Syntheses of Heterocyclic Compounds. Part XXIV.[1] Cyclisation Studies with *ortho*-Substituted Arylcarbene and Arylnitrene Precursors.[2]

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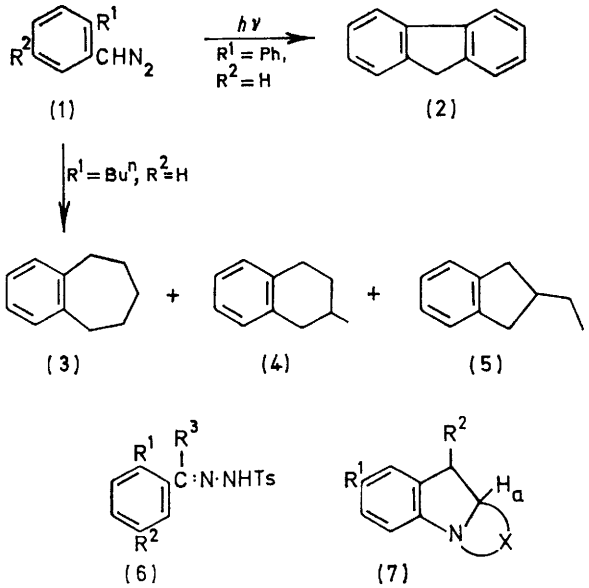
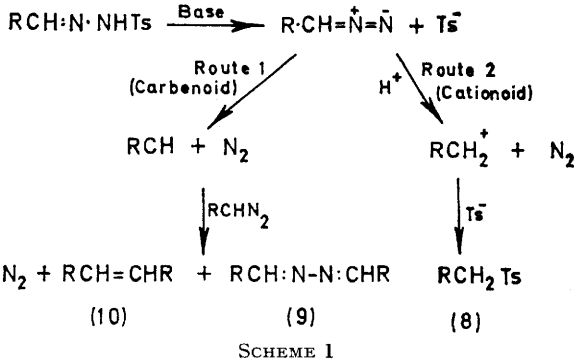
Thermal and photolytic decompositions of the tosyl hydrazones of *o*-dialkylamino-substituted benzaldehydes yield indolines. The scope and mechanism of this cyclisation have been explored. Moreover, benzaldehyde tosylhydrazones with *o*-alkoxy-, *o*-thioalkyl-, and *o*-phosphonate substituents as well as the corresponding diazoalkanes were pyrolysed and photolysed. The products from these carbene precursors were compared with those obtained from the analogous nitrene precursors [*i.e.* ArN_3 or $ArNO_2$ + $(RO)_3P$].

THE intramolecular cyclisation of arylnitrenes generated from suitably *ortho*-substituted aryl azides [3a] or nitroarenes [3b] is a well established and convenient method for preparing various *N*-heterocycles. By contrast, the use of analogous arylcarbene precursors for intramolecular cyclisations has been much less explored. For instance, irradiation of α-diazo-2-phenyltoluene yields fluorene [(1; R^1 = Ph, R^2 = H) ⟶ (2)] in high yield [4] and the α-diazo-2-butyltoluene (1; R^1 = Bu^n, R^2 = H) also undergoes intramolecular C-H insertion on photolysis producing a mixture [5] of the benzosuberan (3), the 2-methyltetralin (4), and the 2-ethylindane (5) in an overall 25% yield.

We now report work designed to assess the scope of the pyrolysis or photolysis of *ortho*-substituted arylcarbene sources for heterocyclic syntheses. Moreover, the results of this study were compared with those observed in the decompositions of arylnitrene precursors, with similar *o*-substituents.



Garner has shown [6] that toluene-*p*-sulphonylhydrazones of benzaldehydes with an *o*-dialkylamino-substituent, for instance (6; R^1 = $C_5H_{10}N$, R^2 = NO_2, R^3 = H) cyclised in the presence of sodium methoxide in boiling diglyme to give the indoline (7; X = $[CH_2]_4$, R^1 = NO_2, R^2 = H) in *ca.* 40% yield. The ring-closure in this Bamford–Stevens reaction [7] was ascribed to an intramolecular insertion into the α-methylene of the *o*-dialkylamino-group by an intermediate arylcarbene (ArCH). This was produced by the base-catalysed decomposition of the hydrazone (6) to give a diazomethane ($ArCHN_2$) followed by loss of nitrogen. The synthetic utility of this cyclisation depends on the extent of side-reactions which can lead to sulphones (8), stilbenes (10), and occasionally azines (9). The former (8) were invariably observed when hydroxylic solvents were used and arise probably from protonation of the intermediate diazoalkane by the solvent (see Scheme 1 route 2: cationoid path) while the latter two products, (9) and (10), result from interaction of the intermediate arylcarbene with the aryl diazomethane (see Scheme 1 route 1: carbenoid path). Photolytic or thermolytic decomposition of the appropriate aryl diazo-compound ($ArCHN_2$) which could be isolated as a stable red solid when a solution of the tosylhydrazone in pyridine was treated with sodium methoxide at 60° gave slightly higher yields.



SCHEME 1

The diazo-compounds could also be prepared from the appropriate arylhydrazone ($ArCH{:}N{\cdot}NH_2$) by oxidation with yellow mercuric oxide in benzene or petrol. Oxidation of the hydrazone in 1,2-dimethoxyethane or tetrahydrofuran led unexpectedly to formation of the corresponding nitrile (ArCN) and a little azine (9) by a

[1] Part XXIII, R. Garner, G. V. Garner, and H. Suschitzky, *J. Chem. Soc.* (*C*), 1970, 825.

[2] Part of this work was presented at the Joint Annual Meeting of the Chemical Society, Edinburgh, 1970.

[3] (*a*) P. A. S. Smith in 'Nitrenes,' (ed. W. Lwowski), Interscience, 1970, p. 99; (*b*) J. H. Boyer, *ibid.*, p. 163.

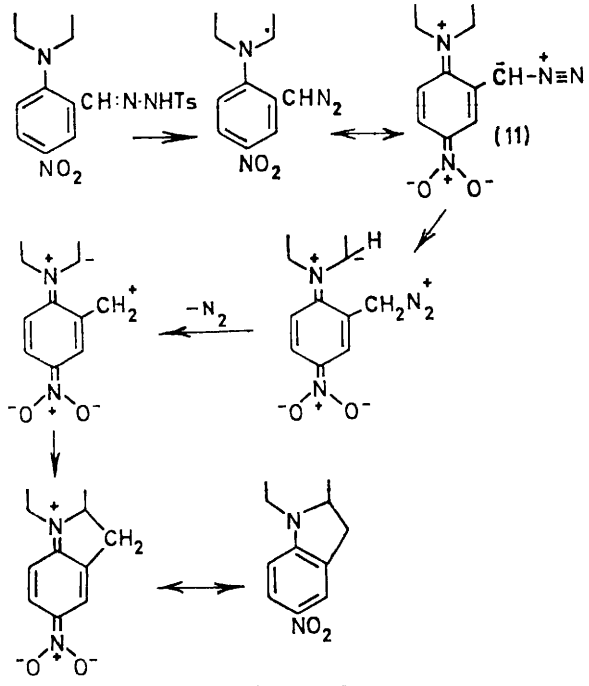
[4] D. B. Denney and P. P. Khemchuk, *J. Amer. Chem. Soc.*, 1958, **80**, 3289.

[5] C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, 1962, **18**, 617.

[6] R. Garner, *Tetrahedron Letters*, 1968, 221.

[7] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735.

reaction sequence on which we reported earlier.[8] The indoline (7; X = $[CH_2]_3$, $R^1 = NO_2$, $R^2 = H$) could only be obtained by photolysis or thermolysis of the pyrrolidino-compound (6; $R^1 = C_4H_8N$, $R^2 = NO_2$,



SCHEME 2

$R^3 = H$) or its diazomethane in dioxan since thermolysis in boiling diglyme gave the corresponding sulphone (8; R = 5-NO_2-2-C_4H_8N·C_6H_3). The indoline (7; X = $[CH_2]_3$, $R^1 = NO_2$, $R^2 = H$) appears to be thermally unstable possibly because of the steric strain of two fused 5-membered rings. In fact, when the compound (7) was heated with sodium toluene-*p*-sulphinate in diglyme at *ca.* 150° the sulphone was produced.

The ketone *p*-tosylhydrazone (6; $R^1 = C_5H_{10}N$, $R^2 = NO_2$, $R^3 = Me$) was also found to decompose under similar conditions to give the methylindoline (7; $R^1 = NO_2$, $R^2 = Me$, X = $[CH_2]_4$) in 37% yield. Its n.m.r. spectrum showed the methyl group to be split into 2 distinct doublets (τ 8·63 and 8·83 in $CDCl_3$). This is probably due to the presence of 2 isomers in which the methyl groups (7; $R^2 = Me$) can be *cis* or *trans* to the vicinal hydrogen (7; H_a). Attempts at separation, however, failed.

Generally, the yields of indolines improve with increasing ring size of the cyclic bases [see (7)] and also by using methane- instead of toluene-sulphonylhydrazones. The nitro-group in the starting material (6; $R^2 = NO_2$) was originally introduced in order to facilitate the synthesis of the parent aldehydes. It was, however, found that without it (6; $R^1 = C_5H_{10}N$, $R^2 = R^3 = H$) indoline formation was suppressed in favour of stilbene (10) and sulphone (8) production, and only in the case of a CF_3- group (6; $R^1 = C_5H_{10}N$, $R^2 = CF_3$, $R^3 = H$) was a small yield (1%) of indoline (7; $R^1 = CF_3$, $R^2 = H$, X = $[CH_2]_4$) observed. In view of the indispensable role of the nitro-group for cyclisation it is doubtful whether indoline formation is the result of carbene insertion. A feasible alternative involving a carbonium ion intermediate as set out (Scheme 2) would be dependent on the dominant part played by the quinonoid form (11) which is accentuated by the presence of a *p*-nitro-group. The activation of the α-methylene group by the t-nitrogen (*cf.* Scheme 2) is an essential, additional factor, reminiscent of other ring-closures which we ascribed to a ' t-amino-effect '.[9] This is borne out by the formation of indolines only (α-cyclisation) even when the possibility of β-cyclisation exists as in the diethylamino-compound (6; $R^1 = NEt_2$). By contrast, without the t-nitrogen, intramolecular insertion into the CH_2-groups along the chain occurs almost randomly [see (1) ⟶ (3) + (4) + (5); $R^1 = Bu^n$]. Also, the hydrazones of mono-alkylaminoaldehydes (6; R^1 = $NHBu^n$ or $NH·C_6H_{11}$) gave no cyclised products but only sulphones probably by the route indicated (Scheme 1; route 2). It could be argued that participation of the *para*-quinonoid form (12) in this case does not activate the α-methylene protons sufficiently for cyclisation to occur by the path described for the t-amino-group (see Scheme 2). Attempts to trap an intermediate carbene by photolysis of the diazomethane (1; $R^1 = C_5H_{10}N$) in cyclohexene failed and gave only the usual products. Since some of the reaction products (9) and (10) are, however, formed *via* carbenes, albeit in small yields, this indicates that route 1 (Scheme A) is only of minor importance. The use of copper as a catalyst [10] for decomposition of the diazomethane (1; $R^1 = C_5H_{10}N$, $R^2 = NO_2$) gave a good yield of the corresponding stilbene (10) but only 1% of the indoline (7; $R^1 = NO_2$, $R^2 = H$, X = $[CH_2]_4$). Thermolytic or photolytic decomposition of the pyridine tosylhydrazone (13) produced the parent aldehyde and corresponding stilbene and no cyclic products. The reaction between aryl carbenes and oxygen to give aryl aldehydes or ketones has been well documented.[11]

In contrast to the limited scope of the above indoline synthesis the analogous cyclisation of dialkylanilines with *ortho*-substituted nitrene precursors is more successful. Pyrolysis or photolysis of the azido-compounds (14; $R = N_3$) or deoxygenation of the nitro-compound (14; $R = NO_2$) with trialkyl phosphite leads to the corresponding benzimidazoles (15) often in good yields regardless of the nature of the substituent in the benzene ring.[1,12] Moreover, the method can also be extended to pyridine [12] and other aromatic ring systems.[13]

[8] D. B. Mobbs and H. Suschitzky, *Tetrahedron Letters*, 1971, 361.

[9] O. Meth-Cohn and H. Suschitzky, *Adv. Heterocyclic Chem.*, vol. XII, eds. A. R. Katritzky and A. J. Boulton, Academic Press, 1971, in the press.

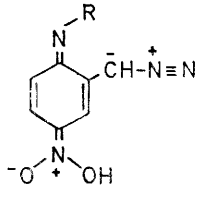
[10] E. Müller and H. Kessler, *Annalen*, 1966, **692**, 58.

[11] W. Kirmse, ' Carbene Chemistry,' Academic Press, 1964, p. 83.

[12] O. Meth-Cohn, R. K. Smalley, and H. Suschitzky, *J. Chem. Soc.*, 1963, 1666.

[13] H. Suschitzky and M. E. Sutton, *J. Chem. Soc.* (*C*), 1968, 3058.

The indoline synthesis can be usefully extended to the preparation of the corresponding indoles (16) by oxidising the products (7) with various reagents (*e.g.* chloranil, Pd/charcoal, and Se). Manganese dioxide was found to be the most convenient agent producing the indole quantitatively after 24 hr. under reflux in light petroleum ether (b.p. 100—120°). The oxidation never proceeded beyond the removal of 1 molar equivalent of hydrogen even with an excess of reagent and the heteroparaffinic ring [see (16)] was thus never affected. Examples of the fully unsaturated indoles are, however, known [*e.g.* (17)] but have been prepared only by direct synthesis.[14] This is analogous to the indolizidines since they also are resistant to direct oxidation.[15] Reduction of the nitro-indolines occurred readily with Pd–hydrazine to give a very unstable amino-compound (7; $R^1 = NH_2$, $R^2 =$ H) of which the acetyl derivative is stable. By contrast, the aminoindole (16; $R = NH_2$) obtained by reduction of the nitro-compound (16; $R = NO_2$) can be kept indefinitely.



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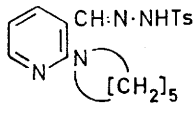

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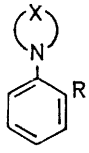

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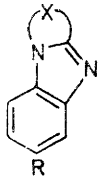

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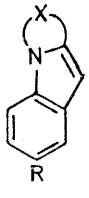

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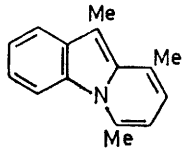


(17)

The u.v. spectra of the indolines (7; $R^1 = NO_2$) and their quaternised derivatives were measured in methanol at 20° (see Table 1). The absorption at *ca.* 400 nm can be assigned to a *para*-quinonoid structure (*cf.* indoline in Scheme 2) by analogy to the spectrum given by *p*-nitrodimethylaniline.[16] It is noteworthy that with increasing ring size (7; $X = [CH_2]_{3-6}$) the highest $\lambda_{max.}$ as well as its ε (due to the *para*-quinonoid form) also increase, an effect which is probably caused by a decreasing strain in the larger ring. Quaternisation of the indolines is reflected in a marked hypsochromic shift since the compound is no longer capable of existing in a quinonoid structure. The spectrum of the indole (16; $R = NO_2$, $X = [CH_2]_4$) differs from that of the corresponding indoline (7; $R^1 = NO_2$, $R^2 = H$, $X = [CH_2]_4$) because of an additional double bond. The $\lambda_{max.}$ value at longest wavelength is now at 333 nm and the extinction coefficient is also reduced (from 17,300 to 8100) relative to the corresponding indoline; this probably reflects the difficulty of the indole to assume a *para*-quinonoid structure because of increased rigidity. The indole cation has no peak above 290 nm as the nitrogen lone-pair is no longer available for co-conjugation.

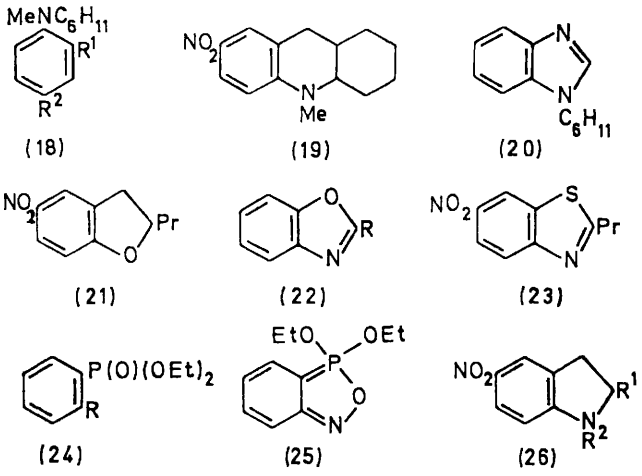
Decomposition of the *N*-cyclohexyl methyl-compound (18; $R^1 = CH{:}N{\cdot}NHTs$, $R^2 = NO_2$) led unexpectedly to the acridine (19). Whilst attack at the t-carbon atom of the cyclohexyl ring or at the methyl group would be favoured in a ' t-amino-mechanism ' (see Scheme 2) no products consistent with this course were found. The molecular geometry which is setting up the α-CH_2-group in a more favourable position than the t-CH-group for intramolecular reaction with the phenyl carbene may be responsible for this selectivity which appeared feasible from inspection of a molecular model. The result is in contrast to the analogous nitrene cyclisation [17] (18; $R^1 = N_3$ or NO_2; $R^2 = H$) which gave the *N*-cyclohexylbenzimidazole (20). The nitrene thus inserts into the methyl group to produce the preferred 5-membered ring in conformity with its usual behaviour.[3] Insertion at the t-CH of the cyclohexyl ring leading to a spiro-cyclohexane-dihydro-benzimidazole though feasible was not established. The only evidence for this reaction was tar formation arising possibly from decomposition of a spiro-structure.

We also investigated the decomposition of benzaldehyde *p*-tosylhydrazones with alkoxy-, thioalkyl-, and an ethyl-side-chain (6; $R^1 =$ OR, SR, or Et, $R^2 = NO_2$, $R^3 =$ H).

Pyrolysis of the 2-methoxy- or the 2-methoxy-5-nitro-benzaldehyde *p*-tosylhydrazone (6; $R^1 =$ OMe, $R^2 =$ H or NO_2, $R^3 = CH{:}N{\cdot}NHTs$) failed to yield cyclised products and gave only the corresponding stilbenes (10; $R = 2\text{-}MeOC_6H_4$ or $2\text{-}MeO\text{-}5\text{-}NO_2{\cdot}C_6H_3$) and sulphones (8; R as in 10). Similarly, extension of the chain to an ethoxy-group gave only the stilbene (10; $R = 2\text{-}EtO\text{-}5\text{-}NO_2{\cdot}C_6H_3$) and the parent aldehyde [see (6)] formed by reaction of the carbene with oxygen in the solvent. However, lengthening of the chain to n-butoxy- (6; $R^1 = Bu^nO$-, R^2, R^3 as before) led to cyclisation by thermolysis or photolysis yielding the benzofuran (21) (27%) and only small amounts of the corresponding stilbene and sulphone [see (10) and (8)]. By contrast, the cyclohexyloxy-derivative (6; $R^1 = O{\cdot}C_6H_{11}$, $R^2 = NO_2$, $R^3 = H$) did not yield any cyclised products but only polymeric material. The tendency of the longer chain to engage in cyclisation to give (21) is presumably due to its ' overhanging ' the reactive site and thereby preventing it from reacting with another molecule. The inductive influence (+*I*) of a longer alkyl chain which will, to some extent, compensate for the electron withdrawal from the α-methylene group by

[14] J. E. Saxton and Sir R. Robinson, *J. Chem. Soc.*, 1950, 3136.
[15] E. T. Borrows and D. O. Holland, *Chem. Revs.*, 1948, **42**, 611.
[16] W. R. Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838.
[17] G. V. Garner and H. Suschitzky, *Tetrahedron Letters*, 1971, 169.

the oxygen may be an additional factor facilitating attack of the electrophilic carbene on the α-carbon atom. If this electronic effect were, however, of prime importance we would expect the cyclohexyl compound (6; R^1 = $O{\cdot}C_6H_{11}$, R^2, and R^3 as before) also to yield a cyclic product, in the form of a 5-(spiro) or 6-membered ring.



The corresponding reactions with nitrenes mirrored the behaviour of the analogous carbene precursors. Thus, neither pyrolysis of the *o*-alkoxyphenylazides (6; R^1 = OMe, OEt, OPr^n, R^2 = H, $R^3{\cdot}C{:}N{\cdot}NHTs$ = N_3) nor deoxygenation of the corresponding nitro-compounds (6; R^1 as before, R^2 = H, $R^3{\cdot}C{:}N{\cdot}NHTs$ = NO_2) with triethyl phosphite gave benzoxazole derivatives. Only the parent amines or corresponding phosphoramidates were isolated. Pyrolysis of *o*-methoxyphenylazide in acetic anhydride results in a sigmatropic rearrangement to give 2-acetamido-3-acetoxyanisole as reported.[18] However, when the chain was lengthened to n-butyl (6; R^1 = OBu^n other substituents as before) the benzoxazole (22; R = Pr^n) was obtained by decomposition of the appropriate azide or deoxygenation of the nitro-compound. We believe that the factors which determine the outcome of these nitrene reactions are similar to those operative in the corresponding carbene precursors (see above).

None of the systems with an S-alkyl side-chain (6; R^1 = SBu^n or SBu^s, R^2 = NO_2, R^3 = H) could be made to cyclise by base-catalysed thermolytic or photolytic conditions. The products were those expected from routes 1 and 2 (see Scheme 1) namely, the corresponding stilbene (10), sulphone (8), and traces of aldehyde formed by oxygen pick-up by an intermediate carbene. Even photolysis of the diazoalkane (1; R^1 = SBu^n, R^2 = NO_2) gave only the stilbene (10; R = $2\text{-}Bu^nS\text{-}5\text{-}NO_2\text{-}C_6H_3$).

The dinitro-compound (6; R^1 = SBu^n, R^2 = NO_2, $R^3{\cdot}C{:}N{\cdot}NHTs$ replaced by NO_2) gave on treatment with trimethyl phosphite a complex mixture. One constituent corresponded in its R_F value to 5-nitro-2-n-propylbenzthiazole (23). This compound (23) was also obtained by a sodium polysulphide reduction of 2,4-dinitrobutylthiobenzene possibly *via* an intermediate nitroso-compound together with 3-nitro-4-thiobutylaniline.

TABLE 1

U.v. spectra of the 5-nitroindolines (7; R^1 = NO_2) and their hydrochlorides in ethanol

		Indoline (7; R^1 = NO_2)		Indoline hydrochloride (7; R^1 = NO_2)	
X	R^2	$\lambda_{max.}$nm.	ε	$\lambda_{max.}$nm.	ε
$[CH_2]_3$	H	208	11,800	210	10,800
		231	6500	257	9000
		390	15,500		
$[CH_2]_4$	H	208	9250	212	16,250
		237	5900	265	12,500
		412	17,300		
$[CH_2]_5$	H	209	12,500	223	30,800
		240	6500	284	21,700
		420	20,800		
$[CH_2]_6$	H	208	11,300	234	31,900
		240	6000	282	15,500
		422	21,000		
$[CH_2]_7$	H	208	17,000	222	42,000
		225	7600	285	24,000
		416	17,900		
$CH_2{\cdot}O{\cdot}CH_2{\cdot}$-$CH_2$	H	210	10,000	230	31,000
		235	6700	287	21,000
		400	15,300		
$[CH_2]_4$	Me	207	10,100	210	16,200
		230	7200	270	16,600
		410	16,600		

The only alkylated compound studied by us was the tosylhydrazone of 2-ethyl-5-nitrobenzaldehyde (6; R^1 = Et, R^2 = NO_2, R^3 = H) which, however, could not be made to cyclise and gave only the expected stilbene (10) and the sulphone (8; R = $2\text{-Et-}5\text{-}NO_2\text{-}C_6H_3$). In view of the report [5] that 2-butyl-α-diazotoluene gives cyclised products the length of the side-chain appears to play an important part as discussed for the analogous case of the alkoxy-compounds (see above). The decomposition of 2-alkylphenyl azides and deoxygenation of 2-alkylnitrobenzenes by phosphite have been studied by several workers.[3a,19] The results generally show that nitrene precursors with a 2-alkyl side-chain have a tendency to form a five-membered ring on thermolysis or photolysis.

We also prepared the *o*-azidophenylphosphonate (24; R = N_3) by reduction of the nitro-compound [20] (24; R = NO_2) with iron and ammonium chloride to the amine, followed by diazotisation and treatment with sodium azide. It was thought that azide decomposition followed by ring-closure might be a concerted process assisted by the P=O group and lead by analogy with the behaviour of *o*-azidophenyl ketones [3] to the heterocycle (25). The azide (24; R = N_3) proved remarkably stable and did not decompose in boiling diglyme or upon irradiation for seven days. When refluxed in *p*-dichlorobenzene an intractable tar was produced. Catalysed decomposition of the azide occurred in moist solvents in

[18] R. K. Smalley and H. Suschitzky, *J. Chem. Soc.*, 1963, 5571.
[19] (*a*) G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, 1964, **29**, 3097; (*b*) D. H. R. Barton, P. G. Sammes, and G. G. Weingarten, *J. Chem. Soc.* (*C*), 1971, 721.
[20] J. I. G. Cadogan, D. J. Sears, and D. M. Smith, *J. Chem. Soc.* (*C*), 1969, 1314.

presence of copper powder or nonacarbonyldi-iron to give a high yield of the amine (24; R = NH_2). We also prepared the aldehyde (24; R = CHO) by conversion of the amine (24; R = NH_2) into the nitrile followed by reduction with Raney nickel and formic acid.[21] The hydrazone (24; CH:N·NH_2) was unexpectedly stable to the usual oxidising agents and could, therefore, not be converted into the diazomethane (24; R = CHN_2) in order to study the behaviour of a carbene towards a P-containing side-chain.

EXPERIMENTAL

2-Dialkylamino-5-nitrobenzaldehydes.—A mixture of 2-chloro-5-nitrobenzaldehyde [22] (1 mol.) and the appropriate amine (1·1 mol.), and sodium hydrogen carbonate (1 mol.) was refluxed in ethanol for 4 hr. On pouring the reaction mixture into water a solid separated which was collected and gave on crystallisation from ethanol the required amino-compound. Condensation products from hepta- and octa-methyleneimine were purified by chromatography on alumina with benzene.

N-Methylcyclohexylamine gave only 10% condensation product in ethanol but a quantitative yield was obtained in sulpholane at 100° for 4 hr. Details of some of the compounds thus prepared and of their toluene-*p*-sulphonylhydrazones have been reported [23] by us and others are listed in Tables 2 and 3.

5-Chloro-2-piperidinobenzaldehyde.— 2-Chloro-5-nitrobenzonitrile [24] (18·4 g.) was boiled with piperidine (18·0 g.) for 4 hr. in ethanol (200 ml.) to yield after work-up as described above *5-nitro-2-piperidinobenzonitrile* (23·0 g.), m.p. 62° (Found: C, 62·2; H, 5·3; N, 18·1. $C_{12}H_{13}N_3O_2$ requires C, 62·4; H, 5·6; N, 18·2%). It (22·0 g.) was reduced in a boiling, aqueous suspension (50 ml.) of reduced iron powder (18·7 g.) and ammonium chloride (3 g.) for 3 hr. Extraction of the reaction mixture with chloroform gave after solvent removal *5-amino-2-piperidinobenzonitrile* (19·0 g.) as pale yellow needles, from benzene, m.p. 147° (Found: C, 71·5; H, 7·6; N, 20·7. $C_{12}H_{15}N_3$ requires C, 71·6; H, 7·5; N, 20·9%). A solution of the amine (15·1 g.) in hydrochloric acid (30 ml.) and water (30 ml.) was diazotised, and the diazotised solution was poured on to copper-bronze (6·0 g.) moistened with hydrochloric acid. The mixture was stirred for 2 hr. and extracted with chloroform. Separation of the solvent layer followed by evaporation gave *5-chloro-2-piperidinobenzonitrile* (9·0 g.), b.p. 195—196°/1 mm. Its *hydrochloride* had m.p. 120° (Found: C, 55·8; H, 5·4; N, 10·9, $C_{12}H_{14}N_2Cl_2$ requires C, 56·0; H, 5·5; N, 10·9%). The nitrile (8·8 g.) was reduced by the method of Backeburg and Staskun [21] with Raney nickel and formic acid to give *5-chloro-2-piperidinobenzaldehyde* (4·5 g.) b.p. 209°/0·75 mm.; this gave a *toluene-p-sulphonylhydrazone*, m.p. 160° (Found: C, 58·3; H, 5·7; N, 10·9. $C_{19}H_{22}N_3ClO_2S$ requires C, 58·2; H, 5·7; N, 10·7%).

2-Piperidino-5-trifluoromethylbenzaldehyde.—A mixture of 4-chloro-3-cyanobenzotrifluoride [25] (10·25 g.) was treated with piperidine (8·5 g.) in hot ethanol for 8 hr. to obtain *3-cyano-4-piperidinobenzotrifluoride* (12·3 g.), b.p. 156°/2 mm. (Found: C, 61·2; H, 5·4; N, 11·1. $C_{13}H_{13}F_3N_2$

TABLE 2

2-Dialkylamino-5-nitrobenzaldehydes

Amino group	Yield (%)	M.p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
Heptamethyleneimino-	86	70°	64·0	6·8	10·8	$C_{14}H_{18}N_2O_3$	64·1	6·9	10·7
Octamethyleneimino-	83	65	64·9	7·4	9·9	$C_{15}H_{20}N_2O_3$	65·2	7·3	10·1
Piperazino-	Quant.	125	56·6	4·3	14·3	$C_{13}H_{16}N_4O_6$	56·2	4·2	14·6
Dimethylamino-	85	102	56·0	5·1	13·9	$C_9H_{10}N_2O_3$	55·7	5·2	14·4
Diethylamino-	88	52	59·5	6·4	13·0	$C_{11}H_{14}N_2O_3$	59·4	6·4	12·6
N-Methyl-*N*-cyclohexylamino-	93	89	64·2	6·7	10·8	$C_{14}H_{18}N_2O_3$	64·1	6·9	10·7

TABLE 3

2-Dialkylamino-5-nitrobenzaldehydetoluene-*p*-sulphonylhydrazones and methanesulphonylhydrazones

Amino group	Yield (%)	M.p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
Toluene-*p*-sulphonylhydrazones									
Heptamethyleneimino-	90	167°	58·6	6·1	13·0	$C_{21}H_{26}N_4O_4S$	58·5	6·0	13·0
Octamethyleneimino-	90	182	59·4	6·6	12·2	$C_{22}H_{28}N_4O_4S$	59·5	6·3	12·6
Piperazino-	66	185	53·6	4·6	15·8	$C_{32}H_{32}N_8O_8S_2$	53·4	4·5	15·6
Dimethylamino-	85	182	53·0	5·0	15·1	$C_{16}H_{18}N_4O_4S$	53·0	5·0	15·6
Diethylamino-	90	129	55·0	5·9	14·3	$C_{18}H_{22}N_4O_4S$	55·4	5·7	13·9
N-Methyl-*N*-cyclohexylamino-	83	183	58·2	6·1	12·8	$C_{21}H_{26}N_4O_4S$	58·6	6·1	13·0
Methanesulphonylhydrazones									
Diethylamino-	80	139	46·0	5·7	—	$C_{12}H_{18}N_4O_4S$	45·8	5·8	17·8
Pyrrolidino-	Quant.	144	46·4	5·1	17·9	$C_{12}H_{16}N_4O_4S$	46·1	5·2	17·9
Piperidino-	Quant.	165	47·8	5·5	16·7	$C_{13}H_{18}N_4O_4S$	47·8	5·5	17·2
Perhydroazepino-	80	156	49·3	5·1		$C_{14}H_{20}N_4O_4S$	49·4	4·9	16·5

[21] B. Staskun and O. G. Backeberg, *J. Chem. Soc.*, 1964, 5880.
[22] H. G. Beard and H. H. Hodgson, *J. Chem. Soc.*, 1926, 147.
[23] D. B. Mobbs and H. Suschitzky, *J. Chem. Soc.* (*C*), 1971, 175.
[24] W. Borsche, *Ber.*, 1921, **54**, 660.
[25] L. Thorpe and E. R. Brunskill, *J. Amer. Chem. Soc.*, **1915**, **37**, 1258.

requires C, 61·4; H, 5·2; N, 11·0%). Its reduction (10·0 g.) as above with formic acid and Raney nickel gave 2-*piperidino*-5-*trifluoromethylbenzaldehyde* (7·8 g.), b.p. 196°/13 mm. Its *toluene*-p-*sulphonylhydrazone* had m.p. 222° (Found: C, 56·6; H, 5·1; N, 9·5. $C_{20}H_{22}F_3N_3O_2S$ requires C, 56·5; H, 5·2; N, 9·9%).

2-*Piperidinobenzaldehyde*.—A solution of *o*-fluorobenzaldehyde (4·0 g.) in dimethyl sulphoxide (10 ml.) was made to react with piperidine (3·0 g.) in the presence of anhydrous potassium carbonate (4·0 g.) at 95° for 6 hr. Water was added to the mixture which was then extracted with chloroform. The solvent layer left after evaporation 2-*piperidinobenzaldehyde* as an oil which was purified by elution from alumina with light petroleum (b.p. 40—60°) (Found: C, 75·9; H, 8·1; N, 7·2. $C_{12}H_{15}NO$ requires C, 76·2; H, 8·0; N, 7·4%). Its *tosylhydrazone* had m.p. 122° (Found: C, 64·1; H, 6·5; N, 12·7. $C_{19}H_{23}N_3O_2S$ requires C, 64·0; H, 6·5; N, 12·9%). Attempts to react *o*-chlorobenzaldehyde with piperidine under similar conditions gave 2-*chloro*-αα-*dipiperidinotoluene* (95%), m.p. 62° (Found: C, 77·3; H, 10·0; N, 10·7. $C_{17}H_{25}ClN_2$ requires C, 77·7; H, 9·6; N, 10·7%).

2-*Piperidinopyridine*-3-*carbaldehyde*.—A mixture of 2-chloronicotinonitrile [26] (13·8 g.), piperidine (17·0 g.), and benzene (100 ml.) were boiled on a steam-bath for 0·5 hr. Piperidine hydrochloride was filtered off and removal of the solvent gave 2-*piperidinonicotinonitrile* as an oil, b.p. 153—54°/12 mm. (16·8 g.) (Found: C, 70·6; H, 6·8; N, 22·5. $C_{11}H_{13}N_3$ requires C, 70·6; H, 7·0; N, 22·4%). Reduction of the nitrile (9·3 g.) with formic acid (150 ml.) and Raney nickel (7·5 g.) as described gave 2-*piperidinopyridine*-3-*carbaldehyde* (7·5 g.), b.p. 146°/0·7 mm.; i.r. $\nu_{max.}$ 1700 cm^{-1} (C:O) (Found: C, 69·7; H, 7·3; N, 14·6. $C_{11}H_{14}N_2O$ requires C, 69·4; H, 7·4; N, 14·7%). Its *toluene*-p-*sulphonylhydrazone* had m.p. 188° (Found: C, 60·3; H, 6·3; N, 15·6. $C_{18}H_{22}N_4O_2S$ requires C, 60·1; H, 6·5; N, 15·6%).

Alkoxy-5-nitrobenzaldehydes.— 2-Methoxy-5-nitrobenzaldehyde [27] m.p. 86° was made by nitration of *o*-methoxybenzaldehyde. The 2-*butoxy*-5-*nitrobenzaldehyde* b.p. 165°/2 mm. (Found: C, 59·4; H, 5·5; N, 6·1. $C_{11}H_{13}NO_4$ requires C, 59·2; H, 5·9; N, 6·3%), the 2-*cyclohexyloxy*-5-*nitrobenzaldehyde*, m.p. 85° (Found: C, 62·3; H, 6·4; N, 5·7. $C_{13}H_{15}NO_4$ requires C, 62·6; H, 6·1; N, 5·6%) and the 2-ethoxy-5-nitrobenzaldehyde,[28] m.p. 70°, were made by interaction of 5-nitrosalicylaldehyde (1 mol.) with the appropriate alkyl toluene-*p*-sulphonate [28-30] (1 mol.) in excess of aqueous sodium hydroxide (10%) under reflux for 2 hr. Ether extraction of the mixture followed by evaporation of the solvent gave the crude product which was purified by distillation. The *toluene*-p-*sulphonylhydrazone* of the *butoxy-compound* had m.p. 170° (Found: C, 55·0; H, 5·4; N, 10·6. $C_{18}H_{21}N_3O_5S$ requires C, 55·2; H, 5·4; N, 10·7%), of the *cyclohexyloxy-compound*, m.p. 140° (Found: C, 58·0; H, 5·5; N, 10·3. $C_{20}H_{23}N_3O_5S$ requires C, 57·6; H, 5·2; N, 10·1%) and of the 2-*ethoxy-compound*, m.p. 154° (Found: C, 53·4; H, 4·9; N, 11·9. $C_{16}H_{17}N_3O_5S$ requires C, 53·0; H, 4·7; N, 11·6%).

5-*Nitro*-2-(*alkylthio*)*benzaldehydes*.— 2-*Chloro*-5-*nitrobenzylideneaniline* was prepared by heating a mixture of equimolar quantities of aniline and 2-chloro-5-nitrobenzaldehyde on a water-bath for 0·5 hr. It had m.p. 95° (Found: C, 59·5; H, 3·7; N, 10·3. $C_{13}H_9ClN_2O_2$ requires C, 59·9; H, 3·5; N, 10·8%). The anil (5·6 g.), n-butanethiol (1·8 g.), and sodium hydroxide (5 ml.) were heated in sulpholane at 110° for 4 hr. Addition of water precipitated a yellow oil which was taken up in chloroform. The solvent layer was separated and gave on evaporation impure 5-*nitro*-2-*butylthiobenzylideneaniline* which was hydrolysed with 4M-sulphuric acid under reflux for 0·5 hr. Extraction with benzene gave a red oil which on purification over alumina with benzene yielded 5-*nitro*-2-(*n-butylthio*)*benzaldehyde* (4·0 g.), m.p. 68° (Found: C, 55·4; H, 5·8; N, 5·7. $C_{11}H_{13}NO_3S$ requires C, 55·2; H, 5·5; N, 5·9%). Its *toluene*-p-*sulphonylhydrazone* had m.p. 162° (Found: C, 53·1; H, 5·5; N, 9·9. $C_{18}H_{21}N_3O_4S_2$ requires C, 53·1; H, 5·2; N, 10·3%). By a similar procedure 5-*nitro*-2-(*s-butylthio*)*benzaldehyde*, m.p. 60° was prepared (Found: C, 55·5; H, 5·7; N, 5·7. $C_{11}H_{13}NO_3S$ requires C, 55·2; H, 5·5; N, 5·9%). Its *toluene*-p-*sulphonylhydrazone* had m.p. 190° (Found: C, 53·1; H, 5·5; N, 9·9. $C_{18}H_{21}N_3O_4S_2$ requires C, 53·1; H, 5·2; N, 10·3%).

2-*Ethyl*-5-*nitrobenzaldehyde*.—2-Ethylbenzaldehyde [31] b.p. 90°/11 mm. was prepared by reduction of 2-ethylbenzonitrile with Raney nickel and formic acid as described above in 62% yield. It (7·0 g.) was nitrated by dropwise addition to a solution of sodium nitrate (6·0 g.) in sulphuric acid (140 g.) at 0—5°; the mixture was poured into water and extracted with chloroform. This yielded 2-ethyl-5-nitrobenzaldehyde (6·0 g.) m.p. 86°. Its *toluene*-p-*sulphonylhydrazone* had m.p. 180° (Found: C, 55·2; H, 4·8; N, 12·0. $C_{16}H_{17}N_3O_4S$ requires C, 55·5; H, 4·9; N, 12·1%). Attempts to prepare 2-cyclohexylbenzaldehyde by reduction of 2-cyclohexylbenzonitrile [32] with Raney nickel and formic acid gave only starting material.

Diethyl o-*Formylphenylphosphonate*.—Diethyl *o*-nitrophenylphosphonate,[20] m.p. 55° (32·5 g.), was slowly added to a vigorously stirred and boiling suspension of reduced iron powder (23 g.) and ammonium chloride (2·75 g.) in water (40 ml.). After 3 hr. the reaction mixture was cooled and extracted with chloroform. The solvent layer was separated and evaporated to leave the unstable amine (25·0 g.) as an oil. Its *hydrochloride* had m.p. 106° (decomp.) (Found: C, 45·3; H, 6·1; N, 5·0. $C_{10}H_{17}ClNO_3P$ requires C, 45·2; H, 6·5; N, 5·3%). The hydrochloride (9·2 g.) was diazotised in 4M-hydrochloric acid at 0—5°. The mixture was then added slowly to a solution of potassium cuprocyanide which was kept at 70°. Extraction of the reaction mixture with chloroform followed by work-up gave *diethyl* o-*cyanophenylphosphonate* (17·0 g.), b.p. 163°/7 mm.; $\nu_{max.}$ 2230 (CN), 1250 (P=O), and 1020 $cm.^{-1}$ (P-O-Et) (Found: C, 55·4; H, 6·1; N, 5·6. $C_{11}H_{14}NO_3P$ requires C, 55·2; H, 5·9; N, 5·9%). A sample (9·6 g.) was reduced in formic acid with Raney nickel as above to yield *diethyl* o-*formylphenylphosphonate*, b.p. 186°/6 mm., with peaks at 1700 (CHO), 1250 (P=O), and 1020 (P-O-Et) (Found: C, 54·5; H, 6·0. $C_{11}H_{15}O_4P$ requires C, 54·6; H, 6·2%). Its *hydrazone* b.p. 148°/2 mm. (Found: C, 52·8; H, 5·5; N, 6·9. $C_{18}H_{23}N_2O_5PS$ requires C, 52·7; H, 5·7; N, 6·8%) could not be oxidised to the diazomethane even on prolonged

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[31] G. Jones, *J. Chem. Soc.*, 1960, 1918.
[32] T. H. McGuine and M. F. Dull, *J. Amer. Chem. Soc.*, 1947, **69**, 1469.

treatment with HgO or MnO_2 in various solvents, but remained unchanged.

Diethyl o-Azidophenylphosphonate.—A diazotised solution of the required amine (4·6 g.) (see above) was slowly added to a solution of sodium azide (1·3 g.) and sodium acetate (50 g.) in water (100 ml.) at 0°. The azide separated as an oil and was purified by chloroform extraction and chromatography (alumina). It showed a strong band at 2120 cm.$^{-1}$ (N_3) apart from the usual peaks. It proved stable to light and heat (see Discussion).

Preparation of Diazoalkanes.—(*a*) To pyridine (20 ml.) at 60° was added the required *p*-tosylhydrazone (2·0 g.) and sodium methoxide (0·5 g.). After being stirred for 0·5 hr. the reaction mixture was diluted with ice–water which caused the diazoalkane to separate. It was filtered off, washed with water, and dried *in vacuo*. Yields were 70—90% and the i.r. spectra showed a peak at *ca.* 2070 cm.$^{-1}$.

(*b*) A mixture of the required hydrazone (2·0 g.), anhydrous sodium sulphate (5·0 g.), ethanolic potassium hydroxide (satd. solution 0·5 ml.), and benzene (50 ml.) was stirred at 10° for 4 hr. The inorganic matter was filtered off and the filtrate was evaporated *in vacuo* to yield the diazoalkane (70—95%). Oxidation with manganese dioxide by a similar procedure was equally successful.

Decomposition Reactions.—(a) *Pyrolysis of* p-*tosylhydrazones in presence of base.* The required tosylhydrazone (1·5 g.) in diglyme or di-n-butyl ether (30 ml.) was added dropwise during 15 min. to a suspension of sodium methoxide (0·5 g.) in boiling diglyme or di-n-butyl ether (20 ml.). Heating was continued for 15 min., the solvent was driven off and the benzene-soluble portion of the residue was chromatographed on alumia to give indolines and other products (see scheme 1) for which details are given in Tables 4, 5, and 6. Details of azines have been reported.[23]

(b) *Pyrolysis with copper.* Decomposition of 5-nitro-2-piperidinobenzaldehyde toluene-*p*-sulphonylhydrazone or its diazomethane were carried out as in (a) in presence of copper which yielded only the corresponding sulphone (28%) stilbene (37%), and a small amount of indoline (1%).

(c) *Pyrolysis of methanesulphonylhydrazones.* This was carried out as in (a).

(d) *Pyrolysis of diazoalkanes.* The diazoalkane was made by adding the required tosylhydrazone (2·0 g.) and sodium methoxide (0·5 g.) to pyridine at 60°. After 0·5 hr. the reaction mixture was diluted with water to deposit the diazoalkane; this was identified from its peak at *ca.* 2070 cm.$^{-1}$. Alternatively, the appropriate hydrazones were oxidised with yellow mercuric oxide.[8] Decomposition was carried out in diglyme as described in (a).

TABLE 4

Indolines (7) or (26) prepared by thermolysis of appropriate toluene-*p*-sulphonylhydrazones (6; $R^2 = NO_2$)

	Hydrazone (6)	Decomp.		Indoline (7) or (26)			Yield		Found (%)				Reqd. (%)		
R^3	R^1	solvent	Base	R^1	R^2	X	(%)	M.p.	C	H	N	Formula	C	H	N
H	Pyrrolidino	Dioxan	KOBu^t	NO_2	H	$[CH_2]_3$	26	47°	64·7	6·1	14·0	$C_{11}H_{12}N_2O_2$	64·7	5·9	13·7
H	Piperidino	Diglyme	NaOMe	NO_2	H	$[CH_2]_4$ *									
		DBE	KOBu^t	NO_2	H	$[CH_2]_4$	37	113	65·8	6·4	13·0	$C_{12}H_{14}N_2O_2$	66·0	6·8	12·8
H	Hexamethylene-imino	Diglyme	NaOMe	NO_2	H	$[CH_2]_5$	38								
		DBE	KOBu^t	NO_2	H	$[CH_2]_5$	45	79	66·7	7·0	11·9	$C_{13}H_{16}N_2O_2$	67·1	6·9	12·1
H	Heptamethylene-imino	DBE	KOBu^t	NO_2	H	$[CH_2]_6$	50	82	68·1	7·5	11·1	$C_{14}H_{18}N_2O_2$	68·2	7·3	11·4
		Diglyme	NaOMe	NO_2	H	$[CH_2]_6$									
H	Octamethylene-imino	DBE	NaOMe	NO_2	H	$[CH_2]_7$	50	132	68·9	7·9	10·8	$C_{15}H_{20}N_2O_2$	69·2	7·7	10·8
H	Morpholino	Diglyme	NaOMe	NO_2	H	$CH_2O[CH_2]_2$	30								
		DBE	KOBu^t	NO_2	H	$CH_2O[CH_2]_2$	35	160	59·8	5·2	13·1	$C_{11}H_{12}N_2O_3$	59·9	5·4	12·8
H	*N*-Methylpiper-azino	Diglyme		NO_2	H	$CH_2NMe[CH_2]_2$	17	87	61·7	6·7	17·7	$C_{12}H_{15}N_3O_2$	61·8	6·4	18·0
Me	Piperidino	DBE	NaOMe	NO_2	Me	$[CH_2]_4$	33	75	67·8	6·5	12·0	$C_{13}H_{16}N_2O_2$	67·3	6·9	12·1
H	Dimethylamino	Diglyme	NaOMe	(H)	(Me)	—	40	126	60·1	5·8	16·1	$C_9H_{10}N_2O_2$	60·6	5·7	15·7
H	Diethylamino	Diglyme	NaOMe	(Me)	(Et)	—	40	60	63·9	6·7	13·6	$C_{11}H_{14}N_2O_2$	64·1	6·8	13·6
H	Piperazino	Diglyme	NaOMe	tar formation											

* Reduction with $SnCl_2$ in acetic anhydride gave the N-*aminoacetylindoline* (7; R^1 = NHAc, R^2 = H, X = $[CH_2]_4$), m.p. 191° (Found: C, 73·1; H, 7·7; N, 12·2. $C_{14}H_{18}N_2O$ requires C, 73·0; H, 7·9; N, 12·2%).

TABLE 5

Aryl sulphones ($ArCH_2SO_2{\cdot}C_6H_4Me$-*p*) obtained from thermolysis of the corresponding toluene-*p*-sulphonylhydrazones or aryldiazoalkanes

Sulphone		Yield	Found (%)				Required (%)		
Ar	M.p.	(%)	C	H	N	Formula	C	H	N
5-NO_2-2-$C_5H_{10}N{\cdot}C_6H_3$-	125°	3·6	61·0	5·9	7·4	$C_{19}H_{22}N_2O_4S$	60·9	5·9	7·5
5-NO_2-2-$C_4H_8N{\cdot}C_6H_3$-	180	51	60·0	5·5	7·9	$C_{18}H_{20}N_2O_4S$	60·0	5·6	7·8
2-MeO-C_6H_4-	144	73	64·9	5·6		$C_{15}H_{16}O_3S$	65·3	5·6	
2-MeO-5-$NO_2{\cdot}C_6H_3$-	154	29	56·0	4·5	4·1	$C_{15}H_{15}NO_5S$	56·1	4·7	4·4
2-Bu^{n}O-5-NO_2-C_6H_3-	164	2·1	59·3	5·8	3·9	$C_{18}H_{22}NO_5S$	59·3	6·0	3·9
2-Bu^{n}S-5-NO_2-C_6H_3-	158	6	56·6	5·8	4·0	$C_{18}H_{22}NO_4S_2$	56·9	5·8	3·7
2-Bu^{s}S-5-NO_2-C_6H_3-	138	8	56·6	5·9	3·4	$C_{18}H_{22}NO_4S_2$	56·9	5·8	3·7
2-Et-5-NO_2-C_6H_3	178	2·3	59·8	5·5	4·5	$C_{16}H_{17}NO_4S$	60·2	5·3	4·4
2-$C_5H_{10}N{\cdot}C_6H_4$-	160	22	69·8	7·1	4·3	$C_{19}H_{23}NO_2S$	69·3	7·0	4·3
5-Cl-2-$C_5H_{10}N{\cdot}C_6H_3$-	180/2·5mm	30	63·1	6·2	3·7	$C_{19}H_{22}ClNO_2S$	62·9	6·1	4·0
2-$C_5H_{10}N{\cdot}C_5H_3N$-3-	160	7	66·0	6·8	8·5	$C_{18}H_{22}N_2O_2S$	65·6	6·7	8·5

(e) *Photolysis.* The required tosylhydrazone (1·5 g.) or diazoalkane (1·5 g.) was photolysed in diglyme (400 ml.), the former compound in presence of sodium methoxide (0·5 g.) for *ca.* 4 hr. using a quartz filter. The products were purified by chromatography over alumina with benzene.

(f) *Photolysis of diazoalkanes in presence of a trap.* α-Diazo-5-nitro-2-piperidinotoluene (2 g.) in cyclohexene was irradiated for 4 hr. at 20° under nitrogen. Removal of the solvent and chromatography of the residue on alumina with light petroleum gave cyclohexene as the only hydrocarbon fraction. Elution with benzene gave the indoline (2·5%) and the *octahydro-10-methyl-7-nitroacridine* (19) (33%), m.p. 50° (benzene) (Found: C, 68·0; H, 7·1; N, 11·7. $C_{14}H_{18}N_2O_2$ requires C, 68·3; H, 7·3; N, 11·4%). Its n.m.r. spectrum showed signals at τ 8·42 (CH_2, broad s), 7·18 (N-Me, s), 7·03 (9-CH_2, s), two sets of doublets centred at 6·84 and 6·40. The aromatic protons had signals at τ 3·83 (5-H), 2·14 (8-H, $J_{6,8}$ 2 Hz), and 2·02 (6-H, $J_{5,6}$ 8·0 Hz).

Photolysis of the 2-piperidino-5-trifluoromethylbenzaldehyde toluene-*p*-sulphonylhydrazone [see (6)] gave the appropriate stilbene (20%), the parent aldehyde (8%), and the *7-trifluoromethyltetrahydropyrido*[1,2-a]*indoline*, m.p. 84° (1%) (Found: C, 64·5; H, 5·9; N, 5·5. $C_{13}H_{14}F_3N$ requires C, 64·8; H, 5·7; N, 5·7%).

TABLE 6

Diarylethylenes (ArCH:CHAr) obtained from thermolysis of the corresponding toluene-*p*-sulphonylhydrazones or aryldiazoalkanes

Diarylethylene Ar	M.p.	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
5-NO_2-2-$C_5H_{10}NC_6H_3$-	279°	4	66·2	6·5	12·5	$C_{24}H_{28}N_4O_4$	66·0	6·8	12·8
2-MeN·C_4H_8N-5-NO_2-C_6H_3-	285	8	61·4	6·2	17·7	$C_{24}H_{30}N_6O_4$	61·8	6·4	18·0
2-MeO·C_6H_4	136 [33]	2							
2-MeO-5-NO_2·C_6H_3-	265	9·5	58·6	4·1	8·7	$C_{10}H_{14}N_2O_6$	58·2	4·3	8·5
2-EtO-5-NO_2·C_6H_3-	200	28	60·0	5·0	7·6	$C_{18}H_{18}N_2O_6$	60·4	5·0	7·8
2-Bu^{n}O-5-NO_2·C_6H_3-	202	7·5	63·6	6·0	6·5	$C_{22}H_{26}N_2O_6$	63·8	6·3	6·8
2-Bu^{n}S-5-NO_2·C_6H_3-	160	28	59·3	5·8	5·9	$C_{22}H_{28}N_2O_4S_2$	59·3	5·9	6·3
2-Bu^{s}S-5-NO_2·C_6H_3-	159	12	59·4	5·7	5·8	$C_{22}H_{28}N_2O_4S_2$	—	—	—
2-Et-5-NO_2·C_6H_3-	150	28	66·3	5·4	8·8	$C_{18}H_{18}N_2O_4$	66·3	5·6	8·6
2-C_5H_{10}N·C_6H_4-	172	0·5	83·1	8·7	8·1	$C_{24}H_{30}N_2$	83·3	8·7	8·0
5-CF_3-2-$C_5H_{10}NC_6H_3$-	125/1mm	20	64·6	5·9	5·4	$C_{26}H_{28}F_6N_2$	64·8	5·8	5·8
2-C_5H_{10}N·C_5H_3N-3-	150	23	76·1	8·0	16·1	$C_{22}H_{28}N_4$	75·9	8·1	16·1
2-C_6H_{11}(Me)N-5-NO_2·C_6H_3-	220	2·5	68·5	7·4	11·0	$C_{28}H_{36}N_4O_4$	68·3	7·3	11·4

TABLE 7

Some examples of the product distribution of the thermal (T) and the photolytic (P) decompositions of *p*-tosylhydrazones and diazoalkanes

Starting material R	Starting material Y	Method	Yield (%) Indoline	Stilbene	Sulphone	Aldehyde Recovered
NO_2	CH:N·NHTs	T	37		2	
NO_2	CH:N·NHTs	T *		37	28	
NO_2	CH:N·NHTs	P	45	9		
NO_2	CHN_2	T	45	4		
H	CH:N·NHTs	T		1	22	
H	CH:N·NHTs	P		0·5	24	22
Cl	CH:N·NHTs	T			30	
Cl	CH:N·NHTs	P			20	7
CF_3	CH:N·NHTs	P	1	20		8

* Decomposition in presence of copper bronze powder.

(4·5%), the stilbene (10%), and 5,5′-dinitro-2,2′-dipiperidinobenzaldehyde azine (14%) m.p. 279° (decomp.) (mixed m.p. with an authentic sample showed no depression).

(g) *Miscellaneous decompositions yielding heterocycles.* 2-Butoxy-5-nitrobenzaldehyde toluene-*p*-sulphonylhydrazone gave by method (a) the stilbene (7·5%), the sulphone (2·1%) (*cf.* Tables 5 and 6), *5-nitro-2-propylbenzofuran* (27%), m.p. 184° (benzene) (Found: C, 63·4; H, 6·4; N, 6·5. $C_{11}H_{13}NO_3$ requires C, 63·8; H, 6·3; N, 6·1%). Its n.m.r. spectrum showed signals at τ 8·96 (C-CH_3, t), 7·9—8·8 (O-C-CH_2·CH_2, m) 6·50 (Ar·CH_2) and at 4·9 (O-CH, m). The aromatic protons [see (21)] gave peaks at τ 3·01 (7-H), 1·78 (6-H) with $J_{6,7}$ 9 Hz and 1·48 (4-H) with $J_{4,6}$ 2·2 Hz.

The *N*-methyl-*N*-cyclohexylamino-toluene-*p*-sulphonylhydrazone [6; R^1 = N(Me)C_6H_{11}, R^2 = NO_2, R^3 = H] when decomposed as in (a) gave the corresponding stilbene

Oxidation of Indolines to Indoles.—The indoline (7; R^1 = NO_2, R^2 = H, X = $[CH_2]_4$) (0·5 g.) and activated manganese dioxide (2·5 g.) were shaken in light petroleum (b.p. 100—120°) (20 ml.) under reflux for 24 hr. The mixture was filtered and the solid was extracted with hot benzene. The filtrate and benzene extract were combined and chromatographed over alumina with benzene to give *1,2,3,4-tetrahydro-7-nitropyrido*[1,2-a]*indole* (quant.) as red plates from light petroleum, m.p. 152° (Found: C, 66·6; H, 5·5; N, 12·9. $C_{12}H_{12}N_2O_2$ requires C, 66·6; H, 5·6; N, 13·0%); τ ($CDCl_3$) 8·00 ($[CH_2]_2$, t), 7·05 (N·CH_2, t) 6·00 (=C-CH_2, t) 3·75 (CH=C, s), 1·65 (8-H), 2·03 (6-H), and 2·78 (9-H) with

[33] M. Jones and S. D. Reich, *J. Amer. Chem. Soc.*, 1967, **89**, 3935.

$J_{6,8}$ 2·2 Hz and $J_{8,9}$ 8·5 Hz; $\lambda_{max.}$ (EtOH) 212 (14,700), 275 (21,500), and 333 (8100); its hydrochloride had $\lambda_{max.}$ 212 (15,500) and 290 (17,500).

Reduction of the title compound (0·5 g.) with hydrazine hydrate (4 ml.) and Pd–charcoal (5%, 0·2 g.) in boiling ethanol (20 ml.) for 15 min. gave the *7-aminoindole* (16; R = NH_2), m.p. 98° (Found: C, 76·9; H, 7·6; N, 14·8. $C_{12}H_{14}N_2$ requires C, 77·3; H, 7·5; N, 15·1%) which slowly darkened on exposure to the atmosphere.

5-Methyl-7-nitro-1,2,3,4-tetrahydropyrido[1,2-a]*indole* was obtained quantitatively from the indoline (7; $R^1 = NO_2$, R^2 = H, X = $[CH_2]_4$) by a similar procedure, m.p. 165° (Found: C, 68·1; H, 6·3; N, 12·2. $C_{13}H_{14}N_2O_2$ requires C, 67·8; H, 6·1; N, 12·2%) τ ($CDCl_3$) 7·83 (Me, s), 8·1 ($[CH_2]_2$, t) 7·10 ($N{\cdot}CH_2$, t), 6·05 ($=C{-}CH_2$, t) and aromatic protons at 1·70 (8-H), 2·03 (6-H), and 2·82 (9-H) with $J_{6,8}$ 2·2 and $J_{8,9}$ 9 Hz.

Preparation and Decomposition of Nitrene Precursors.—(1) *2-Substituted nitrobenzenes and anilines.* Treatment of 2-nitrophenol with the appropriate alkyl halide and potassium carbonate in acetone[34] afforded the alkoxynitrobenzenes which had physical constants close to the reported values.[35] 2-Fluoronitrobenzene (1 mol.), *N*-methylcyclohexylamine (1 mol.), and sodium hydrogen carbonate (1·1 mol.) were heated together in ethanol for 3 hr. Dilution with water and extraction with chloroform gave *N-methyl-N-(2-nitrophenyl)cyclohexylamine* (58%) m.p. 56°, orange prisms from ethanol (Found: C, 66·5; H, 7·6; N, 11·8. $C_{13}H_{18}N_2O_2$ requires C, 66·6; H, 7·7; N, 12·0%). The above nitro-compounds were reduced at atmospheric pressure with palladium under hydrogen to give the 2-substituted anilines listed in Table 8.

Treatment of chloro-2,4-dinitrobenzene with n-butanethiol gave 2,4-dinitrophenyl n-butyl sulphide, m.p. 66° (lit.,[36] 66°). Polysulphide reduction of the latter gave two products separable by chromatography; *5-nitro-2-n-propylbenzthiazole*, m.p. 128° from benzene–cyclohexane (1 : 1). It had resonances at τ 1·45 (4-H), 1·83 (6-H), 2·71 (7-H), 5·89 (CH_2), 8·32 (CH_2), and 9·03 (CH_3) (Found: C, 53·6; H, 5·0; N, 12·3. $C_{10}H_{10}N_2O_2S$ requires C, 54·0; H, 4·5; N, 12·6%). The other product was *4-amino-2-nitrophenyl n-butyl sulphide*, m.p. 87°, red prisms from benzene–cyclohexane (1 : 3); $\nu_{max.}$ 3340, 3420 $cm.^{-1}$ (NH_2) (Found: C, 53·1; H, 6·4; N, 12·2. $C_{10}H_{14}N_2O_2S$ requires C, 53·1; H, 6·2; N, 12·4%).

TABLE 8

2-Substituted anilines

2-Substituent	B.p. (M.p.)	Lit. b.p.	Ref.
OEt	111—113°/2mm	127—128°/14mm	35
OPr^n	118—120°/6mm	125—126°/12mm	35
OBu^n	125°/2mm	141—142°/15mm	35
$MeNC_6H_{11}$ *	(52°)		

* Found: C, 76·8; H, 9·4; N, 14·1. $C_{13}H_{20}N_2$ requires C, 76·4; N, 9·9; N, 13·7%.

(2) *Preparation of azides.* The azides were prepared as previously described.[1] Their i.r. spectra showed a sharp peak at 2100—2140 $cm.^{-1}$ (N_3). The azides were taken up in the decomposition medium without further purification.

(3) *Decomposition of 2-alkoxyphenylazides.* A solution of the azide (2 g.) in diglyme (10 ml.) was added dropwise to boiling diglyme (100 ml.). Refluxing was continued until N_2 evolution had ceased when the solvent was evaporated and the residue chromatographed in light petroleum (b.p. 60—80°) on alumina. Decomposition of the methoxy-, ethoxy- and n-propoxy-derivatives gave the corresponding amine as the major product and much tar was formed. 2-n-Butoxyphenyl azide gave in addition to the amine and tars, 2-n-propylbenzoxazole (6%), identical (i.r., n.m.r.) to an authentic sample.[37]

(4) Deoxygenation of 2-nitrophenyl alkyl ethers. A mixture of 2-nitrophenyl alkyl ether (0·02 mol.) and triethyl phosphite (0·12 mol.) was heated under reflux for 16 hr. in an atmosphere of nitrogen and then cooled. Excess of phosphite was distilled off and the residue was chromatographed on alumina with light petroleum (b.p. 60—80°) as eluant. The products are listed in Table 9.

TABLE 9

Products from the deoxygenation of 2-nitrophenylalkyl-ethers 2-$NO_2{\cdot}C_6H_4{\cdot}OR$ with hot triethylphosphite

	Yield (%)		
R	Starting material	Amine	Phosphoramidate [a]
Me	16	9	12
Et	14	12	19
Pr^n	10	12	16
Bu^n [b]	14	10	8

[a] I.r. and n.m.r. spectra were consistent with the proposed structures. [b] 2-n-Propylbenzoxazole was isolated in 11% yield. It was identical (i.r., n.m.r.) to an authentic sample.[37]

(5) Thermolysis of 2-azido-*N*-cyclohexyl-*N*-methylaniline, was carried out in diglyme as described above. Chromatography of the residue with benzene–ethyl acetate (1 : 1) on alumina gave 1-cyclohexylbenzimidazole from two separate bands. The total yield was 19%, prisms from light petroleum (b.p. 60—80°), m.p. 89° (lit.,[38] 87—89°). Further elution with methanol gave a red-brown tar.

(6) *Trialkyl phosphite reduction of 2,4-dinitrophenyl n-butyl sulphide.* The dinitro-compound in trimethyl phosphite was boiled under nitrogen for 1 hr. The black reaction mixture was extracted with hot benzene; the extracts were concentrated and attempts were made to separate the mixture by t.l.c. The chromatogram showed the reaction product to be a complex mixture, containing starting material and 5-nitro-2-n-propylbenzothiazole.

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