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THE PHOTO-ADDITION OF DIPHENYLACETYLENE TO THREE PHENANTHRENE AND THE PHOTO-DIMERISATION OF 4H-CYCLOPENTA[d,e,f]PHENANTHRENE

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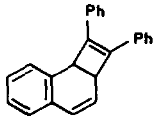
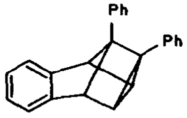
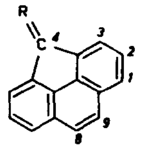
Although bicyclo[4.2.0]octa-2,4,7-trienes have been postulated as intermediates in the light-induced additions of several acetylenes to benzenes (1,2,3,4) and of diphenylacetylene (DPA) to naphthalenes (5,6,7) they have not been detected in such reactions. Under the conditions of the benzene-acetylene additions simple bicyclo[4.2.0]octa-2,4,7-trienes rearrange thermally to the isomeric cyclo-octatetraenes (8), and although the benzobicyclo[4.2.0]octatriene (I), the probable precursor of the naphthalene-DPA adduct (II), is thermally stable up to ca. 150°, it cyclises photochemically under the conditions of the naphthalene-DPA additions to give the adduct (II) quantitatively and no evidence for the formation of (I) in these reactions has been found (6). We now report that the photo-addition of DPA to phenanthrene, 2-methylphenanthrene, and 4H-cyclopenta[d,e,f]phenanthrene (III) gives the 2,3,4,5-dibenzobicyclo[4.2.0]octa-2,4,7-trienes (IV), (V), and (VI), respectively. We also record the formation of the photo-dimer (VII) from (III), an example of the photo-dimerisation of a phenanthrene derivative which is not substituted in the 9-position (cf. 9).



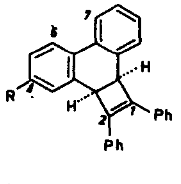
(I)



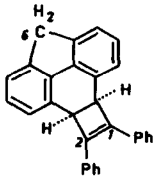
(II)



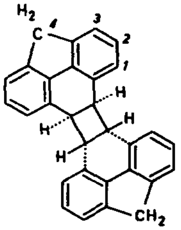
(III; R: H,H)
(VIII; R: O), (IX; R: OH,H)



(IV; R: H) (V; R: Me)



(VI)



(VII)

A solution of phenanthrene (9g) and DPA (1g) in cyclohexane (100 ml) was degassed at its boiling point (7) and irradiated in a pyrex reactor at 30-40° in an atmosphere of "oxygen-free" nitrogen with a Philips HPK lamp (125 W)(7). After 78 hours the reaction mixture was chromatographed on alumina to give starting materials (*ca*. 90%) and a fraction (0.1g), which was eluted by light petrol-benzene (10:1). On crystallisation from methanol it gave colourless plates (0.05g), m.p. 178-179°(10), to which we assign the structure (IV) on the basis of its spectral properties. In particular, its mass spectrum [m/e (% relative abundance): 356 (10; (molecular ion), 279(11) 278(8), 179(20), 178(100), 152(30), 151(29), 149(8); other peaks less than 5%] is analogous to that of (I) [and (II); *cf*. (7)] and its u.v. and p.m.r. spectra show that the addition occurred at the 9,10-double bond. [$\lambda_{max}^{95\%\ EtOH}$ (ε) at 264 (38,000), and 311 mμ (10,300) and a shoulder at 296 mμ (16,000). δ^{CDCl_3} : singlet at 4.68 (2 H, cyclobutene-*H*), and multiplets at 7.1-7.3 (16 H, Ar*H*, and at 7.85-8.05)(2 H, *H*-6, *H*-7)].

2-Methylphenanthrene and DPA were treated similarly to give after crystallisation from benzene-ethanol colourless plates (0.03g), m.p. 168-170°(10), of the adduct (V)[m/e 371(13), 370(45; molecular ion), 192(100), 190(15), 189(20), 178(27), 176(123), 165(11); other peaks less than 6%); $\lambda_{max}^{95\%\ EtOH}$ (ε) at 266-268 (40,200), and at 313 mμ (11,000), and a shoulder at 299mμ (16,600). δ^{CDCl_3} : singlets at 2.27 (3 H, 4-CH_3) and at 4.63 (2H, cyclobutene-*H*); multiplets at 7.0-7.4 (15 H, Ar*H*), and at 7.75-8.0(2 H, *H*-6, *H*-7(11)].

4*H*-Cyclopenta[d,e,f] phenanthrene (III)(2.96g) and DPA (0.9g) in cyclohexane (50 ml) were degassed at room temperature [*cf*.(7)] and irradiated for 72 hours. Chromatography on silicic acid (30:1) gave starting materials (*ca*. 90%) and, on elution with petrol-benzene, a fraction (0.17g) containing compounds (VI) and (VII) in the approximate ratio 2:1.5 (p.m.r. spectrum). Elution with benzene-chloroform (1:1) gave 4,5-phenanthrylene ketone (VIII) (0.05g), m.p.170° [lit, m.p. 170°(12)] [m/e: 204(100; molecular ion), 176(30), 150(63); $\nu_{max}^{CHCl_3}$ 1700 cm^{-1}(C=O); δ^{CDCl_3} : multiplet at 7.35-7.9 (6 H, Ar*H*)(13), and a singlet at 7.67 (2 H, *H*-8, H-9)] and the corresponding carbinol (IX)(0.04g), which separated from ethanol as colourless prisms, m.p.188-190°(10)[m/e: 207(16), 206(100; molecular ion), 205(73), 189(16), 177(23), 176(25), 151(9), 103(7), 87(18): other peaks less than 7%. $\nu_{max}^{CHCl_3}$ 3600, 3300-3400 cm^{-1} (O-H). δ^{CDCl_3}: broad singlet at 6.17 (1 H, C(4)-*H*), which sharpened on addition of D_2O, and a multiplet at 7.4-7.9 (8 H, Ar*H*)(14). The mixture of (VI) and VII) was chromatographed on dry silicic acid to give (VI)(0.04g), colourless needles from acetone/alcohol, m.p. 190-192°(10)(m/e: 368(19); molecular ion), 202(4), 191(17), 190(100), 189(30), and 178(8); other peaks less than 4%). $\lambda_{max}^{95\%\ EtOH}$ (ε) at 264-268 mμ(39,200), a point of inflection at 296 mμ (19,000), and a shoulder at 312 mμ(10,500). δ^{CDCl_3}: singlets at

3.92 (br)(2 H, H_2-6) and 4.87 (2 H, cyclobutene-H, and a multiplet at 7.1-7.6 (16 H, ArH). Compound (VII) was obtained more simply by irradiation of (III) (3.8g) in the absence of DPA in cyclohexane or ethanol when it separated as colourless plates, m.p. 304-305° (50% yield after 24 hours). An analytical sample, m.p. 304-305°(10) was crystallised from benzene-ethanol. Its dimeric nature is demonstrated by its mass spectrum [significant peaks at m/e 380(0.1; molecular ion), 374(0.80), 190(100), 163(4), 149(10), and 95(20)]. Bond formation between C-8 and C-9 is suggested by the u.v. spectrum($\lambda_{max}^{CH_2Cl_2}$ (ε) at 274 mμ (36,000), a point of inflection at 285 mμ (25,000), and shoulders at 303 (4,000) and at 313 mμ (7,000))and by its p.m.r. spectrum (δ^{CDCl_3}: singlet at 3.95 (br.) (4 H, C(4)-H_2 and C(4')-H_2) and at 4.20 (4 H, cyclobutene-H), and a multiplet at 7.1-7.4 (12 H, ArH). This conclusion is confirmed by the failure of (VII) to undergo oxidation with cold potassium permanganate or reduction with hydrogen-palladium/carbon, and by its quantitative conversion to (III) on being heated at its m.p. for 3-5 minutes. The similarity of the methylene signals in the p.m.r. spectra of (VII), (VI), and (III) [singlet (br.) at 3.95 (2 H, C(4)-H_2)] appears to rule out any shielding of the methylene groups in (VII), possibly suggesting that the dimer is a trans-cyclobutane as shown in (VII)[cf. (9)]. We attribute the formation of bicyclo[4.2.0]octatrienes in the phenanthrene-DPA additions to two factors. Firstly, the direct excitation of the adducts (IV), (V), and (VI), which might lead to further photochemical changes, cannot occur to any extent during the photo-additions because these compounds absorb light only at shorter wavelengths than those of the ^1L_b band systems of the phenanthrenes which are present in more than 500-fold molar excess. By comparison, the benzobicyclo[4.2.0]octatriene (I) has a broad absorption maximum which extends beyond the ^1L_b band of naphthalene.

Secondly, thermal rearrangements of the adducts (IV), (V), and (VI) can be excluded as these compounds are thermally even more stable than the benzo-derivative (I)[e.g., (VI) is not affected by being heated at 210° for 10 minutes (cf. (6)]. Formally, the thermal rearrangement of a bicyclo[4.2.0]octa-2,4,7-triene to the isomeric cyclo-octatetraene can be regarded as the isomerisation of a cyclobutene to the corresponding butadiene, or as the rearrangement of a cyclohexadiene to the related hexatriene but provided that the process is concerted the stereochemistry of the reactants demands the latter course (15). On this basis the thermal isomerisation of the dibenzobicyclo[4.2.0]octatrienes (IV), (V), and (VI) to the corresponding dibenzocyclo-octatetraenes would require the conversion of the Kekulè structures of the annellated benzene rings into a quinonoid system, a pathway that would require more energy than is needed for the corresponding isomerisation of the benzobicyclo[4.2.0]octatriene (I)(16).

Compared to the naphthalene-DPA additions (5,7) the efficiencies in the phenanthrene additions are very low but this is consistent with the previously proposed mechanism (7,17) of the naphthalene-DPA addition, of which the key step is the formation of an excited complex between the aromatic hydrocarbon in its first excited singlet state and the acetylene in its ground state. As the separation between these energy levels is greater with phenanthrenes than with naphthalenes excited complex formation should be less favoured.

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10. Satisfactory microanalytical data have been obtained for this compound.
11. This multiplet contains a doublet centered at 7.85 p.p.m. (J= 8.5 Hz), which can be assigned to H-6
12. H. Medenwald, Chem. Ber., 86, 287 (1953).
13. This multiplet consists of three doublet of doublets. The apparent line positions (arithmetical mean values), splitting patterns, and our tentative assignments are as follows: 7.45 p.p.m. (7.5 and 6.8 Hz; H-2, H-6); 7.72 p.p.m. (6.8 and 1.4 Hz; H-1, H-7); and 7.82 p.p.m. (7.5 and 1.4 Hz; H-3, H-5).
14. This includes a prominent singlet at 7.76 p.m. which is assigned to H-8 and H-9.
15. R.B. Woodward and R. Hoffman, J.Amer.Chem.Soc., 87, 395 (1965).
16. This argument was suggested to one of us by Professor Dr. R. Huisgen to account for the increased stability of (I) compared to that of bicyclo[4.2.0]octa-2,4,7-triene.
17. R.J. MacDonald and B.K. Selinger, Tetrahedron Letters, 4791 (1968)