813. *Cyclopentadienes, Fulvenes, and Fulvalenes. Part II.*[1] 1,1′-*Dihydro-2,3,5,2′,3′,5′-hexa- and* 1,1′-*Dihydro-2,3,4,5,2′,3′,4′,5′-octaphenylfulvalenes.*

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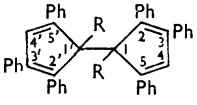
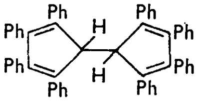
Methods described in the preceding paper that gave fulvalenes from 1,2,3-triphenylcyclopentadiene, yielded only dihydrofulvalenes or derivatives of these when applied to 1,2,4-tri- and 1,2,3,4-tetra-phenylcyclopentadiene. Attempts to convert these into fulvalenes failed. This is attibuted to steric factors.

The ready formation[1] of 2,3,4,2′,3′,4′-hexaphenylfulvalene prompted attempts to use the same methods with 1,2,4-triphenyl- and 1,2,3,4-tetraphenyl-cyclopentadiene. However, both these compounds were readily converted into the corresponding 1,1′-dihydrofulvalenes [bi(cyclopenta-2,4-dienyls)] (I and II), and attempts to convert these into substituted fulvalenes failed. The most striking difference between these two compounds and that of the preceding paper[1] is the steric crowding about the 1,1′-bond in the former pair. Coplanarity of the 2,5,2′,5′-substituents is impossible and accounts, we believe, for our inability to introduce a 1,1′-double bond.

In contrast to its isomer[1] which affords the corresponding fulvalene in each case, 1,2,4-triphenylcyclopentadiene is converted into the 1,1′-dihydrofulvalene (I; $R = H$; isomer " A ") when its lithio-derivative is treated with iodine or oxygen, or when ts 5-bromo-derivative is debrominated with zinc in boiling benzene. Its dibromo-derivative[2] yields a dibromodihydrofulvalene. If the starting material is 5,5-dibromo-1,2,4-triphenylcyclopentadiene as expected, then this must be the 1,1′-dibromo-1,1′-dihydro-compound (I; $R = Br$; isomer A), and the lack of reactivity of its bromine atoms despite their allylic position must be due to steric hindrance. Alternative positions for the bromine atoms in both compounds cannot, however, be ruled out with certainty on the available evidence. 1,2,3,4-Tetraphenylcyclopentadiene behaved very similarly, yielding the corresponding dihydrofulvalene (II) when its 5-halogeno-derivatives were dehalogenated with zinc in benzene, but its 5,5-dibromo-derivative did not give a readily isolable product.



(I)



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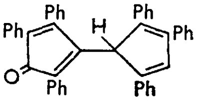

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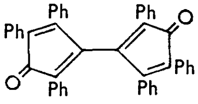

(IV)

When 1,2,3,4-tetraphenylcyclopentadienyl-lithium was treated with iodine, only 5-iodo-1,2,3,4-tetraphenylcyclopentadiene[3] was isolated and analogous iodo-derivatives may be intermediate in the corresponding reactions in both the 1,2,3- and the 1,2,4-triphenyl series. A more notable difference from these less highly substituted compounds was observed when the same lithio-derivative was treated with oxygen. Tetracyclone was the only product isolated, rather than a fulvalene or dihydrofulvalene. The same behaviour was encountered with the dihydrohexaphenylfulvalene (I; $R = H$) which is likewise a tetrasubstituted cyclopentadiene derivative. Its monolithio-derivative (obtained by use of phenyl-lithium) was oxygenated in one ring to afford the cyclopentadienone derivative (III, or a tautomer thereof), and its dilithio-derivative (obtained by use of n-butyl-lithium) gave the symmetrical bi-compound (IV). This behaviour contrasts with the reaction of

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[1] Part I, preceding paper.
[2] Newman, *Annalen*, 1898, **302**, 237.
[3] Kainer, *Annalen*, 1952, **578**, 232.

oxygen with the dilithio-derivative of unsubstituted dihydrofulvalene, which resulted in the first synthesis of fulvalene.[4]

Bromination of the dihydrohexaphenylfulvalene (IA; R = H) afforded a dibromo-compound (isomer B) which differed from the isomer (A) described above. Since carbon-1 and -1′ in compound (I) are asymmetric and equivalent, a *meso*- and a racemic form are expected. It is not known with certainty whether the compounds isolated are the two stereoisomers or whether one is a position isomer (*e.g.*, the 1,4′-dibromo-1,4′-dihydro-compound derivable by allylic rearrangement). The dibromo-compound (isomer B) was subjected to three debromination procedures. Copper in benzene gave intractable products. Sodium iodide in acetone did not result in the desired debromination, but led instead to reductive debromination giving a dihydrohexaphenylfulvalene isomeric (isomer B) with the product (isomer A) mentioned above; again these may be either steroisomers or position isomers. Zinc dust in ethanol likewise led to reductive debromination but afforded isomer A. Reduction was expected in the latter case, having been observed with 5,5-dibromo-1,2,3-triphenylcyclopentadiene.[1] The same behaviour of the halogenated 1,2,4-tri- and 1,2,3,4-tetra-phenylcyclopentadienes has also been demonstrated.

Finally 5-diazo-1,2,4-triphenylcyclopentadiene has been prepared, but unlike its isomer,[1] failed to give the desired fulvalene or other tractable products on thermal decomposition.

EXPERIMENTAL

For general remarks see Part I.

5-*Bromo*-1,2,4-*triphenylcyclopentadiene*.—A mixture of 1,2,4-triphenylcyclopentadiene (1·51 g., 0·005 mole) and *N*-bromosuccinimide (1·09 g., 0·006 mole) in carbon tetrachloride (50 ml.) was refluxed for 2 hr. After cooling, the precipitated succinimide was filtered off, and the red filtrate was evaporated. The residue crystallised from cyclohexane, to give 5-*bromo*-1,2,4-*triphenylcyclopentadiene* as bright red cubes (1·3 g.), m. p. 133—134°. Recrystallisation raised the m. p. to 140—141° (Found: C, 73·9; H, 5·0; Br, 21·5. $C_{23}H_{17}Br$ requires C, 74·0; H, 4·6; Br, 21·4%).

The 5,5-dibromo-derivative obtained from the hydrocarbon with bromine [2] had m. p. 159—160° (lit.,[2] 157°) and was recovered unchanged after 2 hours' refluxing with *N*-bromosuccinimide in carbon tetrachloride.

1,1′-*Dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene* [2,3,5,2′,3′,5′-*Hexaphenylbi*(*cyclopenta*-2,4-*dienyl*)] (I; R = H; *isomer A*).—(a) *By reaction between* 1,2,4-*triphenylcyclopentadienyl-lithium and iodine*. 1,2,4-Triphenylcyclopentadiene (5·29 g., 0·018 mole) in benzene (100 ml.) was added dropwise to a stirred solution of phenyl-lithium prepared from lithium (0·29 g., 0·042 g.-atom) and bromobenzene (3·1 g., 0·02 mole) in ether, and the mixture refluxed with stirring for 2 hr. After cooling, iodine (4·6 g., 0·018 mole) in ether was added dropwise and the mixture stirred overnight. Water was then added and the organic layer separated, washed with sodium thiosulphate solution, and dried (Na_2SO_4). Removal of the solvent gave a red gum (7·3 g.). This was dissolved in benzene and chromatographed, giving a single orange band. On elution with benzene and evaporation of the solvent a red gum (6·7 g.) was obtained. Acetone was added and the mixture was boiled for several minutes. Filtration of the cooled suspension yielded 1,1′-*dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene* [2,3,5,2′,3′,5′-*hexaphenylbi*(*cyclopenta*-2,4-*dienyl*)], *isomer A* (1·2 g.). Recrystallisation from benzene gave pale yellow plates, m. p. 281—283° (Found: C, 94·0; H, 5·9. $C_{46}H_{34}$ requires C, 94·1; H, 5·8%), $\lambda_{max.}$ 250 and 356 mμ (log ε 4·56 and 4·45), very sparingly soluble in most organic solvents in the cold, but dissolving in hot benzene or chloroform.

(b) *By reaction between* 1,2,4-*triphenylcyclopentadienyl-lithium and oxygen*. 1,2,4-Triphenylcyclopentadiene (4·70 g., 0·016 mole) in dry benzene (150 ml.) was added to a solution of phenyl-lithium [from lithium (0·29 g., 0·042 g.-atom) and bromobenzene (3·14 g., 0·02 mole)] in ether, and the mixture was refluxed for 2 hr. After cooling, oxygen was passed into the solution for 2½ hr. The brown mixture was poured into water, and the organic layer was separated and

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[4] Doering, in "Theoretical Organic Chemistry," Butterworth, London, 1958.

dried (Na_2SO_4). Evaporation of the solvent left a dark gum (4·9 g.). The infrared spectrum of a solution of this crude product showed a maximum in the carbonyl stretching region at 1739 cm.$^{-1}$. The gum was chromatographed in benzene. The main yellow band was eluted with benzene and recovered as a brown solid (3·0 g.). Acetone was added and filtration gave the dihydrohexaphenylfulvalene as a pale yellow solid (1·7 g.), m. p. 281—283° (from benzene). Other fractions eluted from the column yielded intractable gums.

(c) *From* 5-*bromo*-1,2,4-*triphenylcyclopentadiene.* This bromo-compound (1·0 g., 0·0027 mole) and zinc dust (4·8 g., 0·074 g.-atom) were refluxed in benzene (75 ml.) overnight. The mixture was filtered and the residue washed with chloroform. The filtrate was washed with water, dried (Na_2SO_4), and evaporated, yielding a solid (0·94 g.). This was triturated with acetone and the undissolved portion (0·2 g.) filtered off. Recrystallisation from benzene gave the pure dihydrohexaphenylfulvalene as pale yellow plates, m. p. and mixed m. p. 281—283°.

The infared spectra of the products prepared by the above three methods were indistinguishable.

1,1′-*Dihydro*-2,3,4,5,2′,3′,4′,5′-*Octaphenylfulvalene* [2,3,4,5,2′,3′,4′,5′-*Octaphenylbi*(*cyclopenta*-2,-4-*dienyl*)] (II).—5-Bromo-1,2,3,4-tetraphenylcyclopentadiene [3] (4·50 g., 0·01 mole) and zinc dust (16·3 g., 0·25 g.-atom) in benzene (200 ml.) were refluxed overnight. The mixture was filtered and the residue washed with hot benzene. The combined benzene solutions were washed with water, dried (Na_2SO_4), and evaporated, giving a pale yellow solid (4·0 g.). Recrystallisation from ethanol yielded the *dihydro-octaphenylfulvalene* as pale yellow plates m. p. 180—182° (depressed on admixture with tetraphenylcyclopentadiene) (Found: C, 94·1; H, 5·9. $C_{58}H_{42}$ requires C, 94·3; H, 5·7%), $\lambda_{max.}$ 250 and 350 mμ (log ε 4·54 and 4·33).

1,1′-*Dibromo*-1,1′-*dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene* (I; R = Br).—(i) *Isomer A.* A mixture of zinc dust (16·2 g., 0·25 g.-atom) and 5,5-dibromo-1,2,4-triphenylcyclopentadiene (2·26 g., 0·005 mole) in benzene (100 ml.) was refluxed overnight, then filtered, and the residue was washed with hot benzene. The benzene extracts were combined, washed with water, and dried (Na_2SO_4); evaporation yielded a pale yellow solid (1·9 g.). Digesting this with acetone left an insoluble colourless solid (0·23 g.) that, recrystallised from cyclohexane, afforded the *dibromodihydrohexaphenylfulvalene* as colourless needles, m. p. 174·5—175·5° (Found: C, 74·9; H, 5·0; Br, 21·2. $C_{46}H_{52}Br_2$ requires C, 74·2; H, 4·3; Br, 21·5%), $\lambda_{max.}$ 248, 260, and 334 mμ (log ε, 4·61, 4·61, and 4·38).

(ii) *Isomer B. N*-Bromosuccinimide (0·85 g., 0·0048 mole) and 1,1′-dihydro-2,3,5,2′,3′,5′-hexaphenylfulvalene (1·2 g., 0·002 mole) were refluxed in carbon tetrachloride (100 ml.) for 2 hr. After cooling, succinimide was filtered off. When the filtrate was evaporated to a small volume 1,1′(?)-*dibromo*-1,1′(?)-*dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene, isomer* B, crystallised in orange plates (0·54 g.), m. p. 148—151°. Recrystallisation from cyclohexane or acetone raised the m. p. to 149·5—151·5° (Found: C, 74·5; H, 4·2; Br, 21·7. $C_{46}H_{32}Br_2$ requires C, 74·2; H, 4·3; Br, 21·5%). The same product resulted (in lower yield) on attempted monobromination with the same reagent or with bromine in carbon disulphide, the calculated amount being used in each case.

Debromination of 1,1′-*Dibromo*-1,1′-*dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene* (I; R = Br) (*isomer B*).—(a) *With copper.* To the dibromo-compound (1·27 g., 0·0017 mole), in benzene (100 ml.), copper powder (10·9 g., 0·17 g.-atom) was added, and the mixture was refluxed overnight. The copper powder was filtered off and washed with hot benzene. The benzene solution was orange-yellow with a strong green fluorescence. Evaporation gave an orange solid (1·07 g.). This was chromatographed in light petroleum–benzene (1 : 3). Two orange bands were developed. Evaporation of the solutions obtained on elution yielded intractable orange gums (0·53 and 0·28 g.).

(b) *With sodium iodide.* Sodium iodide (1·17 g., 0·0078 mole) in acetone (50 ml.) was added to the dibromo-compound (2·24 g., 0·003 mole) in acetone (250 ml.). The solution darkened immediately and a white precipitate was formed. The mixture was refluxed for 5 hr. On evaporation to a small volume pale yellow 1,1′(?)-*dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene, isomer B* (0·6 g.), crystallised, having m. p. 262—264°. Several recrystallisations from cyclohexane raised the m. p. to 279—280° (depressed on admixture with isomer A) (Found: C, 94·1; H, 5·9%; *M*, 576. $C_{46}H_{34}$ requires C, 94·2; H, 5·8%; *M*, 586), $\lambda_{max.}$ 248 and 320 mμ (log ε 4·69 and 4·56). The acetone filtrate afforded a brown solid (1·0 g.), resolved into several non-crystalline fractions on chromatography.

Zinc–Ethanol Debrominations.—Solutions of each of the compounds (0·002 moles) were refluxed overnight in ethanol (*ca.* 100 ml.) with an excess (0·01—0·2 g.-atom) of zinc dust. The products were worked up by pouring the mixtures into water, extracting them with chloroform, and evaporating the washed and dried (Na_2SO_4) extracts. 5-Bromo- and 5,5-dibromo-1,2,4-triphenylcyclopentadiene, 5-bromo-1,2,3,4-tetraphenylcyclopentadiene and 1,1′-dibromo-1,1′-dihydro-2,3,5,2′,3′,5′-hexaphenylfulvalene (isomer B) yielded 1,2,4-triphenylcyclopentadiene (m. p. 149°; from ethanol), 1,2,3,4-tetraphenylcyclopentadiene (m. p. 178°, from ethanol), and 1,1′-dihydro-2,3,5,2′,3′,5′-hexaphenylfulvalene (isomer A, m. p. 274—276°), respectively. Yields were excellent and the products were identified by mixed m. p.s or comparison of infrared spectra.

Reaction between Tetraphenylcyclopentadiene, Phenyl-lithium, and Iodine.—1,2,3,4-Tetraphenylcyclopentadiene (2·78 g., 0·0075 mole) in benzene (50 ml.) was added dropwise to a stirred solution of phenyl-lithium [from lithium (0·12 g., 0·017 g.-atom) and bromobenzene (1·3 g., 0·0084 mole)] in ether. The mixture was refluxed for 2 hr., then cooled in ice. Iodine (0·95 g., 0·0075 g.-atom) in ether (50 ml.) was added dropwise, and the mixture was stirred overnight. The red mixture was poured into water, and the benzene layer was separated and washed with sodium thiosulphate solution. After drying (Na_2SO_4), evaporation of the solvent gave a yellow solid (3·1 g.), m. p. 147—150° (decomp.). Recrystallisation from acetone yielded 5-iodo-1,2,3,4-tetraphenylcyclopentadiene as yellow needles, m. p. 163—165° (decomp.) (Found: C, 69·7; H, 4·5; I, 25·9. Calc. for $C_{29}H_{21}I$: C, 70·1; H, 4·3; I, 25·6%).

Reaction between 1,1′-*Dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene, Phenyl-lithium, and Oxygen.*—A solution of the hydrocarbon, isomer A (5·46 g., 0·0093 mole), in benzene (200 ml.) was added dropwise to a solution of phenyl-lithium [from lithium (0·30 g., 0·043 g.-atom) and bromobenzene (3·2 g., 0·02 mole)] in ether and the mixture was refluxed for 3 hr. After cooling, dry oxygen was passed into the mixture which rapidly became dark red. Water was then added and the organic layer separated, dried (Na_2SO_4), and evaporated. The residue, a dark solid, was dissolved in benzene and chromatographed. Two bands were obtained, and were eluted with benzene: (*a*) A pale yellow band which yielded starting material. (*b*) A purple band which gave a dark red solid (0·3 g.). Recrystallisation from methanol gave dark red cubes, m. p. 193—195°, believed to be 2,3,5-*triphenyl*-4-(2,3,5-*triphenylcyclopenta*-2,4-*dienyl*)*cyclopentadienone* (III) (Found: C, 91·6; H, 5·8. $C_{46}H_{32}O$ requires C, 91·9; H, 5·4%), $\nu_{max.}$ 1715 cm.$^{-1}$ (C=O), $\lambda_{max.}$ 258 and 342 mμ (log ε 4·59 and 4·34). A solution of the compound in ether was instantly decolorised on addition of lithium aluminium hydride or phenyl-lithium solution.

Reaction between 1,1′-*Dihydro*-2,3,5,2′,3′,5′-*hexaphenylfulvalene, Butyl-lithium and Oxygen.*—The hydrocarbon, isomer A (5·27 g., 0·009 mole), in benzene–tetrahydrofuran (100 ml.; 1 : 3) was added dropwise to a solution of butyl-lithium (0·018 mole) in ether, and the mixture was refluxed for 4 hr. After cooling, dry oxygen was passed into the mixture for 1 hr. The dark red mixture was poured into water, and the organic layer was separated and dried (Na_2SO_4). Evaporation gave a dark solid (6·6 g.). This was chromatographed in benzene. Two bands were eluted with benzene: (*a*) An orange-brown band which yielded a brown solid (1·2 g.). Recrystallisation from benzene gave unchanged material. (*b*) A dark red band which gave a deep red solid (0·7 g.) that, recrystallised from ethanol and then from cyclohexane, gave dark red plates (almost black), m. p. 235·5—237°, believed to be 3,3′-*dioxo*-2,4,5,2′,4′,5′-*hexaphenylbi*(*cyclopentadienyl*) (IV) (Found: C, 90·1; H, 5·4. $C_{46}H_{30}O_2$ requires C, 89·9; H, 4·9%), $\nu_{max.}$ 1715 cm.$^{-1}$ (C=O), $\lambda_{max.}$ 262, 376, and 554 mμ (log ε 4·62, 4·14, and 2·31). An ethereal solution of this compound was rapidly decolorised on the addition of phenyl-lithium or lithium aluminium hydride solution.

Reaction between Tetraphenylcyclopentadiene, Phenyl-lithium, and Oxygen.—To phenyl-lithium (0·0075 mole) in ether 1,2,3,4-tetraphenylcyclopentadiene (2·77 g., 0·0075 mole) in benzene (100 ml.) was added dropwise, and the mixture was refluxed for 2 hr. Dry oxygen was passed into the cooled solution which soon became dark red. After a further 7 hr. the mixture was poured into water. The organic layer was separated, dried (Na_2SO_4), and evaporated, to yield a dark red solid (2·9 g.). This was chromatographed in benzene. Two bands were eluted with benzene: (*a*) A pale yellow band yielded unchanged tetraphenylcyclopentadiene. (*b*) A purple band gave dark red crystals (1·5 g.). Recrystallisation from benzene–ethanol gave tetracyclone as dark red clusters, m. p. and mixed m. p. 219—220°.

5-*Diazo*-1,2,4-*triphenylcyclopentadiene.*—To phenyl-lithium in ether [from lithium (0·29 g., 0·042 g.-atom) and bromobenzene (3·14 g., 0·02 mole)], 1,2,4-triphenylcyclopentadiene (5·29 g., 0·018 mole) in benzene (100 ml.) was added, and the whole refluxed for 2 hr. After cooling, the mixture was added dropwise in 1 hr. to a stirred solution of toluene-*p*-sulphonyl azide (3·55 g., 0·018 mole) in ether (15 ml.). A yellow precipitate was formed and the solution became deep red. The mixture was stirred for a further $\frac{1}{4}$ hr. The pale yellow precipitate was filtered off and washed with ether. The dark red organic solution was washed with water and dried (Na_2SO_4). Evaporation gave a dark red solid (5·65 g.). Recrystallisation from methanol yielded 5-*diazo*-1,2,4-*triphenylcyclopentadiene* as brick red prisms, m. p. 131—133° (decomp.), $\nu_{max.}$ 2088 cm.$^{-1}$ (diazo) (Found: C, 86·4; H, 5·4; N, 8·6. $C_{23}H_{16}N_2$ requires C, 86·2; H, 5·0; N, 8·7%). This compound (0·1 g.) decomposed with frothing at 140°/0·1 mm. in 2 min., as indicated by disappearance of the 2088 cm.$^{-1}$ band, but no crystalline product was isolated.

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