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## Part XX.<sup>1</sup> Polyhalogenoaromatic Compounds. Some Reactions of **Decachlorobiphenyl**

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Decachlorobiphenyl is reduced at the 4,4'-positions when treated with excess of lithium aluminium hydride, n-butyl lithium, or magnesium followed by hydrolysis. With molar proportions of these reagents inseparable mixtures of mono- and di-substituted compounds were obtained. The lithio-derivatives were converted into the methyl derivatives with dimethyl sulphate, and also underwent thermal elimination of LiCl to give the corresponding arynes. The title compound reacted readily with both piperidine and methoxide to give the 4- and 4,4'-substituted polychlorobiphenyls. Oxidation of the piperidino-derivatives gave the corresponding nitro-compounds.

WHILE the chemistry of polyfluorobiphenyls is comparatively well known<sup>2</sup> that of the analogous polychlorocompounds has been little explored. Our interest in this field has led us to study the behaviour of decachlorobiphenyl (I), which has been known for sometime.<sup>3</sup> A few scattered reports,<sup>4,5</sup> mainly in the patent literature, describe nucleophilic substitution occurring preferentially at the 4,4'-positions. This orientation can be rationalised by regarding decachlorobiphenyl as a substituted pentachlorobenzene ( $R-C_6Cl_5$ ). When all the possible Wheland-type intermediates, the  $I_{\pi}$  repulsion of chlorine, and the steric bulk of the negative C<sub>6</sub>Cl<sub>5</sub>-substituent are considered, nucleophilic substitution in decachlorobiphenyl is most likely to occur at the 4-position involving the *para*-quinonoid intermediate (II). Similar factors have been successfully applied to explain the orientation in other aromatic polyhalogeno-compounds.<sup>6</sup> Thus, with



<sup>&</sup>lt;sup>3</sup> F. L. W. Van Roosemalen, Rec. trav. Chim., 1934, 53 359.

Part XIX, D. J. Berry, B. J. Wakefield, and J. D. Cook, Chem. Soc. (C), 1971, 1227.
 G. M. Brooke and W. K. R. Musgrave, J. Chem. Soc., 1965,

<sup>1864;</sup> D. E. Fenton, A. J. Park, D. Shaw, and A. G. Massey, J. Organometallic Chem., 1964, 2, 437; S. C. Cohen, D. E. Fenton, Tomlinson, and A. G. Massey, J. Organometallic Chem., 1966, 6, 301, and papers cited therein.

<sup>&</sup>lt;sup>4</sup> Belg.P. 671,608/1966; U.S.P. 2,644,015/1953.

<sup>&</sup>lt;sup>5</sup> Belg.P. 643,938/1964.
<sup>6</sup> D. T. Clark, J. N. Murrell, and J. M. Tedder, J. Chem. Soc., 1963, 1250; J. Burdon, Tetrahedron, 1965, 21, 3373.



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alcoholic sodium hydroxide, 4-hydroxynonachlorobiphenyl is first produced followed by the 4,4'-dihydroxyderivative.<sup>4</sup> Similarly, treatment with an excess of 2,2bishydroxymethylbutanol and sodium hydroxide in hot dioxan yields the octachlorobiphenyl (III).<sup>5</sup> Ballester <sup>7</sup> has successfully chlorinated 4,4'-bistrichloromethylbiphenyl to give perchloro-p,p,-bitolyl and by treatment with oleum converted it into the 4,4'-dicarboxylic acid, which undergoes pyrolysis to yield octachlorobiphenyl (V). Roosemalen's <sup>3</sup> early synthesis of a number of polychlorobiphenyls using a benzidine rearrangement of the appropriate polychlorohydrazobenzenes has been found to be complicated by accompanying diphenyline formation<sup>8</sup>.

We have carried out a series of reactions on decachlorobiphenyl (I) and our results are set out in the Scheme. Orientation and separation of the reaction products proved difficult since mixtures of the mono- and the di-substituted derivatives were often formed. The constituents were usually distinguishable by spectroscopy but behaved similarly on chromatographic columns.

In one method the octachlorobiphenyl (V) was prepared by heating 2,3,5,6-tetrachloroiodobenzene with copper bronze in a sealed tube at 190° for 15 hr. Unfortunately, analogous reactions to obtain the corresponding isomers in which the 3,3'- and 2,2'-positions were nonchlorinated were unsuccessful. The octachloro-derivative (V) gave rise to a sharp singlet at  $\tau 2.27$  (CDCl<sub>2</sub>) in the n.m.r. spectrum; it also showed a breakdown pattern in the mass spectrum similar to that observed for the title compound (I) and arising from successive loss of 2Cl atoms from the parent ion (m/e 430).

Decachlorobiphenyl (I) was readily reduced by lithium aluminium hydride in tetrahydrofuran at room temperature to give a mixture of polychlorobiphenyls in proportion almost identical to that from other reductions using the same molar ratio of reagent to starting material. These include treatment with butyl-lithium of the title compound (I) followed by addition of water and hydrolysis of the Grignard reagent of (I) obtained by the entrainment technique.<sup>9</sup> The n.m.r. spectrum of the reaction products obtained by using a molar quantity of reducing agents contains 2 singlets at  $\tau$  2.27 and 2.35, in the ratio 5:3, the former corresponding to the octachloro-derivative (V). Evidence from mass spectral and i.r. measurements showed the presence of some starting material (30%) together with strong peaks in the mass spectrum corresponding to nonachloro- (m/e 465) and octachlorobiphenyls. The second product was therefore identified as the nonachlorobiphenyl (IV). With an excess of reagent (2 mol.), both n.m.r. and mass spectral evidence showed almost exclusive formation of the octachloro-compound (V). These reaction products could not be separated satisfactorily by conventional chromatographic methods.

7 M. Ballester, U.S. Airforce (Aerospace Research) project report, 1964, 17. <sup>8</sup> R. B. Carlin and W. O. Forshey, jun., J. Amer. Chem. Soc.,

Similarly, when a solution of BuLi (1 mol.) in hexane was allowed to react with decachlorobiphenyl in ether suspension at low temperature, hydrolysis gave a mixture of the nonachloro- (IV), and the octachloro- (V) derivatives, together with starting material in the ratio 1.3:1:1respectively, whereas with an excess of BuLi (2 mol.) octachlorobiphenyl (V) was produced almost exclusively. This tendency towards dilithiation is similar to that observed in another perhalogenobiphenyl, namely, 2,2'dibromo-octafluorobiphenyl.<sup>10</sup> It may be due to the solubility of the monolithio-derivatives of (I) being greater in the solvent than the starting material. The mixed mono- and di-lithio derivatives, on treatment with an excess of dimethyl sulphate gave the expected mixture of 4-mono- and 4,4'-di-methylpolychlorobiphenyl [(VI) and (VII)]. Again these derivatives could not be separated chromatographically. However, a pure sample of 4,4'-dimethyloctachlorobiphenyl (VII) was prepared by treating (I) with an excess of butyl-lithium (2 mol.) followed by reaction with dimethyl sulphate.

From the lithio-derivatives we were able to generate both the corresponding mono- and di-arynes by thermal elimination of lithium chloride, and trap these intermediates as the 1,2,4,5-tetramethylbenzene adducts in high yields (50-60%). For instance with an excess of butyl-lithium (2 mol.), the 4,4'-dilithio-derivative of (I) when heated with 1,2,4,5-tetramethylbenzene gave the bis-adduct (IX). Its n.m.r. spectrum showed two weak singlets centred at  $\tau 5.24 (J 3 \text{ Hz}, 4\text{H})$  and a strong broad singlet at  $\tau 8.12$  (8 Me). We attribute the nonequivalence of the bridge-head H atoms to the asymmetry of the molecule. Similar behaviour has been observed in the 1.2.4. 5-tetra-methylbenzene adducts of trichloropyrid-3,4yne.<sup>11</sup> With a molar proportion of butyl-lithium, under the same conditions we derived inseparable mixtures of mono- and bis-1,2,4,5-tetramethylbenzene adducts (3:5), distinct both in their mass spectral (*m/e* 560) and 621) and their n.m.r. behaviour  $\tau$  5.31 (2s, J 3 Hz) and 5.24 (2s, J 3 Hz).

An equivalent of piperidine in dimethylformamide gave 4-piperidinononachlorobiphenyl (X) when heated under reflux with the title compound (I). Almost quantitative conversion into the 4,4'-dipiperidinoderivative (XI) followed reaction with an excess of piperidine at high temperature and pressure. There was little tripiperidino-substitution (detectable in the mass spectrum). Oxidation of the mono- and the di-piperidino-derivatives with 30% H2O2 in a mixture of chloroform-trifluoroacetic acid readily produced the corresponding nitro-compounds.

Decachlorobiphenyl reacted under comparatively mild conditions with sodium methoxide in hot pyridine, in analogous fashion to hexachlorobenzene.<sup>12</sup> The monoand di-methoxy-derivatives (XIV) and (XV), though giving superposable n.m.r. singlets at  $\tau$  5.95, (OMe), and

<sup>1950, 72, 793.</sup> 

<sup>9</sup> H. Heaney and J. M. Jablonski, J. Chem. Soc. (C), 1968, 1895.

<sup>&</sup>lt;sup>10</sup> S. C. Cohen and A. G. Massey, J. Organometallic Chem., 1967, 10, 471.
 <sup>11</sup> J. D. Cook, B. J. Wakefield, H. Heaney, and J. M. Jablonski, J. Chem. Soc. (C) 1968, 2727.
 <sup>12</sup> A. L. Rocklin, J. Org. Chem., 1956, 21, 1478.

poorly resolved molecular ions  $(m/e \ 494.5 \text{ and } 490.0 \text{ respectively})$  gave distinct i.r. spectra.

## EXPERIMENTAL

Mass spectra were recorded on an A.E.I. MS 12 instrument and <sup>1</sup>H n.m.r. spectra were measured at 60 MHz with tetramethylsilane as internal standard.

Preparation of 2,2',3,3',5,5',6,6'-Octachlorobiphenyl (V). 2,3,5,6-Tetrachloroaniline (8 g.), prepared by reduction with iron-hydrochloric acid of 2,3,5,6-tetrachloronitrobenzene <sup>13</sup> in ethanol, was dissolved in acetic acid (200 ml.) with warming. The solution was vigorously stirred and diazotised at 10° with a solution of sodium nitrite (2·3 g.) in concentrated sulphuric acid (100 ml.). The diazo-solution was poured into a saturated solution of potassium iodide and the mixture was warmed gently on a water-bath for 30 min. 2,3,5,6-Tetrachloroiodobenzene (60%) was precipitated from the cool solution and was purified by column chromatography [silica gel G-light petroleum (b.p. 60-80°)], m.p. 96-97° (Found: C, 21·45; H, 0·5. C<sub>6</sub>HCl<sub>4</sub>I requires C, 21·05; H, 0·3%).

An intimate, finely ground mixture of 2,3,5,6-tetrachloroiodobenzene (1 g.) and activated copper bronze (0.185 g.) in a sealed glass tube was heated at 190° for 15 hr. N.m.r. examination of the reaction product obtained by extraction with hot chloroform showed a little starting material (5%;  $\tau$  2.33), 1,2,4,5-tetrachlorobenzene (15%;  $\tau$  2.41), and the major product (73%) giving rise to a singlet at  $\tau$  2.27. Fractional sublimation (90°/1 mm.) removed the more volatile component, 1,2,4,5-tetrachlorobenzene, and chromatography of the residue (silica gel G-hexane) gave 2,2',3,3',-5,5',6,6'-octachlorobiphenyl (65%), m.p. 159—160° (Found: C, 33.0; H, 0.9. C<sub>12</sub>H<sub>2</sub>Cl<sub>8</sub> requires C, 33.5; H, 0.55%).

Reactions of Decachlorobiphenyl.—(a) With lithium aluminium hydride. A mixture of decachlorobiphenyl (2 g., 0.004 mol.) and lithium aluminium hydride (0.15 g., 0.004 mol.) was stirred in dry tetrahydrofuran (200 ml.) at room temperature for 16 hr. Water was added to the reaction mixture followed by dilute hydrochloric acid; the organic layer was separated, dried, and evaporated. The spectral properties of the crude reaction product (see Discussion) indicated a mixture of starting material (ca. 30%), nonachlorobiphenyl (IV) (39%) and octachlorobiphenyl (V) (31%); chromatography on silica gel G with hexane as eluant failed to separate these polychlorobiphenyls.

The reduction was repeated with an excess of lithium aluminium hydride (2 mol.), when the major product isolated was octachlorobiphenyl (V) (70–80%) together with a little of the derivative (IV) (10%).

(b) Grignard formation. Decachlorobiphenyl (2 g.) and magnesium (0.15 g.) in tetrahydrofuran (75 ml.) were heated under reflux with dibromoethane (0.2 g.) and a crystal of iodine until reaction commenced. A further quantity of dibromoethane (0.6 g.) in tetrahydrofuran (10 ml.) was added dropwise and the reaction mixture was heated under reflux for 30 min. Addition of a saturated solution of ammonium chloride to the mixture, followed by separation of the organic layer which was then dried and evaporated gave a mixture of starting material (30%), nonachlorobiphenyl (IV) (39%), and the octachloro-derivative (V) (31%).

With a 2 mol. excess of dibromoethane under the same conditions, octachlorobiphenyl was obtained as the major <sup>13</sup> A. T. Peters, F. M. Rowe, and D. M. Stead, *J. Chem. Soc.*, 1943, 233.

product (V) (80%) together with small amounts (ca. 10%) of derivative (IV).

(c) With butyl-lithium. A solution of n-butyl-lithium (2 ml., 0.0052 mol.) in hexane was added to a vigorously stirred suspension of decachlorobiphenyl (2 6 g., 0.0052 mol.) in ether (sodium-dried, 100 ml.) under nitrogen, at  $-75^{\circ}$ . The mixture was stirred at  $-75^{\circ}$  for 10 min.; it was then allowed to warm up to room temperature and stirred for a further hour. The following reactions were performed. (i) Hydrolysis. The mixture was recooled to  $-75^{\circ}$  and water was added. The contents of the flask were allowed to warm to room temperature and were then extracted with ether. Drying (over MgSO<sub>4</sub>) of the extract and removal of the solvent gave a mixture of starting material (30%), octachlorobiphenyl (V) (31%), and nonachlorobiphenyl (IV) (39%).

With an excess of butyl-lithium (2 mol.) the same procedure gave mainly the octachloro-derivative (V) 70—80%) with a little nonachlorobiphenyl (IV, 10%).

(ii) Methylation. The solution, prepared as described above, was cooled to  $-15^{\circ}$  and excess of dimethyl sulphate (10 ml.) was added. The reaction mixture was allowed to warm to room temperature, and was then stirred for 1 hr. before addition of water. The ether layer was washed well with dilute ammonia solution, dried, and evaporated. The n.m.r. spectrum of the reaction product showed two strong signals at  $\tau$  (CDCl<sub>3</sub>) 7.32 and 7.4 in the ratio 5 : 3 respectively. I.r. evidence showed the presence of some starting material (ca. 30%). Mass spectral measurements provided evidence for methylnonachlorobiphenyl (VI) (m/e 478.5) and octachlorodimethylbiphenyl (VII) (m/e 458). Column chromatography failed to separate the reaction products.

With an excess of butyl-lithium (2 mol.) a similar procedure gave 4,4'-dimethyloctachlorobiphenyl (VII) in good yield (74%) purified by column chromatography (silica gel G, light petroleum, b.p. 60-80°),  $\tau$  (CDCl<sub>3</sub>) 7.32 (Found: C, 36.8; H, 1.6. C<sub>14</sub>H<sub>6</sub>Cl<sub>8</sub> requires C, 36.7; H, 1.3%).

(iii) Aryneformation and adducts with 1,2,4,5-tetramethylbenzene. The solution of mixed lithio-derivatives, obtained as described above was cooled to  $-30^{\circ}$  and on excess of 1,2,4,5-tetramethylbenzene in ether solution was added with stirring. The reaction mixture was allowed to warm up and after the ether had been distilled off was heated at  $120^{\circ}$  for 4-5 hr. The mixture was cooled and extraction of the solid material with hexane removed some of the residual 1,2,4,5-tetramethylbenzene. Ether extraction gave an impure mixture which was further purified by column chromatography (1% ether in hexane) followed by sublimation to remove traces of 1,2,4,5-tetramethylbenzene. N.m.r. and mass spectral measurements showed it to be a mixture of 1,2,4,5-tetramethylbenzene adducts (VIII) and (IX).

With an excess of butyl-lithium (2 mol.) and the same technique employed above, the yield of the bis-adduct (IX) was increased (50%) and it was found possible to separate a pure sample from the accompanying mono-1,2,4,5-tetra-methylbenzene adduct (VIII) (10%) by column chromatography (silica gel G with hexane as eluant) m.p. >250°,  $\tau$  5.24 (2s, J 3 Hz) (Found: C, 61.8; H, 3.4. C<sub>32</sub>H<sub>24</sub>Cl<sub>6</sub> requires C, 61.9; H, 3.9%).

(d) With piperidine. (i) In dimethylformamide. Decachlorobiphenyl (I) (5 g.) was heated under reflux in dimethylformamide with piperidine (2 mol.) for 48 hr. The cooled mixture was poured into water to precipitate a brown solid in almost quantitative yield. This was filtered off, washed

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well with water, and subjected to column chromatography [silica gel G-light petroleum (b.p.  $60-80^{\circ}$ )]. A pale yellow glassy material was obtained, which resisted further attempts at purification. Mass spectral measurements showed it consisted mainly of the monopiperidino-derivative (X) (*m/e* 548.5) contaminated with a little dipiperidino-compound (XI) (*m/e* 598).

Oxidation <sup>14</sup> of the reaction products (5 g.) was carried out by stirring them with hydrogen peroxide (30%, 60 ml.), in a mixture of trifluoroacetic acid (150 ml.) and chloroform (150 ml.) for 16 hr. at room temperature; the temperature was then raised to 60° for 3 hr. The solution was neutralised with 50% (w/v) aqueous potassium carbonate. The two layers were separated and the aqueous layer was extracted with chloroform. The combined chloroform layers were extracted with potassium carbonate solution, dried, and evaporated to give 4-*nitrononachlorobiphenyl* (XII) (purified by column chromatography) (ca. 40%), m.p. 215-217° (Found: C, 28·8; N, 2·8. C<sub>12</sub>Cl<sub>9</sub>NO requires C, 28·3; N, 2·8%).

(ii) By an autoclave reaction.<sup>14</sup> Decachlorobiphenyl (I) (100 g.) was heated and stirred in a 1 l. autoclave with an excess of piperidine (250 ml.) at 175° for 16 hr. The product was filtered and the excess of base was evaporated off from the filtrate. The combined solids were treated with sulphuric acid (100 ml.; d 1.84). Very little insoluble decachlorobiphenyl (<5%) was obtained and the acid <sup>14</sup> D. J. Berry, I. Collins, S. M. Roberts, H. Suschitzky, and

B. J. Wakefield, J. Chem. Soc. (C), 1969, 1289.

fraction was poured onto ice giving 4,4'-dipiperidino-octachlorobiphenyl (XI) which was purified by column chromatography (silica gel G-hexane), m.p. 106°, m/e 598 (Found: C, 44·7; H, 3·8. C<sub>22</sub>H<sub>22</sub>Cl<sub>8</sub>N<sub>2</sub> requires C, 44·2; H, 3·7%).

Oxidation of the dipiperidino-derivative (XI) by the above method gave 4,4'-dinitro-octachlorobiphenyl (XIII), m.p. 234-235°, m/e 520 (Found: C, 28.2; N, 5.4. C<sub>12</sub>Cl<sub>8</sub>N<sub>2</sub>O<sub>4</sub> requires C, 27.7; N, 5.4).

(e) With sodium methoxide. Sodium hydroxide (0.8 g.) dissolved in methanol (5 ml.) at 50° was added quickly, to a gently boiling and stirred mixture of the title compound (I) (1 equiv.) in pryidine.<sup>12</sup> After 1 min., the mixture was cooled to room temperature and filtered to remove sodium chloride. Evaporation of the pyridine left the crude product which was purified by column chromatography to give mainly 4-methoxynonachlorobiphenyl (XIV) (90%), m.p. 203°, m/e 494·5 (Found: C, 32·0; H, 1·0. C<sub>13</sub>H<sub>3</sub>Cl<sub>9</sub>O requires C, 31·6; H, 0·6%).

By the same procedure, decachlorobiphenyl gave 4,4'dimethoxyoctachlorobiphenyl (XV, 90%), m.p. 227—229°, on reaction with 2 mol. of sodium methoxide (Found: C, 33.8; H, 1.3.  $C_{14}H_6Cl_8O_2$  requires C, 34.3; H, 1.2%).

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