

Intramolecular Nitrene Insertions into Aromatic and Heteroaromatic Systems. Part 4.¹ Insertions using Triphenylmethanes, Unactivated or Bearing Electron-donating Groups

By Robert N. Carde, Gurnos Jones,* William H. McKinley, and Cynthia Price, Chemistry Department, University of Keele, Keele, Staffordshire ST5 5BG

Thermal decompositions of the *o*-azidotriphenylmethanes (5), (6), (11), and (12) have given 9-phenylacridans, 9-phenylacridines, and 11-phenyl-10*H*-azepino[1,2-*a*]indoles. From azides (6) and (11) the tetracyclic compounds (21) and (30) were also obtained. Photolytic decomposition of azides (5) and (6), and thermolysis of azide (5) at different temperatures and in various solvents leads to the suggestion that acridans and acridines are derived from triplet nitrene, while azepinoindoles and tetracyclic compounds (21) and (3) are derived from singlet nitrene. Further transformations of compounds (21) and (30) have given 11-arylazepino[1,2-*a*]indol-8-one (24) and dihydroazepinoindolones (20) and (31). Decomposition of *o*-azidodiphenyl[²H₂]methane (40) gave [10,11-²H₂]azepino[1,2-*a*]indole (41).

We have reported^{2,3} that thermal decomposition of *o*-azidodiphenylmethanes gives azepinoindoles, except when an *o*'-methoxy group is present in the ring receiving the intermediate nitrene. When such an *o*'-methoxy group is present acridans (and acridines) become the dominant product;² benzacridans are virtually the only products when a naphthalene receives the nitrene.³ In other similar systems (*o*-azidodiphenyl sulphides for example⁴) ring expansion products were not observed. We have now prepared and decomposed a number of *o*-azidotriphenylmethanes; we report here on those in which the 'receiving' ring is unactivated or bears electron-donating groups, and discuss the results in the light of the dichotomy previously observed.

We have obtained the azides (5), (6), (11), and (12) by the routes shown in Schemes 1 and 2; for Scheme 2 the

¹ Part 3, R. N. Carde and G. Jones, *J.C.S. Perkin I*, 1975, 519.

² G. R. Cliff and G. Jones, *J. Chem. Soc. (C)*, 1971, 3418.

³ R. N. Carde and G. Jones, *J.C.S. Perkin I*, 1974, 2066.

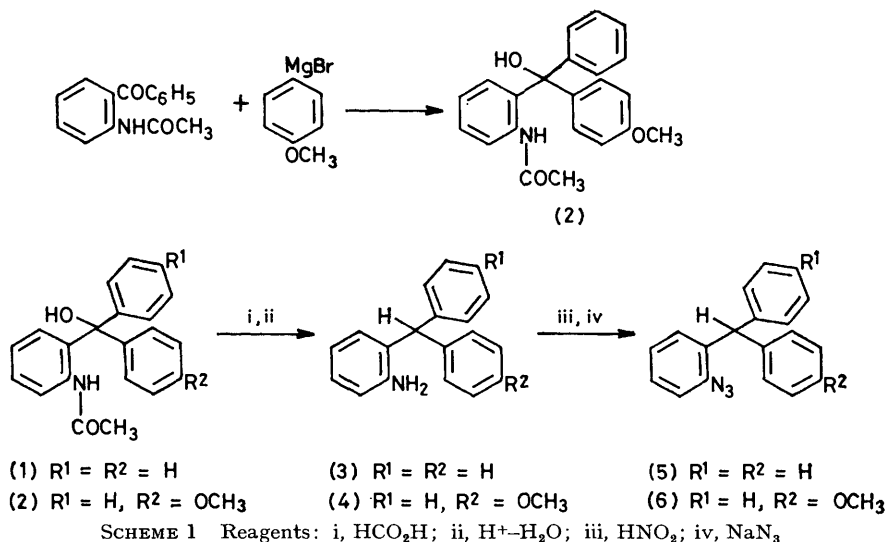
benzene ring must contain a strong electron-donating group R¹. All azides have been thermolysed in trichlorobenzene at 190–200°. Additionally azide (5) has been thermolysed at 156° and in a variety of solvents; azides (5) and (11) have been photolysed. We discuss first the products obtained from the standard thermolyses, then the non-standard decompositions, and their bearing on the mechanism of the insertion.

Thermal decomposition (190°; trichlorobenzene) of azide (5) gave a mixture. Major products were 11-phenyl-10*H*-azepino[1,2-*a*]indole (13), 9,10-dihydro-9-phenylacridine (14), and the corresponding acridine (15); minor products were the amine (3), and azo-2,2'-bis(diphenylmethyl)benzene (16). In contrast to the observed decompositions of *o*-azidodiphenylmethanes²

⁴ M. Messer and D. Farge, *Bull. Soc. chim. France*, 1968, 2832; J. I. G. Cadogan, S. Kulik, C. Thomson, and M. J. Todd, *J. Chem. Soc. (C)*, 1970, 2437; J. I. G. Cadogan, and S. Kulik, *ibid.*, 1971, 2671.

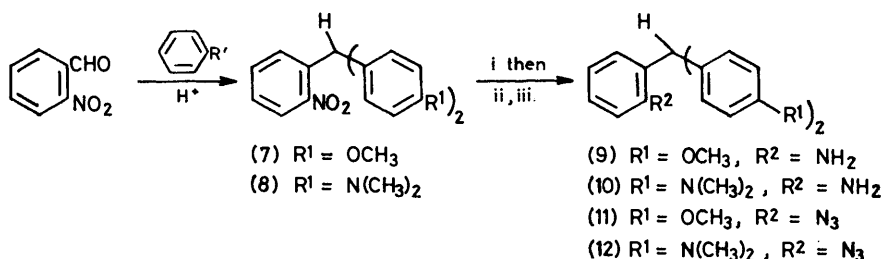
where azepinoindoles were the major isolated products, the triphenylmethane decomposition gave roughly equal proportions of acridan and acridine and of azepinoindole. Decomposition of the bis-*p*-methoxyphenyl azide (11) gave 9,10-dihydro-3-methoxy-9-(*p*-methoxyphenyl)-acridine (17), the acridine (18), but very little of the

amine (4), both the possible 9,10-dihydroacridines (25) and (26), both the acridines (27) and (28), the azepinoindole (29), and the tetracyclic compound (30). Of the dihydroacridine and acridine pairs, one in each case was obtained pure, the other in each case pure enough for spectral characterisation. A point which must be



azepinoindole (19); attempted purification of compound (19) gave the dihydroazepinoindolone (20). A substantial amount of a product, $C_{21}H_{19}NO_2$, was formed; this compound showed in the 1H n.m.r. spectrum an ABCX system, best fitted by the tetracyclic structure (21). The signals at δ 0.6, 1.83, 2.8, and 5.7 showed

established for the acridines (18) and (27) is the position of the methoxy group on the acridine ring (at position 2 or 3, the former being a possible position if a spirodiene intermediate is involved). The addition of $Eu(fod)_3$ shift reagent to the solution of compound (18) caused a large downfield shift in two absorptions, one a subsplit



couplings J_{AB} 4.8, J_{AC} 5.8, J_{BC} 10.2, and J_{CX} 2 Hz, and these couplings agree well with those of the model compounds (22) and (23) reported by Steigl and his co-workers.⁵ J_{CX} is a long range coupling; inspection of Dreiding models shows clearly the coplanarity of the **W** arrangement. No previously prepared azepinoindoles have shown any tendency to form such tautomers. We have established by long heating of compound (21) that it is not an intermediate in the formation of azepinoindole (19). Many products were formed (t.l.c.) but there was no evidence of the presence of azepinoindole (19). The only identified product was the azepinoindolone (24).

Decomposition of the 'mixed' azide (6) gave the

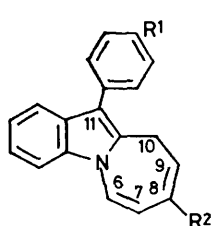
⁵ J. A. Steigl, J. Sauer, D. A. Kleier, and G. Binsch, *J. Amer. Chem. Soc.*, 1972, **94**, 2770.

doublet (major coupling 8 Hz), the other a doublet (J 2 Hz) which must be due to 4-H and therefore shows *meta* coupling only, because of the presence of methoxy at position 3. Similar results were found with compound (27). The tetracyclic compound (30), which showed very similar spectral characteristics to those of compound (21) was rapidly hydrolysed by aqueous acid with opening of the cyclopropane ring and formation of the dihydroazepinoindolone (31). Reduction of compound (13) gave the tetrahydro derivative (32).

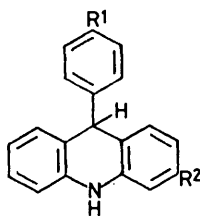
Decomposition of the *o*-azidophenylbis-(*p*-dimethylaminophenyl)methane (12) was the only reaction to give a poor total recovery of identified material. The major identified materials were isomers, $C_{23}H_{23}N_3$, both deep red compounds showing a green fluorescence in solution. The isomers were identified as 2- and 3-dimethylamino-

9-(*p*-dimethylaminophenyl)acridine, (33) and (34), by their visible and ^1H (100 MHz) n.m.r. spectra. Both isomers showed in the n.m.r. spectrum an A_2B_2 pattern characteristic of the *p*-dimethylaminophenyl residue. Compound (33) showed an upfield doublet at δ 6.75 (J 2.5 Hz), coupled to a doublet of doublets at δ 7.55 (J 2.5 and

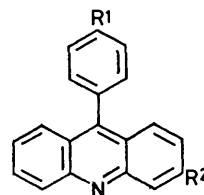
on the ring nitrogen) caused a larger bathochromic shift in the longest wavelength absorption of compound (33), but a much greater increase in intensity of the longest wavelength absorption in compound (34); this is in accord with observations on 2-amino- and 3-aminoacridine.⁶ Compound (33) is thus the first example of a



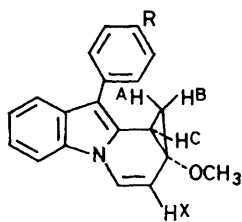
- (13) $\text{R}^1 = \text{R}^2 = \text{H}$
 (19) $\text{R}^1 = \text{R}^2 = \text{OCH}_3$
 (29) $\text{R}^1 = \text{OCH}_3, \text{R}^2 = \text{H}$



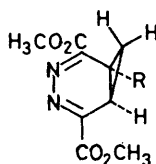
- (14) $\text{R}^1 = \text{R}^2 = \text{H}$
 (17) $\text{R}^1 = \text{R}^2 = \text{OCH}_3$
 (25) $\text{R}^1 = \text{H}, \text{R}^2 = \text{OCH}_3$
 (26) $\text{R}^1 = \text{OCH}_3, \text{R}^2 = \text{H}$



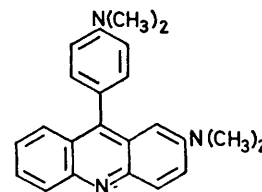
- (15) $\text{R}^1 = \text{R}^2 = \text{H}$
 (18) $\text{R}^1 = \text{R}^2 = \text{OCH}_3$
 (27) $\text{R}^1 = \text{H}, \text{R}^2 = \text{OCH}_3$
 (28) $\text{R}^1 = \text{OCH}_3, \text{R}^2 = \text{H}$
 (34) $\text{R}^1 = \text{R}^2 = \text{N}(\text{CH}_3)_2$



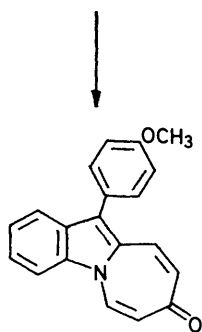
- (21) $\text{R} = \text{OCH}_3$
 (30) $\text{R} = \text{H}$



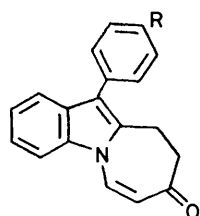
- (22) $\text{R} = \text{H}$
 (23) $\text{R} = \text{CH}_3$



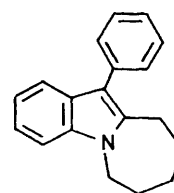
(33)



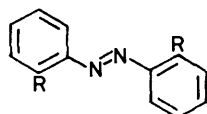
(24)



- (20) $\text{R} = \text{OCH}_3$
 (31) $\text{R} = \text{H}$



(32)



- (16) $\text{R} = (\text{C}_6\text{H}_5)_2\text{CH}$
 (35) $\text{R} = (4\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{CH}$

9.5 Hz), which was in turn coupled to a doublet at δ 8.12 (J 9.5 Hz); this pattern clearly establishes the position of the dimethylamino group at position 2. Compound (34) had an aromatic pattern similar to that of compound (18). Most significantly, there was only a one proton signal at δ 8.1 (5-H), the signal for 4-H being moved upfield by the dimethylamino group.

In the visible spectrum protonation (expected to occur

're-arranged' acridine obtained in our work and must arise *via* a spirodiene intermediate such as has been invoked in the phenothiazine syntheses.⁴

DISCUSSION

The formation of two series of products, in one of which the benzene ring receiving the nitrene is expanded,

⁶ D.M.S. U.V. Atlas, Butterworth-Verlag Chemie, Weinheim and London, 1966, vol. 1.

in the other unexpanded, has not been explained. The most obvious conclusion is that two precursors are involved, and that these are singlet nitrene (for ring expansion) and triplet nitrene (for acridan and acridine formation). The clear participation of the two nitrene states has been well demonstrated for decomposition of

benzylphthalenes where we have shown³ that 100% acridine + acridan production is normal.

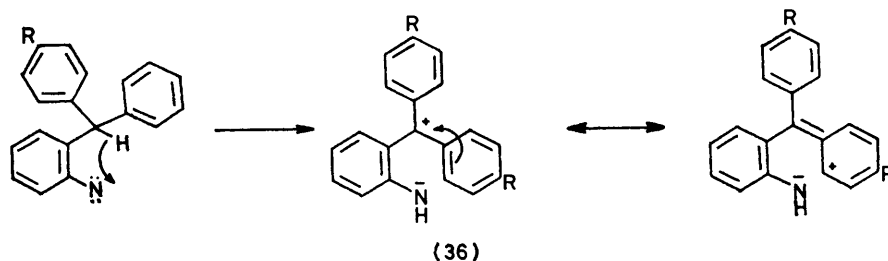
The final point to be explained is the difference between product ratios observed for *o*-azidodiphenylmethanes (virtually exclusive azepinoindole formation) and *o*-azidotriphenylmethanes (approximately equal

Solvent	Solvent triplet energy (kJ mol ⁻¹)	T/°C	% Azepinoindole (A)	% Acridan + acridine (B)	Ratio A/B
Bromobenzene		156	v. low	> 95	0.0
TCB	330	156	35	65	0.55
TCB	330	190	48	52	0.98
<i>p</i> -Dibromobenzene	327	190	35–55	65–45	~0.6
Naphthalene	251	190	13	87	0.15
Biphenyl	271	190	33	66	0.5

TCB = 1,2,4-Trichlorobenzene.

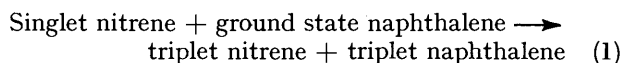
azidobiphenyls by Lindley *et al.*,⁷ and we present here only a brief discussion. The azides (5) and (11) were photolysed in benzene solutions, with and without added acetophenone. In both cases the principal product was the azo-compound, (16) and (35) respectively, which have been regarded as derived from triplet azide. The azo-compounds are shown in the *trans*-form, though *cis*- and *trans*-forms were present. The yield of other products was disappointingly small; however no azepines were found, although acridans and acridines were present in both cases, and this would accord with the hypothesis that acridans and acridines are triplet

amounts of singlet and triplet products) when decompositions were performed under the same conditions. A possible explanation lies in the differing stability of diphenylmethyl and triphenylmethyl carbonium ions. A five-membered transition state is available for singlet nitrene to abstract a hydrogen atom from the bridging carbon atom, but its success would depend on the C–H bond strength. Such an abstraction would produce the ionic species (36), which in another mesomeric form is well set up for cyclisation for acridan. A small contributory piece of evidence comes from the considerably increased acridan : azepinoindole ratio in decompositions



derived. A series of thermal decompositions was conducted with azide (5), using differing solvents at 156 and at 190°. The percentages of products are given in the Table (azepine + acridan + acridine = 100), along with the triplet energies of the solvent, where this is available.

Several trends can be seen from the Table. As has been shown elsewhere⁷ increased temperature leads to increasing yields of singlet insertion products. At the lower temperature a very considerable 'heavy atom' effect is shown by bromobenzene. At the higher temperature this effect is small (dibromobenzene) compared with that of naphthalene. We suggest that this may be a reflection of the low triplet energy of naphthalene, enabling the transformation (1) to proceed; a less



marked, but noticeable change in product ratio for the decomposition in biphenyl accords with the higher triplet energy of this solvent. Such an aid to inter-system crossing is provided *par excellence* in the *o*-azido-

of azides (11), where the *p*-methoxy groups contribute to still greater stability for an ion of type (36). Unfortunately, deuteration studies, successfully used in the diphenylmethane series and in insertion studies using *o*-carbenes of diphenylmethanes,⁸ cannot be used to establish the intermediacy of a carbonium ion because of the lability of the acridan NH.

Finally, we have established, by deuterium labelling experiments, that the hydrogen transfer, essential in the conversion of *o*-azidodiphenylmethane (37) to 10*H*-azepino[1,2-*a*]indole (38), is regiospecific. The deuteriated amine (39) was prepared from the corresponding *o*-aminobenzophenone by reduction with lithium aluminium deuteride and aluminium chloride. The azide (40) was then thermally decomposed. The azepinoindole (41) was purified by recrystallisation and showed, in the ¹H n.m.r. spectrum, no signal for 11-H, and a signal integrating for only one hydrogen at δ 3.30–3.43 (10-H). Within the limits of the integration,

⁷ J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Perkin I*, 1977, 2194.

⁸ W. D. Crow, personal communication.

no deuterium was found at any other position, so that a stepwise transfer seems unlikely, as does intermolecular transfer leading to the most stable tautomer (we have shown elsewhere that 6*H*- and 8*H*-isomers can exist in special circumstances).

EXPERIMENTAL

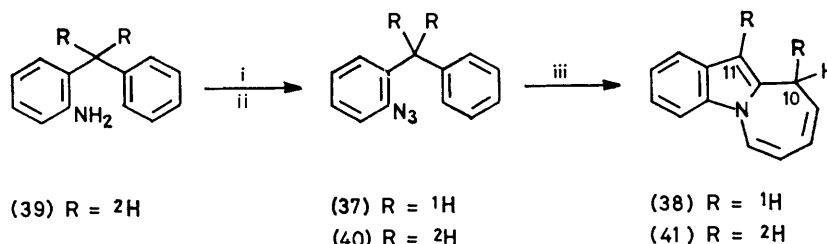
All m.p.s were determined on a Kofler hot stage apparatus, and are uncorrected. Thin and thick layer chromatography was performed with Merck silica gel PF₂₅₄, column chromatography was on Woelm alumina, activity IV. U.v. absorption spectra were in 95% EtOH.

2-Acetamido-4'-methoxytriphenylmethanol (2).—A solution of *o*-acetamidobenzophenone (44 g) in THF (100 ml) was slowly added under nitrogen to a vigorously stirred, boiling solution of the Grignard reagent from *p*-bromoanisole (105 g) and magnesium (14 g) in ether (500 ml). Boiling was continued for 4 h; the cooled, stirred mixture was treated with a saturated solution of ammonium chloride in ammonia (*d* 0.88). Separation of the organic layer and extraction of the aqueous layer with several small portions

dried (MgSO₄), and evaporated. The residue, a red oil, was purified by column chromatography (benzene). The dimethoxynitrotriphenylmethane (7) failed to crystallise (Found: C, 72.45; H, 5.4; N, 4.3. C₂₁H₁₉NO₄ requires C, 72.2; H, 5.45; N, 4.0%); δ (CDCl₃) 3.75 (6 H, OCH₃), 6.18 (1 H, s), and 6.7–7.9 (12 H); ν_{\max} (film) 3 100–2 860, 2 840, and 1 610 cm⁻¹; λ_{\max} 230 (log ϵ 4.39) and 268 (4.04) nm; *m/e* 349 (*M*⁺).

2-Aminotriphenylmethane (3).—Prepared by reduction of the triphenylmethanol (1) using formic acid¹⁰ in 74% yield, the amine (3) had m.p. 126.5–127.5° (lit.,¹¹ 129°) (Found: C, 87.8; H, 6.55; N, 5.2. Calc. for C₁₉H₁₇N: C, 88.0; H, 6.6; N, 5.4%); δ (CDCl₃) 3.22br (2 H, s, exch. NH₂), 5.26 (1 H, s), and 6.4–7.3 (14 H); ν_{\max} (mull) 3 440, 3 360, 1 620, and 1 598 cm⁻¹; λ_{\max} 212 (log ϵ 4.40), 235sh (3.86), and 286 nm (3.38); *m/e* 259 (*M*⁺).

2-Amino-4'-methoxytriphenylmethane (4).—A solution of the triphenylmethanol (2) (30 g) in 98% formic acid (250 ml) was boiled (24 h) under reflux. The acid was removed *in vacuo* and the residue dissolved in methanol (250 ml) with concentrated hydrochloric acid (250 ml). The resulting solution was boiled under reflux (5 h), cooled, basified with aqueous ammonium hydroxide, and extracted with



Reagents: i, HNO₂; ii, NaN₃; iii, TCB, 187°.

of ether gave a combined organic solution which was dried (Na₂SO₄), and the solvent evaporated. The residue was triturated with methanol to give a solid; crystallisation from light petroleum (b.p. 60–80°–CCl₄) gave the acetamidomethoxytriphenylmethanol (2), m.p. 158–160° (22 g, 35%) (Found: C, 73.7; H, 5.9; N, 3.7. C₂₂H₂₁NO₄·½H₂O requires C, 74.1; H, 6.2; N, 3.9%); δ (CDCl₃) 1.52 (3 H, s, COCH₃), 3.72 (3 H, s, OCH₃), 4.78 (1 H, exch. OH), 6.5–7.5 (12 H, m), 8.0 (1 H, d, *J* 7 Hz), and 9.1br (1 H, exch. NH); ν_{\max} (mull) 3 450–3 100, 1 665, 1 608, and 1 585 cm⁻¹; λ_{\max} 212 (log ϵ 4.48), 230.5 (4.26), 245sh, 271sh, and 282sh nm, *m/e* 347 (*M*⁺).

4,4'-Dihydroxy-2''-nitrotriphenylmethane.—Prepared as described⁹ in a crude yield of 63%, the crude material was used to prepare the dimethyl ether. A sample of the dihydroxy compound was purified by column chromatography (benzene), m.p. 161° (from chloroform) (lit.,⁹ 163°) (Found: C, 71.3; H, 4.55; N, 4.3. Calc. for C₁₉H₁₅NO₄: C, 71.0; H, 4.65; N, 4.35%); ν_{\max} (mull) 3 360br, 1 610, and 1 590 cm⁻¹; λ_{\max} 228 (log ϵ 4.33) and 283 (3.64) nm; δ ([²H₆]acetone) 6.04 (1 H), 6.65–7.85 (12 H), and 8.14 (2 H, exch.); *m/e* 321 (*M*⁺).

4,4'-Dimethoxy-2''-nitrotriphenylmethane (7).—A solution of the dihydroxynitrotriphenylmethane (28 g) and methyl iodide (42 g) in dry acetone (500 ml) was boiled and stirred with anhydrous potassium carbonate (42 g) for 2 h. Methyl iodide (20 g) was added, and stirring and boiling continued (3 h). The cooled mixture was filtered, acetone evaporated, and the residue in chloroform (200 ml) washed with dilute aqueous NaOH (2 × 150 ml) and water (3 × 150 ml),

chloroform. The combined organic extracts were dried (MgSO₄), and evaporated to give a yellow oil; the amine (4) (85%) had b.p. 170–180° at 0.1 mmHg; *m/e* 289 (*M*⁺); δ (CDCl₃) 3.39br (2 H, exch. NH₂), 3.69 (3 H, s, OCH₃), 5.42 (1 H, s), and 6.5–7.4 (13 H); ν_{\max} (film) 3 465, 3 355, 1 618, and 1 250 cm⁻¹; λ_{\max} 229.5 (log ϵ 4.34), 252sh, 275sh, 286sh, and 374 nm (3.40).

2-Amino-4',4''-dimethoxytriphenylmethane (9).—(a) A solution of the nitro compound (7) (12.5 g) in 95% EtOH (1 l) was hydrogenated over 10% Pd–C at atmospheric temperature and pressure till ca. 3 l of hydrogen had been absorbed. Evaporation of the filtered solution gave as a red oil almost pure amine (9) (11.4 g, 98%); a sample distilled for analysis had b.p. 270–280° at 35 mmHg (Found: C, 79.2; H, 6.3; N, 4.4. C₂₁H₂₁NO₂ requires C, 79.1; H, 6.6; N, 4.2%); δ (CDCl₃) 3.6 (8 H, s, exch. 2 H), 5.29 (1 H, s), and 6.4–7.0 (12 H); ν_{\max} (film) 3 370br cm⁻¹; λ_{\max} 230 (log ϵ 4.39) and 278 nm (3.79); *m/e* 319 (*M*⁺).

(b) Hydrazine hydrate (5 ml, 98%) was added dropwise to a stirred solution of the nitro compound (7) (4 g) in 95% EtOH (200 ml) at 50°. To the solution was added 10% Pd–C (0.1 g) and the mixture was boiled (2 h), further catalyst (0.1 g) added, and boiling continued. From the filtered solution, by evaporation, the amine (9) was obtained in 70% yield.

N'N'N''-Tetramethyl-2,4',4''-triaminotriphenylmethane (10).—This was prepared as described for a similar com-

⁹ J. E. Driver and S. F. Mok, *J. Chem. Soc.*, 1955, 3924.

¹⁰ S. T. Bowden and T. F. Watkins, *J. Chem. Soc.*, 1940, 1333.

¹¹ A. Baeyer and V. Villiger, *Ber.*, 1904, **37**, 3192.

pound by Zn dust reduction¹² from the nitro compound (8).¹³

2-Azidotriphenylmethane (5).—To a cooled (-5°), stirred solution of 2-aminotriphenylmethane (3) (5 g) in a mixture of 4*N*-sulphuric acid (250 ml) and purified 1,4-dioxan (250 ml) was added sodium nitrite (1.45 g) in water (50 ml). After 15 min a solution of sodium azide (1.4 g) in water (50 ml) was added, and the mixture gently warmed to 30° . The azide was extracted from the cooled solution by ether, the ether extracts dried (MgSO_4) and evaporated. The residual oil was percolated through alumina [200 g, light petroleum (b.p. $40-60^{\circ}$)]. Evaporation of the eluate at 30° under reduced pressure in a foil-wrapped flask gave the azide (5) (4 g, 73%), m.p. $94.5-95.5^{\circ}$ [from light petroleum (b.p. $40-60^{\circ}$)] (Found: C, 80.4; H, 4.9; N, 14.6. $\text{C}_{19}\text{H}_{15}\text{N}_3$ requires C, 80.0; H, 5.3; N, 14.7%); $\delta(\text{CDCl}_3)$ 5.8 (1 H, s) and 6.7–7.4 (14 H, m); ν_{max} (mull) 2 125 and 1 285 cm^{-1} ; λ_{max} 222sh, 253.5 (log ϵ 4.03), 263sh, 280sh, and 289sh nm; m/e 285 (1%), and 257 (100, $M - 28$).

2-Azido-4'-methoxytriphenylmethane (6).—Prepared as described for compound (5), from amine (4) in 87% yield, the azide (6) did not solidify (Found: C, 76.4; H, 5.85; N, 12.9. $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}$ requires C, 76.2; H, 5.45; N, 13.3%); $\delta(\text{CDCl}_3)$ 3.75 (3 H, s), 5.75 (1 H, s), and 6.8–7.4 (13 H, m); ν_{max} (film) 2 130, 1 298, 1 282, and 1 250 cm^{-1} ; λ_{max} 230sh, 252 (log ϵ 4.01), 264sh, 280sh, and 290sh nm; m/e 315 (10%), 287 (43, $M - 28$), and 286 (100, $M - 29$).

2-Azido-4',4''-dimethoxytriphenylmethane (11).—This was prepared as described for compound (5) in 93% yield from amine (9). Elution from the column required 15% benzene in light petroleum (b.p. $40-60^{\circ}$) and gave the azide (11) (Found: C, 72.8; H, 5.5; N, 12.0. $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2$ requires C, 73.1; H, 5.5; N, 12.2%); $\delta(\text{CDCl}_3)$ 3.76 (6 H, s), 5.74 (1 H, s), and 6.2–7.2 (12 H, m); ν_{max} (mull) 2 125 cm^{-1} ; λ_{max} 230 (log ϵ 4.44) nm; m/e 345 (13%), 318 (39), and 317 (100, $M - 28$).

2-Azido-4',4''-bis(dimethylamino)triphenylmethane (12).—Prepared as described for a benzothiofen azide¹⁴ in 35% yield from the amine (10), the azide (12) had m.p. $109-111^{\circ}$ [light petroleum (b.p. $60-80^{\circ}$)] (Found: C, 74.7; H, 6.65; N, 18.9. $\text{C}_{23}\text{H}_{25}\text{N}_5$ requires C, 74.35; H, 6.8; N, 18.85%); $\delta(\text{CDCl}_3)$ 2.95 (12 H, s), 5.6 (1 H, s), and 6.5–7.15 (12 H, m); ν_{max} (CHCl_3) 2 120 cm^{-1} ; m/e 371 (M^+ , 22%), 343 (64), 342 (84), 341 (100), 282 (72), 239 (62), and 223 (80).

Thermolysis of Azide (5) in 1,2,4-Trichlorobenzene at 190° .—A solution of the azide (3.8 g) in trichlorobenzene (100 ml) was added dropwise to vigorously stirred trichlorobenzene (1 l) maintained at 190° (45 min); a stream of dry nitrogen was passed through the solution. After 4 h at 190° the solvent was removed at 1 mmHg; the residue was chromatographed on alumina (200 g) in benzene. Major fractions (A) (1 l) and (B) (500 ml) were taken.

Fraction (A), evaporated, gave an oil, which on trituration with light petroleum gave 9,10-dihydro-9-phenylacridine (14) (0.41 g), m.p. $170-171^{\circ}$ [light petroleum (b.p. $60-80^{\circ}$)] (lit.,¹⁵ 170°) (Found: C, 88.65; H, 5.7; N, 5.5. Calc. for $\text{C}_{19}\text{H}_{15}\text{N}$: C, 88.65; H, 5.9; N, 5.45%); $\delta(\text{CDCl}_3)$ 5.28 (1 H, s, H₉), 6.1br (1 H, s, exch. NH), and 6.6–7.3 (13 H, m); ν_{max} (mull) 3 375, 1 608, 1 604, and 1 582 cm^{-1} ; λ_{max} 224sh, 254sh, 289 (log ϵ 4.13), and 312sh nm; m/e 257 (M^+).

Fraction (B), evaporated, gave a yellow solid which was

recrystallised from light petroleum (b.p. $60-80^{\circ}$) to give 9-phenylacridine (15) (0.38 g), m.p. $183-184^{\circ}$ (lit.,¹⁵ 184°) (Found: C, 89.35; H, 5.1; N, 5.4. $\text{C}_{19}\text{H}_{15}\text{N}$ requires C, 89.4; H, 5.1; N, 5.5%); ν_{max} (mull) 1 630 and 1 608 cm^{-1} ; λ_{max} 219sh, 253.5 (log ϵ 5.10), and 359 (4.00) nm; m/e 255 (M^+ , 100%).

The combined crystallisation residues were evaporated and chromatographed on alumina (200 g) with light petroleum (b.p. $60-80^{\circ}$); 500 ml of eluant were evaporated to give 11-phenyl-10H-azepino[1,2-a]indole (13) (1.05 g), m.p. $74-75^{\circ}$ (light petroleum) (Found: C, 88.9; H, 5.85; N, 5.4. $\text{C}_{19}\text{H}_{15}\text{N}$ requires C, 88.65; H, 5.9; N, 5.45%); $\delta(\text{CDCl}_3)$ 3.49 (2 H, d, J 5 Hz, 10-H), 5.6–6.3 (3 H, m), and 7.0–7.7 (10 H, m); λ_{max} 234 (log ϵ 4.41), 270.5 (4.24), 305sh, and 325sh nm; m/e 257 (M^+ , 100%).

The column was stripped (CHCl_3) and the recovered material (850 mg) applied to three preparative plates (20 × 40 cm). Elution (toluene) gave five bands. These were extracted and in order of decreasing R_F were (1) unidentified, (2) the azo compound (16) (18 mg), m.p. $119-122^{\circ}$ [light petroleum (b.p. $60-80^{\circ}$); m/e (514, M^+); λ_{max} 257 (log ϵ 4.66), 268sh (4.64), 287 (4.54), 310 (4.49), 342 (4.28), and 390 nm (3.76)]; (3) dihydroacridine (14) (130 mg); (4) 2-aminotriphenylmethane (3), identical with an authentic specimen (260 mg); (5) acridine (15) (100 mg). Total yields were:

Compound	(13)	(14)	(15)	(16)	(3)
Yield (%)	31	19	14	1	7.5

Thermolysis of Azide (6) at 185° .—Thermolysed for 4 h as described for azide (5), the crude products were chromatographed on alumina (300 g) with light petroleum-benzene (1 : 1). After a little trichlorobenzene, a single compound (t.l.c.) was eluted, and shown to be 11-(*p*-methoxyphenyl)-10H-azepino[1,2-a]indole (29) (17%), m.p. $97-99^{\circ}$ [light petroleum (b.p. $60-80^{\circ}$)] (Found: C, 83.85; H, 6.2; N, 4.7. $\text{C}_{20}\text{H}_{17}\text{NO}$ requires C, 83.6; H, 6.0; N, 4.85%); $\delta(\text{CDCl}_3)$ 3.44 (2 H, d, 10-H), 3.62 (3 H, s, OCH_3), 5.5–6.1 (3 H, m, 7-, 8-, 9-H), and 6.8–7.6 (9 H, m); λ_{max} 234.5 (log ϵ 4.45), 267.5 (4.29), 296sh, 325sh, and 335sh nm; m/e 287 (M^+ , 100%). Further elution gave mixtures, then 8,9-dihydro-8,9-methano-8-methoxy-10-phenylpyrido[1,2-a]indole (30) (34%), m.p. $155-157^{\circ}$ [light petroleum (b.p. $60-80^{\circ}$)] (Found: C, 83.4; H, 5.8; N, 4.95. $\text{C}_{20}\text{H}_{17}\text{NO}$ requires C, 83.6; H, 6.0; N, 4.85%); $\delta(\text{CDCl}_3)$ 0.59 (1 H, dd, 11a-H), 1.83 (1 H dd, 11b-H), 2.68 (1 H, m, 9-H), 3.22 (3 H, s, OCH_3), 5.65 (1 H, dd, 7-H), and 6.9–7.9 (10 H, m); $J_{11a,11b}$ 4.8, $J_{11b,9}$ 5.8, $J_{11b,8}$ 10.2, $J_{9,7}$ 2.0, and $J_{6,7}$ 8.0 Hz; λ_{max} 227.5 (log ϵ 4.41), 256 (4.49), 285sh, and 314 (4.18) nm; m/e 287 (M^+ , 100%). Further elution gave a mixture of two compounds; slow cooling of a light petroleum solution gave 9,10-dihydro-9-(*p*-methoxyphenyl)acridine (26), m.p. $181-182^{\circ}$ (12%) (Found: C, 82.1; H, 5.7; N, 4.75. $\text{C}_{20}\text{H}_{17}\text{NO}$ requires C, 83.6; H, 6.0; N, 4.85%); $\delta(\text{CDCl}_3)$ 3.71 (3 H, s), 5.24 (1 H, s, 9-H), 6.1br (1 H, s, NH), and 6.6–7.2 (12 H, m); ν_{max} (mull) 3 380, 1 610, and 1 581 cm^{-1} ; λ_{max} 228 (log ϵ 4.3), 285.5 (4.15), and 315sh nm; m/e 287 (M^+ , 37%) and 180 ($M - \text{C}_7\text{H}_7\text{O}$, 100). Spectral information on the second component of this mixture identified it as 9,10-dihydro-3-methoxy-9-phenylacridine (25) (14%); $\delta(\text{CDCl}_3)$ 3.77 (3 H, s, OCH_3), 5.24 (1 H, s, 9-H), and 5.95br (1 H, s, NH).

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¹³ O. Fischer and C. Schmidt, *Ber.*, 1884, **17**, 1889.

¹⁴ B. Iddon, H. Suschitzky, D. S. Taylor, and M. W. Pickering, *J.C.S. Perkin I*, 1974, 575.

¹⁵ A. Bernthsen, *Annalen*, 1884, **224**, 13.

Further elution gave another pair of isomers, one of which crystallised slowly from light petroleum solution, identified as 9-(*p*-methoxyphenyl)acridine (28) (6%), m.p. 213–214° (lit.,¹⁶ 213°); $\delta(\text{CDCl}_3)$ 3.87 (3 H, s, OCH₃) and 6.9–8.3 (12 H, m); λ_{max} 220 (log ϵ 4.41), 227sh, 253 (5.01), 343sh, and 356 nm (3.97); m/e 285 (M^+ , 100%). The second component was identified from its spectra as 3-methoxy-9-phenylacridine (27) (10%); $\delta(\text{CDCl}_3)$ 3.95 (3 H, s, OCH₃) and 6.9–8.3 (12 H, m). The final product eluted was identified as the amine (4), by comparison with an authentic specimen.

Thermal Decomposition of Azide (11) at 190°.—The crude product (5 g) was chromatographed on alumina (350 g; 1 m column); elution with benzene–light petroleum (1 : 1) gave, successively, four products. In order of elution these were (a) 8-methoxy-11-(*p*-methoxyphenyl)-10H-azepino[1,2-*a*]indole (19), unstable to p.l.c., characterised by its spectra; $\delta(\text{CDCl}_3)$ 3.2 (3 H, s, OCH₃), 3.3–3.6 (5 H, s on d, OCH₃ and 10-H), 4.62 (1 H, t, 9-H), 5.45 (1 H, d, 7-H), and 6.6–7.5 (9 H, m); ν_{max} (film) 3 055, 3 010, 1 655, and 1 635 cm⁻¹; λ_{max} 227 (log ϵ 4.38), 257 (4.21), and 351.5 (4.02) nm; (b) 8,9-dihydro-8,9-methano-8-methoxy-10-(4-methoxyphenyl)pyrido[1,2-*a*]indole (21) (13.6%), m.p. 159–160° (light petroleum) (Found: C, 79.4; H, 5.95; N, 4.4. C₂₁H₁₉NO₂ requires C, 79.6; H, 6.0; N, 4.4%); $\delta(\text{CDCl}_3)$ 0.54 (1 H, dd, 11a-H), 1.81 (1 H, dd, 11b-H), 2.72 (1 H, m, 9-H), 3.18 (3 H, s, OCH₃), 3.70 (3 H, s, OCH₃), 5.61 (1 H, m, dd, 7-H), and 6.7–7.8 (9 H, m); ν_{max} (mull) 3 035, 1 650, and 1 610 cm⁻¹; λ_{max} 229 (log ϵ 4.35), 257.5 (4.47), and 313 nm (4.16); m/e 317 (M^+ , 100%); (c) 9,10-dihydro-3-methoxy-9-(4-methoxyphenyl)acridine (17) (8.8%), m.p. 158–160° (light petroleum) (Found: C, 79.1; H, 5.9; N, 4.35. C₂₁H₁₉NO₂ requires C, 79.5; H, 6.0; N, 4.4%); $\delta(\text{CDCl}_3)$ 3.65 (6 H, s), 5.1 (1 H, s, 9-H), 6.2br (1 H, s, NH), and 6.4–7.3 (11 H, m); (d) 3-methoxy-9-(*p*-methoxyphenyl)acridine (18) (28%), m.p. 168–170° (light petroleum–CCl₄) (Found: C, 79.8; H, 5.3; N, 4.35. C₂₁H₁₇NO₂ requires C, 80.0; H, 5.39; N, 4.45%); $\delta(\text{CDCl}_3)$ 3.95 (3 H, s), 4.05 (3 H, s), and 7.0–8.3 (11 H, m); λ_{max} 226 (log ϵ 4.08), 260 (4.50), and 355 nm (3.56); m/e 315 (M^+ , 100%).

Thermal Decomposition of Azide (12) at 190°.—The crude product was a brown polymer-like substance. Chromatography of the crude product on alumina, eluting with light petroleum and light petroleum–benzene mixtures, collecting 500 ml fractions gave a rough separation; all fractions darkened rapidly on keeping. Fractions 26–28 gave three components on t.l.c. separated on preparative plates [ethyl acetate–toluene (1 : 1)]. The major component was the orange-red acridine (33), m.p. 220–222° (Found: M^+ , 341.1896. C₂₃H₂₃N₃ requires M , 341.1892); λ_{max} 244 (log ϵ 4.53), 281 (4.68), and 464 nm (3.66); λ_{max} (0.2% conc. HCl added) 240 (log ϵ 4.44), 300 (4.59), 392 (3.66), and 576 nm (3.83); $\delta(\text{CDCl}_3)$ 2.96 (6 H, s, CH₃N), 3.08 (6 H, s, CH₃N), 6.75 (1 H, d, $J_{1,3}$ 2.5 Hz, 1-H), 6.9 (2 H, d, J 9.5 Hz, 2'-, 6'-H), 7.32 (2 H, d, J 9.5 Hz, 3'-, 5'-H), 7.25–7.39 (1 H, m, 7-H), 7.55 (1 H, q, J 2.5 and 9.5 Hz, 3-H), 7.51–7.67 (1 H, m, 6-H), 7.72br (1 H, d, $J_{7,8}$ 9.5 Hz, 8-H), 8.12 (1 H, d, $J_{3,4}$ 9.5 Hz, 4-H), and 8.16br (1 H, d, $J_{5,6}$ 8.5 Hz, 5-H). From fractions 31–36 (eluted with benzene), after p.l.c. [ethyl acetate–benzene (1 : 1)] the major component was acridine (34), m.p. 222–227° (Found: M^+ , 341.1892. C₂₃H₂₃N₃ requires M , 341.1892); λ_{max} 241 (log ϵ 4.19), 283 (4.26), and 455 (3.37) nm; λ_{max} (added 0.2% conc. HCl) 241 (log ϵ 4.31), 296 (4.28), 360 (3.62), 378 (3.69), and 492 nm

(3.99); $\delta(\text{CDCl}_3)$ 3.06 (6 H, s, CH₃N), 3.12 (6 H, s, CH₃N), 6.88 (2 H, d, J 9 Hz, 2'-, 6'-H), 7.29 (2 H, d, J 9 Hz, 3'-, 5'-H), 7.05–7.34 (3 H, m), 7.57–7.79 (3 H, m), and 8.11br (1 H, d, $J_{5,6}$ 8 Hz, 5-H).

Thermolysis of Compound (21).—A solution of compound (21) (0.65 g) in trichlorobenzene (5 ml) was heated at 186° (22 h), the solvent evaporated, and the residue examined by g.l.c. Seven components were present. Repeated attempts at separation by p.l.c. gave only one identifiable compound, the azepinoindolone (24), m/e 301 (M^+); $\delta(\text{CDCl}_3)$ 3.87 (3 H, s, OCH₃), 5.8 (1 H, dd, J 10 and 3 Hz, 7-H), 6.18 (1 H, dd, J 12 and 3 Hz, 9-H), 6.8–7.7 (9 H, m), and 7.72 (1 H, d, J 10 Hz, 6-H).

9,10-Dihydro-11-phenyl-8H-azepino[1,2-*a*]indol-8-one (31).—Compound (30) (0.2 g) dissolved in concentrated hydrochloric acid (25 ml) to give a red solution. The acid was neutralised with ammonia, extracted with ether, and the ethereal extracts dried (MgSO₄) and evaporated. The yellow solid (0.15 g) crystallised from methanol to give the dihydroazepinoindolone (31), m.p. 144–144.5° (Found: C, 83.25; H, 5.85; N, 5.0. C₁₉H₁₅NO requires C, 83.5; H, 5.55; N, 5.15%); λ_{max} 227 (log ϵ 4.45), 251sh, 275.5 (4.19), 279sh, and 347 nm (4.20); ν_{max} (mull) 1 650, 1 626, and 1 605 cm⁻¹; $\delta(\text{CDCl}_3)$ 2.82 (2 H, m, 10-H), 3.22 (2 H, m, 9-H), 5.71 (1 H, d, J 10 Hz, 7-H), 7.2–7.8 (10 H, m); m/e 273 (M^+ , 100%), 245 (75), and 244 (93).

6,7,8,9-Tetrahydro-11-phenyl-10H-azepino[1,2-*a*]indole (32).—A solution of the azepinoindole (13) (0.25 g) in methanol (10 ml) containing 10% palladium–charcoal (0.1 g) was hydrogenated at atmospheric temperature and pressure until absorption ceased. The filtered solution was evaporated, and the residue crystallised from light petroleum (b.p. 60–80°) to give the tetrahydro derivative (32) (0.22 g, 87%), m.p. 107.5–108.5° (Found: C, 87.15; H, 7.25; N, 5.3. C₁₉H₁₉N requires C, 87.3; H, 7.35; N, 5.35%); λ_{max} 230 (log ϵ 4.47), 277sh, and 282.5 nm (4.12); $\delta(\text{CDCl}_3)$ 1.7–2.0 (6 H, m, 7-, 8-, 9-H), 2.9–3.2 (2 H, m, 10-H), 4.1–4.5 (2 H, m, 6-H), and 7.1–7.9 (9 H, m, aromatic); m/e 261 (M^+ , 100%), 260 (20), 232 (13), and 184 (55).

2-Azidodiphenyl[²H₂]methane (40).—A complex of lithium aluminium deuteride with aluminium chloride was prepared by adding the deuteride (4 g) to a solution of anhydrous aluminium chloride (20 g) in dry ether (100 ml). A solution of *o*-aminobenzophenone in ether was added dropwise to the vigorously stirred solution until coagulation occurred and a solid precipitated (ca. 7 g of *o*-aminobenzophenone). Excess of lithium aluminium deuteride was destroyed using wet ether, then water, the ether layer separated, and the aqueous layer washed with ether. The combined ether extracts were dried and evaporated to give crude amine (39) (6.1 g, 93%). A small sample was distilled, b.p. 114–116° at 0.35 mmHg (Found: C, 84.2; ¹H/²H, 7.2; N, 7.5. C₁₃¹H₁₁²H₂N requires C, 84.25; H, 7.0; N, 7.55%); m/e 186 (16%), 185 (100), 184 (47), 183 (11), 182 (9), and 181 (9). The n.m.r. spectrum showed no absorption at δ 6.0 due to 2-NH₂C₆H₄CH₂C₆H₅. Diazotisation of the amine in dioxan–sulphuric acid as described before² gave the azide (40) (73%), as an oil; m/e 183 (29%), 182 (90), 181 (100), 180 (50), and 179 (12); no n.m.r. absorption at δ 6.0–6.1.

10,11-Dideuterio-10H-azepino[1,2-*a*]indole (41).—The azide (40) (5 g) was decomposed at 187° in trichlorobenzene. Evaporation of the solvent and recrystallisation of the residue gave the dideuterated azepinoindole (41), m.p. 91.5–92.5° (Found: C, 85.3; H, 6.1; N, 7.65. C₁₃¹H₉²H₂N requires C, 85.2; ¹H/²H, 6.0; N, 7.65%); m/e 184 (12%),

¹⁶ J. M. Birchall and D. H. Thorpe, *J. Chem. Soc.*, 1968, 2900.

183 (80), 182 (100), 181 (65), and 180 (18); $\delta(\text{CCl}_4; 200 \text{ MHz})$ 3.32—3.43 (1 H, m, 10-H), 5.59 (1 H, dd, J 9 and 5.5 Hz, 9-H), 5.72—5.86 (1 H, m, 8-H), 5.9 (1 H, dd, J 10.2 and 5.5 Hz, 7-H), and 6.98—7.46 (5 H, m). No signal was present at δ 6.1 due to 11-H.

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