111. *Liquid-phase Photolysis. Part VI.*[1] *Preparation of Cyclo-octatetraenes by the Photoaddition of Acetylenes to Benzene: Dimerisation of Phenylacetylene to* 1-*Phenylazulene and* 1-*Phenylnaphthalene.*

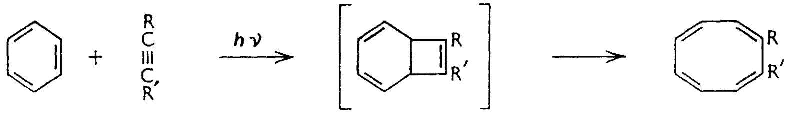
By D. Bryce-Smith and J. E. Lodge.

Methyl propiolate, dimethyl acetylenedicarboxylate, and phenylacetylene add to benzene under the influence of ultraviolet radiation to give the corresponding cyclo-octatetraenes. Evidence has been obtained for the formation of a trace of cyclo-octatetraene from the irradiation of a solution of acetylene in a mixture of acetone and benzene. This ring-expansion is considered to involve initial 1,2-addition of the acetylene followed by isomerisation of the intermediate bicyclo[4,2,0]octa-2,4,7-triene derivative. The addition of dimethyl acetylenedicarboxylate to benzene, unlike that of maleic anhydride,[1] appears not to involve photoexcitation of an intermediate charge-transfer complex.

Phenylacetylene photodimerises to a 5 : 1 mixture of 1-phenylazulene and 1-phenylnaphthalene.

Maleic anhydride reacts with benzene under the influence of ultraviolet radiation by successive 1,2- and 1,4-additions,[2,3] and Ayer and Büchi have described in a patent the 1,2-photoaddition of various ethylenes to benzonitrile.[4] A report [5] of a lecture given by Büchi refers to the formation of 1-cyano-2,3-diethylcyclo-octatetraene by photoaddition of hex-3-yne to benzonitrile; evidence for the structure of this product has been given by Atkinson in a thesis.[6] Grovenstein and Rao described the production of a 1 : 1 photo-adduct from dimethyl acetylenedicarboxylate and benzene, and formulated it as dimethyl cyclo-octatetraene-1,2-dicarboxylate.[7] The present workers independently reported this addition and some related examples of it; and the cyclo-octatetraene structure for one of the adducts was established rigorously.[8]

These reactions, which can be represented by the annexed sequence, are now more fully described.



Methyl Propiolate.—Irradiation of a solution of methyl propiolate in benzene under nitrogen for 20 hr. at 53° in a quartz cell fitted with a quartz-wool scouring device [1] gave methyl cyclo-octatetraenecarboxylate as a yellow oil having an infrared spectrum wholly identical with that previously reported.[9] The derived acid had m. p. and mixed m. p. 72·5° (lit.,[9] 72·5°), and infrared and ultraviolet spectra identical with those of material prepared by carboxylation of cyclo-octatetraenyl-lithium.[9] It was not found possible to prepare this acid directly by irradiation of propiolic acid in benzene.

Dimethyl Acetylenedicarboxylate.—Irradiation of dimethyl acetylenedicarboxylate in benzene gave a yellow solid, m. p. 109·5—110·5°. This is formulated as dimethyl cyclo-octatetraene-1,2-dicarboxylate for the following reasons. The elemental analysis and

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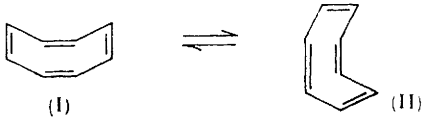
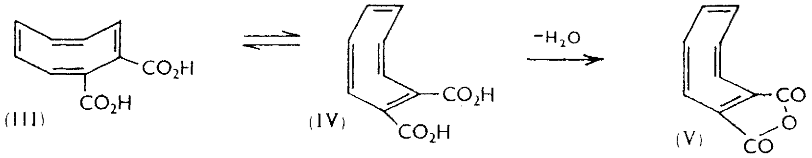
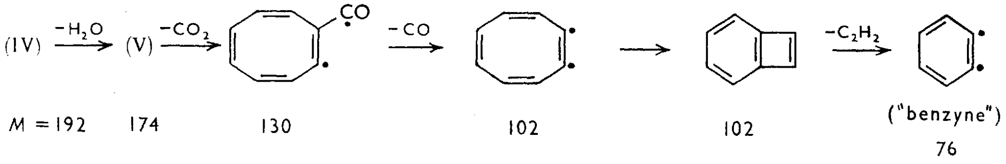
[1] Part V, Bryce-Smith and Lodge, *J.*, 1962, 2675.
[2] Angus and Bryce-Smith, *Proc. Chem. Soc.*, 1959, 326; *J.*, 1960, 4791.
[3] Grovenstein, Rao, and Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 1705.
[4] Ayer and Büchi, U.S.P. 2,805,242/1957.
[5] Wirz, *Chimia*, 1958, **12**, 282, reporting a lecture given by Büchi on 19th June, 1958, to the Basler Chemische Gesellschaft.
[6] Atkinson, Ph.D. Thesis, Massachusetts Institute of Technology, 1962.
[7] Grovenstein and Rao, *Tetrahedron Letters*, 1961, No. 4, 148.
[8] Bryce-Smith and Lodge, *Proc. Chem. Soc.*, 1961, 333.
[9] Cope, Burg, and Fenton, *J. Amer. Chem. Soc.*, 1952, **74**, 173.

molecular weight were consistent with a 1 : 1 adduct, as was the equivalent of the derived acid, m. p. 207·5—208·5°. The infrared spectra of the ester and acid were markedly similar to those of methyl cyclo-octatetraenecarboxylate and cyclo-octatetraenecarboxylic acid, respectively. The ultraviolet spectrum of the adduct acid quantitatively resembled that of cyclo-octatetraenecarboxylic acid. Anet has shown that the two (identical) forms (I) and (II) of cyclo-octatetraene superficially analogous to the Kekulé forms of benzene are very rapidly interconvertible at 20°.[10] Models show that, of the two corresponding tautomers (III) and (IV) of the dicarboxylic acid, only form (IV) could give a relatively unstrained anhydride (V). The skew angle of the carboxylate groups in form (III) is about 70°. The dicarboxylic acid could not be converted into an anhydride by conventional means. Thus, acetic anhydride gave a product which from its infrared spectrum was an anhydride but appeared to contain acetate groups. Prolonged treatment with acetic anhydride led to gross decomposition. In a mass spectrometer, the acid gave, as expected, no peak corresponding to structure (IV) (M 192), but principal peaks corresponding to particles of mass 174, 130, 102, and 76 were observed. No particle of mass 77 was detected: thus benzene, which would appear as the phenyl radical, was not formed. The decomposition path illustrated is consistent with these results.

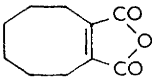


(*via* a strained planar form)

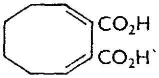




The course of catalytic hydrogenation of the dicarboxylic acid [(III), (IV)] was dependent on the catalyst employed. The use of 10% palladium–charcoal led consistently to the smooth uptake of 2·7 mol. of hydrogen. Further absorption was then very slow. The product was a 2 : 1 mixture of a colourless oil and a colourless solid. This oil was cyclo-oct-1-ene-1,2-dicarboxylic anhydride (VI). The mass spectrograph showed a single peak corresponding to the calculated mass of 180. The nuclear magnetic resonance spectrum of this anhydride in carbon tetrachloride ($SiMe_4 = 0$) showed two peaks at 1·65 and 2·65 p.p.m. in the ratio 2 : 1. The former is correlated with the grouping $-CH_2-CH_2^*-CH_2$ and the latter with $-CH_2-CH_2^*-C=$, in agreement with the assigned structure (VI). Attempts to prepare the corresponding acid gave only the anhydride.



(VI)



(VII)

The solid product, m. p. 245°, from the above hydrogenation was cyclo-octa-1,3-diene-2,3-dicarboxylic acid (VII). This assignment rests, *inter alia*, on elemental analysis,

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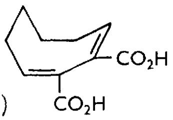
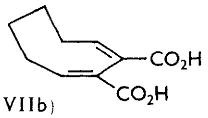
[10] Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 672.

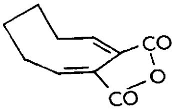
equivalent weight, and mass spectrographic determination of the molecular weight. Only one peak, corresponding to a mass of 178, appeared in the mass spectrum: this is the value calculated for the anhydride of acid (VII). Two conformations (a) and (b) for acid (VII) are possible, of which (b) can be shown by models to be somewhat the more strained.† The consequent supposition that acid (VII) exists mainly in conformation (a) is supported by its ultraviolet spectrum ($\lambda_{\text{max.}}$ 210 mμ; ε 12,500) which indicates little or no interaction between the ethylenic groups. The anhydride of acid (VII) which was evidently formed in the mass spectrometer was also formed when the acid was heated at 240° for five minutes under nitrogen. This anhydride, a sweet smelling oil, gave a nuclear magnetic resonance spectrum showing three peaks at 6·3, 2·65, and 1·65 p.p.m. in the ratio 1 : 2 : 2. These correspond to the features $=CH^*-CH_2-$, $=CH-CH_2^*-CH_2-$, and $-CH_2-CH_2^*-CH_2-$, respectively, and accord with the suggested structure. The skew angle of the carboxyl groups in conformation (VIIa) is *ca.* 80° and is zero in conformation (VIIb); so the anhydride might be expected to exist in a preferred conformation (VIII). This expectation is supported by the ultraviolet spectrum [$\lambda_{\text{max.}}$ 206, 255 (shoulder), 305 mμ; ε 14,000, 2800, 4000] which indicates a more extended conjugation in the anhydride (VIII) than in the parent acid (VIIa). The acid (VII) was recovered unchanged from an attempted hydrogenation at 50 atmospheres over palladium–charcoal. Cyclo-octenes seem to be generally abnormally resistant to hydrogenation; but this example of a resistant 1,3-diene seems most unusual.‡



(VIIa)



(VIIb)



(VIII)

Some early experiments in which Adams catalyst was used for hydrogenation of the dicarboxylic acid [(III), (IV)] led to the smooth uptake of 4 mol. of hydrogen. A micro-hydrogenator was employed, and no attempts were then made to isolate the reduced acid. Subsequent experiments have led to erratic results with this catalyst, as previously reported,[8] and only *ca.* 2·5—3·5 mol. of hydrogen tended to be consumed at a conveniently measurable rate. Despite much work, no satisfactory explanation for these variations in catalytic activity has emerged.

Acetylene.—Formation of cyclo-octatetraene by photoaddition of acetylene to benzene should in principle provide the simplest example of the present reaction. In practice, the only evidence for the formation of cyclo-octatetraene in this way came from an experiment in which acetylene was passed through an irradiated mixture of benzene and acetone at 52—56°. (No fulvene was formed,[11] although it was produced when acetone was omitted.) Examination of the products of b. p. >80·5° by gas chromatography indicated the presence of a trace of cyclo-octatetraene. The significance of this is doubtful as it would not be possible without isotopic labelling to distinguish between a photoaddition to benzene and the known phototetramerisation of acetylene.[12]

Phenylacetylene.—Irradiation of a solution of phenylacetylene in benzene gave phenylcyclo-octatetraene, 1-phenylazulene, and 1-phenylnaphthalene, together with other products still under investigation. The named products were separated by preparative gas-chromatography on silicone gum rubber. The azulene and naphthalene derivatives are dimers of phenylacetylene, and are further discussed below. Phenylcyclo-octatetraene

† Distortion of form (VIIb) can give rise to either form (VIIa) or its enantiomorph.

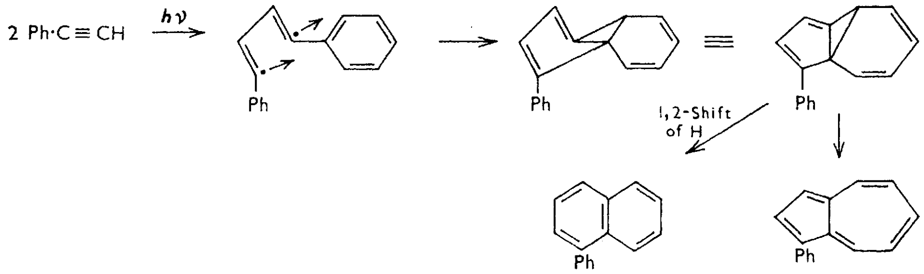
‡ The production of a 2 : 1 mixture of compounds (VI) and (VII) by hydrogenation demonstrates the existence of the parent acid in forms (III) and (IV); but nothing can be safely deduced from this ratio concerning the relative proportions of the forms or the ease of their interconversion.

[11] Angus, Blair, and Bryce-Smith, *J.*, 1960, 2003; cf. Blair and Bryce-Smith, *Proc. Chem. Soc.*, 1957, 287.

[12] Kuri and Shida, *Bull. Chem. Soc. Japan.*, 1952, **25**, 116; Kuri, *J. Chem. Soc. Japan.*, 1955, **76**, 944.

was identified through the known adducts with *p*-benzoquinone and silver nitrate, the absorption of 4 mol. of hydrogen on catalytic hydrogenation to give phenylcyclo-octane, and the identity of the ultraviolet and infrared spectra with those of authentic material prepared by Cope and Kinter's method.[13] Difficulty was experienced in the preparation of derivatives when the material was contaminated with 1-phenylnaphthalene.

Dimerisation of Phenylacetylene.—The formation of 1-phenylazulene and 1-phenylnaphthalene in the foregoing experiment was confirmed as arising from photodimerisation of phenylacetylene. Irradiation of phenylacetylene in cyclohexane gave these dimers in the same ratio (5 : 1), as in the experiment with benzene as solvent. 1-Phenylnaphthalene and 1-phenylazulene were found not to be interconvertible when irradiated separately in cyclohexane. Each compound was free from detectable amounts of nuclear isomers, so the dimerisation is evidently stereospecific. The annexed reaction path is suggested.



It can readily be shown that an initial *trans*-dimerisation could have led by corresponding steps to 2-phenylazulene and 2-phenylnaphthalene. Professor Büchi kindly informs the writers that he has observed the photodimerisation of tolan to 1,2,3-triphenylazulene and 1,2,3-triphenylnaphthalene, and the phototrimerisation to hexaphenylbenzene.[14] Triphenylbenzenes have not been found on irradiation of phenylacetylene in the present work. Assony and Kharasch's observation that tolan dimerises to 1,2,3-triphenylazulene under the influence of a mixture of 2,4-dinitrobenzenesulphenyl chloride and aluminium chloride [15] is relevant to these results, although it seems unlikely that there can be a common mechanism.

Mechanism of the Photoaddition of Acetylenes to Benzene.—The initial 1,2-addition of acetylenes to benzene had been expected in the light of previous evidence that maleic anhydride also undergoes a corresponding 1,2-addition; but the suggested intermediate bicyclo-octatriene is at present purely hypothetical. Several differences from the addition of maleic anhydride have been noted. Thus, photoaddition of maleic anhydride to benzene has recently been shown to involve photoactivation of an intermediate charge-transfer complex,[1] whereas the ultraviolet spectra of solutions of dimethyl acetylenedicarboxylate and phenylacetylene in cyclohexane, benzene, and cyclohexane–benzene mixtures reveal no absorption attributable to charge-transfer complexes. This unexpected result may imply that photoactivation of individual molecules of the reactants plays a greater part in the addition of acetylenes than in the addition of maleic anhydride. It may be significant that benzophenone, which photosensitises the addition of maleic anhydride to benzene,[16] inhibits the corresponding addition of dimethyl acetylenedicarboxylate.[1]

EXPERIMENTAL

The irradiation apparatus was the water-cooled form of that described in Part I; [17] quartz wool was used as in Part V.[1] Benzene was sulphur-free and was redistilled before use. Methyl

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[13] Cope and Kinter, *J. Amer. Chem. Soc.*, 1951, **73**, 3424.
[14] Büchi, private communication.
[15] Assony and Kharasch, *J. Amer. Chem. Soc.*, 1958, **80**, 5978.
[16] Schenck and Steinmetz, *Tetrahedron Letters*, 1960, No. 21, 1.
[17] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

propiolate was prepared essentially as described for dimethyl acetylenedicarboxylate,[18] an equivalent proportion of propiolic acid being used in place of the monopotassium salt of acetylenedicarboxylic acid

The nuclear magnetic resonance spectra were obtained with a Varian A-60 Mc. spectrometer.

Addition of Methyl Propiolate to Benzene.—Irradiation of methyl propiolate (5·0 g.) in benzene (140 ml.) under nitrogen for 20 hr. at 53° gave methyl cyclo-octatetraenecarboxylate (0·8 g.) as a yellow oil, b. p. 89°/0·4 mm., n_D^{25} 1·5388 (lit.,[9] 1·5398) (Found: C, 74·2; H, 6·5. Calc. for $C_{10}H_{10}O_2$: C, 74·0; H, 6·25%). This had the correct infrared spectrum.[9] Hydrolysis with N/200-sodium hydroxide gave cyclo-octatetraenecarboxylic acid, m. p. and mixed m. p. 72·5° (lit.,[9] 72·5°) (Found: equiv., 148. Calc. for $C_9H_8O_2$: equiv., 148). The ultraviolet and infrared spectra were superimposable upon those of authentic material prepared by carboxylation of cyclo-octatetraenyl-lithium.[9]

Addition of Dimethyl Acetylenedicarboxylate to Benzene.—Irradiation of dimethyl acetylenedicarboxylate (4·0 g.) in benzene (150 ml.) under nitrogen for 20 hr. at 50—55° gave dimethyl cyclo-octatetraene-1,2-dicarboxylate (2·0 g.) as a yellow solid, m. p. 109·5—110· ° [Found: C, 65·5; H, 5·45%; *M* (mass spectrograph), 220. $C_{12}H_{12}O_4$ requires C, 65·45; H, 5·5%; *M*, 220]. The infrared spectrum (Nujol mull) qualitatively resembled that of methyl cyclo-octatetraenecarboxylate. The main peaks were at 5·8s, 6·1w, 7·0s, 7·7m, 7·9s, 8·2m, 9·1m, 9·5s, 9·9w, 10·1w, 10·2w, 10·5w, 10·7w, 10·8w, 11·0w, 12·5s, 12·6m, 13·8s, 14·6s μ. Hydrolysis of this ester gave pale yellow cyclo-octatetraene-1,2-dicarboxylic acid, m. p. 207·5—208·5° (decomp.) (Found: C, 62·3; H, 4·2%; equiv., 95·5. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%; equiv., 96). The ultraviolet spectrum (in ethanol) had $\lambda_{max.}$ 208·8, 227, 300 mμ (shoulder) (log ε 4·21, 4·16, 3·10, respectively), and $\lambda_{min.}$ 220 mμ (log ε 4·14). The infrared spectrum, $\lambda_{max.}$ (Nujol mull) 3·8m, 3·95m, 5·9s, 6·15s, 7·05m, 7·8s, 8·3m, 9·0w, 9·6m, 9·9w, 10·3w, 10·8s, 11·9m, 12·4m, 12·7m, 13·3m, 13·9m, and 14·8s μ, broadly resembled that of cyclo-octatetraenecarboxylic acid. The mass spectrum of the acid showed peaks at 174 (corresponding to the anhydride), 130, 102, and 76.

The acid (0·68 g.) was heated with acetic anhydride (5 ml.) under reflux for 1 min. The resulting orange solution was poured into cyclohexane (100 ml.), to give a yellow pasty solid which when treated repeatedly with cyclohexane gave a yellow solid *substance* (0·6 g.) of indefinite m. p. (Found: C, 64·5; H, 4·77. Calc. for the cyclic anhydride, $C_{10}H_6O_3$: C, 68·9; H, 3·5%). More prolonged treatment with acetic anhydride gave only tar. Attempts to decarboxylate the acid by standard methods also gave only tars.

*Catalytic Hydrogenation of Cyclo-octatetraene-*1,2-*dicarboxylic Acid.*—The acid (0·788 g.) with 10% palladium–carbon (0·05 g.) in methanol (10 ml.) and water (1 ml.) absorbed 2·7 mol. of hydrogen in 2 hr.; absorption then virtually ceased. Removal of solvents, etc., gave a sweet-smelling paste (0·78 g.). Treatment with carbon tetrachloride (20 ml.) gave colourless *cyclo-octa-*1,3-*diene-*2,3-*dicarboxylic acid* (VII) (0·26 g.), m. p. 216—218°. Recrystallisation from water raised the m. p. to a constant 245° [Found: C, 60·5; H, 6·05%; equiv., 97·5. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%; equiv. (dibasic), 98·0]. The mass spectrum showed a single peak at 178 corresponding to the anhydride ($C_{10}H_{10}O_3$ requires *M*, 178). The ultraviolet spectrum in ethanol showed a single maximum at 210 mμ (log ε 4·1) and closely resembled those of maleic and fumaric acid. The infrared spectrum (Nujol mull) had principal maxima at 4·0s, 6·5s, 6·2s, 7·6s, 7·8s, 8·0m, 8·5w, 9·4w, 9·6w, 10·0w, 10·5w, 10·9m, 11·2m, 12·1m, 12·4w, 12·6m, 13·1m, 13·3w, and 13·7m μ. The acid, when heated at 240° under nitrogen, gave a distillate of *cyclo-octa-*1,3-*diene-*2,3-*dicarboxylic anhydride* (Found: C, 67·8; H, 5·7. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). Details of the nuclear magnetic resonance spectrum of this anhydride have been given in the main text. The ultraviolet spectrum in cyclohexane showed $\lambda_{max.}$ 206, 255 (shoulder), 305 mμ (log ε 4·15, 3·45, and 3·60, respectively), and $\lambda_{min.}$ 272 mμ (log ε 3·38).

Evaporation of solvent from the carbon tetrachloride extract of the hydrogenation products gave *cyclo-octene-*1,2-*dicarboxylic anhydride* as a colourless sweet-smelling oil [Found: C, 66·7; H, 6·75%; *M* (mass spectrograph), 180. $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·65%; *M*, 180]. The ultraviolet spectrum in 0·1N aqueous sodium hydroxide showed $\lambda_{max.}$ 218 mμ (log ε 4·0). The infrared spectrum had principal maxima at 3·5s, 5·5s, 5·7s, 6·1m, 7·0s, 7·1m, 7·4w, 7·8s, 8·0s, 8·3m, 8·5m, 8·7w, 9·1w, 9·4w, 9·6m, 9·7m, 10·4m, 10·8s, 11·0s, 11·3m, 11·8m, 12·5w, 12·9w, 13·2m, 13·4s, 13·7s, 14·5w μ. The nuclear magnetic resonance spectrum has been given

[18] *Org. Synth.*, **32**, 55.

in the main text. The corresponding acid could not be obtained as it appeared spontaneously to form the anhydride. Thus, acidification of a well-cooled solution of the anhydride in aqueous sodium hydroxide re-formed the anhydride as an insoluble oil (infrared spectrum).

Irradiation of Acetylene in Benzene–Acetone.—A slow current of dry acetylene was passed through an irradiated mixture of benzene (50 ml.) and acetone (110 ml.) at 52—56° for 29 hr. Distillation of the orange-yellow product showed the absence of fulvene. A pale yellow fraction of camphoraceous odour, b. p. 100—150° (0·2 g.), was collected. Gas-chromatography (5% of dinonyl phthalate on Celite) indicated the presence of *ca.* 1% of cyclo-octatetraene in this fraction.

Addition of Phenylacetylene to Benzene: Dimerisation of Phenylacetylene.—A solution of phenylacetylene (4·7 g.) in benzene (130 ml.) was irradiated for 20 hr. at 40° under nitrogen. A strong initial fluorescence soon disappeared, and the final solution was brown. The products from four such experiments were combined.

Benzene and most of the unchanged phenylacetylene were removed by fractional distillation under a reduced pressure of nitrogen. The residual oil was shaken vigorously with cyclohexane (150 ml.) to give a green solution and a brown insoluble solid (3·0 g.). The green solution was chromatographed on alumina (Brockmann activity 2). Elution with cyclohexane gave fractions (i) (colourless), (ii) (yellow), and (iii) (deep blue). Fraction (i) contained unchanged phenylacetylene (ultraviolet and infrared spectra). Fraction (ii) was evaporated under nitrogen to give a yellow oil (0·55 g.). This was separated by preparative gas-chromatography on silicone gum rubber (programmed from 175° to 225°) into two products (A and B) which were collected in a by-pass to the detector. The more volatile product A (0·2 g.) was phenylcyclo-octatetraene, a yellow oil of characteristic odour (Found: C, 93·4; H, 6·25. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·65%). The infrared and ultraviolet spectra were identical with those of authentic material.[13] It was demonstrated that the authentic material was stable under the conditions used for the separation. The silver nitrate adduct had m. p. and mixed m. p. 146° (decomp.) [lit.,[13] 146° (decomp.)] (Found: C, 48·0; H, 3·35. Calc. for $C_{14}H_{12}AgNO_3$: C, 48·0; H, 3·45%). The adduct with *p*-benzoquinone had m. p. and mixed m. p. 171°. (The recorded value is 192—192·5°.[13] An authentic specimen prepared exactly as reported had an initial m. p. 191—192°. After recrystallisation from ethanol, the m. p. fell to 171°, and was unchanged at this figure after further recrystallisation. This seems to be a case of dimorphism.) Catalytic hydrogenation of material A (10% palladium–charcoal) proceeded at the same rate as that of authentic phenylcyclo-octatetraene with the consumption of 4·0 mol. of hydrogen, and the formation of phenylcyclo-octane, m. p. and mixed m. p. 8° (lit.,[13] 8°), having the correct infrared spectrum.

Product B, an almost colourless oil, was 1-phenylnaphthalene (0·21 g.) (Found: C, 94·0; H, 6·0. Calc. for $C_{16}H_{12}$: C, 94·1; H, 5·9%). The ultraviolet spectrum was identical with that reported [19] and was further checked against that of authentic material. The absence of 2-phenylnaphthalene was clearly shown: the 1- and the 2-isomer differ markedly in their ultraviolet spectra. The infrared spectrum was identical with that of authentic 1-phenylnaphthalene. Mixtures of material B with authentic 1-phenylnaphthalene were not resolved on a range of gas-chromatograph columns.

The blue fraction (iii) was re-chromatographed as above, and a middle fraction of eluted material was collected. Cyclohexane was removed under reduced pressure of nitrogen to give 1-phenylazulene (1·2 g.) as a blue oil (Found: C, 93·9; H, 6·1. Calc. for $C_{16}H_{12}$: C, 94·1; H, 5·9%). The ultraviolet,[20] visible,[20] and infrared [21] spectra were identical with those previously reported. The series of maxima in the visible spectrum has been shown by Plattner *et al.*[20] to be very characteristic of the 1-isomer, and no trace of maxima characteristic of other nuclear isomers was perceptible.

Irradiation of phenylacetylene (2·0 g.) in cyclohexane (100 ml.) under nitrogen at 60° for 2 hr. gave by procedures similar to those detailed above 1-phenylnaphthalene (0·04 g., 2%) and 1-phenylazulene (0·2 g., 10%).

Irradiation of 1-phenylnaphthalene (0·2 g.) in cyclohexane (100 ml.) under nitrogen at 60° for 2 hr. produced no detectable chemical change.

Irradiation of 1-phenylazulene (0·2 g.) in cyclohexane (100 ml.) under nitrogen at 60° for

[19] Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

[20] Plattner, Gordon, and Zimmermann, *Helv. Chim. Acta*, 1950, **33**, 1910.

[21] Arnold and Pahls, *Chem. Ber.*, 1956, **89**, 121.

2 hr. gave a green solution from which 1-phenylazulene (0·15 g.) was recovered. An ill-defined brown substance, apparently polymeric, was formed, but no trace of 1-phenylnaphthalene was detected.

Ultraviolet Spectrum of Dimethyl Acetylenedicarboxylate in the Presence of Benzene.—The ultraviolet spectra of dimethyl acetylenedicarboxylate in benzene, and in cyclohexane containing 0·4% or 0·1% of benzene over the ranges 280—350, 225—350, 200—350 mμ, respectively, were identical with those of solutions in pure cyclohexane, absorption due to benzene being compensated in the reference beam of the spectrometer: $\lambda_{max.}$ 205, 215 (shoulder), 225 mμ (shoulder); log ε 3·77, 3·67, 3·54, respectively; absorption was negligible at wavelengths longer than 300 mμ.

Similar solutions of phenylacetylene showed corresponding behaviour.

Solutions of naphthalene and anthracene in the colourless dimethyl acetylenedicarboxylate had faint yellow colours suggestive of the presence of charge-transfer complexes; but the colours were much less intense than those of liquid mixtures of maleic anhydride and these hydrocarbons.

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