Benzene Isomers from the Thermal Rearrangement of Hexa-1,5-diyne

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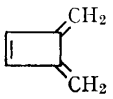
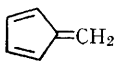
THE thermal rearrangement of hexa-1,5-diyne at 350° to give 3,4-dimethylenecyclobutene (I) in 85% yield was described by Huntsman and Wristers.[1] We have effected the rearrangement at 380° and report that a mixture of (I), fulvene (II), and benzene is produced, and at 420° benzene is the sole isolable product. Similarly (I) is converted into benzene at 400°. We also report the n.m.r., vapour-phase ultraviolet, and more highly resolved[2] infrared spectra of (I).



(I)



(II)

The thermal rearrangements of the diyne at 380° and 420° were effected using the procedure described by Huntsman and Wristers,[1] though with reduced nitrogen flow rates (~80 ml./hr). At 380° an intractable tar (~40%) condensed at room temperature and the products were carried over and condensed at −40° and −78°. The n.m.r. spectrum of the mixture exhibits bands at τ 2·84, due to benzene, at τ 3·28, 5·23, and 5·33 due to (I) and τ 3·66, 3·87, and 4·30 due to (II).[3] Broad low-intensity absorption occurred between τ 7·0 and 9·2, due to unidentified impurities. The v.p.c. trace of the mixture exhibited three major and two minor bands. In the cases of benzene and (I) assignment was made on the basis of retention times compared with authentic specimens. The components are benzene (50%), (I) (25%), (II) (20%), and unidentified product (5%). The ratio of products is sensitive to temperature change [*e.g.*, at 390° the yields are benzene (70%), (I) (20%), and (II) (5%)].

The rearrangement of the diyne at 420° and of (I) at 400° gave rise to benzene (50%) and an intractable tar. As expected, the rearrangement of (I) compares with the rearrangement of dimethylenebenzocyclobutene to naphthalene.[4]

The n.m.r. spectrum of (I) exhibits bands at τ 5·30 and 5·41 (exomethylene protons) and τ 3·16 (ring protons). It is suggested that the relatively low-field absorption of the ring methines (cyclobutene, ring methine protons τ 4·05[5]) might be attributed to the anisotropy of the carbon atoms[6] and not to the induced π-electron circulation (*cf.*, fulvene, ring protons τ 3·56 and 3·89, exomethylene protons τ 4·22, and Kitahara's[7] discussion on the virtual absence of ring currents in fulvene derivatives). The high-field exomethylene absorptions compare with those presented by Griffin and Peterson[8] for a number of dimethylenecyclobutene derivatives, and are indicative of olefinic character. A more detailed discussion of these effects will be presented shortly.

The vapour-phase ultraviolet spectrum of (I) determined at 50 microns of Hg pressure (10 cm. cell), exhibits maxima at 204·8 mμ (log ϵ, 5·0), 212·6 mμ (log ϵ, 4·8), and 240·2 mμ (log ϵ, 4·2).

The infrared spectrum of pure (I) (b.p. 72°/759 mm. Hg) determined at 7 cm. pressure (10 cm. cæsium iodide cell) exhibits more—and sharper—bands than the previously published spectrum.[2*] On standing, a strong band at 1090 cm.$^{-1}$ and a medium band at 610 cm.$^{-1}$ appear as a result of polymer formation.

Detailed theoretical, vacuum-ultraviolet, high-resolution infrared, and microwave-spectroscopic studies of (I) and (II) are at present in progress. It is also hoped to extend the thermal rearrangement of substituted diynes to yield corresponding fulvene derivatives.

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* Absorption bands exhibited at 3322 (v.w.), 3098 (s), 3000 (s), 1840 (w), 1820 (w), 1810 (w), 1770 (m), 1755 (m), 1705 (s), 1692 (s), 1665 (s), 1659 (s), 1432 (w), 1415 (w–m), 1405 (w), 1381 (w), 1370 (w), 1245 (s), 1055 (m), 1045 (m), 880 (s), 866 (s), 853 (s), 791 (s), 777 (m–s), 685 (m), 670 (m–s), 660 (m) cm.$^{-1}$

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