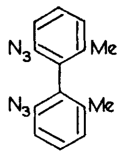
219. *The Decomposition of Some* ortho-*Substituted Azido- or Azidomethyl-biphenyls.*

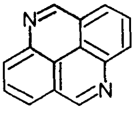
By B. Coffin and R. F. Robbins.

The pyrolysis and photolysis of some *ortho*-substituted azido- or azidomethyl-biphenyls has been studied. Reaction paths in the latter case are evidently complex and may involve the rearrangement of an azene intermediate $ArCH_2N$.

The decomposition of organic azides by heat,[1] or by ultraviolet radiation,[1] and the related decomposition by reagents such as ferrous oxalate [2] or triethyl phosphite [3] of suitable nitro-compounds has given elegant syntheses of many heterocyclic compounds. Thus, the pyrolysis of 2-azido-2′,4′,6′-trimethylbiphenyl in boiling biphenyl ether gave a 48% yield [4] of 5,7-dimethylphenanthridine. When however, 2,2′-diazido-6,6′-dimethylbiphenyl (I) was heated alone or in a number of solvents tar rather than the expected 4,9-diazapyrene (II) was obtained. Neither did (II) result from the ultraviolet irradiation of various solutions of (I) or from the reaction of 2,2′-dimethyl-6,6′-dinitrobiphenyl with either ferrous oxalate or with triethyl phosphite. The latter reagent, however, gave 1,10-dimethylbenzo[*c*]cinnoline. So perhaps better to understand some of these reactions and thereby arrive at an improved synthesis of 4,9-diazapyrene a study of the pyrolysis and photolysis of 2-azido-2′-methylbiphenyl, 2-azidomethylbiphenyl, and 2,2′-di(azidomethyl)-biphenyl was initiated. These azides were prepared by standard, although sometimes tedious, methods and were photolysed in solutions of either diethyl ether or cyclohexane. Photolysis was usually a less satisfactory experimental procedure than pyrolysis. Thus photolysis gave more unchanged starting material and poorer product yields presumably as a result of the successive reduction of the penetration of light as dark coloured irradiation products precipitated. For the pyrolyses biphenyl ether was the solvent of choice.



(I)



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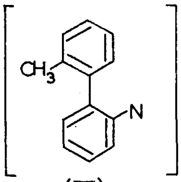

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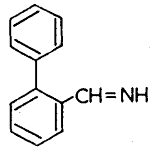

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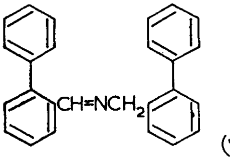

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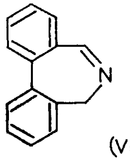

(VII)

From any one pyrolysis or photolysis several products usually resulted and these were separated by chromatography on alumina.

In all those cases where nitrogen evolution was measured (mainly pyrolyses) the evolution appeared to follow a first-order rate.

In the decomposition of 2-azido-2′-methylbiphenyl the azene (III) first formed might

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[1] Horner and Christmann, *Agnew. Chem. internat. Edn.*, 1963, **2**, 599, contains most of the important references.

[2] Abramovitch, Ahmed, and Newman, *Tetrahedron Letters*, 1961, 752.

[3] Cadogan and Cameron-Wood, *Proc. Chem. Soc.*, 1962, 78.

[4] Smolinsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4717.

be substituted at the 6′-hydrogen to give a carbazole, or abstract hydrogen from the 2′-methyl group. Intramolecular coupling in the latter case would then give dihydrophenanthridine. So easily is this oxidised that formation of phenanthridine would follow. Alternatively, the azene (III) might abstract hydrogen from the solvent (or from dihydrophenanthridine) to give 2-amino-2′-methylbiphenyl. However, the pyrolysis of 2-azido-2′-methylbiphenyl gave 4-methylcarbazole in 91% yield with no phenanthridine or 2-amino-2′-methylbiphenyl formation. The absence of formation of amine in this pyrolysis and in all other reported pyrolyses of 2-azidobiphenyls which have 6′-hydrogen and no strongly nucleophilic group in position 2′ indicates the ease of carbazole formation in such reactions. Even when 2-azido-5-bromobiphenyl[5] was pyrolysed in phenol, diethyl malonate, or toluene-ω-thiol, 3-bromocarbazole was the only product. While obviously the stereochemistry of these reactions is important such results do lend force to the suggestion that in such reactions leading to carbazoles the azene derived from a 2-azidobiphenyl acts as a carbene-like electrophile rather than as a biradical. The alternative suggestion that loss of nitrogen and ring closure are so concerted as not to require discrete azene formation is contrary to the kinetic evidence provided by Smith and Hall.[6]

Quite commonly the azenes produced from decomposing azides are believed to function as biradicals. This appeared so with the azene produced on photolysing 2-azidomethylbiphenyl

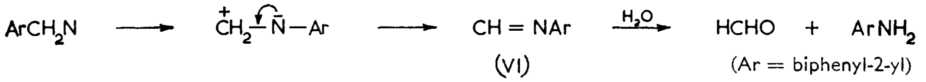
$$\mathrm{ArCH_2{\cdot}N_3 \longrightarrow ArCH_2{\cdot}N}\ (\mathrm{Ar} = \text{biphenyl-2-yl})$$

for by characteristic[1] intramolecular hydrogen abstraction the azene formed the imine (IV) (8%). However under the presumably more energetic conditions of pyrolysis in boiling biphenyl ether 2-azidomethylbiphenyl evolved hydrazoic acid and gave two products. One of these was the anil (V) (as was proved by acid hydrolysis and identification of the fragments) while the other product, isolated in small yield as the hydrochloride, was shown (by paper chromatography and infrared absorption spectroscopy) to be 2-aminobiphenyl. Anil (V) formation may be explained as due to the coupling of the appropriate azene with a radical produced by elimination of hydrazoic acid from 2-azidomethylbiphenyl. Thus:

$$\mathrm{ArCH_2{\cdot}N_3 \longrightarrow ArCH_2{\cdot}N + ArCH \longrightarrow ArCH_2{\cdot}N{=}CHAr}\ (\mathrm{V})$$

Favouring this formulation rather than an alternative explanation involving attack of the carbene upon the original azide is some work due to Curtius and Erhart.[7] The nature and multiplicity of the products they isolated from the presumably related decomposition of benzyl azide seem best explained in terms of the further reaction of $\mathrm{PhCH_2N}$ and PhCH.

The azene from 2-azidomethylbiphenyl might on rearrangement give the formaldehyde anil (VI; Ar = biphenyl-2-yl). Easy hydrolysis during working up of this anil then seems likely. This suggestion would explain the presence of 2-aminobiphenyl in the pyrolysis products of 2-azidomethylbiphenyl. The rearrangement as postulated has not previously been observed in the thermal decomposition of aralkyl azides although rearrangements such as $\mathrm{Ar_3CN_3 \longrightarrow Ar_2C{=}NAr}$ are well known.



$$\mathrm{ArCH_2N \longrightarrow \overset{+}{C}H_2{-}\bar{N}{-}Ar \longrightarrow CH{=}NAr \xrightarrow{H_2O} HCHO + ArNH_2}$$

(VI) (Ar = biphenyl-2-yl)

Conceivably the formaldehyde anil (VI; Ar = biphenyl-2-yl) formation might involve, as does the decomposition[8] of $\mathrm{Ar_3CN_3}$, a degree of aryl participation in the loss of nitrogen from the parent azide.

When 2,2′-di(azidomethyl)biphenyl was heated in boiling biphenyl ether, or in boiling

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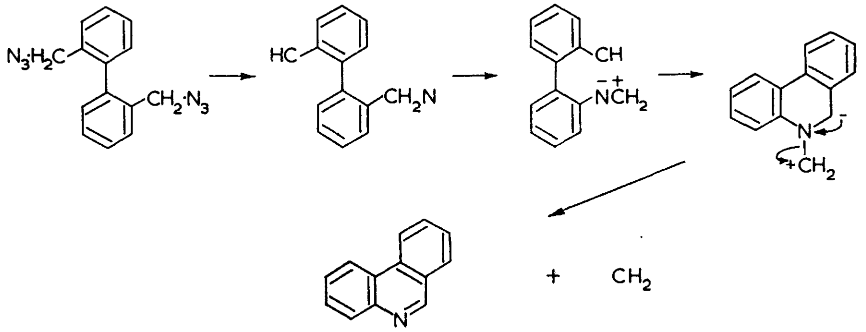
[5] Smith and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 2435.
[6] Smith and Hall, *J. Amer. Chem. Soc.*, 1962, **84**, 480.
[7] Curtius and Erhart, *Ber.*, 1922, **55**, 1559.
[8] Saunders and Ware, *J. Amer. Chem. Soc.*, 1958, **80**, 3328.

biphenyl, hydrazoic acid was evolved and phenanthridine and 5*H*-dibenz[*c*,*e*]azepine (VII) was obtained. The structure (VII) for the latter pyrolysis product is consistent with the observed infrared and nuclear magnetic resonance spectral data while its ultraviolet absorption curve is similar to that of its carbocyclic analogue. Furthermore on catalytic reduction(H_2–Pt) the dibenzazepine (VII) took up two gram-equivalents of hydrogen and gave a cyclic secondary amine identical with one produced by treating 2,2′-di(bromomethyl)biphenyl with ammonia under pressure (the amines were compared as their toluene-*p*-sulphonates derivatives).

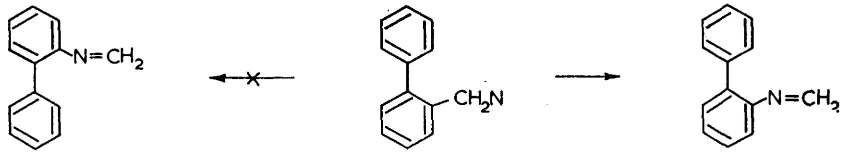
Vapour-phase pyrolysis (about 400°/0·02 mm.) of 2,2′-di(azidomethyl)biphenyl commonly gave phenanthridine. In experiments which differed only in scale and possibly in the rate at which vapour was distilled into the decomposition chamber good yields of 5*H*-dibenz[*c*,*e*]azepine (VII) were obtained. Heated alone the dibenzazepine (VII) gave no phenanthridine.

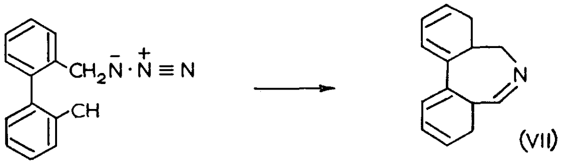
There exists a formal analogy between the pyrolysis products of 2-azidomethylbiphenyl and 2,2′-di(azidomethyl)biphenyl. Thus dibenzazepine (VII) formation might be regarded as the intramolecular analogue of anil (V) formation while phenanthridine formation may involve an azene rearrangement similar to that already described, the rearrangement product on intramolecular attack then expelling a methylene group. Thus:



As a consequence of the above scheme it follows that the rearrangement of the azene formed by pyrolysing 2-azidomethylbiphenyl cannot utilise the 2′-position of the other ring.

The exit gases from the pyrolysis of 2,2′-di(azidomethyl)biphenyl contained no ethylene (aqueous $KMnO_4$) while other attempts to confirm the presence of methylene (*e.g.*, by trapping with acenaphthylene) gave only uncharacterisable polymeric material. To this extent the above scheme for phenanthridine formation must remain tentative. However, it compares with a suggested rationalisation by Abramovitch and Davis[9] of an earlier





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[9] Abramovitch and Davis, *Chem. Rev.*, 1964, **64**, 170.

report [10] that carbonyl azide and benzene on heating in an autoclave give pyridine. This suggestion also involves rearrangement and expulsion of methylene.

That the formation of 5*H*-dibenz[*c,e*]azepine (VII) may involve intramolecular carbene attack on an azidomethyl group cannot be easily dismissed. In the absence of further and probably difficult kinetic analysis this reaction path and an analogous one for anil (V) formation is worthy of consideration.

EXPERIMENTAL

Ultraviolet absorption spectra were measured in methanol on a Uvispek apparatus while infrared spectra were usually determined for Nujol mulls with a Perkin-Elmer " Infracord."

Preparation of the Azides.—*2,2'-Diazido-6,6'-dimethylbiphenyl.* 2,2'-Diamino-6,6'-dimethylbiphenyl (1 g.) (from 2,2'-dimethyl-6,6'-dinitrobiphenyl [11] by reduction with hydrazine hydrate and Raney nickel in dilute ethanol solution [12]) was dissolved in acetic acid (10 ml.) and sulphuric acid (2 ml.; *d* 1·84). To this at 5° was added dropwise a solution of sodium nitrite (0·76 g.) in water (10 ml.), and after 1 hour's stirring water (50 ml.) and sufficient urea to remove the excess of nitrous acid (starch–iodide paper) were added. Slow addition of sodium azide (1·3 g.) in water (20 ml.) then gave after 1 hr. at 0° and 12 hr. at room temperature *2,2'-diazido-6,6'-dimethylbiphenyl* (1·1 g.; 88%). Crystallisation (ethanol) gave brown needles, m. p. 56—57° (Found: C, 63·3; H, 4·8; N, 32·0. $C_{14}H_{12}N_6$ requires C, 63·6; H, 4·6; N, 31·8%).

2-Azido-2'-methyldiphenyl. After the diazotisation of 2-amino-2'-methylbiphenyl [13] (1 g.) in 5N-sulphuric acid (10 ml.) at 5° with sodium nitrite solution (0·4 g. in 5 ml. of water) and stirring for 30 min. the excess of nitrous acid was removed as before. The addition of sodium azide (0·4 g.) in water (5 ml.) afforded after 1 hr. at 0° and 12 hr. at room temperature an oil which was isolated by ether extraction of the solution. Its further purification was effected by passage down a short alumina column. Removal of the solvent from the eluate gave the azide as an oil (1·04 g.; 91%) with a characteristic strong infrared absorption at 2128 cm.$^{-1}$ (azido).[14] It decomposed on attempted distillation (118°/0·01 mm.) and satisfactory analyses could not be obtained. Its reactions leave no doubt as to its character. For subsequent experiments the oil was used as prepared.

2-Azidomethylbiphenyl. Biphenyl-2-carboxylic acid [15] (20 g.) in tetrahydrofuran (100 ml.) was slowly added (1 hr.) to a stirred refluxing solution of lithium aluminium hydride (4 g.) in tetrahydrofuran (100 ml.), cooled as necessary. After 3 hr. the mixture was poured on to ice, acidified (5N-H_2SO_4) and extracted (ether). After washing and drying (Na_2SO_4), removal of the solvent gave 2-hydroxymethylbiphenyl (14·9 g.; 81%), b. p. 133°/0·2 mm. (lit., b. p. 176°/17 mm.).[16]

The reaction of this product (4 hr.) with hydrobromic acid and isolation in the usual way gave 2-bromomethylbiphenyl (13 g.; 65%) (b. p. 127°/0·4 mm.; lit., b. p. 129°/0·4 mm.).[17] This was dissolved in ethanol (150 ml.), and sodium azide (4 g.) in water (50 ml.) was added. After boiling, sufficient sodium azide was added to provide a saturated solution. After refluxing for 24 hr. water (300 ml.) was added and the mixture extracted with ether.

After washing, the dry (Na_2SO_4) ethereal solution was evaporated to give *2-azidomethylbiphenyl* (7·8 g.; 63%), b. p. 91°/0·2 mm. (Found: N, 19·7. $C_{13}H_{11}N_3$ requires N, 20·1%).

2,2'-Di(azidomethyl)biphenyl. As in the foregoing reduction, biphenic acid (31 g.) in tetrahydrofuran (100 ml.) was treated with lithium aluminium hydride (10 g.) in tetrahydrofuran (100 ml.) to give 2,2'-di(hydroxymethyl)biphenyl (23·3 g.; 83%), as needles, m. p. 110—112° (lit., m. p. 110—112°),[18] from benzene. Treatment of this alcohol with hydrobromic acid gave 2,2'-di(bromomethyl)biphenyl (27·5 g.; 75%) as needles, m. p. 91—93° (lit., m. p. 91—93°),[18] from light petroleum (b. p. 60—80°).

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[10] Curtius and Bertho, *Ber.*, 1926, **59**, 565.

[11] (*a*) Carlin and Foltz, *J. Amer. Chem. Soc.*, 1956, **78**, 1999; (*b*) Kenner and Stubbings, *J.*, 1921, 593.

[12] Moore and Furst, *J. Org. Chem.*, 1958, **23**, 1504.

[13] Shuttleworth, *J.*, 1944, 71.

[14] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., p. 273.

[15] Fillig and Osteimayer, *Annalen*, 1873, **166**, 374; Guitsche and Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 2239.

[16] Goldschmidt and Veer, *Rec. Trav. chim.*, 1948, **67**, 489.

[17] Cookson and Mann, *J.*, 1949, 2891.

[18] Turner and Hall, *J.*, 1930, 711.

After the bromo-compound had dissolved in 2-ethoxyethanol (100 ml.), sodium azide (18 g.) in water (25 ml.) was added;[19] and after stirring for 24 hr. at 95° water was added and the mixture extracted with ether. After washing and removal of the solvent from the dry ethereal solution (Na_2SO_4) 2,2′-*di(azidomethyl)biphenyl* (18·1 g.; 85%) was obtained as an oil, b. p. 148°/0·09 mm. (Found: N, 31·8. $C_{14}H_{10}N_6$ requires N, 31·8%).

Pyrolysis of the Azides.—The azide dissolved in dry biphenyl ether was heated under nitrogen in a container jacketed by boiling biphenyl ether (b. p. 248—250°). The evolution of nitrogen from the reaction could be measured by means of an attached mercury manometer. When nitrogen evolution had ceased, heating was usually continued for a further 10 min., and the products were isolated as described below.

(*a*) 2,2′-*Diazido*-6,6′-*dimethylbiphenyl.* The dilution of the pyrolysis solution of this diazide (1·5 g.) with light petroleum (b. p. 60—80°) gave a brown amorphous product (0·8 g.) which could not be characterised. The attempted pyrolysis in solvents such as ligroin or xylene gave similar material. Furthermore the considerable variation of azide concentration effected no improvement.

(*b*) 2-*Azido*-2′-*methylbiphenyl.* After pyrolysis of a solution of the azide (1 g.) in biphenyl ether (5 ml.), the mixture was diluted with light petroleum (b. p. 60—80°) (25 ml.) and afforded 4-methylcarbazole (0·82 g., 91%) as needles, m. p. 128° (lit., m. p. 129·5—130°) (Found: C, 86·1; H, 5·9; N, 8·0. Calc. for $C_{13}H_{11}N$: C, 86·2; H, 6·1; N, 7·7%), from light petroleum (b. p. 60—80°). It formed a red picrate (methanol), m. p. 168° (lit., m. p. 168°).[20]

(*c*) 2-*Azidomethylbiphenyl.* The pyrolysis of 2-azidomethylbiphenyl (1·4 g.) in biphenyl ether (5 ml.) gave, after pouring into light petroleum (b. p. 60—80°) (25 ml.), a dark coloured solid. This was filtered off and the filtrate, after chromatography on alumina (60 g.) [eluted first with light petroleum (100 ml.) and then with a 10% solution of benzene in light petroleum), gave N-2-*biphenylylmethyl*-2-*biphenylylmethyleneamine* (V) (0·75 g., 65%) as needles, m. p. 125° (Found: C, 89·8; H, 5·8; N, 4·0. $C_{26}H_{21}N$ requires C, 89·9; H, 6·0; N, 4·0%). With Brady's reagent it gave 2-phenylbenzaldehyde 2,4-dinitrophenylhydrazone as red needles (HOAc) (Found: C, 62·6; H, 4·5; N, 15·5. $C_{19}H_{14}N_4O_4$ requires C, 62·6; H, 3·9; N, 15·4%), m. p. 206° undepressed on admixture with an authentic sample.

The hydrolysis (10—15 min. at 100°) of (V; 0·2 g.) with 50% sulphuric acid (5 ml.) gave, after dilution with water and extraction with ether, 2-phenylbenzaldehyde identified *via* its 2,4-dinitrophenylhydrazone (0·182 g., 87%). The basification of the acid fraction gave after extraction with ether, 2-*aminomethylbiphenyl* (0·082 g., 77%) which after sublimation under vacuum melted at 48° (Found: C, 85·4; H, 6·6; N, 7·9. $C_{13}H_{13}N$ requires C, 85·7; H, 6·6; N, 7·7%).

If, in the above chromatographic procedure, after elution with 10% benzene in light petroleum the column was eluted with ethanol, then evaporation of the solvent from the eluate gave an oil (0·148 g., 19%) which was purified by vacuum distillation (b. p. 118°/0·2 mm.). On passing hydrogen chloride into its ethereal solution 2-*aminobiphenyl hydrochloride* resulted; it had m. p. 201° after vacuum sublimation (Found: C, 70·1; H, 6·2. $C_{12}H_{12}NCl$ requires C, 70·1; H, 5·9%). Chromatography on paper (Whatman No. 3) of the above using methanol–n-pentyl alcohol–benzene–water (4 : 1 : 1 : 1) and development with 0·2% sodium nitrite and dilute hydrochloric acid followed by *N*-ethylnaphthylamine hydrochloride[21] in alcohol gave a spot of R_F 0·98. (An authentic sample of 2-aminobiphenyl also gave R_F 0·98.) Similarly comparison with authentic samples of both the base and its hydrochloride by infrared spectroscopy showed them to be 2-aminobiphenyl and the corresponding hydrochloride.

When in the above pyrolysis the exit gases were passed into aqueous ferric chloride a blood red coloration due to hydrazoic acid was observed. The evolution of nitrogen on passing the gases into potassium permanganate solution and the resulting loss of colour again showed the presence of hydrazoic acid. The absence of formaldehyde in the exit gases was shown by passing them into a solution of chromotropic acid in concentrated sulphuric acid.

Differing concentrations of azide in the biphenyl ether seemed not to alter the yields of the various pyrolysis products nor did a change of solvent to biphenyl. Attempts to trap possible reaction intermediates, for example by adding either indene or acenaphthylene to the reaction mixture gave only high-melting uncharacterisable products.

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[19] Lieber, Tai Siang Chao, and Ramachandran Rao, *J. Org. Chem.*, 1957, **22**, 238.

[20] Campaigne and Lake, *J. Org. Chem.*, 1959, **24**, 478; Pansacker and Robinson, *J.*, 1947, 1557.

[21] Ekman, *Acta Chem. Scand.*, 1948, **2**, 383.

(*d*) 2,2′-*Di*(*azidomethyl*)*biphenyl*. The pyrolysis of 2,2′-di(azidomethyl)biphenyl (3·5 g.) in biphenyl ether (6 g.) gave, after pouring the mixture into light petroleum (b. p. 60—80°; 100 ml.) and filtering, a filtrate which was chromatographed on an alumina column (60 g.). Elution of the column with light petroleum gave first biphenyl ether and then phenanthridine (0·49 g., 21%) (Found: C, 87·0; H, 5·0; N, 7·6. Calc. for $C_{13}H_9N$: C, 87·1; H, 5·1; N, 7·8%), as shown from its infrared absorption and m. p. and mixed m. p. 108°.[22] Further elution of the column with 10% benzene in light petroleum gave, after distillation under vacuum (b. p. 138—140°/0·08 mm.), 5H-*dibenz*[c,e]*azepine* (0·74 g., 29%) as an oil. It formed a *methiodide* (Found: C, 53·3, 53·5; H, 4·2, 4·1; N, 4·1, 3·2. $C_{14}H_{13}NI$ requires C, 53·8; H, 4·2; N, 4·2%), as yellow needles (methanol), m. p. 217°, and a p-*nitrobenzyl bromide*, m. p. 234° (as needles from ethanol/ether) (Found: C, 61·8; H, 4·2. $C_{21}H_{17}N_2O_2Br$ requires C, 61·6; H, 4·2%.)

On catalytic (Adams platinum oxide, 0·1 g.) reduction the foregoing dibenz[*c,e*]azepine (0·355 g.) absorbed one mol. of hydrogen to give, after removal of solvent, a gum. Dissolved in pyridine (5 ml.) and treated with toluene-*p*-sulphonyl chloride (0·4 g.) it gave 6-*toluene*-p-*sulphonyl*-6,7-*dihydro*-5H-*dibenz*[c,e]*azepine* (0·57 g., 89%) as needles (methanol), m. p. 164° (Found: C, 71·8; H, 5·7; N, 3·9; S, 9·2. $C_{21}H_{19}NO_2S$ requires: C, 72·2; H, 5·5; N, 4·0; S, 9·2%) as shown by mixed m. p. and the similarity of its infrared absorption to the *p*-tosyl derivative prepared from an authentic sample of 6,7-dihydro-5*H*-dibenz[*c,e*]azepine.[23]

The distillation of 2,2′-di(azidomethyl)biphenyl (0·36 g.) at 0·02 mm. through a tube packed with glass beads maintained at 380° gave a distillate which after chromatography on alumina (40 g.) (elution with 10% benzene in light petroleum) afforded 5*H*-dibenz[*c,e*]azepine (0·149 g., 57%). On a larger scale another vapour-phase pyrolysis of the diazide (1·0 g.) afforded phenanthridine (0·52 g., 77%).

Photolysis of the Azides.—(*a*) 2,2′-*Diazido*-6,6′-*dimethylbiphenyl*. The u.v. irradiation (Hanovia U.V.S. model 500A lamp) for 24 hr. of the diazide (0·5 g.) in pure cyclohexane (20 ml.) and contained under nitrogen in a silica flask gave only dark, presumably polymeric, material which could not be characterised.

(*b*) 2-*Azido*-2′-*methylbiphenyl*. The photolysis as in (*a*) of this azide (0·5 g.) in cyclohexane (20 ml.) gave after removal of the solvent an oil which on trituration with light petroleum (10 ml.) yielded 4-methylcarbazole (0·186 g., 43%), needles, m. p. 128° (from light petroleum).

(*c*) 2-*Azidomethylbiphenyl*. After photolysis (48 hr.) in cyclohexane (20 ml.) and evaporation of the solvent, 2-azidomethylbiphenyl (0·5 g.) afforded 2-iminomethylbiphenyl which on treatment with Brady's reagent gave 2-formylbiphenyl 2,4-dinitrophenylhydrazone (0·069 g., 8%) as red needles, m. p. and mixed m. p. 206°, from glacial acetic acid.

1,10-*Dimethylbenzo*[c]*cinnoline*.—2,2′-Dimethyl-6,6′-dinitrobiphenyl (0·64 g.) in triethyl phosphite (5 g.) was heated at 160° under nitrogen for 12 hr. The resulting solution was then evaporated under reduced pressure to yield a dark brown gum which was dissolved in benzene (30 ml.) and chromatographed on alumina (40 g.). Elution with benzene gave 1,10-dimethylbenzo[*c*]cinnoline (0·054 g., 11%) as needles [from light petroleum (b. p. 60—80°)], m. p. and mixed m. p. 96° (lit., m. p. 96—97°).[11b]

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[22] "Chemistry of Carbon Compounds," edited by Rodd, Vol. IVA, Elsevier, London, p. 694.

[23] Cohen, Dimwoodie, and McKeever, *J. Org. Chem.*, 1962, **27**, 3385.