

30. *Cyclobutadienes. Part I. Addition of Tetramethylcyclobutadiene to Acetylenes and Some Preliminary Experiments on Tetraphenylcyclobutadiene.*

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Reduction of dichlorotetramethylcyclobutene with zinc in the presence of acetylenes gives the tetramethylbenzenes (XII; R = Me or CO₂Me). Tetraphenylthiophen dioxide is pyrolysed to the high-melting dimer of tetraphenylcyclobutadiene.

Of all possible routes to derivatives of bicyclo[2,2,0]hexa-2,5-diene (I), Dewar's structure¹ for benzene,* the most promising seemed to be (i) 1,2-elimination from (II), *e.g.*, base-catalysis where X = H, Y = halogen or ⁺NMe₃, reduction where X = Y = halogen or equivalent, oxidation where X = Y = CO₂H,² (ii) photo-isomerisation of a benzene derivative,³ or (iii) addition of a cyclobutadiene to an acetylene.⁴ Because it also involved the interesting chemistry of cyclobutadienes and their dimers, we have given most attention to the last, (iii).

Amongst the syntheses of cyclobutadienes that were attempted were removal of the metal from known cyclobutadiene complexes,^{5,6} reduction of dihalides (III) and (IV), elimination of a stable molecule (X = CO, CO₂, SO₂, N₂, etc.) from a heterocycle (V) or its valence-tautomer (VI), condensation between a 1,2-dimetallo- and a 1,2-dihalogeno-olefin (VII), and cyclisation of a 1-metallo-4-halogeno-butadiene (VIII).

We first examined the tetramethyl series.⁷ Reduction of the dichloride^{8,9} (IX) with lithium amalgam in ether containing but-2-yne gave an almost quantitative yield of the *syn*-dimer¹⁰ (X), which is also formed in the absence of but-2-yne. Treatment of the

* Although Dewar's name has become attached to this structure (I), in fact he listed it in 1866¹ only as one of seven formulæ (including Kekulé's) for benzene to illustrate the use of his molecular models with (planar) quadrivalent carbon atoms, remarking that "This little device is the mechanical representative of Dr. C. Brown's well-known graphic notation."

¹ Dewar, *Proc. Roy. Soc. Edinburgh*, 1866, 82.

² van Tamelen and Pappas, *J. Amer. Chem. Soc.*, 1963, **85**, 3297.

³ van Tamelen and Pappas, *J. Amer. Chem. Soc.*, 1962, **84**, 3789.

⁴ Berkoff, Cookson, Hudec, and Williams, *Proc. Chem. Soc.*, 1961, 312; Williams, Ph.D. Thesis, Southampton, 1961.

⁵ Criegee and Schröder, *Annalen*, 1959, **623**, 1.

⁶ Hübel, Braye, Clauss, Weiss, Krüerke, Brown, King, and Hoogzand, *J. Inorg. Nuclear Chem.*, 1959, **9**, 204; Dodge and Schomaker, *Nature*, 1960, **186**, 798; Malatesta, Santarella, Vallarino, and Zingales, *Angew. Chem.*, 1960, **72**, 34.

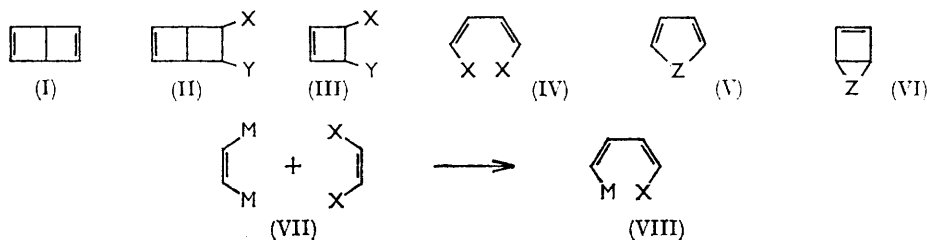
⁷ Criegee has recently reviewed his extensive work in this field, *Angew. Chem.*, 1962, **74**, 703.

⁸ Smirnof-Samkof, *Proc. Akad. Sci. (U.S.S.R.)*, 1952, **83**, 869.

⁹ Criegee and Moschel, *Chem. Ber.*, 1959, **92**, 2181.

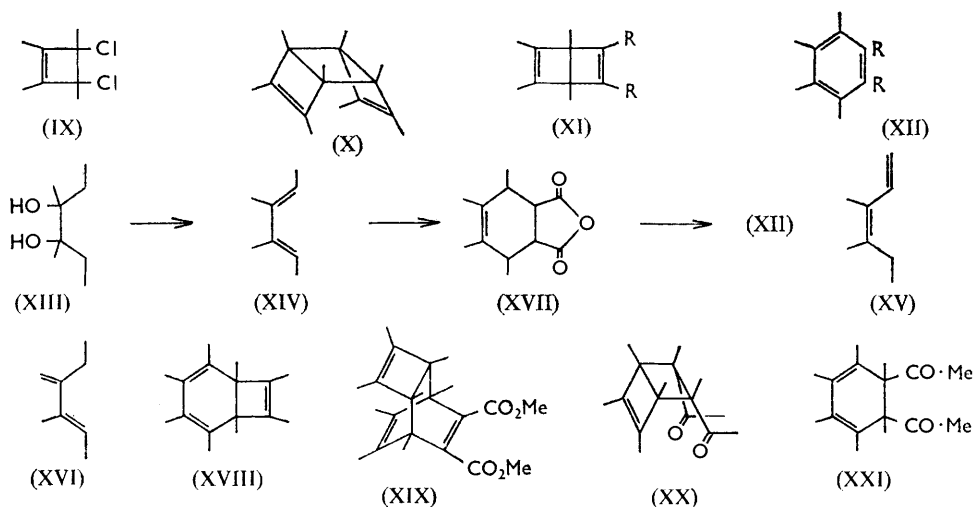
¹⁰ Criegee and Louis, *Chem. Ber.*, 1957, **90**, 417.

dichloride (IX) with activated zinc dust in but-2-yne produced red polymer and some liquid hydrocarbon. In the presence of ether, however, hexamethylbenzene (XII; R = Me) (20%) was also formed. The stability of the liquid hydrocarbon mixture to acid and to heat ruled out its being the Dewar isomer (XI) which may be an intermediate in



the formation of compounds (XII). Reduction under similar conditions in the presence of dimethyl acetylenedicarboxylate yielded dimethyl tetramethylphthalate (XII; R = CO₂Me), an authentic sample of which was made as follows. Dehydration of the diol¹¹ (XIII) gave a mixture of dienes from which 3,4-dimethylhexa-2,4-diene (XIV) was separated by fractional distillation. It was found pure by gas chromatography and by the complete absence of the strong absorption at 890 cm.⁻¹ present in the infrared spectra of the isomers (XV) and (XVI). Addition to maleic anhydride gave the anhydride (XVII), which was converted into the dimethyl ester and dehydrogenated over palladium-charcoal.

The infrared spectra (CCl₄) of both hexamethylbenzene and dimethyl tetramethylphthalate contained an unexpected band at 2993 cm.⁻¹, as well as that normally associated with methyl groups at 2925 cm.⁻¹ (XII; R = Me) or 2940 cm.⁻¹ (XII; R = CO₂Me). This high-frequency band presumably arises from congestion between hydrogen atoms on *ortho*-methyl groups.¹²



When the *syn*-dimer (X) was treated with dimethyl acetylenedicarboxylate in boiling *n*-butyl acetate it gave an adduct that could be pyrolysed to the tetramethylphthalate (XII; R = Me). We assumed⁴ that the adduct had structure (XIX), formed by addition to the valence tautomer¹³ (XVIII). However, this hydrocarbon (XVIII) has since been

¹¹ McCullum and Whitby, *Trans. Roy. Soc. Canada*, 1928, **22**, 39.

¹² Kivelson, Winstein, Bruck, and Hansen, *J. Amer. Chem. Soc.*, 1961, **83**, 2938; de Vries and Ryason, *J. Org. Chem.*, 1961, **26**, 621; Bird, Cookson, and Crundwell, *J.*, 1961, 4809.

¹³ Cf. Avram, Mateescu, and Nenitzescu, *Annalen*, 1960, **636**, 174; Cookson, Hudec, and Marsden, *Chem. and Ind.*, 1961, 21.

isolated¹⁴ and found not to react¹⁵ with the acetylene ester under the conditions of the addition. Further work will be needed to check the structure of the adduct and to find out how it is formed.

Under the mildest conditions possible for the reaction of the dichloride (IX) with zinc and substituted acetylene no Dewar isomer (XI) of the products could be extracted. If it is indeed an intermediate, its isomerisation to (XII) may be catalysed by the zinc chloride inevitably produced at the same time.

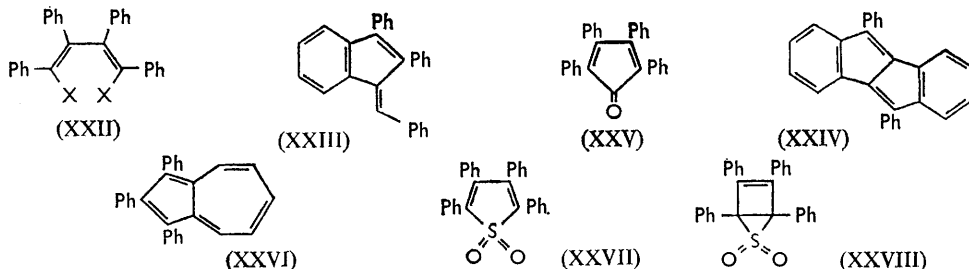
Some interaction between the two double bonds in Criegee's *syn*-dimer (X) was indicated by the strong end-absorption in the ultraviolet spectrum; *e.g.*, at 230 m μ in ethanol ϵ was 2200, and in cyclohexane it was 2500. However, irradiation of the dimer (X) through silica without a sensitizer, or through Pyrex in the presence of benzophenone, gave no sign of conversion into the saturated cubic hydrocarbon, octamethylpentacyclo-octane. The diketone (XX), made from the adduct of the dimer (X) with osmium tetroxide,¹⁰ also had an interesting spectrum (see Table). The heavy substitution and strain in the cyclobutene

Ultraviolet absorption bands (m μ) (ϵ in parentheses) of the diketone (XX).

Ethanol		Cyclohexane	
$\pi(\text{C}=\text{C}) \longrightarrow \pi^*(\text{C}=\text{O})$	$n \longrightarrow \pi^*$	$\pi(\text{C}=\text{C}) \longrightarrow \pi^*(\text{C}=\text{O})$	$n \longrightarrow \pi^*$
239 (1440)	300 (421)	239 (1750)	294 (250) 301 (275) 311 (244)

double bond combine to lower its ionisation potential and to produce the charge-transfer absorption at unusually long wavelength. There is also enhancement of the $n \longrightarrow \pi^*$ intensity. That the mixing between the two transitions¹⁶ is apparently greater in ethanol than in the less polar cyclohexane, is expected from the smaller difference in energy between them in the more polar solvent. [The tautomeric structure (XXI) is excluded by the ultraviolet spectrum and by the presence in the infrared spectrum of the band at 1689 cm.⁻¹, characteristic of tetramethylcyclobutenes.]

Since substitution by phenyl groups should stabilise cyclobutadiene, we also made some preliminary experiments on possible syntheses of the tetraphenyl compounds. On pyrolysis, the di-iodotetraphenylbutadiene (XXII; X = I) lost iodine to form the hydrocarbons (XXIII) and (XXIV) (the former was dehydrogenated to the latter when heated in air), and the course of the reaction was not changed in the presence of nickel powder: there was no trace of the highly coloured tetraphenylcyclobutadiene-nickel di-iodide complex. The di-iodide (XXII; X = I) did not react with nickel bromide in boiling triglyme (triethylene glycol trimethyl ether), but treatment with nickel carbonyl gave



tetraphenylcyclopentadienone (XXV) in high yield, perhaps through a cyclobutadiene-nickel complex although there is no definite evidence: however, tetraphenylcyclobutadiene-nickel complexes are converted into the dienone (XXV) by nickel carbonyl.¹⁷ Reduction

¹⁴ Criegee, Wirth, Engel, and Brune, *Chem. Ber.*, 1963, **96**, 2230.

¹⁵ Prof. R. Criegee, personal communication (see also ref. 7).

¹⁶ Labhardt and Wagnière, *Helv. Chim. Acta*, 1959, **42**, 2219; Mason, *Quart. Rev.*, 1961, **15**, 287; Cookson and Hudec, *J.*, 1962, 429.

¹⁷ Maitlis and Games, *J. Amer. Chem. Soc.*, 1963, **85**, 1887.

of the di-iodide (XXII; X = I) with lithium amalgam only gave tetraphenylbutadiene (XXII; X = H), but with zinc dust in tetrahydrofuran this was accompanied by 1,2,3-triphenylazulene¹⁸ (XXVI).

Attempts to add potassium to diphenylacetylene in 1,2-dimethoxyethane under various conditions in the hope of obtaining $\alpha\alpha'$ -dipotassio-stilbene for condensation with dihalides caused trimerisation to hexaphenylbenzene and dismutation to 1,2,3,4-tetraphenylbutane and 5,10-diphenylindeno[2,1-*a*]indene (XXIV).

Tetraphenylthiophen dioxide (XXVII) and tetraphenylcyclopentadienone (XXV) did not react with nickel bromide in boiling triglyme. The dioxide (XXVII) survived long ultraviolet irradiation, which might have led to loss of sulphur dioxide, perhaps through the valence tautomer (XXVIII), although a sulphur-free product was slowly produced. Irradiation in air gave a mixture of *cis*- and *trans*-dibenzoylstilbene.

Pyrolysis of the dioxide (XXVII) gave the high-melting dimer of tetraphenylcyclobutadiene, which will be described in a later Paper.

EXPERIMENTAL

3,4-Dichloro-1,2,3,4-tetramethylcyclobutene (IX).—The reaction was carried out as described by Criegee and Moschel⁹ but with some modifications. But-2-yne (108 g., 2 mole) was placed in a 250 ml. three-necked flask fitted with stirrer, gas inlet bubbler, and Drikold condenser. The flask was cooled in Drikold-acetone at -30 to -25° and boron trifluoride etherate (5 ml.) and water (0.5 ml.) were added to the stirred acetylene. Liquid chlorine (100 g., 1.4 mole) at -34° was bubbled in through a concentrated sulphuric acid drier, for 3 hr. The temperature was kept below -20° : towards the end of the addition hydrogen chloride was evolved. After the addition, the pink semi-solid mixture was cooled to -70° and filtered rapidly through a sintered glass funnel. The pale pink mass was sucked free of mother-liquors and recrystallised from light petroleum (b. p. 40 — 60°) containing 8% methylene chloride at -70° to give the cyclobutene (71 g.), m. p. 57 — 58° .

syn-Octamethyltricyclo[4,2,0,0^{a,5}]octa-3,7-diene (X).—Lithium amalgam was prepared by carefully heating a mixture of lithium metal (2 g.) and mercury (800 g.) under hydrogen in a 1-litre flask until amalgamation occurred. The amalgam formed at about 185° . The dichloride (IX) (30 g.), dissolved in absolute ether (500 ml.), was added to the cooled amalgam and the mixture shaken for 24 hr. The mixture was filtered to remove mercury and lithium chloride, and the ethereal solution evaporated to dryness, when the octamethyltricyclo-octadiene was obtained (18 g., 97%), m. p. 197 — 198° (from acetone).

Reaction between 3,4-Dichloro-1,2,3,4-tetramethylcyclobutene and Dimethyl Acetylenedicarboxylate in the Presence of Activated Zinc Dust.—Zinc dust was activated by adding AnalaR zinc dust to 1:1 hydrochloric acid, stirring for $\frac{1}{2}$ min., and decanting the acid. The zinc was washed many times with distilled water, several times with alcohol, and finally with ether. The dichloride (IX) (6 g., 0.033 mole) was added slowly during 45 min. to a stirred mixture of dimethyl acetylenedicarboxylate (10.7 g., 0.15 mole) and activated zinc dust (15 g.). Heat was evolved during the addition of the dichloride and the temperature was kept below 50° by cooling when necessary. After about half the dichloride had been added the mixture became very viscous and stirring difficult. When the addition was complete, benzene was added and the mixture filtered. The benzene solution was washed several times with water, dried, and distilled to yield fractions (i) (6.2 g.) b. p. $90^\circ/10$ mm. and (ii) (1.55 g., 18.7%) b. p. $138.9^\circ/0.1$ mm. Fraction (i) was unreacted diester. Fraction (ii) was dimethyl tetramethylphthalate, m. p. 128 — 129° (from light petroleum), identical (m. p., mixed m. p., and infrared spectrum) with an authentic sample.

Reaction of Dichlorotetramethylcyclobutene with Butyne and Zinc Dust.—To activated zinc dust (9 g.) was added cold but-2-yne (50 ml.) and the dichloro-compound (2 g.). Almost immediately a reaction ensued, and the butyne began to distil. The mixture was cooled and set aside in a stoppered vessel, in the dark, for 30 hr. The butyne was then removed and the residue, which contained red polymer, extracted with light petroleum. The extract was chromatographed on silica, yielding an off-white solid (350 mg.) which was recrystallised from light petroleum to give hexamethylbenzene (XII; R = Me) (19.3%), m. p. 162 — 166° , identical

¹⁸ Cf. Freedman, *J. Org. Chem.*, 1962, **27**, 2298.

(mixed m. p. and infrared and ultraviolet spectra) with an authentic sample (kindly supplied by Dr. M. C. Whiting). Some polymeric gums and a pale yellow liquid were also isolated. The liquid had ν_{\max} 1058, 1373, 1440, and 1645 cm^{-1} . The ultraviolet spectrum had only end-absorption.

Control Experiments on But-2-yne.—(a) Activated zinc dust (3.0 g.) was mixed with zinc chloride (0.5 g.) and cold but-2-yne (3.0 g.) added. The mixture was stirred for 48 hr. in the dark at room temperature, diluted with ether, filtered through Kieselguhr, and concentrated *in vacuo*. The residue, which contained zinc chloride, was dissolved in ether, and the ethereal solution washed with water and dried. Removal of the ether yielded a white gum (8%). This was chromatographed through silica in light petroleum, when a few colourless crystals (10 mg., <1% yield) were isolated. Infrared and ultraviolet spectroscopy showed that the crystals were hexamethylbenzene.

(b) A mixture of zinc chloride (3.0 g.) and but-2-yne (10 ml.) was stirred at room temperature for 48 hr. Working up in the usual way yielded 75 mg. of a semi-solid product. Infrared and ultraviolet spectroscopy showed that it was not hexamethylbenzene.

(c) Activated zinc dust (2.5 g.), zinc chloride (0.5 g.), and butyne (10 ml.) were stirred at room temperature for 48 hr. The product (80 mg.) was recrystallised from light petroleum giving pure hexamethylbenzene, (22 mg., 1%), m. p. 163—167°.

3,4-Dimethylhexane-3,4-diol (XIII).—Dry magnesium turnings (48 g., 2 moles) and anhydrous benzene (600 ml.) were placed in a 3-litre 3-necked round-bottomed flask fitted with stirrer, dropping funnel, and reflux condenser. Mercuric chloride (42 g., 0.15 mole) was dissolved in dry ethyl methyl ketone (437 ml., 4.4 moles) and the solution added slowly to the stirred mixture. After the initial induction period, the ketone was added at such a rate as to maintain a gentle reflux. When the addition was complete, a further 200 ml. of benzene was added, and the mixture was heated on a steam-bath for 2 hr. The cooled semi-solid mixture was decomposed by adding to ice-water containing sodium hydroxide (160 g., 4 moles). The organic layer was separated, dried over sodium hydroxide, and distilled to remove benzene and unreacted ethyl methyl ketone. The residue was distilled under vacuum and the fraction, b. p. 120—135°/15 mm., collected (180 gm.).

3,4-Dimethylhexa-2,4-diene (XIV)—The diol (XIII) (146 g., 1 mole) was treated with 1 drop of 20% sulphuric acid and distilled at 120—140°. The oil was separated, dried (CaCl_2), and distilled, b. p. 70—76°/100 mm. (80 g.). Gas chromatography showed the presence of two isomers. Pure 3,4-dimethylhexa-2,4-diene was obtained by careful fractional distillation, b. p. 135—136°, ν_{\max} 797 cm^{-1} .

1,2,3,6-Tetrahydro-3,4,5,6-tetramethylphthalic Anhydride (XVIII).—Maleic anhydride (5 g. was added slowly with cooling to 3,4-dimethylhexa-2,4-diene (XIV) (5.5 g.). Heat was evolved. After the addition, the mixture was heated at 100° for 15 min. and cooled giving the *anhydride* (8.8 g.) (from light petroleum) (Found: C, 69.1; H, 7.8. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.2; H, 7.7%), ν_{\max} 1780 and 1850 cm^{-1} and strong bands at 953 and 1200 cm^{-1} .

Dimethyl 1,2,3,6-Tetrahydro-3,4,5,6-tetramethylphthalate.—The foregoing anhydride (4 g.) was dissolved in methanol (25 ml.) containing sulphuric acid (0.1 ml.), boiled under reflux for 1 hr., and the bulk of the alcohol removed. The residue was poured into sodium hydrogen carbonate solution and extracted with ether (3 × 30 ml.). The extract was dried (Na_2SO_4) and distilled to dryness giving the *diester* (4.0 g.), m. p. 51—52° (from light petroleum) (Found: C, 66.0; H, 8.55. $\text{C}_{14}\text{H}_{22}\text{O}_4$ requires C, 66.1; H, 8.7%) ν_{\max} 1745, 1178, 1190, and 1215 cm^{-1} .

Dimethyl Tetramethylphthalate (XII; R = CO_2Me).—The tetrahydro-ester (2 g.) and 30% palladium-charcoal (1 g.) were heated together under nitrogen for 2 hr. at 220—240°. After cooling, the mixture was extracted several times with ether. Removal of the ether yielded 1.8 g. of a white solid which gave the *diester* (1.35 g.), m. p. 124—125° (from light petroleum) (Found: C, 67.4; H, 7.2%; *M*, 250.7. $\text{C}_{14}\text{H}_{18}\text{O}_4$ requires C, 67.2; H, 7.2%; *M*, 250), ν_{\max} 1729, 1034, 1222, 1323, and 1580 cm^{-1} . The infrared spectrum in CCl_4 also showed an abnormal band at 2992 cm^{-1} .

Reaction between Dimethyl Acetylenedicarboxylate and syn-Octamethyltricyclo[4,2,0,0^{2,5}]octa-3,7-diene.—The diene (1.09 g., 0.005 mole) and n-butyl acetate (5 ml.) were mixed with dimethyl acetylenedicarboxylate (1.42 g., 0.01 mole) and boiled under reflux for 48 hr. Butyl acetate was removed by distillation under low pressure and the residue chromatographed on alumina. Elution with light petroleum gave the diene (100 mg.). Further elution with 25% benzene-light petroleum afforded a white adduct (650 mg.), m. p. 97—98° (from light petroleum) (Found:

C, 73.95; H, 8.35%; *M*, 354.2. Calc. for $C_{22}H_{30}O_4$: C, 73.7; H, 8.4%; *M*, 358, ν_{\max} . 1025, 1263, 1280, 1605, and 1715 cm^{-1} .

Pyrolysis of the Above Adduct.—The adduct (358 mg., 0.01 mole) was heated under nitrogen at 330–350° for 30 min. An attempt was made to trap any tetramethylcyclobutadiene which might have been evolved in silver nitrate solution, but no complex was formed. The residue from the reaction was distilled, when a fraction, b. p. 230–250°, was obtained. A small amount of a higher-boiling fraction was also collected. The lower-boiling fraction was chromatographed on alumina. Elution with 25% benzene–light petroleum gave pure dimethyl tetramethylphthalate (30 mg.), m. p. 126–128°, identified by infrared spectrum and mixed m. p.

2,3-Diacetylhexamethylbicyclo[2,2,0]hex-5-ene (XX).—Following the method of Criegee and Louis,¹⁰ the *syn*-octamethyltricyclo-octadiene (X) (0.88 g.) and osmium tetroxide (1.03 g.) were dissolved in absolute ether (25 ml.) and set aside for 24 hr. The osmate ester was filtered off, and added to a solution of anhydrous sodium sulphite (5 g.) in 50% ethanol (90 ml.). The mixture was boiled under reflux for 4 hr., cooled, and filtered. The inorganic residue was washed several times with small amounts of ethanol and the filtrate and washings evaporated to small bulk under vacuum. The oil which separated was extracted with ether and the ethereal solution dried and distilled. The residue was purified by repeated vacuum sublimation. The diketone (65 mg.), m. p. 54–55°, was obtained free from the diol, ν_{\max} . 1100, 1145, 1688, and 1710 cm^{-1} , λ_{\max} . (EtOH) 239 and 300 μ (ϵ 1435 and 421), λ_{\max} . (cyclohexane) 239 and 301 μ (ϵ 1745 and 275).

Irradiation of syn-Octamethyltricyclo[4,2,0,0^{2,5}]octa-3,7-diene (X).—(a) *In solution.* A solution of the diene (10 g.) in absolute ether (100 ml.), in a quartz flask fitted with an efficient reflux condenser, was irradiated under nitrogen by a 400 w mercury vapour lamp for 1 week. Aliquots were taken at daily intervals and examined by infrared spectroscopy and gas chromatography. No change was observed. After a week the ether was evaporated off and the diene was recovered quantitatively.

(b) *In the crystalline state.* A small amount of the diene was irradiated in a quartz flask under nitrogen for several days. Only starting material and a small amount of polymeric material were found in the product.

Thermal Decomposition of 2,3,4,5-Tetraphenylthiophen 1,1-Dioxide (XXVII).—The dioxide (3.5 g.) in a dry, oxygen-free, nitrogen atmosphere, was heated at 370–380° in a Woods metal bath for 3 hr. The resultant brown oil deposited tetraphenylcyclobutadiene dimer (38 mg.) on solution first in chloroform, and then in benzene–light petroleum. After removal of the dimer, the filtrate was applied in light petroleum containing the minimum of benzene to an alumina column in light petroleum. Elution with light petroleum (5 × 250 ml.) gave an oil (0.810 g.) that crystallised from chloroform–ethanol as plates. The infrared spectrum of this solid was superimposable on that of authentic tetraphenylfuran. Continued elution with light petroleum (6 × 250 ml.) afforded a partly crystalline oil (404 mg.) which gave needles, m. p. 252–254° (from chloroform–ethanol).

Elution with benzene (2 × 250 ml.) gave a dark brown oil (1.27 g.).

Experiments with 1,4-Di-iodo-1,2,3,4-tetraphenylbutadiene (XXII; X = I).—*Reaction with lithium amalgam.* The diene¹⁹ (0.5 g.), in anhydrous ether, was shaken with lithium amalgam (100 g.) for 12 hr. The washed ether solution was dried ($MgSO_4$) and evaporated. Chromatography on alumina in light petroleum, and elution with light petroleum gave white needles (83 mg.) (from ethanol) identified as 1,2,3,4-tetraphenylbutadiene by mixed m. p. and infrared spectrum.

Thermal decomposition. The diene (0.2 g.) was slowly heated to 230–240° for 15 min. *in vacuo*. Iodine was evolved and the melt assumed a dark red colour. This product, in light petroleum containing the minimum of benzene, was applied to an alumina column in light petroleum. Elution with the latter solvent gave two bands. The first band afforded a yellow oil (30 mg.) that crystallised from ethanol as a mixture of yellow needles and prisms, m. p. 184–185°, shown to be 1-benzylidene-2,3-diphenylindene²⁰ (XXIII) by comparison with a synthetic sample. The second band afforded a dark red oil (22 mg.) that recrystallised from chloroform–ethanol as long, red-brown needles (17 mg.), m. p. 260–261°. This compound had m. p. and ultraviolet spectrum identical with those reported for 5,10-diphenylindeno[2,1-*a*]indene (XXIV). Addition of nickel powder had no effect on the pyrolysis.

¹⁹ Bray, Hübel, and Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.

²⁰ Orechhoff, *Ber.*, 1914, **47**, 93.

Reaction with Nickel Carbonyl.—The di-iodo-compound (3 g.) in anhydrous benzene (50 ml.) was treated with nickel carbonyl (5 ml.) under nitrogen. The mixture was refluxed for 8 hr., filtered, the filtrate evaporated, and the black residue crystallised from chloroform-ethanol as black shiny plates of the cyclopentadienone (XXV) (1.35 g.), m. p. 220—221°.

Reaction with Anhydrous Nickel Bromide.—Anhydrous nickel bromide was prepared by direct union of the elements in dry ether. The resultant etherate was dried *in vacuo*.

The diene (0.5 g.) in 1,2-dimethoxyethane (15 ml.) was heated in a nitrogen-flushed sealed tube at 200° for 18 hr. in the presence of a molar proportion of anhydrous nickel bromide. No complex formation was observed. The filtered product gave tetraphenylfuran²¹ (0.31 g.) on crystallisation from ethanol with the help of chloroform.

The mother-liquor deposited yellow needles (0.12 g.), m. p. 184—185° (after repeated recrystallisation), undepressed on admixture with authentic 1-benzylidene-2,3-diphenylindene (XXIII).

Reaction with Zinc.—The diene (1 g.) in tetrahydrofuran (30 ml.) was refluxed under nitrogen with zinc dust (2 g.) for 20 hr. The filtered solution was evaporated and the residue taken up in ether. The solution was washed with water, dried (MgSO₄), and evaporated, and the residue crystallised from chloroform-ethanol to give the indene (XXIII), needles (242 mg.), m. p. and mixed m. p. 183°. The evaporated mother-liquor was chromatographed on alumina. Light petroleum eluted a blue band (99 mg.) that crystallised from nitromethane as blue prisms and white needles. The latter [tetraphenylbutadiene, (33 mg.)] dissolved on warming. The blue prisms were 1,2,3-triphenylazulene²² (XXVI), m. p. and mixed m. p. 215—216°.

Reaction with Nickel.—The diene (0.16 g.) in triglyme (5.5 ml.) was refluxed with finely divided nickel (0.2 g.) for 40 min. No coloration indicating formation of a complex was observed, and filtration of the nickel followed by aqueous work-up gave starting material (83 mg.), m. p. 203—204°.

Heating of 1-Benzylidene-2,3-diphenylindene.—The indene (XXIII) (0.2 g.) was heated with a small flame until molten and maintained at this temperature for 2—3 min. Chromatography then afforded starting material (93 mg.) and the indenoindene (XXIV), (43 mg.).

Irradiation of 1-Benzylidene-2,3-diphenylindene.—The indene (XXIII) (0.2 g.) in ethyl acetate (50 ml.) was irradiated with a medium-pressure mercury arc through quartz for 24 hr. Removal of solvent gave a dark brown gum, that gave, on trituration with ethanol, a white powder (42 mg.), m. p. 265° (decomp.) (from chloroform-ethanol) (Found: C, 94.0; H, 5.7%; M (Rast), 356). Chromatography of the portion soluble in ethanol gave only oils.

Reaction of Potassium with Diphenylacetylene.—Diphenylacetylene (2 g.) in 1,2-dimethoxyethane (25 ml., dried over potassium and distilled) was shaken with an excess of freshly cut potassium for 3 hr. The solution rapidly became yellow, then blue, and finally dark brown after 3 hr. The mixture was carefully poured into absolute alcohol. Evaporation of the alcohol and solvent gave a brown gum that was taken up in ether, washed with water, dried (Na₂SO₄), and chromatographed on alumina in light petroleum. Elution with this solvent (750 ml.) gave a pale yellow oil (78 mg.) containing some diphenylacetylene. Further elution with light petroleum (1250 ml.) gave a yellow gum (0.23 g.) that crystallised from chloroform-methanol as white needles (110 mg.), m. p. 185°, shown to be identical with 1,2,3,4-tetraphenylbutane by comparison with a synthetic specimen.²³ Continued elution with light petroleum (750 ml.) gave further quantities (0.09 g.) of the yellow oil from which ~5 mg. of white crystals, m. p. 180—182° could be obtained by addition of ethanol. Elution with light petroleum-benzene (9 : 1; 1 l.) gave a yellow band that afforded a dark oil (0.426 g.). Crystallised from chloroform-methanol, this gave first the indenoindene (XXIV) (30 mg.) then hexaphenylbenzene (21 mg.).

Elution with benzene-light petroleum (1 : 4; 750 ml.) gave a fraction (0.154 g.) that crystallised from chlorobenzene as needles (9 mg.), m. p. >300°, infrared spectrum identical with that of a sample of hexaphenylbenzene prepared by trimerisation of diphenylacetylene.²⁴

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