Tetrahedron Letters No.14, pp. 1689-1693, 1968. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND PHOTO-ISOMERISATION OF 7,8-DIPHENYL-2,3-BENZOBICYCLO[4.2.0]OCTA-2,4,7-TRIENE AND 4,5-DIPHENYLBENZOCYCLO-OCTATETRAENE

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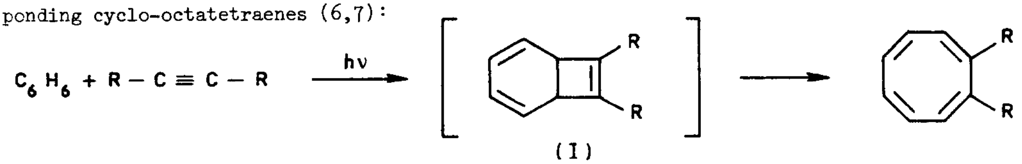
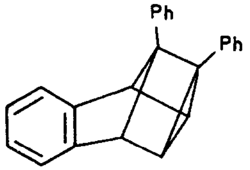
(Received in UK 18 December 1967)

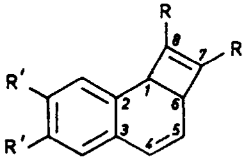
Derivatives of bicyclo[4.2.0]octa-2,4,7-triene (I) have been invoked as intermediates in the light-induced formation of cyclo-octatetraenes from certain acetylenes and benzene (1,2,3) or benzonitrile (4) as well as in the photochemical synthesis of 1:1 adducts [e.g., (II)] from tolan (diphenylacetylene) and naphthalenes (5). In the context of benzene-acetylene photo-additions this concept appears to be consistent with the properties of the valence tautomerism that links simple derivatives of bicyclo[4.2.0]octa-2,4,7-triene with the corresponding cyclo-octatetraenes (6,7):



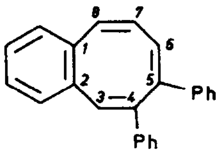
(I)



(II)



(III) R=Ph—; R'=H—.
(VI) R=H ; R'=CH_3OOC—.



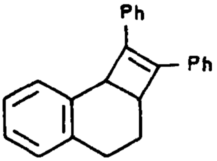
(IV)

However, the suggestion that the naphthalene-tolan photo-adduct (II) is formed by intramolecular photo-cyclisation of the intermediate bicyclo-octatriene (III) (5) does not account for the difference in the outcome of photo-additions of acetylenes to benzenes and to naphthalenes unless additional assumptions are made. Thus, one could postulate that the photocyclisation (III) ⟶ (II) is so fast that the thermal isomerisation (III) ⟶ (IV) cannot compete; or, if it did, one could assume that (IV) undergoes rapid photocyclisation to give (II). The results now recorded indicate that the first of these assumptions is fulfilled. However, the benzocyclo-octatetraene (IV) has been obtained from (II) and (III) at higher temperatures and has been found to form the adduct (II) exclusively on irradiation.

The present work rests on the finding that the benzobicyclo [4.2.0] octa-2,4,7-triene (III) and the benzocyclo-octatetraene (IV) are formed in the thermolysis of the naphthalene-tolan photo-adduct (II). In these experiments the best yields were obtained when degassed samples of (II) (up to 1 g) were heated at 220° for ten minutes. Under these conditions two isomers are formed in 70 and 20% yield, respectively. These hydrocarbons were separated by crystallisation and by chromatography on alumina, which had been impregnated with silver nitrate (10% w/w). On the basis of the following evidence we assign to the main product the structure (III); the other hydrocarbon is suggested to be 4.5-diphenyl-benzocyclo-octatetraene (IV).

7,8-Diphenyl-2,3-benzobicyclo [4.2.0] octa-2,4,7-triene (III)(8,9) separated from methanol in colourless needles, m.p. 98-98.5°. The mass spectrum of (III), which established its molecular weight as 306, closely resembled that of the adduct (II). In particular, intense peaks occurred at m/e 178 (tolan) and 128 (naphthalene). The ultraviolet spectrum of (III) (in 96% ethanol) exhibited a broad, unsymmetrical maximum at 262-266 mμ(ε 19,000) with a shoulder at 293-295 mμ(ε 12,000). In the p.m.r. spectrum of (III) (10) a multiplet between 7.0 and 7.6 p.p.m. accounted for fourteen aromatic protons. The four non-aromatic protons gave rise to an ABCD system. This agreed within experimental error with the theoretical ABCD spectrum that was computed from the following parameters: H-1, 4.48 p.p.m.; H-6, 4.07 p.p.m.; H-5, 6.18 p.p.m.; H-4, 6.30 p.p.m.; $J_{1,6}$ = 5.0 c/s; $J_{5,6}$ = 4.2 c/s; $J_{6,4}$ = -1.1 c/s; and $J_{4,5}$ = 9.9 c/s. These data provide convincing support for the structural assignment. The coupling between H-4 and H-5 and their chemical shift positions agree with values obtained for olefinic protons in a related dihydronaphthalene (11). The vinylic and allylic coupling constants ($J_{5,6}$ and $J_{6,4}$, respectively), are in accord with the empirical relationships developed by Garbisch, Jr. (dihedral angle between the protons attached to C-5 and C-6 ca.60°)(12), and the value of $J_{1,6}$ lies in the range observed with the corresponding protons in cyclobutenes (13).

Chemical support for the structure (III) was obtained by catalytic hydrogenation in the presence of palladium-on-carbon (ambient temperature and pressure). Uptake of one mole of hydrogen gave the hydrocarbon (V)(8), which separated from methanol in colourless prisms, m.p. 108-109°. Its p.m.r. spectrum exhibited a multiplet between 6.8 and 7.6 p.p.m.



(V)

(14 protons), a doublet at 4.15 p.p.m. (1 proton; J = 4.5 c/s), a multiplet between 3.6 and 3.85 p.p.m. (1 proton) and another multiplet between 1.3 and 2.9 p.p.m. (4 protons). The conclusion that the unsubstituted double bond in (III) had been reduced was confirmed by the ultraviolet spectrum of (V) (λ_{max} 294-295 mμ, ε 14,200) and by the mass spectrum, the most intense peaks of which occurred at m/e 130 (naphthalene and two protons) and 178 (tolan). Continued hydrogenation gave an oily hydrocarbon (molecular ion m/e 310) which was transparent at wavelengths greater than ca. 285 mμ.

4,5-Diphenylbenzocyclo-octatetraene (IV) (8) crystallised from methanol in colourless needles, m.p. 94-95°. The base peak in its mass spectrum was the molecular ion peak (m/e 306). Fragmentation paths, which were prominent, included the loss of 26, 77, 102 (phenyl-acetylene), 128 (naphthalene), and 178 (tolan). The ultraviolet spectrum of (IV) consisted of a broad, ill defined maximum 252-258 mμ(ε29,000), which extended towards longer wavelengths (ε 3,900 at 300 mμ; ε 200 at 340 mμ). The p.m.r. spectrum of (IV) exhibits a multiplet (15 protons) between 6.9 and 7.4 p.p.m., which is assigned to the 14 aromatic protons and the proton at C-3. A doublet of doublets (one proton) is centered at 6.20 p.p.m. (separation 11.0 and 3.3 c/s), and two doublets, each corresponding to one proton, centered at 6.38 and 6.60 p.p.m., respectively (separation 3.3 and 11.0 c/s, respectively). The complete analysis of this spectrum is in progress but it is clear that the apparent chemical shift positions and coupling constants are consistent with the pattern to be expected from the protons at C-6, C-7 and C-8 in structure (IV). On catalytic hydrogenation (IV) took up three moles of hydrogen (9). The product appeared to be homogeneous (gas chromatography) but it could not be crystallised, possibly because of the presence of stereoisomers.

Attempts to improve the yields of (IV) by heating the adduct (II) or the bicyclo-octatriene (III) either for periods longer than ten minutes (at 220°) or at temperatures above 220° failed, possibly because of the formation of another product under more forcing conditions. This compound is being examined currently.

The adduct (II) and the bicyclo-octatriene (III) isomerise already at 170° (80-90% conversion of (II) to (III) after 10 hours; 30-40% conversion of (III) to (IV) after 100 hours) but (III) was not detectably changed after being kept at 120° for 19 hours. At this temperature the benzobicyclo-octatriene (VI) has been reported to rearrange to the corresponding benzocyclo-octatetraene (14). This comparison shows that the thermal stability of (III) is related to the presence of the annellated benzene ring and the stilbene moiety.

Irradiation of solutions (in cyclohexane) of either the bicyclo-octatriene (III) or the benzocyclo-octatetraene (IV) in Pyrex tubes with an external Philips HPK 125 W lamp gave the adduct (II) in quantitative yield. These reactions are fast compared to the formation of the adduct (II) from its components and under the conditions used for the intramolecular cyclisations the formation of the adduct (II) from naphthalene and tolan could not be detected. The presence of naphthalene and tolan did not interfere with the formation of (II) from (III). These facts account for the failure to detect the bicyclo-octatriene (III) among the products of the irradiation of mixtures of naphthalene and tolan, even on a preparative scale (20 g).

At intermediate stages of the cyclisation of (IV) the presence of ca. 10% of the bicyclo-octatriene (III) was established by p.m.r. spectroscopy. Therefore at least part of the cyclo-octatetraene (IV) is converted to the adduct (II) by way of the bicyclo-octatriene (III). Irradiation of either (III) or (IV) in quartz tubes gave mixtures containing naphthalene and tolan (gas chromatography). The photo dissociation of (IV) and the formation of (III) from (IV) are reminiscent of the photochemistry of other cyclo-octatetraenes (15,16).

Although other pathways cannot at present be excluded, the results obtained are entirely consistent with the proposal that the naphthalene-tolan photo-adduct (II) is formed by way of the benzobicyclo-octatriene (III)(5). If this hypothesis is accepted, the difference in the products formed in the photo-additions of acetylenes to benzenes on the one hand, and of tolan to naphthalenes on the other, can be related to the thermal stability of the diphenylbenzobicyclo-octatriene (III) relative to that of simpler bicyclo-octatrienes, e.g., (I).

A full account of this work and its extension to substituted naphthalene-tolan photo-adducts will be given elsewhere.

Acknowledgment - We thank Dr. S. Sternhell for computing facilities, Dr. J.S. Shannon for mass spectra, and Miss P.E. Rosevear for ultraviolet spectra.

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9. All new compounds described were characterised by their mass spectra, recorded with an Atlas CH-4 mass spectrometer.
10. All p.m.r. spectra were recorded at concentrations of 10-15% in carbon tetrachloride with a Varian A-60 spectrometer. Chemical shifts are given as p.p.m. against TMS as internal standard.
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