-(*o*-aminophenyl)ethyl benzoate (5) were also formed and represent typical products from a triplet nitrene intermediate.[8]

Inhibition of the triplet nitrene pathway is difficult, since singlet-excited azides tend to produce singlet nitrenes faster than intersystem crossing to the triplet excited azide occurs. Once formed the singlet nitrene species can collapse to a triplet nitrene which cannot be 'quenched' in the normal sense but which could react with a quencher molecule, thus redirecting its normal decay processes. Nevertheless any triplet azide species present should be quenched to the ground state, and more of the desired insertion reaction should be observed. Photolysis of the benzoate ester (1; R = Bz) in the presence of penta-1,3-diene gave a striking suppression of azo-compound (4) formation and, in one case (run 8, Table 1), an increased yield of benzoic acid. A new compound was also isolated during the quenching experiments. It was a fairly polar oil, the



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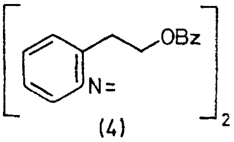

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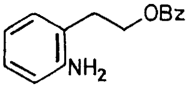

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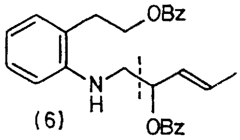

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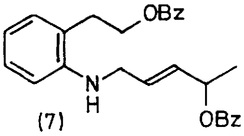

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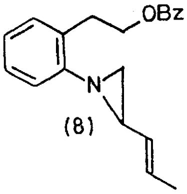

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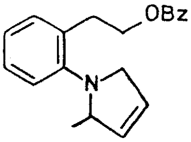

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[4] G. Smolinsky and B. I. Feuer, *J. Amer. Chem. Soc.*, 1964, **86**, 3085.

[5] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 1961, 3030.

[6] P. A. S. Smith and B. B. Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 2438.

[7] G. F. Smith, *Chem. and Ind.*, 1954, 1451.

[8] J. S. Swenton, *Tetrahedron Letters*, 1968, 3421; A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, 1968, **64**, 3265.

i.r. spectrum of which showed the presence of a secondary amine and two carbonyl groups. Mass spectral analysis gave the molecular formula as $C_{27}H_{27}NO_4$. The ^1H n.m.r. spectrum was consistent with either structure (6) or (7); however the mass spectral fragmentation pattern showed a strong peak at 175 mass units below the parent ion, only consistent with structure (6) and formed by the allylic cleavage indicated. The piperylene adduct (6) is derived from addition of benzoic acid to the aziridine (8) or the dihydropyrrole (9). Since the conditions of the photolysis favoured formation of an intimate ion pair, addition to the aziridine intermediate is more likely.[9] Such an intermediate could arise from addition of either the singlet [10a] or the triplet nitrene [10b] to the quenching agent (pentadiene).

Since the quenching experiments did not lead to a dramatic increase in the yield of benzoic acid, alternative substrates were sought. Although carbon–hydrogen insertion reactions are usually associated with singlet nitrene intermediates,[11] it does not necessarily follow that, in the absence of alternative reaction paths, triplet nitrene species cannot undergo a similar carbon–hydrogen insertion by a two-step process. For example, allylic carbon–hydrogen bonds are readily attacked by triplet nitrene species. Thus in the sensitised photolysis of ethylazidoformate in cyclohexene, high yields of 2,2′-bicyclohexenyl and *O*-ethylurethane are formed by hydrogen abstraction.[12a] If the initial hydrogen abstraction were to proceed intramolecularly a triplet diradical species would form (see Scheme), similar to the diradical intermediate postulated for addition of triplet nitrenes to olefins.[12b] Provided such a diradical intermediate is held together closely in space it can eventually collapse by spin inversion with formation of a further carbon–nitrogen bond.

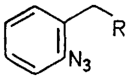
In order to test this possibility the photochemistry of a second model substrate, *o*-azidobenzyl alcohol (10; R = OH) and its corresponding benzoate (10; R = BzO), was examined. These substrates were derived from *o*-azidotoluene by refluxing its solution in dry benzene containing *N*-bromosuccinimide, to give the bromide (10; R = Br). Benzene was preferred as a solvent to carbon tetrachloride since the latter reacts with azides under radical conditions.[13] Treatment of the bromide with sodium benzoate in dimethylacetamide gave the benzoate (10; R = BzO). The alcohol could be obtained from this either by hydrolysis or by treatment of *o*-azidotoluene with *N*-bromosuccinimide in wet solvent. Photolysis of the alcohol (10; R = OH) in benzene gave only the unstable *o*-aminobenzaldehyde and a polymer probably derived from it.[14] This result suggested that irradiation of *o*-azidobenzyl benzoate in the presence of a polar solvent, such as water, might give benzoic acid *via* production of the intermediate (11) followed by hydrolysis. The results of the photolyses are summarised in Table 2. Only moderate yields of benzoic acid were isolated under the best conditions found (run 11, Table 2). Again an azo-compound (12) and *o*-aminobenzyl benzoate (13) were also isolated. The yield of the azo-compound increased substantially when the photolysis was sensitised with acetone, consistent with the generalisation that azo-compound formation arises from a triplet nitrene species.[8] The major product in all these reactions was another brown polar material shown by its i.r. spectrum to retain the benzoate group. In the presence of methanol no methyl benzoate was formed, demonstrating the absence of activated ester intermediates during photolysis. Possibly the predicted intermediate (11) polymerises before hydrolysis of the benzoate group. In agreement with this suggestion hardly any *o*-aminobenzaldehyde could be detected in the product mixture.

TABLE 2

Photolysis of *o*-azidobenzyl benzoate (10; R = OBz)

Run	Solvent	Conditions [a]	Time (hr.)	Products
9	Hexane-water	A	3·0	Benzoic acid 12%; (12) 6%
10	Acetone	A	4·0	Benzoic acid 0%; (12) 16%
11	Methanol	A	0·75	Benzoic acid 32%; (12) 8%
12	Methanol	C	0·1	Benzoic acid 17%; (12) 9%
13	Tetrahydrofuran–water	B	25 [b]	Benzoic acid 18%; (12) 0%; (13) 31%
14	Acetone	B	18 [c]	Benzoic acid 0%; (12) 22%

[a] As for Table 1. [b] Recovered 45% starting azide. [c] Recovered 43% starting azide.



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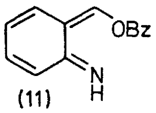

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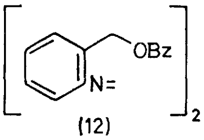

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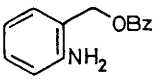

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One final model substrate, based on the *peri*-substituted naphthalene structure (14), was investigated. Such *peri*-substituted compounds have a strong tendency

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[9] Only one authentic case of 1,4-addition of a nitrene to a diene system appears to be known (A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1965, **87**, 5512).

[10] (*a*) K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 1964, 3953; (*b*) A. Misliva, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, 1968, **33**, 481.

[11] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1966, **88**, 2322; W. Lwowski and R. C. Johnson, *Tetrahedron Letters*, 1967, 871; I. Brown and O. E. Edwards, *Canad. J. Chem.*, 1967, **45**, 2599; *cf.* J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Amer. Chem. Soc.*, 1968, **90**, 5313.

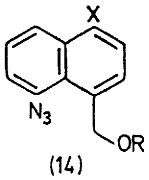
[12] (*a*) W. Lwowski and T. W. Mattingly, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 1947; (*b*) J. S. McConaghy and W. Lwowski, *ibid.*, 1967, **89**, 2357, 4450.

[13] J. E. Leffler and H. H. Gibson, *J. Amer. Chem. Soc.*, 1968, **90**, 4117.

[14] For the pyrolysis of *o*-azidobenzyl alcohol, see G. Smolinsky, *J. Org. Chem.*, 1961, **26**, 4108.

to cyclise.[15] In the present instance this steric pressure should enhance insertion by the singlet nitrene intermediate formed on photolysis and, furthermore, increase the chance of cyclisation of any triplet species by the two-step mechanism already outlined.

The initial approach was aimed at a synthesis of 1-azido-8-benzoyloxymethylnaphthalene (14; X = H, R = Bz) *via* the corresponding alcohol. Ozonolysis of acenaphthalene in methanol,[16] followed by reduction of the intermediate ozonide with dimethyl sulphide, gave the compound (15; R = MeO) which, after crystallisation from water, afforded the hydrate (15; R = HO). Treatment with base gave the naphthopyrone (15; R = H) in good yield by a Cannizzaro reaction. More of the naphthopyrone could also be obtained by an intermolecular reduction of the compound (15; R = OH) and (15; R = OMe) with formalin and base. However, the naphthopyrone was inert to the Schmidt reaction under a variety of conditions; none of the desired alcohol (16; X = H, Y = OH) was formed. For this reason the reduction of 2-hydroxybenz[*cd*]indole was attempted. This was produced by a method superior to that previous employed.[17] Treatment of naphthalene-1,8-dicarboxylic anhydride with hydroxylamine gave the hydroxamic acid; (17; R = H). Treatment with toluene-*p*-sulphonyl chloride gave, quantitatively, the corresponding tosylate (17; R = *p*-Me-C_6H_4·SO_2) which reacted with methanolic potassium hydroxide to give 2-hydroxybenz[*cd*]indole.[18] Hydrolysis with aqueous base gave the amino-acid (18). Reductions of the amino-acid, 2-hydroxybenz[*cd*]indole, or the tosylate (17; R = MeC_6H_4·SO_2) with lithium aluminium hydride under a variety of conditions all gave complex mixtures. The major component of these, thought to be 1,2-dihydrobenz[*cd*]indole, was readily oxidised in air to a blue compound formulated as (19).[19] Evidently the amino-alcohol (16; X = H, Y = OH) initially formed by reduction is unstable and is rapidly dehydrated to give 1,2-dihydrobenz[*cd*]indole.



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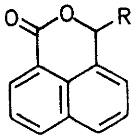

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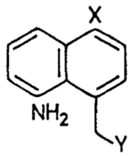

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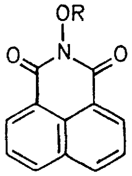

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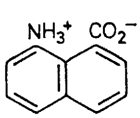

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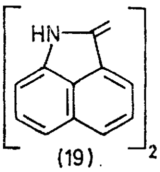

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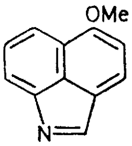
As an alternative system the known, stable methoxy-substituted naphthalene derivative (16; X = MeO, Y = OH) was prepared by a slightly modified procedure.[20] Acetylation and methylation of 1-amino-5-hydroxynaphthalene was followed by chloromethylation to give the *N*-acetyl derivative of the unstable chloride (16; X = MeO, Y = Cl). Reaction with sodium acetate in acetic acid gave the corresponding acetate, which was hydrolysed to the alcohol (16; X = MeO, Y = OH). Diazotisation of this amine by sodium nitrite in acetic acid followed by reaction with sodium azide afforded an excellent yield of the azido-alcohol (14; X = MeO, R = H) which could be readily acylated, with benzoyl chloride in pyridine, or alkylated, with ethanol in the presence of hydrochloric acid, the latter reaction indicating the stability of the naphthylic carbonium ion derived from compound (14; X = MeO, R = H). The ethyl ether could also be prepared by alkylation of the amino-alcohol (16; X = MeO, Y = H) followed by conversion into the azide.

Irradiation of the azido-ether (14; X = MeO, R = Et) in ether (Pyrex filter) rapidly gave one major, readily air-oxidised product. This was presumed to be 5-methoxybenz[*cd*]indole (20), produced *via* the carbinolamine (21), but too unstable to be isolated directly.[21] The crude photolysis mixture was therefore reduced with lithium aluminium hydride and then acetylated with acetic anhydride to give the *N*-acetyl derivative (22) in 39% overall yield. Ethanol was eliminated during the photolysis and was characterised as ethyl 3,5-dinitrobenzoate.



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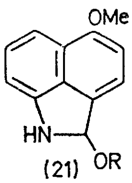

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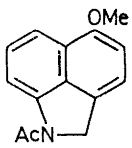

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Photolysis of the benzoate (14; X = MeO, R = Bz) in ether also proceeded smoothly with formation of the same unstable benzindole (20) and with liberation of 65—70% of benzoic acid. The remaining benzoic acid was retained as the ester of a polar product, but it could be readily liberated by hydrolysis with base. The photolysis was faster in ether than in benzene but very slow in ether containing penta-1,3-diene. The presence of the quenching agent did not alter the yield of benzoic acid formed, implying that either a singlet azide species was formed which reacted by loss of nitrogen and insertion faster than intersystem crossing to a triplet state could occur, or that any triplet nitrene species was

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[15] V. Balasubramanyan, *Chem. Rev.*, 1966, **66**, 567.

[16] J. K. Stille and R. T. Foster, *J. Org. Chem.*, 1963, **28**, 2703.

[17] F. Ullman and F. Cassirer, *Ber.*, 1910, **43**, 439.

[18] J. E. Baldwin, D. H. R. Barton, and J. K. Sutherland, *J. Chem. Soc.*, 1965, 1787.

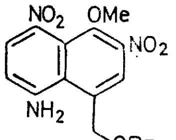
[19] A. Stoll, T. Petrzilka, and J. Rutschmann, *Helv. Chim. Acta*, 1950, **33**, 2254.

[20] C. A. Grob and J. Voltz, *Helv. Chim. Acta*, 1950, **33**, 1796.

[21] C. A. Grob, B. Hofner, and P. Payot, *Experientia*, 1951, **7**, 373.

also reacting to give the carbinolamine (21; R = Bz). No amine or azo-compounds corresponding to alternative triplet nitrene products could be detected.

This result confirmed the initial hypothesis with respect to the importance of steric environment on the course of the reaction. Since the naphthalene azide was stable to light of wavelengths longer than *ca.* 350 nm. an attempt was made to introduce a nitro-chromophore into the naphthalene nucleus in order to sensitise the molecule to light of lower energy. However, nitration of the azide precursor (16; X = MeO, Y = OAc), as its *N*-acetyl derivative, under a variety of mild conditions could only be induced to give a dinitro-derivative, identified on the basis of its ^{1}H n.m.r. properties as either (23) or (24; R = Ac, X = H), together with a small quantity of the zwitterion (25). That the dinitro-compound had the latter structure (24; R = Ac, X = H) was demonstrated by nitration of the deuteriated acetate (26; R^1 = Me, R^2 = CH_2·OAc, X = D) prepared from the deuteriated phenol (26; R^1 = H, R^2 = X = D). Nitration with 2N-nitric acid at room temperature gave, principally, the dinitro-derivative (24; R = Ac, X = D) in which the deuterium label was retained.



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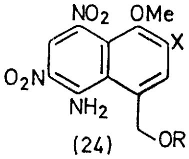

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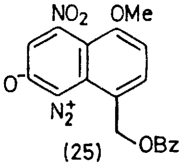

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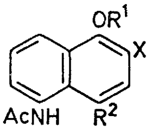

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EXPERIMENTAL

M.p.s were measured with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Unicam SP 200 spectrometer, for Nujol mulls (solids) or films (liquids), and u.v. spectra with a Unicam SP 800B instrument for solutions in absolute ethanol. Unless otherwise specified ^{1}H n.m.r. spectra were determined with a Varian A60 instrument for solutions in deuteriochloroform. Deuterium oxide was used to test for exchangeable protons. Mass spectra were determined with an A.E.I. MS9 instrument. T.l.c. was carried out with Merck GF_{254} silica gel. Light petroleum refers to the fraction of boiling range 60—80°. Solvents used in irradiations were freshly redistilled before use.

β-(o-*Aminophenyl)ethyl Methyl Ether*.—Reduction [22] of β-(*o*-nitrophenyl)ethyl methyl ether [5] with tin(II) chloride gave the corresponding amine (83%), $\nu_{max.}$ 3450, 3350, and 1625 cm.$^{-1}$. The amine was purified as its *hydrochloride*, m.p. (from ethanol) 112—114°; $\nu_{max.}$ 2250 and 1110 cm.$^{-1}$; τ (CCl_4) 6·68 (3H, s), 6·87 (2H, t, *J* 7 Hz), 6·35 (2H, t, *J* 7 Hz), and 2·05—2·75 (4H, m) (Found: C, 57·4; H, 7·4; Cl, 19·3; N, 7·3. $C_9H_{14}ClNO$ requires C, 57·5; H, 7·45; Cl, 19·0; N, 7·45%.

β-(o-*Azidophenyl)ethyl Methyl Ether* (1; R = Me).—The foregoing amine was diazotised and treated with sodium azide.[4,6] The azide (77%) was extracted into ether and stored as such. The solvent was distilled from portions of the stock solution as required. A portion of the azide obtained in this way had $\nu_{max.}$ 2140 and 1120 cm.$^{-1}$; τ (CCl_4) 6·73 (3H, s), 7·24 (2H, t, *J* 7 Hz), 6·55 (2H, t, *J* 7 Hz), and 2·92 (4H, m).

Photolysis of β-(o-*Azidophenyl)ethyl Methyl Ether* (1; R = Me).—A typical run was as follows. The azide (203 mg.) in dry benzene (25 ml.) was irradiated in a Pyrex flask with a medium-pressure mercury lamp. Dry oxygen-free nitrogen was bubbled through the solution during irradiation. The solution soon darkened to a light brown colour. The progress of the reaction was monitored by the disappearance of the azide chromophore in the i.r. ($\nu_{max.}$ 2150 cm.$^{-1}$). After reaction the crude mixture of products was separated by preparative t.l.c. with benzene as solvent. Indole (33 mg.) was isolated; corrected for evaporation during isolation this was equivalent to 42 mg. (43%); its picrate had m.p. 146—148°, identical with that of an authentic sample. β-(*o*-Aminophenyl)ethyl methyl ether (5 mg.) was also isolated from the t.l.c. plate.

β-(o-*Azidophenyl)ethyl Alcohol* (1; R = H).—β-(*o*-Nitrophenyl)ethyl alcohol [23] (3·76 g.) was stirred with conc. hydrochloric acid (50 ml.) and tin(II) chloride (23 g.) at room temperature for 15 hr. 4N-Sodium hydroxide was added carefully until the white tin complex had just dissolved. The solution was extracted with ether (5 × 100 ml.) and the extract was washed with water, dried (Na_2SO_4), filtered, and evaporated to give a yellow oil (2·37 g.). This was immediately converted into the *azide* (2·34 g., 64%) by the standard procedure; [4,6] $\nu_{max.}$ 3400 and 2150 cm.$^{-1}$ (Found: C, 58·9; H, 5·6; N, 25·75. $C_8H_9N_3O$ requires C, 58·8; H, 5·6; N, 25·7%).

β-(o-*Azidophenyl)ethyl Benzoate* (1; R = Bz).—Benzoylation of the alcohol (2·25 g.) with benzoyl chloride (10 g.) in dry pyridine (50 ml.) for 6 hr. at room temperature in the dark gave, after work-up by ether extraction in the normal manner, the oily benzoate. Filtration through alumina (grade 3; 100 g.), with benzene–light petroleum (2 : 1) as eluant, gave the *benzoate* (3·1 g., 86%) as an oil. A sample, after distillation at 90°/0·05 mm., had $\nu_{max.}$ 2150, 1720, and 1390 cm.$^{-1}$, $\lambda_{max.}$ 207, 231, 250sh, 278sh, and 287 nm. (ε 20,900, 15,600, 10,600, 2990, and 1960), ε_{300} 130; τ 6·99 (2H, t, *J* 7 Hz), 5·54 (2H, t, *J* 7 Hz), and 2·1—3·0 (9H) (Found: C, 67·3; H, 5·0; N, 15·5. $C_{15}H_{13}N_3O_2$ requires C, 67·4; H, 4·9; N, 15·7%).

Photolysis of β-(o-*Azidophenyl)ethyl Benzoate* (1; R = Bz).—The results are summarised in Table 1. The general procedure was as already described. The progress of the photolysis was followed by t.l.c. and by the disappearance of the azide peak in the i.r. spectrum. When photolysis was complete the solution was extracted (× 2) with aqueous sodium hydrogen carbonate. The aqueous layer was washed with ether (× 2) before acidification and re-extraction with ether (× 2). The latter ether extract was washed with water, dried (Na_2SO_4), and evaporated to give benzoic acid, identical with an authentic sample, m.p. 122°.

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[22] V. M. Zubarovskii, T. M. Vebovskaya, and A. I. Kiprianov, *Zhur. obshchei. Khim.*, 1961, **31**, 2849.

[23] S. T. Ravshevskaya, E. S. Kascheeva, and E. I. Mostostavskaya, *Zhur. obshchei Khim.*, 1963, **33**, 3998.

The initial ether extract was evaporated to small bulk under reduced pressure before preparative t.l.c. [benzene–light petroleum (9 : 1)]. The most polar, brown material, $\nu_{max.}$ 3400 and 1720 cm.$^{-1}$, was rejected. The next band was further separated by t.l.c. into two amino-benzoates, β-(*o*-aminophenyl)ethyl benzoate (5) and the ester (3). The next band contained the orange azo-compound (4), and the least polar band contained indole.

β-(*o*-Aminophenyl)ethyl benzoate was an oil, $\nu_{max.}$ 3490, 3410, and 1715 cm.$^{-1}$; τ 7·08 (2H, t, *J* 7 Hz), 6·2br (2H, exchangeable), 5·57 (2H, t, *J* 7 Hz), and 2·1—3·5 (9H).

2-(o-*Aminophenyl*)-1,1-*bisbenzoyloxyethane* (3) had m.p. (from benzene–light petroleum) 168—169°; $\nu_{max.}$ 3490, 3400, 1740, 1710, and 1630 cm.$^{-1}$, τ (100 MHz; CCl_4) 6·85 (2H, d, *J* 5·5 Hz coupled to a proton at τ 3·0), 6·5 (2H, exchangeable), 2·5—3·5 (11H), and 2·03 (4H, m) (Found: C, 73·0; H, 5·15; N, 3·7. $C_{22}H_{19}NO_4$ requires C, 73·1; H, 5·3; N, 3·9%).

β-(o-*Azophenyl*)*ethyl benzoate* (4) had m.p. (from ether) 126—127°, $\nu_{max.}$ 1710 cm.$^{-1}$, $\lambda_{max.}$ 207, 231, 275sh, 283sh, and 332 nm. (ε 35,800, 47,200, 7280, 8470, and 25,000) (Found: C, 75·2; H, 5·4; N, 5·85. $C_{30}H_{26}N_2O_4$ requires C, 75·3; H, 5·5; N, 5·85%).

When the photolysis was carried out in the presence of redistilled penta-1,3-diene (as a mixture of *cis*- and *trans*-isomers) another polar product (6) was isolated in small amounts as an oil, $\nu_{max.}$ 3470, 1720, 1710, 1605, 1590, 1280, and 1170 cm.$^{-1}$; τ (CCl_4) 8·27 (3H, m), 7·18 (2H, t, *J* 8 Hz), 5·74 (2H, t, *J* 8 Hz), 6·55 (2H, m), 4—4·5 (3H, m), 5·2br (1H, exchangeable), 2·5—3·6 (10H, m), and 1·9—2·3 (4H, m); *m/e* 429·1932 ($C_{27}H_{27}NO_4$ requires *M*, 429·1940), 359 (9%), 307 (15), 268 (50), 254 (100), 204 (11), 186 (8), 185 (9), 170 (10), 146 (45), and 132 (90).

o-*Azidobenzyl Bromide* (10; R = Br).—*o*-Azidotoluene (3·9 g.), *N*-bromosuccinimide (5·5 g.), and benzoyl peroxide (3·4 g.) were heated in the dark under nitrogen in refluxing dry benzene (30 ml.). The reaction was complete after 4·5 hr. The mixture was poured into water and ether and the ether layer was dried (Na_2SO_4) and chromatographed through alumina (grade 3; 100 g.) with benzene–light petroleum (1 : 1) as eluant. The first product eluted was the required *bromide* (4·7 g., 76%), m.p. (from light petroleum) 71—72°; $\nu_{max.}$ 2150 cm.$^{-1}$; τ (CCl_4) 5·63 (2H, s) and 2·6—3·1 (4H, m); $\lambda_{max.}$ 207, 226, and 255 nm. (ε 15,800, 12,600, and 10,100) (Found: C, 39·8; H, 3·1; Br, 38·0; N, 19·7. $C_7H_6BrN_3$ requires C, 39·7; H, 2·9; Br, 37·7; N, 19·8%).

Further elution afforded o-*azidobenzyl benzoate* (10; R = BzO) (0·5 g., 7%), m.p. (from light petroleum) 63—64°; $\nu_{max.}$ 2150, 1715, and 1280 cm.$^{-1}$; $\lambda_{max.}$ 205, 230, 251, and 281 nm. (ε 19,400, 13,250, 8900, and 2000); τ 4·69 (2H, s), 2·5—2·9 (7H, m), and 1·9—2·1 (2H, m) (Found: C, 66·3; H, 4·5; N, 16·45. $C_{14}H_{11}N_3O_2$ requires C, 66·4; H, 4·4; N, 16·6%).

The benzoate could also be made by treatment of the bromide with sodium benzoate in dimethylacetamide at 100° under nitrogen for 3 hr.

o-*Azidobenzyl Alcohol* (10; R = OH).—*o*-Azidotoluene (1·3 g.), *N*-bromosuccinimide (1·8 g.), and benzoyl peroxide (0·6 g.) were heated in refluxing carbon tetrachloride (10 ml.) in the presence of water (10 ml.) and in the absence of light. After 3 days the products were separated by chromatography through alumina (grade 3; 50 g.) with benzene containing small quantities of methanol as eluant. The first product eluted was unchanged starting material (0·3 g.); this was followed by *o*-azidobenzyl alcohol (0·6 g., 51%), m.p. 50—52° (lit.,[24] 52—53°); $\nu_{max.}$ 3300, 2150, 1050, and 1020 cm.$^{-1}$; $\lambda_{max.}$ 209, 252, 277, and 286 nm. (ε 18,200, 10,200, 2730, and 1920); τ (CCl_4) 7·24 (1H, s), 5·48 (2H, s), and 2·5—3·2 (4H, m).

Photolysis of o-*Azidobenzyl Alcohol*.—Freshly sublimed azide (10; R = OH) (0·34 g.) in dry benzene (200 ml.) was irradiated under nitrogen in a silica reactor with a low-pressure mercury lamp. The azide peak at $\nu_{max.}$ 2150 cm.$^{-1}$ diminished as a new peak at 1680 cm.$^{-1}$ was formed. The photolysis became slower with time. After 44 hr. the solution was concentrated under reduced pressure before separation by preparative t.l.c. [benzene–acetone (9 : 1)]. Besides recovered starting material (0·08 g., 23%), *o*-aminobenzaldehyde (0·05 g., 24%) was isolated, $\nu_{max.}$ 3380 and 1665 cm.$^{-1}$; τ 4·4br (2H, exchangeable), 2·5 (4H, m), and 0·2 (1H, s). The phenylhydrazone had m.p. (from ethanol) 222—223° (lit.,[24] 223—224°).

Photolysis of o-*Azidobenzyl Benzoate* (10; R = BzO).—The results are summarised in Table 2. The method was essentially as already described. No external cooling was applied and so the irradiation with the medium-pressure lamp was carried out at reflux. Benzoic acid was isolated as described previously. The other products were isolated chromatographically.

o-Aminobenzyl benzoate (13) had $\nu_{max.}$ 3500, 3400, 1720, and 1630 cm.$^{-1}$; τ 5·47 (2H, exchangeable), 4·71 (2H, s), and 1·9—3·5 (9H, m).

o-*Azobenzyl benzoate* (12) had m.p. (from light petroleum) 113—114°; $\nu_{max.}$ 1710 and 1280 cm.$^{-1}$; $\lambda_{max.}$ 205, 230, 273, 282, and 324 nm. (ε 25,400, 32,000, 5500, 6500, and 14,250); τ 4·0 (4H, s) and 1·8—2·8 (18H, m) (Found: C, 74·65; H, 5·1; N, 6·1. $C_{28}H_{22}N_2O_4$ requires C, 74·65; H, 4·9; N, 6·2%).

Ozonolysis of Acenaphthalene.[16]—Acenaphthalene (10 g.) in methanol (200 ml.) was ozonised at −30° until the yellow colour of the solution had disappeared (40 hr.). The precipitated peracetal (1·1 g.) was treated with excess of dimethyl sulphide at room temperature for 24 hr. and the product (15; R = MeO) (0·88 g.) was filtered off; m.p. 106—107°; τ 6·33 (3H, s), 6·13 (1H, s), 3·7—4·15 (2H, m), and 2·1—2·8 (6H, m). After recrystallisation from water several times this was converted into the hydrate (15; R = OH), m.p. 133—135°; $\nu_{max.}$ 3330 and 3200 cm.$^{-1}$; τ 3·72 (1H, d, *J* 6 Hz, collapsed to a singlet after shaking with D_2O), 3·44 (1H, d, *J* 6 Hz, collapsed to a singlet after shaking with D_2O), 3·5—4·0 (2H, exchangeable), and 2·1—2·6 (6H, m). When the hydrate (0·55 g.) was kept at room temperature in the presence of 2N-sodium hydroxide (20 ml.) for four days, then acidified with conc. hydrochloric acid (6 ml.), 1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-one (15; R = H) was formed (0·38 g.), m.p. (from methanol) 153—154°; $\nu_{max.}$ 1710 cm.$^{-1}$; τ 5·01 (2H, s) and 2·3—3·5 (6H, m). More of the naphthopyrone (4·55 g.) could be obtained by treatment of the filtrate from the ozonolysis mixture with formalin and base.[25] Purification on alumina (grade 3) with benzene–acetone (9 : 1) as eluant gave material, m.p. 156—157°. The naphthopyrone was stable to the Schmidt reaction[26] with sodium azide in sulphuric acid.

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[24] G. Smolinsky, *J. Org. Chem.*, 1961, **26**, 4108.

[25] R. H. Callighan, M. F. Tarker, and M. H. Wilt, *J. Org. Chem.*, 1961, **26**, 1379.

[26] H. Wolff, *Org. Reactions*, 1946, **3**, 307.

2-p-*Tolylsulphonyloxy*-1H-*benz*[de]*isoquinoline*-1,3(2H)-*dione* (17; R = p-$MeC_6H_4{\cdot}SO_2$).—2-Hydroxy-1*H*-benz-[*de*]isoquinoline-1,3-(2*H*)-dione (17; R = H) (5 g.) was treated with toluene-p-sulphonyl chloride (5·5 g.) in dry pyridine (50 ml.) at room temperature for 14 hr. The yellow precipitate was filtered off and water was added to the filtrate to give a further precipitate. The combined solids were recrystallised from benzene to give the *toluene*-p-*sulphonate* (7·7 g., 89%), m.p. 228—229°; $\nu_{max.}$ 1715, 1705, 1330, 1380, 1230, and 1020 cm.$^{-1}$ (Found: C, 62·3; H, 3·7; N, 3·7; S, 8·5. $C_{19}H_{13}NO_4S$ requires C, 62·1; H, 3·6; N, 3·8; S, 8·7%).

Treatment of the sulphonate (5·4 g.) with methanol (300 ml.) containing potassium hydroxide (5·7 g.) at room temperature overnight gave a white precipitate.[18] The solvent was evaporated off *in vacuo* and the residue was digested with chloroform. After filtration and evaporation of solvent the filtrate was chromatographed through alumina (grade 3; 100 g.), with benzene-chloroform mixtures as eluant. The 2-hydroxybenz[*cd*]indole (1·4 g., 60%) isolated had m.p. (from benzene) 180—182° (lit.,[17] 181°).

8-Aminonaphthalene-1-carboxylic acid (18) was prepared [27] quantitatively from this product.

Reductions with Lithium Aluminium Hydride.—The ester (17; R = p-$MeC_6H_4{\cdot}SO_2$) (400 mg.) was treated with lithium aluminium hydride (400 mg.) in refluxing ether (100 ml.) under nitrogen for 2 hr. Wet ether was added and the ether layer was separated. Evaporation of the ether extract gave an oil (120 mg.) shown to be a mixture by t.l.c. and which turned blue on exposure to air. In a similar manner the amino-acid (18) was reduced with lithium aluminium hydride in refluxing ether overnight. When an attempt was made to evaporate the ether extract obtained after reaction the solution turned dark blue and eventually afforded a blue solid which was soluble in acid. The product was a complex mixture (t.l.c.). A similar result was obtained on attempted reduction of 2-hydroxybenz[*cd*]indole.

5-*Acetamido*-4-*chloromethyl*-1-*methoxynaphthalene*.— 5-Acetamido-1-methoxynaphthalene (35·8 g.) in warm (40°) glacial acetic acid (500 ml.) was added dropwise during 2 hr. to a solution of paraformaldehyde (10 g.) in glacial acetic acid (130 ml.) at room temperature while a stream of dry hydrogen chloride was passed through the mixture. The solution warmed up during the initial stages of the reaction (to 40°) but gradually returned to ambient temperature as the reaction progressed. After addition was complete the mixture was stirred for a further 6 hr. while the passage of hydrogen chloride gas was continued. The mixture was then cooled to 5° and the product was filtered off, washed with a little ether, and dried under reduced pressure ($CaCl_2$). The product (33·4 g., 77%) had m.p. 155—165° (lit.,[20] 140—170°), $\nu_{max.}$ 3250, 1650, 1540, and 1040 cm.$^{-1}$.

5-*Acetamido*-4-*acetoxymethyl*-1-*methoxynaphthalene* (26; R^1 = Me, R^2 = $CH_2{\cdot}OAc$, X = H).—The foregoing chloride (35·8 g.) was dissolved in hot glacial acetic acid (2·2 l.) and sodium acetate (38 g.) and acetic anhydride (5 ml.) was added in portions. The stirred mixture was kept at 60° for 1 hr. The precipitated sodium chloride was filtered off and the filtrate was left overnight with a further portion of acetic anhydride (75 ml.). After addition of water, the mixture was extracted with chloroform. The extract afforded the diacetate (27 g., 65%), m.p. (from ethanol) 149—150°; $\nu_{max.}$ 3250, 1730, and 1645 cm.$^{-1}$; τ 7·94 (3H, s), 7·80 (3H, s), 6·27 (3H, s), 4·62 (2H, s), 1·55 (1H, s), 3·33 (1H, d, J 8 Hz), 2·45—2·70 (3H, m), 2·20 (1H, d, J 8 Hz), and 1·78 (1H, d, J 8 Hz).

Heating the diacetate (27 g.) in refluxing ethanol (1·25 l.) containing sodium ethoxide [from sodium (7 g.)] for 5 hr. under nitrogen followed by evaporation and extraction with ether gave the amino alcohol (16; X = MeO, Y = OH). This was purified by extraction with 6N-hydrochloric acid, work-up with ether, and then rebasification of the aqueous phase with solid sodium hydrogen carbonate. Recrystallisation of the precipitate from ethanol gave the amine (14·8 g., 78%), m.p. 121—122° (lit.,[20] 123—124°); $\nu_{max.}$ 3320, 3080, and 1600 cm.$^{-1}$; τ 6·07 (3H, s), 5·05 (2H, s), and 2·1—3·5 (5H, m). The broad OH and NH_2 peaks showed exchange with deuterium oxide.

5-*Azido*-4-*ethoxymethyl*-1-*methoxynaphthalene* (14, X = MeO, R = Et).—The alcohol (16; X = MeO, Y = OH) was converted into the corresponding ethoxy-ether (16; X = MeO, Y = EtO) by the method of Grob and Voltz.[20] The product had m.p. 76—77°; $\nu_{max.}$ 3410 and 3320 cm.$^{-1}$; τ 8·77 (3H, t, J 7 Hz), 7·42 (2H, q, J 7 Hz), 6·08 (3H, s), 5·12 (2H, s), 4·68br (2H, exchangeable), and 2·2—3·4 (5H, m).

The amine was converted [6] into the corresponding *azide* (89%), m.p. (from ethanol) 56—57°, $\nu_{max.}$ 2120 cm.$^{-1}$; $\lambda_{max.}$ 210, 232, and 317 nm. (ε 30,000, 33,000, and 8000); τ 8·71 (3H, t, J 7 Hz), 6·33 (2H, q, J 7 Hz), 6·06 (3H, s), 4·92 (2H, s), and 1·9—3·3 (5H, m) (Found: C, 65·4; H, 5·9; N, 16·2. $C_{14}H_{15}N_3O_2$ requires C, 65·4; H, 5·8; N, 16·3%)

5-*Azido*-4-*hydroxymethyl*-1-*methoxynaphthalene* (14; X = MeO, R = H).—Treatment of the amino-alcohol (16; X = MeO, Y = OH) with sodium nitrite in glacial acetic acid, followed by reaction with sodium azide [6] gave the *azide* (88%), m.p. (from ethanol) 142—144°, $\nu_{max.}$ 3300 and 2130 cm.$^{-1}$; $\lambda_{max.}$ 207, 232, and 317 nm. (ε 32,700, 46,200, and 10,500); τ 7—7·4 (1H, exchangeable), 6·07 (3H, s), 4·97 (2H, s), and 1·8—3·3 (5H, m) (Found: C, 62·6; H, 5·0; N, 18·1. $C_{12}H_{11}N_3O_2$ requires C, 62·9; H, 4·8; N, 18·3%).

This alcohol could also be converted into the corresponding ethyl ether (14; X = MeO, R = Et) by dissolving in ethanol containing a small quantity of concentrated hydrochloric acid.

5-*Azido*-4-*benzoyloxymethyl*-1-*methoxynaphthalene* (14; X = MeO, R = Bz).—The azido-alcohol (14; X = MeO, R = H) (2·0 g.) was dissolved in pyridine (100 ml.) containing freshly distilled benzoyl chloride (10 g.) in the absence of light. After 1 hr. at room temperature the solution was poured into ice–water, acidified, and extracted with ether. After work-up in the normal manner the extract afforded, from light petroleum, crystals of the *benzoate* (2·1 g., 71%), m.p. 111—112°; $\nu_{max.}$ 2150 and 1703 cm.$^{-1}$; $\lambda_{max.}$ 232 and 319 (ε 63,340 and 12,800); τ 6·04 (3H, s), 4·07 (2H, s), and 1·7—3·4 (10H, m) (Found: C, 68·6; H, 4·5; N, 12·5. $C_{19}H_{15}N_3O_3$ requires C, 68·5; H, 4·5; N, 12·6%).

Photolysis of 5-*Azido*-4-*hydroxymethyl*-1-*methoxynaphthalene* (14; X = MeO, R = H).—The alcohol (62 mg.) in dry ether (25 ml.) was photolysed in a Pyrex cell under nitrogen with a medium-pressure mercury lamp for 35 min. Lithium aluminium hydride (100 mg.) was added and the solution was heated to reflux under nitrogen for 1·5 hr.

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[27] E. Bamberger and M. Philip, *Ber.*, 1887, **20**, 237.

Wet ether, then water, were added, and the ether phase was separated and dried (Na_2SO_4) under nitrogen. The solution was filtered under nitrogen and acetic anhydride (5 ml.) was added before the ether was evaporated off *in vacuo* at room temperature. The solution was left overnight, then the acetic anhydride was distilled off under reduced pressure and the residue was purified by preparative t.l.c. to give, as the major product, *N*-acetyl-1,2-dihydro-5-methoxybenz[*cd*]indole (22) (20 mg., 35%), m.p. (from ethanol) 146°, identical with an authentic sample;[20] $\nu_{max.}$ 1655 cm.$^{-1}$; $\lambda_{max.}$ 231, 317, and 336 nm. (ε 45,400, 13,700, and 13,000); τ 7·72 (3H, s), 6·05 (3H, s), 4·95 (2H, s), and 2—3·3 (5H, m).

Photolysis of 5-*Azido*-4-*ethoxymethyl*-1-*methoxynaphthalene* (14; X = MeO, R = Et).—The azide (80 mg.) was photolysed as described for the foregoing alcohol. Reduction and acetylation afforded *N*-acetyl-1,2-dihydro-5-methoxybenz[*cd*]indole (22) (27 mg., 39%). In another run the solvent was distilled off and pyridine and 3,5-dinitrobenzoyl chloride were added to the distillate. The mixture was refluxed for 15 min. then water was added, and the ether layer was separated and washed with 2N-hydrochloric acid, 2N-sodium hydroxide, and water, dried (Na_2SO_4), and filtered. Evaporation afforded ethyl 3,5-dinitrobenzoate (4 mg.), m.p. 87—90°, identical with an authentic sample.

Photolysis of 5-*Azido*-4-*benzoyloxymethyl*-1-*methoxynaphthalene* (14; X = MeO, R = Bz). The benzoate (120 mg.) was irradiated as described for the alcohol. Irradiation was complete in 25 min. The solution was quickly extracted with cold 4N-sodium hydroxide and water, and the alkaline layers were acidified and re-extracted into ether. (Control experiments showed that the benzoate ester was not hydrolysed under these conditions.) The acid extract afforded benzoic acid (27 mg., 65%), m.p. 122°.

In dry ether photolysis of the azide (0·67 g.) with a Philips 125 W high-pressure mercury lamp (type HPK) took 40 min. and again gave benzoic acid (0·15 g., 65%). Hydrolysis of the neutral fraction with sodium ethoxide in ethanol for 2 hr. gave, after work-up, a further quantity of benzoic acid (60 mg., 25%). On exposure to air the neutral fraction from the photolysis rapidly turned a dark blue.

5-*Acetamido*-4-*acetoxymethyl*-2-*deuterio*-1-*methoxynaphthalene* (26; R^1 = Me, R^2 = CH_2·OAc, X = D).—5-Acetamido-1-naphthol (1·85 g.) was heated with triethylamine (1·1 g.), deuterium oxide (3·0 g., 99·5%), and dimethyl formamide to reflux under nitrogen for 5 hr. The solution was cooled and acidified with 6N-hydrochloric acid. Water was added and the solution was extracted (× 5) with ether. The product isolated from the ether extract was crystallised from chloroform; m.p. 176—177°; τ $[(CD_3)_2SO]$ 7·84 (3H, s), 2·80 (s, H-3), 2·75 (1H, d, *J* 8 Hz), 2·45 (1H, m), 1·92 (d, *J* 8 Hz, H-8), 0·76br (1H, exchangeable), and 0·50br (1H, exchangeable), *m/e* 203 (M^+, corresponding to [2,4-$^2H_2$]).

This material was alkylated with an excess of ethereal diazomethane and then chloromethylated and treated with sodium acetate in glacial acetic acid as already described to give the required acetoxymethylated naphthalene (overall yield 30%), m.p. 150—151°; τ $[(CD_3)_2SO]$ τ 7·99 (3H, s), 7·84 (3H, s), 4·57 (2H, s), 2·62 (s, H-3), 2·6 and 2·3 (m, H-6 and H-7), 1·85 (d, *J* 8 Hz, H-8), and 1·5br (1H, exchangeable). A small peak at τ 3·36 (d, *J* 8 Hz) was attributed to the 2-proton in some of the undeuteriated material; *m/e* 288 and 287 (65% of peak at 288).

Nitration of 5-*Acetamido*-4-*acetoxymethyl*-1-*methoxynaphthalene* (26; R^1 = Me, R^2 = CH_2·OAc, X = H) *and its* 2-*Deuterio-derivative*.—The undeuteriated ester was nitrated under a variety of conditions. Typically the ester (100 mg.) was heated with 2N-nitric acid (5 ml.) at room temperature for 22 hr. The yellow crystalline precipitate was purified by t.l.c. [benzene–acetone (9 : 1)] to give 5-*amino*-4-*acetoxymethyl*-6,8-*dinitro*-1-*methoxynaphthalene* (24; R = Ac, X = H) (70 mg., 60%), m.p. (from ethyl acetate) 207—208°; $\nu_{max.}$ 3420, 3310, 1730, 1550, 1370, and 850 cm.$^{-1}$; $\lambda_{max.}$ 212, 273, 334, and 435 nm. (ε 17,300, 15,200, 5150, and 8050); τ 7·83 (3H, s), 6·08 (3H, s), 4·46 (2H, s), 2·78 (1H, d, *J* 8 Hz), 2·27 (1H, d, *J* 8 Hz), and 1·72 (1H, s) (Found: C, 50·3; H, 3·8; N, 12·4. $C_{14}H_{13}N_3O_7$ requires C, 50·15; H, 3·9; N, 12·5%).

A small quantity of the *diazo-ketone* (25) was also isolated from the t.l.c. plate. This was recrystallised from benzene to give yellow needles of 5-*acetoxymethyl*-4-*diazo*-8-*methoxy*-1-*nitronaphthalene*-3(4H)-*one*, m.p. 155—156°; $\nu_{max.}$ 2150, 1735, 1625, 1555, and 855 cm.$^{-1}$; $\lambda_{max.}$ 208, 240, 267, 377, 408, and 421 nm. (ε 28,900, 35,500, 10,000, 6460, 5960, and 3000); τ 7·81 (3H, s), 6·16 (3H, s), 4·75 (2H, s), 3·34 (s, 2-H), and 3·25 and 2·43 (ABq, *J* 8 Hz, H-6 and H-7) (Found: C, 53·3; H, 3·5; N, 13·3. $C_{14}H_{11}N_3O_6$ requires C, 53·0; H, 3·5; N, 13·3%).

In attempts to purify the dinitro-amine (24; R = Ac, X = H) through alumina (grade 3), with benzene as eluant, hydrolysis to the *alcohol* (24; R = X = H) occurred. The alcohol (from benzene) gave yellow needles, m.p. 221—222°; $\nu_{max.}$ 3500, 3360, 3280, 1550, and 845 cm.$^{-1}$ (Found: C, 49·0; H, 3·9; N, 14·0. $C_{12}H_{11}N_3O_6$ requires C, 49·15; H, 3·8; N, 14·3%).

On repeating the nitration with the deuteriated material (26; R^1 = Me, R^2 = CH_2·OAc, X = D) a similar result was obtained. The principal dinitrated product was compound (24; R = Ac, X = D), m.p. 198—199°; τ 7·87 (3H, s), 6·10 (3H, s), 4·50 (2H, s), 2·29 (s, H-3), and 1·76 (s, H-7). A small AB quartet pattern at τ 2·68 and 2·29 (*J* 8 Hz) was assigned to some of the undeuteriated material; *m/e* 336 and 335 (63% of peak at 336).

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