Intramolecular Nitrene Insertions into Aromatic and Heteroaromatic Systems. Part III.[1] Photochemical Decomposition of Azido-indanes and Azido-1,2-dihydrobenzocyclobutenes

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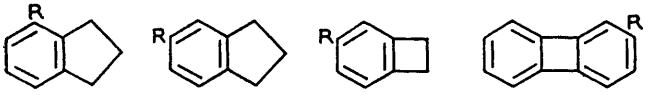
Photochemical decomposition of 4-azidoindane (3) in diethylamine gave 5-diethylamino-1,2,3,6-tetrahydro-4-aza-azulene (22), 4-diethylamino-1,2,3,3a- (19), and 4-diethylamino-1,2,3,8-tetrahydro-5-aza-azulene (20). Similar decomposition of 5-azidoindane (7) gave a mixture of 5-diethylamino-1,2,3,4-tetrahydro-6-aza-azulene (26) and 6-diethylamino-1,2,3,7-tetrahydro-5-aza-azulene (24). From 4-azido-1,2-dihydrobenzocyclobutene (11) a good yield of 4-diethylamino-1,2-dihydro-3*H*-5-azacyclobutacycloheptene (30) was obtained; 2-azidobiphenylene (13) gave no azepines, only 2-aminobiphenylene (31) and a little 2,2'-azobisbiphenylene (35).

WE have reported [1,2] reactions in which thermally generated nitrenes insert intramolecularly into neighbouring aromatic rings, giving azepines in some cases. As part of a general programme aimed at the production of aza-azulenes, and also of azacyclobutacycloheptenes, we have examined the photochemical decomposition of azidoindanes and azido-1,2-dihydrobenzocyclobutenes in diethylamine solution.

The azides were prepared by two general methods. Nitration of indane gave a mixture of nitro-compounds (1) and (5); this was reduced to a mixture of amines (2) and (6), which were readily separated as fumarate salts.[3] The amine (2) gave, *via* the diazonium salt, the azide (3); the amine (6) gave the azide (7). The azide (3) was also obtained from the bromo-compound (4),[4] *via* the Grignard reagent which was treated with tosyl azide.[5] The azidodihydrobenzocyclobutene (11) was

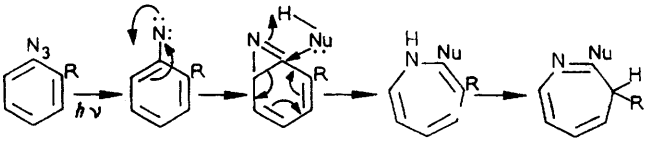


(1) R=NO_2 (5) R=NO_2 (8) R=Br (12) R=Br
(2) R=NH_2 (6) R=NH_2 (9) R=NO_2 (13) R=N_3
(3) R=N_3 (7) R=N_3 (10) R=NH_2 (31) R=NH_2
(4) R=Br (11) R=N_3

prepared both from the nitro-compound (9) [6] *via* the amine (10),[6] and from the bromide (8) [7] *via* the Grignard reagent. Azidobiphenylene (13) was obtained in good yield from 2-bromobiphenylene [8] (12). All four azides were decomposed in solution in diethylamine, in a Rayonet reactor (quartz vessel), by using light of maximum intensity at 300 nm.

DISCUSSION

Studies of the photochemical and thermal decomposition of aryl azides by Huisgen,[9] Maier,[10] and Sundberg [11,12] have established a mechanism in which insertion by the nitrene intermediate into an *ortho*-substituted benzene ring (14) gives reversibly a benzazirine (15) which, when a nucleophile is present, affords a 1*H*-azepine (16) and thence in almost all cases a 3*H*-azepine (17).



(14) (15) (16) (17)

For our purpose, the most notable feature of Sundberg's work [12] was the regiospecificity, giving almost entirely one of the possible isomeric azepines; our own precursor azides were all unsymmetrically substituted, and could thus give more than one bicyclic compound. Unfortunately, in two cases out of the three where ring expansion was achieved, our experience differs from that of Sundberg and his co-workers. Decomposition of the azide (3) gave a mixture from which three isomeric aza-azulenes were isolated. The structures were elucidated primarily by a study of n.m.r. spectra, and particularly of the shifts produced by addition of $Eu(fod)_3$. The shift reagent must be complexed between ring and side chain nitrogen atoms, and this is confirmed by the large shift shown in all cases by the $N{\cdot}CH_2{\cdot}CH_3$ signals. The major product from the azide (3) (49% of the azepines produced) was the 5-aza-azulene (19). The n.m.r. spectrum showed signals at δ 5·68 (m, H-7), 6·1 (d, H-8), and 6·9 (d, H-6); of the possible azepines only compound (19) has such a sequence of three alkene protons. The second product (20% of total azepines) was the 4-aza-azulene (22); two n.m.r. signals at δ 4·5—5·0 (m) and 6·14 (d, *J* 8·5 Hz) were due to H-7 and -8; addition of $Eu(fod)_3$ caused

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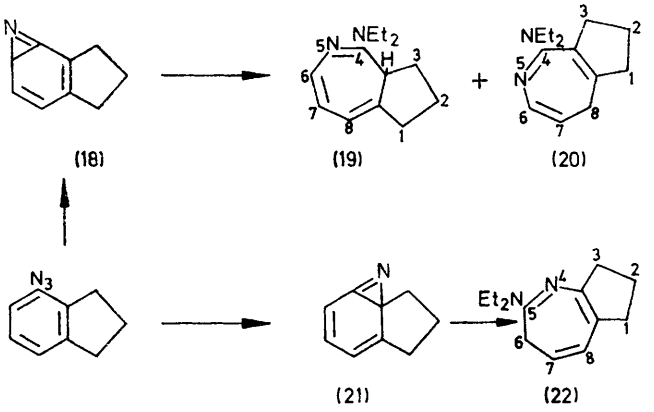
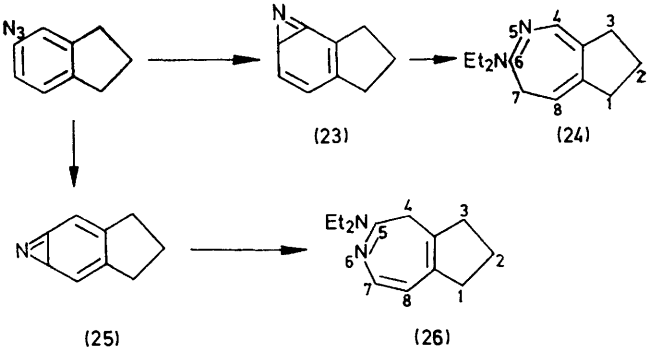
a large downfield shift in one component (2H, t, H-3) of a 6-proton multiplet originally at δ 2·4—2·8, and revealed a 2-proton doublet, which must be assigned to H-6. The third azepine (20) (31%) was of the abnormal '4*H*-azepine' type. A doublet at δ 6·4 (*J* 7 Hz, H-6) was shifted to low field by addition of $Eu(fod)_3$; the only other alkene signal, at δ 4·4—4·9, was a multiplet (H-7), and hence the sequence $N{\cdot}CH{=}CH{\cdot}CH_2$ must be present. These products are the result of nitrene insertion to give the two possible benzazirines (18) and (21), in which, in accord with Sundberg's observations,[12]



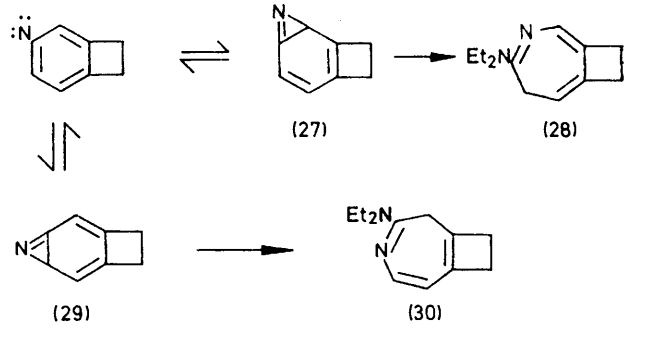
insertion occurs predominantly away from the *ortho*-substituent (80% of azepines formed). Formation of the 4*H*-azepine isolated by Sundberg [12] was attributed to unfavourable interaction between a bulky mesityl group and the diethylamine residue in the 1*H*-azepine intermediate, but we can find no such interaction in models of the precursor to the azepine (20), and its formation remains unexplained.

Decomposition of the azide (7) gave a mixture of two azepines, which could not be separated, but the n.m.r. spectrum of the mixture enabled structures to be assigned and proportions to be estimated. An apparent doublet at δ 6·8 separated on treatment with $Eu(fod)_3$ to a singlet and a doublet; both had moved considerably downfield and hence each proton is next to a ring nitrogen atom. The doublet at δ 6·8, due to the isomer in major proportion, was seen to be coupled (*J* 8 Hz) to a 1-proton signal (d) at δ 5·49 and hence could be due only to the 6-aza-azulene (26). The singlet at δ 6·85, due to the second isomer, suggests that this isomer is the 5-aza-azulene (24); analytical g.l.c. indicated a ratio of 85 : 15 for the two isomers. They would be formed *via* the benzazirines (25) and (23) respectively.

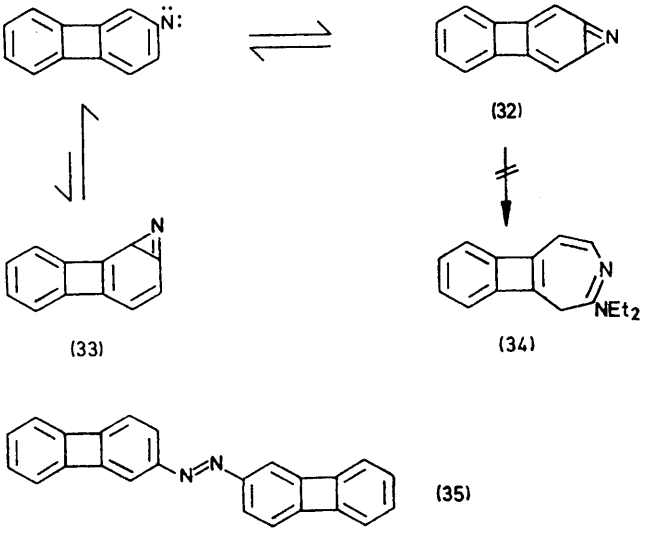
Decomposition of 4-azido-1,2-dihydrobenzocyclobutene (11) showed an altogether simpler picture. One product was isolated in good yield (55%); the presence of a second component in trace quantities in the crude mixture was noted. The major product had n.m.r. signals at δ 6·81 and 5·40, both doublets (*J* 7·5 Hz), and a singlet (2H) at δ 2·69. The similarity to the spectrum of the aza-azulene (26) was striking, and the product is formulated as 4-diethylamino-1,2-dihydro-3*H*-5-aza-cyclobutacycloheptene (30). The preponderance of one isomer in this case could reflect the 'fixed-bond'



character of the benzene ring in 1,2-dihydrobenzocyclobutene; in the intermediate benzazirine (27), reversibly formed *en route* to isomer (28), the double bond is forced into the cyclobutane ring, and this is energetically unfavourable.



All attempts to introduce further unsaturation into the dihydroazacyclobutacycloheptene (30) (with *N*-



bromosuccinimide, dichlorodicyanobenzoquinone, or triphenylmethyl fluoroborate) were unsuccessful.

We considered that the problems of performing a final oxidation stage, which proved insuperable with compound (30), might be overcome by using the biphenylene system. Decomposition of the azide (13), however, gave no azepines. The main isolated product was 2-aminobiphenylene (31). A small amount of coloured material identified by mass spectrum as azobisbiphenylene (35) was also obtained. We have experienced similar difficulties in attempts to expand the naphthalene ring by nitrene insertion.[2] Here the obstacle to ring expansion is less obvious since insertion into the 2,3-double bond giving the azirine (32) appears as energetically feasible as the successful insertion into dihydrobenzocyclobutene; the azirine (33) would be at least as disfavoured as the azirine (27). Apparently the barrier to ring expansion in the biphenylene system must rest with the azepine (34); this observation reflects the instability of benzocyclobutenes.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. Column chromatography was carried out on alumina [Fluka; activity shown thus: (IV)]. Preparative layer chromatography (p.l.c.) was performed on 40 cm plates of Merck silica PF_{254}. U.v. spectra were determined for solutions in 95% ethanol; $\lambda_{max.}$ values are recorded with $\log_{10} \varepsilon$ in parentheses. Liquid azides were generally too unstable for analysis, losing weight on the balance; such azides were characterised by spectral data.

4- and 5-Nitroindane [(1) *and* (5)].—Nitration of indane (100 g) [13] was followed by percolation of the crude mixture through an alumina column (300 g; IV) in petroleum (b.p. 60—80°) giving mixed 4- and 5-nitroindane (45 g).

4- and 5-Aminoindane [(2) *and* (6)].—A solution of the mixed nitroindanes (16·3 g) in methanol (150 ml) was hydrogenated over palladium–charcoal (1·0 g) at atmospheric temperature and pressure till absorption ceased. The filtered solution was treated with fumaric acid, as described by Rhomberg and Berger,[3] to give 4-aminoindane (2) (4·5 g), b.p. 65° at 0·1 mmHg; $\nu_{max.}$ (film) 3450, 3362, and 1620 cm^{-1}; $\lambda_{max.}$ 237 (3·83) and 283 nm (3·19); δ (CCl_4) 1·7—2·25 (2H, m, H-2), 2·35—3·0 (4H, m, H-1 and -3), 3·55br (2H, s, exch. D_2O, NH_2), 6·23 (1H, d, *J* 7·5 Hz, H-5), 6·52 (1H, d, *J* 7·5 Hz, H-7), and 6·84 (1H, t, H-6). 5-Aminoindane (6) had m.p. 34° (lit.,[3] 33—34°); $\nu_{max.}$ (film) 3420, 3345sh, and 1616 cm^{-1}; $\lambda_{max.}$ 236·5 (3·88) and 293 nm (3·39); δ (CCl_4) 1·8—2·2 (2H, m, H-2), 2·73br (4H, t, H-1 and -3), 3·25br (1H, s, exch. D_2O, NH_2), 6·28 (1H, d of d, *J* 2 and 8 Hz, H-6), 6·37br (1H, s, H-4), and 6·84 (1H, d, *J* 8 Hz, H-7).

4-Azidoindane (3).—(*a*) A solution of 4-aminoindane (2) (0·05 mol) in a mixture of 4N-sulphuric acid (250 ml) and purified dioxan (250 ml) was cooled (−5°) and diazotised with sodium nitrite (0·055 mol) in water (50 ml). After 15 min a solution of sodium azide (0·06 mol) in water (50 ml) was added and the solution warmed to 30°. The azide was extracted from the cooled solution with ether; the extracts were dried ($MgSO_4$) and evaporated at 30° under reduced pressure. The residual oil was percolated through alumina (200 g; IV; column length 0·2 m) in petroleum (b.p. 40—60°). Evaporation of the eluate under reduced pressure gave *4-azidoindane* (3) as a yellow oil (60%) (Found: C, 67·5; H, 6·1. $C_9H_9N_3$ requires C, 67·9; H, 5·7%); $\nu_{max.}$ (film) 2105 and 1295 cm^{-1}; $\lambda_{max.}$ 252·5 (4·0), 278·5 (3·47), and 288 nm (3·38); δ ($CDCl_3$) 1·8—2·4 (2H, m, H-2), 2·6—3·1 (4H, m, H-1 and -3) and 6·7—7·2 (3H, m); *m/e* 159 (M^+, 20%), 132 (15), 131 (100), 130 (20), and 102 (20).

(*b*) The Grignard reagent from 4-bromoindane (4) [4,14] (29·3 g) and magnesium (7·41 g) in dry ether (200 ml) was added at −5° to a stirred solution of toluene-*p*-sulphonyl azide (32·3 g) in dry ether (500 ml). The precipitated triazene salt was filtered off, washed with ether, and vacuum-dried. Saturated aqueous sodium pyrophosphate (500 ml) was added dropwise to a cold (−5°), stirred, suspension of the dried triazene salt in dry ether. The mixture was stirred (24 h), the ether layer removed, and the aqueous layer extracted with ether (2 × 200 ml). The combined extracts were dried ($MgSO_4$) and evaporated at 30° under reduced pressure. Purification as in (*a*) gave 4-azidoindane (3) (6·5 g, 27%), identical with that prepared as in (*a*).

5-Azidoindane (7).—Prepared by method (*a*) (above) from 5-aminoindane (6) in 22% yield, 5-azidoindane (7) was a yellow oil, $\nu_{max.}$ (film) 2105 and 1298 cm^{-1}; $\lambda_{max.}$ 250 (4·00), 280 (3·45), and 290 nm (3·30); δ (CCl_4) 1·8—2·2 (2H, m, H-2), 2·5—2·9 (4H, m, H-1 and -3), and 6·8—7·2 (3H, m); *m/e* 159 (M^+, 10%), 132 (20), 131 (100), 130 (10), and 102 (15).

4-Bromo-1,2-dihydrobenzocyclobutene (8).—This was prepared as described by Lloyd and Ongley [7] in 74% yield from 1,2-dihydrobenzocyclobutene.[15,16]

1,2-Dihydro-4-nitrobenzocyclobutene (9).—This was prepared by nitration of 1,2-dihydrobenzocyclobutene in acetic acid,[6] with modified work-up. The crude nitration mixture was chromatographed (200 g; IV) with petroleum (b.p. 40—60°)–methylene chloride (4 : 1) as eluant. The mixture obtained from the eluate was distilled to give 1,2-dihydro-4-nitrobenzocyclobutene (9), b.p. 70—85° at 0·1 mmHg (lit.,[6] 60—85° at 0·05 mmHg) (10 g, 26%); $\nu_{max.}$ (film) 1515 and 1345 cm^{-1}; $\lambda_{max.}$ 221 (3·92) and 275 nm (3·82); δ (CCl_4) 3·22 (4H, s, H-1 and -2), 7·08 (1H, d, *J* 8 Hz, H-6), 7·72 (1H, s, H-3), and 7·96 (1H, d of d, *J* 2 and 8 Hz, H-5).

4-Amino-1,2-dihydrobenzocyclobutene (10).—Reduction of the nitro-compound (9) in methanol over palladium–charcoal gave a 98% yield of 4-amino-1,2-dihydrobenzocyclobutene (10), b.p. 85—90° at 0·15 mmHg; $\nu_{max.}$ (film) 3420, 3340, 3200, 1605, and 1590 cm^{-1}; $\lambda_{max.}$ 236 (3·76), and 293 nm (3·35); δ (CCl_4) 3·1 (4H, s, H-1 and -2), 3·32 (2H, s, exch. D_2O, NH_2), and 6·2—6·8 (3H, m).

4-Azido-1,2-dihydrobenzocyclobutene (11).—(*a*) Prepared as described for 4-azidoindane, in 74% yield, the 4-azidodihydrobenzocyclobutene (11) was a yellow oil; $\nu_{max.}$ (film) 2109 and 1292 cm^{-1}; $\lambda_{max.}$ 251·5 (4·01) and 282·5 nm (3·56); δ (CCl_4) 3·1 (4H, s, H-1 and -2) and 6·6—7·0 (3H, m); *m/e* 145 (M^+, 18%), 120 (26), 119 (100), 118 (89), 117 (44), 116 (27), 104 (13), 103 (15), 93 (13), 92 (21), 91 (49), 90 (37), 77 (27), 65 (27), and 51 (29).

(*b*) Prepared from 4-bromo-1,2-dihydrobenzocyclobutene

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[15] J. A. Oliver and P. A. Ongley, *Chem. and Ind.*, 1965, 1024.
[16] A. Sanders and W. P. Giering, *J. Org. Chem.*, 1973, **38**, 3055.

via the Grignard reagent and tosyl azide in 11% yield, the azidodihydrobenzocyclobutene (11) was identical with the material derived from the amine.

2-*Bromobiphenylene* (12).—This was prepared in 50% yield from biphenylene [17] by the reported procedure.[8]

2-*Azidobiphenylene* (13).—The Grignard reagent from 2-bromobiphenylene (12) (7 g) and magnesium (0·88 g) in dry tetrahydrofuran (200 ml) was filtered and added dropwise to a stirred, cold (0°), solution of tosyl azide (13 g) in dry ether (250 ml). Petroleum (b.p. 40—60°; 250 ml) was then added and the mixture stirred (0·5 h) till precipitation was complete. The orange triazene was filtered off, washed with dry ether, and vacuum-dried. Decomposition of the triazene with pyrophosphate as described for the preparation of 4-azidoindane gave, after percolation through alumina, 2-*azidobiphenylene* (13) as a yellow solid [from petroleum (b.p. 60—80°)], m.p. 80—81° (2·6 g, 44%) (Found: C, 74·5; H, 4·05; N, 21·4. $C_{12}H_7N_3$ requires C, 74·6; H, 3·65; N, 21·75%); $\nu_{max.}$ (CCl_4) 2100 and 1288 cm^{-1}; $\lambda_{max.}$ 239 (4·34), 261·5 (4·66), 353 (3·88), and 363 nm (3·88); δ (CCl_4) 6·2—6·8 (m); *m/e* 193 (M^+, 30%), 167 (14), 166 (18), 165 (100), 164 (84), 139 (21), and 137 (12).

Photochemical Decomposition of Azides: Standard Procedure.—A solution of the azide in diethylamine (concentration 2·5—7 g in 600 ml) was irradiated in a Rayonet Preparative Photochemical Reactor with 16 RUL-3000A lamps (maximum intensity at 300 nm). Evaporation left an oil or tar which was subjected to column or preparative layer chromatography.

Decomposition of 4-*azidoindane* (3). The residue from photoreaction of the azide (3) (6·5 g) (40 h) was chromatographed on alumina (300 g; IV) in benzene. Four main fractions were collected (A—D), and each fraction was further separated by p.l.c. with benzene–acetone (4 : 1) as solvent.

Fraction B (1 g) gave two major bands on p.l.c. The one of lower R_F value gave the aza-azulene (22) (20 mg) (see below). The one of higher R_F value gave the aza-azulene (19) (110 mg) (see below).

Fraction C (1·4 g) gave three major identified bands on p.l.c. In order of increasing R_F value these were: (a) 4-*diethylamino*-1,2,3,8-*tetrahydro*-5-*aza-azulene* (20) (170 mg), b.p. 90° at 0·02 mmHg (Found: N, 13·7. $C_{13}H_{20}N_2$ requires N, 13·7%); $\nu_{max.}$ (film) 1638 and 1587 cm^{-1}; $\lambda_{max.}$ 225 (4·02) and 284 nm (3·80); δ (CCl_4) 1·11 (6H, t, $CH_2{\cdot}CH_3$), 1·6—2·2 (2H, m, H-2), 2·2—2·7 (6H, m, H-1, -3, and -8), 3·26 (4H, q, $N{\cdot}CH_2{\cdot}CH_3$), 4·6br (1H, q, H-7), and 6·41 (1H, d, *J* 7 Hz, H-6); *m/e* 205 (20%), 204 (M^+, 100%), 203 (20), 202 (10), 189 (69), 176 (20), 175 (98), 161 (25), 147 (18), 134 (12), 133 (38), 132 (41), 131 (12), 130 (16), 120 (24), 105 (16), 91 (16), 77 (20), and 72 (35); (b) 5-*diethylamino*-1,2,3,6-*tetrahydro*-4-*aza-azulene* (22) (200 mg), b.p. 110° at 0·1 mmHg (Found: C, 77·1; H, 9·85; N, 13·7. $C_{13}H_{20}N_2$ requires C, 76·45; H, 9·85; N, 13·7%); $\nu_{max.}$ (film) 1602 and 1555 cm^{-1}; $\lambda_{max.}$ 219 (4·08), 278 (3·85), and 290sh nm (3·84); δ ($CDCl_3$) 1·1 (6H, t, $CH_2{\cdot}CH_3$), 1·6—2·1 (2H, m, H-2), 2·4—2·8 (6H, m H-1, -3, and -6), 3·34 (4H, q, $N{\cdot}CH_2{\cdot}CH_3$), 4·80br (1H q, H-7), and 6·15 (1H, d, *J* 8·5 Hz, H-8); *m/e* 205 (25%)' 204 (M^+, 100%), 203 (13), 189 (66), 176 (13), 175 (97)' 161 (25), 159 (25), 147 (19), 134 (13), 133 (50), 132 (53) 131 (13), 130 (25), 120 (25), 118 (13), 117 (19), 105 (19), 91 (28), 79 (26), 78 (13), 77 (28), and 72 (38); (c) 4-diethylamino-1,2,3,3a-tetrahydro-5-aza-azulene (19) (420 mg), b.p. 100° at 0·1 mmHg, giving variable results on analysis, and decomposing rapidly; $\nu_{max.}$ (film) 1575 and 1570 cm^{-1}; $\lambda_{max.}$ 228 (3·94), 250sh, and 285 nm (3·75); δ ($CDCl_3$) 0·7—1·3 (6H, t, $CH_2{\cdot}CH_3$), 1·7—2·5 (6H, m, H-1, -2, and -3), 2·6—3·4 (5H, m, $N{\cdot}CH_2{\cdot}CH_3$ and H-3a), 5·68 (1H, d of d, *J* 8 and 6 Hz, H-7), 6·1br (1H, d, *J* 6 Hz, H-8), and 6·9 (1H, d, *J* 8 Hz, H-6); *m/e* 205 (8%), 204 (M^+, 41%), 189 (27), 176 (16), 175 (100), 161 (20), 134 (16), 133 (37), 132 (33), 131 (12), 130 (12), 120 (12), 117 (18), 105 (24), 104 (16), 91 (16), 79 (16), 78 (14), 77 (18), and 72 (43).

Fraction D (0·5 g) on p.l.c. yielded one main band, identified as the aza-azulene (20) (170 mg). Total yields of aza-azulenes were: (19) (530 mg); (20) (340 mg); (22) (220 mg); total recovery 1·09 g (13% yield).

Decomposition of 5-*azidoindane* (7). After irradiation of the azide (7) (2·4 g) (17 h) and evaporation of the solvent a black oil remained. Distillation gave a yellow oil (0·92 g, 31%), b.p. 87—90° at 0·3 mmHg, showing two overlapping peaks on g.l.c. (estimated ratio 85 : 15). No chromatographic separation could be achieved. The major product was identified as 5-diethylamino-1,2,3,4-tetrahydro-6-aza-azulene (26) (Found: C, 76·4; H, 9·5; N, 13·7. $C_{13}H_{20}N_2$ requires C, 76·45; H, 9·85; N, 13·7%); $\nu_{max.}$ (film) 1620 and 1565 cm^{-1}; $\lambda_{max.}$ 219 (4·20) and 294 nm (3·86); δ (CCl_4) 1·13 (6H, t, $CH_2{\cdot}CH_3$), 1·6—2·25 (2H, m, H-2), 2·44 (4H, t, H-1 and -3), 2·61 (2H, s, H-4), 3·35 (4H, q, $N{\cdot}CH_2{\cdot}CH_3$), 5·49 (1H, d, *J* 8 Hz, H-8), and 6·79 (1H, d, *J* 8 Hz, H-7); *m/e* 205 (16%), 204 (M^+, 94%), 203 (73), 202 (13), 189 (15), 176 (19), 175 (100), 161 (13), 160 (11), 159 (13), 147 (19), 134 (11), 133 (32), 132 (41), 131 (13), 120 (16), 118 (13), 117 (13), 105 (11), 104 (19), 102 (13), 91 (19), 79 (13), 78 (11), 77 (19), and 72 (40). Mass spectra for both isomers were obtained by use of a g.l.c.-linked instrument.

N.m.r. peaks to the minor product, 6-diethylamino-1,2,3,7-tetrahydro-5-aza-azulene (24) appeared at δ 3·33 (4H, q, $N{\cdot}CH_2{\cdot}CH_3$), 4·73 (1H, t, H-8), and 6·85 (1H, s, H-4). This isomer had *m/e* 205 (16%), 204 (M^+, 100%), 203 (16), 190 (6), 189 (46), 176 (20), 175 (92), 161 (23), 160 (7), 159 (10), 148 (13), 147 (19), 134 (17), 133 (76), 132 (60), 131 (14), 130 (13), 120 (30), 118 (17), 117 (10), 106 (19), 105 (39), 104 (15), 103 (16), 102 (7), 91 (20), 79 (24), 78 (17), 77 (28), and 72 (47).

Decomposition of 4-*azido*-1,2-*dihydrobenzocyclobutene* (11). Irradiation of the azide (11) (5·6 g) (20 h) followed by evaporation of the solvent gave a red oil. Chromatography on alumina (200 g; IV) with petroleum (b.p. 40—60°; 300 ml) then petroleum–benzene (4 : 1; 600 ml) as eluants gave 4-*diethylamino*-1,2-*dihydro*-3H-5-*azacyclobutacycloheptene* (30), m.p. 52—53° [from petroleum (b.p. 60—80°)] (4·0 g, 55%) (Found: C, 75·45; H, 9·85; N, 15·0. $C_{12}H_{18}N_2$ requires C, 75·8; H, 9·5; N, 14·7%); $\nu_{max.}$ (Nujol) 1628 cm^{-1}; $\lambda_{max.}$ 220·5 (4·16) and 293·5 nm (3·96); δ ($CDCl_3$) 1·11 (6H, t, $CH_2{\cdot}CH_3$), 2·54 (4H, s, H-1 and -2), 2·69 (2H, s, H-3), 3·32 (4H, q, $N{\cdot}CH_2{\cdot}CH_3$), 5·40 (1H, d, *J* 7·5 Hz, H-7), and 6·81 (1H, d, *J* 7·5 Hz, H-6); *m/e* 190 (M^+, 50%), 189 (100), 175 (11), 161 (22), 120 (16), 119 (14), 118 (32), 117 (11), 106 (11), 99 (14), 92 (17), 91 (43), 78 (11), 77 (16), and 72 (30).

Decomposition of 2-*azidobiphenylene* (13). The azide (13) (2·6 g) was irradiated (40 h); removal of solvent gave a black tar, which on p.l.c. (benzene–acetone, 1 : 1) gave 1 major and 2 minor bands. The major band was shown to

[17] F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12.

contain 2-aminobiphenylene (31), m.p. 126° (lit.,[18] 123—124°); $\nu_{max.}$ (Nujol) 3400, 3320, 1660, and 1603 cm^{-1}; $\lambda_{max.}$ 258·5 (4·57), 357sh, and 366 nm (3·91); δ (CCl_4) 3·2br (2H, s, exch. D_2O, NH_2) and 5·7—6·6 (7H, m).

[18] W. Baker, M. P. V. Boarland, and J. F. W.McOmie, *J. Chem. Soc.*, 1954, 1476.

A minor band (orange) was shown by its mass spectrum to contain an azobiphenylene: *m/e* 331 (4%), 330 (M^+, 16%), 303 (26), 302 (100), and 151 (37).

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