812. *Cyclopentadienes, Fulvenes, and Fulvalenes. Part I. A Hexaphenylfulvalene.*

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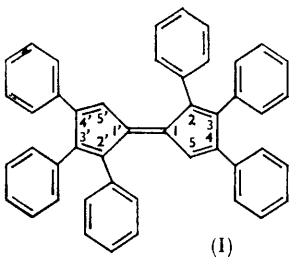
2,3,4,2′,3′,4′-Hexaphenylfulvalene, regarded as the *trans*-isomer, has been obtained from 1,2,3-triphenylcyclopentadiene by way of its diazo-, 5,5-dibromo-, or lithium derivative. The preparation of the starting material has been improved.

Interest in fulvalene derivatives was stimulated by Brown's theoretical work [1] on this system. After our own unsuccessful attempt,[2] preparations of fulvalene have been

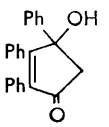
[1] Brown, *Trans. Faraday Soc.*, 1950, **46**, 146; *Nature*, 1950, **165**, 566.
[2] Kealy and Pauson, *Nature*, 1951, **168**, 1039.

reported by Doering,[3] by De More, Pritchard, and Davidson,[4] and more doubtfully by Kosower and Ramsay.[5] In each case only dilute solutions have been obtained and evidence has been provided [3,4] that the compound is not sufficiently stable to permit isolation under ordinary conditions. It therefore remains of interest to prepare more complex fulvalenes, in order to establish the degree of substitution necessary to produce stability, and for study of the chemical properties of the simplest stable derivatives.

Of the few known derivatives the simplest are fluorenylidenecyclopentadiene [6] and 2,3,4,5-tetraphenylfulvalene.[7] Others [8,9] are so heavily substituted that they cannot be even approximately planar about the central double bond. In the present paper we describe the ready formation from 1,2,3-triphenylcyclopentadiene of a hexaphenylfulvalene. In view of its ease of formation, particularly in contrast with the experiments with 1,2,4-triphenylcyclopentadiene described in the following paper, we regard this product as the relatively unhindered (and hence presumably near-planar) *trans*-isomer (I) of 2,3,4,2′,3′,4′-hexaphenylfulvalene.



(I)



(II)

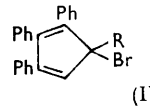
The previous synthesis [10] of 1,2,3-triphenylcyclopentadiene was improved by condensing the methiodide of β-dimethylaminopropiophenone rather than β-chloropropiophenone with deoxybenzoin. This afforded the intermediate 1,2,5-triphenylpentane-1,5-dione in 76% yield. However, pinacol reduction of this diketone failed to give consistent yields of crystalline 1,2,3-triphenylcyclopentane-1,2-diol greater than 50%. An alternative method was developed in which 4-hydroxy-2,3,4-triphenylcyclopent-2-enone (II), obtained by an improved procedure from benzil and phenylacetone, was reduced first with hydriodic acid [11] to 2,3,4-triphenylcyclopent-2-enone, and then with borohydride to the corresponding alcohol. The latter, presumably a mixture of both epimers, was smoothly dehydrated by alcoholic hydrogen chloride.

Conversion of 1,2,3-triphenylcyclopentadiene into the fulvalene (I) was first observed during an unsuccessful attempt [10] to prepare 1,2,3,1′,2′,3′-hexaphenylferrocene. In this experiment methyl-lithium, prepared in ether from methyl iodide, was allowed to react with the cyclopentadiene, and anhydrous ferric chloride was then added. The ferric chloride reacts in ether with the lithium iodide present, to liberate iodine, and we find that the latter itself converts the cyclopentadienyl-lithium into the product (I). Oxygen effected the same conversion. The direct formation of this compound from both these reactions is striking. It contrasts with the isolation at the corresponding stage in the unsubstituted series [3] of dihydrofulvalene, which had then to be converted into a lithium derivative and oxidised again to introduce the central double bond.

[3] Doering, in " Theoretical Organic Chemistry," Butterworths, London, 1958.
[4] De More, Pritchard, and Davidson, *J. Amer. Chem. Soc.*, 1959, **81**, 5874.
[5] Kosower and Ramsay, *J. Amer. Chem. Soc.*, 1959, **81**, 856.
[6] Courtot, *Ann. Chim. Phys.*, 1915, **4**, 218.
[7] Schreiber and Becker, *J. Amer. Chem. Soc.*, 1954, **76**, 3354, 6125.
[8] Bergman in Cook, ed., " Progress in Organic Chemistry," Vol. III, Butterworths, London, 1955.
[9] McBee, Roberts, and Idol, *J. Amer. Chem. Soc.*, 1955, **77**, 4942.
[10] Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.
[11] Koelsch and Geissman, *J. Org. Chem.*, 1938, **3**, 480.

An alternative route consisted of converting triphenylcyclopentadiene into its azo-derivative [12] (III). But whereas De More *et al.*[4] converted diazocyclopentadiene into fulvalene by low-temperature irradiation, its triphenyl derivative (III) readily decomposed to the correspondingly substituted fulvalene (I) in boiling alcohol.

(III)



(IV)

1,2,3-Triphenylcyclopentadiene with one mol. of bromine in carbon disulphide afforded the 5-bromo-derivative (IV; R = H). Use of *N*-bromosuccinimide or of two mol. of bromine afforded the 5,5-dibromo-compound (IV; R = Br). The latter is also formed by disproportionation when the former (IV; R = H) is refluxed in benzene. This presumably accounts both for the fact that only the dibromo-derivative was isolated when one mol. of *N*-bromosuccinimide (in boiling carbon tetrachloride) was employed, and for the formation of some fulvalene (I) by the action of zinc dust in boiling benzene on the monobromide (IV; R = H). But whereas similar treatment with copper converted the dibromotriphenylcyclopentadiene (IV; R = Br) exclusively into the hexaphenylfulvalene (I), the monobromo-compound (IV; R = H) affords a mixture of this compound and the expected 9,10-dihydro-derivative. The latter resembles 1,2,3-triphenylcyclopentadiene in its ultraviolet and infrared spectra. The use of zinc dust in ethanol, in place of benzene, leads to reductive debromination of the dibromo-compound to the parent cyclopentadiene. 1,2,3-Triphenylcyclopentadiene with an excess of bromine affords the 4,5,5-tribromo-derivative.

Experimental

Nitrogen was used as an inert atmosphere in all experiments involving the use of lithium alkyls and aryls. Spence's grade H and May and Baker's activated alumina were used for chromatography. Infrared spectra were measured for potassium chloride discs unless otherwise stated. Ultraviolet spectra were measured for chloroform solutions unless otherwise stated. M. p.s were determined in sealed evacuated tubes.

β-*Dimethylaminopropiophenone Methiodide.*—Methyl iodide (16·9 g., 0·12 mole) in ether (50 ml.), added to β-dimethylaminopropiophenone (20·5 g., 0·12 mole) in cold 3 : 1 ether–benzene (200 ml.), precipitated the *methiodide* (27·8 g.), flakes (from methanol), m. p. 261—264° (decomp.) (Found: C, 45·0; H, 5·5; N, 4·5. $C_{12}H_{18}INO$ requires C, 45·1; H, 5·7; N, 4·4%).

1,2,5-*Triphenylpentane*-1,5-*dione.*—Sodium hydroxide (15·0 g., 0·37 mole) in methanol (150 ml.) was added to deoxybenzoin (58·8 g., 0·3 mole) and β-dimethylaminopropiophenone methiodide (95·7 g., 0·3 mole) in methanol (750 ml.), and the mixture refluxed for 36 hr., then, while still warm, acidified with acetic acid, filtered, and left overnight. The buff-coloured crystals of 1,2,5-triphenylpentane-1,5-dione were filtered off and washed with cold methanol (yield 75·0 g., 76%; m. p. 95°).

4-*Hydroxy*-2,3,4-*triphenylcyclopent*-2-*enone.*—Benzil (21·0 g., 0·1 mole) and phenylacetone (26·8 g., 0·2 mole) in absolute alcoholic 0·5% potassium hydroxide (250 ml.) were kept at room temperature for a week. The crystalline precipitate (14·5 g., 44·5%), when filtered off and washed with cold ethanol, had m. p. 166—167° (lit.,[11] 164—165°).

2,3,4-*Triphenylcyclopent*-2-*en*-1-*ol.*—Sodium borohydride (9·0 g.) in water (100 ml.) was added to 2,3,4-triphenylcyclopent-2-en-1-one (8·9 g.) in dioxan (300 ml.) and the mixture left for 3 days at room temperature. The yellow solution became colourless. It was concentrated under reduced pressure, poured into water, and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to give 2,3,4-triphenylcyclopent-2-en-1-ol as a colourless oil (9·0 g.), almost certainly a mixture of epimers, $\nu_{max.}$ 3571 and 3448 (OH) $cm.^{-1}$.

1,2,3-*Triphenylcyclopentadiene.*—Concentrated hydrochloric acid (22·5 ml.) was added to

[12] Doering and De Puy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.

2,3,4-triphenylcyclopent-2-en-1-ol (9·0 g.) in ethanol (225 ml.). Crystals appeared and the mixture was refluxed for 1 hr. After cooling, 1,2,3-triphenylcyclopentadiene was filtered off as colourless needles (6·2 g.), m. p. and mixed m. p. with an authentic sample [10] 165—165·5°.

5-Diazo-1,2,3-triphenylcyclopentadiene.—1,2,3-Triphenylcyclopentadiene (1·18 g., 0·004 mole) in benzene (50 ml.) was added dropwise to phenyl-lithium (0·004 mole) in ether, and the mixture was refluxed for 2 hr., allowed to cool, added during 1 hr. to a stirred solution of toluene-*p*-sulphonyl azide (0·87 g., 0·004 mole) in ether (5 ml.), and stirred overnight. The yellow precipitate was filtered off and washed with ether. The organic solution was washed with water, dried (Na_2SO_4), and evaporated, giving a red-brown solid (1·4 g.). This was chromatographed in benzene. The main yellow band was eluted with benzene and yielded an orange solid (0·6 g.). This recrystallised from cyclohexane as orange-red plates of *5-diazo-1,2,3-triphenylcyclopentadiene*, m. p. 165—167° (decomp.) (Found: C, 86·5; H, 5·3; N, 8·8. $C_{23}H_{16}N_2$ requires C, 86·2; H, 5·0; N, 8·7%), $\nu_{max.}$ 2083 cm.$^{-1}$ (diazo). This compound decomposes partially on recrystallisation from organic solvents.

5-Bromo-1,2,3-triphenylcyclopentadiene.—To 1,2,3-triphenylcyclopentadiene (7·0 g., 0·024 mole) in carbon disulphide (276 ml.), bromine (3·80 g., 0·024 mole) in carbon disulphide (276 ml.) was added in 1 hr. Next morning the solvent was evaporated, to yield a yellowish-brown solid. Recrystallisation from light petroleum (b. p. 60—80°) afforded yellow-brown plates of *5-bromo-1,2,3-triphenylcyclopentadiene* (5·3 g.), m. p. 147° (decomp.) (Found: C, 74·5; H, 4·6; Br, 21·3. $C_{23}H_{17}Br$ requires C, 74·0; H, 4·6; Br, 21·4%).

5,5-Dibromo-1,2,3-triphenylcyclopentadiene.—(*a*) 1,2,3-Triphenylcyclopentadiene (0·75 g., 0·0025 mole) and *N*-bromosuccinimide (0·55 g., 0·003 mole) in carbon tetrachloride (25 ml.) were heated under reflux for 2 hr. The precipitated succinimide was filtered from the cooled solution, and the solvent was evaporated to yield a brown solid. Recrystallisation from cyclohexane afforded pale yellow needles of *5,5-dibromo-1,2,3-triphenylcyclopentadiene* (0·41 g.), m. p. 198° (Found: C, 61·4; H, 3·9; Br, 35·6. $C_{23}H_{16}Br_2$ requires C, 61·1; H, 3·6; Br, 35·4%).

(*b*) 1,2,3-Triphenylcyclopentadiene (0·01 mole) and bromine (0·02 mole) in carbon disulphide (240 ml.) gave, in 3 hr., the dibromo-derivative (3·6 g.), m. p. and mixed m. p. 198°.

(*c*) 5-Bromo-1,2,3-triphenylcyclopentadiene (1·2 g.) in benzene (40 ml.) was refluxed overnight. The solvent was evaporated to give a dark brown solid. Recrystallisation from acetone afforded yellow needles of the 5,5-dibromo-derivative (0·5 g.), m. p. and mixed m. p. 198°.

Reaction of 5,5-Dibromo-1,2,3-triphenylcyclopentadiene with Zinc and Ethanol.—A mixture of zinc dust (7·0 g., 0·11 g.-atom) and 5,5-dibromo-1,2,3-triphenylcyclopentadiene (0·5 g., 0·0011 mole) in ethanol (50 ml.) was refluxed for 4 hr. The solution was filtered from zinc which was washed with boiling ethanol. The combined ethanolic solutions were evaporated to a small volume. 1,2,3-Triphenylcyclopentadiene (0·09 g.) crystallised and had m. p. 164—165° (mixed m. p. 165—166°).

4,5,5-Tribromo-1,2,3-triphenylcyclopentadiene.—Bromine (2·6 g., 0·0165 mole) in carbon disulphide (70 ml.) was added in portions to 1,2,3-triphenylcyclopentadiene (1·61 g., 0·0055 mole) in carbon disulphide (70 ml.). The solution was left for 2 hr., then evaporated to yield a brown solid. After this had been dried over soda-lime *in vacuo*, ethanol was added and the yellow solid (1·98 g.) was filtered off. Recrystallisation from cyclohexane gave *4,5,5-tribromo-1,2,3-triphenylcyclopentadiene* as yellow needles, m. p. 184—186° (Found: C, 52·3; H, 3·0; Br, 45·3. $C_{23}H_{15}Br_3$ requires C, 52·0; H, 2·9; Br, 45·2%).

2,3,4,2′,3′,4′-Hexaphenylfulvalene (I).—(*a*) 1,2,3-Triphenylcyclopentadiene (1·47 g., 0·005 mole) in benzene (30 ml.) was added to butyl-lithium (0·005 mole) in ether, and the mixture was refluxed for 2 hr. After cooling, iodine (1·27 g., 0·005 mole) in ether was added dropwise and the mixture stirred overnight. Water was added and the organic layer was separated, washed with sodium thiosulphate solution, and dried (Na_2SO_4). Evaporation yielded a dark coloured solid (1·43 g.). This was chromatographed in benzene. The main yellow-green band was eluted with benzene and recovered, yielding *2,3,4,2′,3′,4′-hexaphenylfulvalene* as a dark yellow-green solid. Recrystallisation from benzene or acetone gave dark khaki needles, m. p. 279—282° (Found: C, 94·2; H, 5·7. $C_{46}H_{32}$ requires C, 94·5; H, 5·5%), $\lambda_{max.}$ 264 and 412 mμ (log ε 4·48 and 4·51). The compound dissolves in benzene to a red solution with a strong green fluorescence. It gives a characteristic, intense blue colour with sulphuric acid; ultraviolet maxima in this solvent appear at 212, 290, 336, 394, 464, 580, and 655 mμ (log ε 4·66, 4·20, 4·09, 4·11, 4·15, 4·72, and 4·38).

In a similar experiment an intermediate iodine-containing compound, m. p. 110° (decomp.),

was isolated. Attempts to purify it by recrystallisation caused decomposition (Found: C, 61·3; H, 4·3. Calc. for $C_{23}H_{17}I$: C, 65·7; H, 4·1%). It had $\lambda_{max.}$ 252 mμ (log ε 4·30).

(*b*) To phenyl-lithium (0·01 mole) in ether 1,2,3-triphenylcyclopentadiene (2·94 g., 0·01 mole) in benzene (70 ml.) was added, and the mixture was refluxed for 2 hr. After cooling, dry oxygen was passed into the mixture for 2½ hr. The solution cleared and then gradually darkened. It was poured into water, and the organic layer was separated and dried (Na_2SO_4). Removal of the solvent left a dark brown gum (3·4 g.). An infrared spectrum of this showed maxima in the carbonyl stretching region at 1773 and 1695 cm.$^{-1}$. The gum was chromatographed in benzene. The main yellow-green band was eluted with benzene, to give a dark red solution which had a strong green fluorescence. Evaporation gave a dark green-brown solid (0·65 g.). Recrystallisation from acetone afforded dark khaki needles of 2,3,4,2′,3′,4′-hexaphenylfulvalene, m. p. 279—282°. Other fractions from the column yielded only intractable gums.

(*c*) 5-Diazo-1,2,3-triphenylcyclopentadiene (5·0 g.) in ethanol (800 ml.) was heated to the b. p. After 3—4 hr. a brownish-green solid separated and was filtered off (m. p. *ca.* 260°). Recrystallisation from acetone gave khaki needles of 2,3,4,2′,3′,4′-hexaphenylfulvalene, m. p. 279—282°.

(*d*) Copper powder (15·8 g., 0·25 g.-atom) was refluxed with 5,5-dibromo-1,2,3-triphenylcyclopentadiene (2·3 g., 0·005 mole) in benzene (100 ml.) overnight. The solution became dark red with a strong green fluorescence. The copper powder was filtered off and washed with hot benzene. The benzene extracts were combined, washed with water, dried (Na_2SO_4), and evaporated. The resulting dark solid was chromatographed in benzene. The main yellowish-green band was eluted with benzene and obtained as a dark brown solid (0·7 g.). Recrystallisation from acetone afforded dark greenish-yellow needles of 2,3,4,2′,3′,4′-hexaphenylfulvalene, m. p. 279—281°.

The infrared and ultraviolet spectra of samples prepared by each of the above methods were identical.

2,3,4,2′,3′,4′-*Hexaphenylbi*(*cyclopenta*-2,4-*dienyl*).—Zinc dust (4·8 g., 0·074 g.-atom) was refluxed with 5-bromo-1,2,3-triphenylcyclopentadiene (1·1 g., 0·003 mole) in benzene (75 ml.) overnight. The solution became dark red with a strong green fluorescence. The zinc dust was filtered off and washed with hot benzene. The benzene solutions were combined, washed with water, dried (Na_2SO_4), and evaporated. Fractional crystallisation of the brown solid (0·8 g.) from acetone gave two compounds. The less soluble (2,3,4,2′,3′,4′-hexaphenylfulvalene) was obtained as dark khaki needles, m. p. and mixed m. p. 279—282°. The other, the *bi*(*cyclopentadienyl*), (1,1′-dihydro-2,3,4,2′,3′,4′-hexaphenylfulvalene) crystallised in pale yellow needles, m. p. 268·5—270° (Found: C, 94·0; H, 6·0. $C_{46}H_{34}$ requires C, 94·1; H, 5·9%), $\lambda_{max.}$ at 264, 324, and 366 mμ.

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