Formation of Benzene and Fulvene through the Bicyclo[3,1,0]hex-2-ene Diradical

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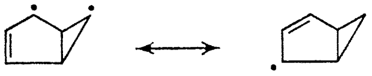
IT has been suggested[1,2] that the intermediate involved in the photoisomerization of benzene to fulvene is a singlet diradical with structure (I):



(I)

Both benzene and fulvene[‡] are formed in the reaction of carbon atoms with cyclopentadiene,[3] apparently through an intermediate having the same configuration as that suggested in the photochemical work.

Free carbon atoms in the form of ^{11}C (half-life 20·5 min.) were produced by nuclear recoil techniques.[4,5] The products were separated and analyzed by means of radio-gas chromatography and identified by comparison with known compounds.[6] The effect on the product spectrum was investigated for changes in pressure and phase, scavenging by oxygen, and moderation of the kinetic energy of the carbon atoms with inert gases (Table).[5]

The principal reactions of the carbon atom with unsaturated hydrocarbons are addition to C=C bonds and insertion into C–H bonds.[5] Since the carbon atoms may be in either

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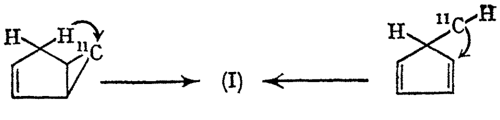
[‡] Benzvalene (tricyclo[3,1,0,$0^{2,6}$]hex-3-ene), which has been detected in the photochemical studies, is not expected to survive the chromatographic analysis used in the carbon atom studies (H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, 1968, **90**, 1085).

a singlet or a triplet state, the resulting adducts may have either multiplicity. Two of the intermediates which will be formed in the cyclopentadiene case[3] are (II) and (III):



(II) (III)

Because the reactions leading to these species are highly exothermic, the adducts will be in excited vibrational states. The subsequent simple rearrangements to (I), indicated by the arrows, are thus expected to be easy. Additional driving force for the isomerization is available, owing to the resulting relocalization of one of the electrons.

If intermediate (I) is formed from a singlet precursor, it may then isomerize, *e.g.* to fulvene, or undergo a transition to the $^1A_{1g}$ ground state of benzene. On the other hand, a triplet intermediate will not form benzene directly, since the difference in the symmetry properties of the intermediate and the closest lying triplet state of benzene prevents a favourable adiabatic transition.[1,2] It has been postulated, however, that the triplet is in dynamical equilibrium with the singlet intermediate.[1] Through this pathway the triplet adducts formed in the carbon atom reactions may also lead to formation of benzene. The reduction of the benzene yield when oxygen is added to the system is consistent with the suggestion that a part of the benzene is formed by a mechanism involving a triplet intermediate. The effect is particularly marked in the moderated system where the initial triplet adducts, being formed with less energy, are less prone to fragmentation and where the triplet to singlet carbon atom ratio may be higher.[7] While the possibility cannot be excluded that oxygen is reacting with the singlet diradical itself, oxygen had no effect on the quantum yield for benzene disappearance in the photochemical system.[8]

The contribution to the fulvene yield from isomerization of intermediate (I) is difficult to determine. Fulvene may alternatively be formed from a singlet adduct of type (III) by a simple hydrogen atom shift, in contrast to benzene formation where no such direct rearrangement is possible. The yield is substantially larger in the high-pressure gas-phase experiments than is expected from the photochemical results, where no fulvene was detected from irradiation of a 0·1 cm. benzene–20 cm. propane sample.[8,§] This difference, however, may reflect merely that the diradical is more highly excited in the carbon atom case.

The changes in the fulvene yield with changes in pressure and addition of oxygen are in qualitative agreement with photolysis measurements on the steady state concentration of fulvene.[8,9] The yield is enhanced by the addition of oxygen and goes through a maximum with increasing pressure, if one considers the condensed phase results comparable to high pressure studies. The most straightforward explanation of these effects is that fulvene is formed in a high vibrational state and is sensitive to reaction by radicals which are eliminated by the addition of oxygen.[6,8] Thus, while these changes give some information about the fate of the fulvene molecule once it is formed, little is indicated about the intermediate involved in its formation.

Benzene and fulvene yields from the reaction of ^{11}C *and cyclopentadiene*(CPD)[3,6]

	Product yield[a] (% of total volatile yield) Benzene	Fulvene	Total volatile yield[a,b]
CPD (30 cm.)	17·4 ± 1·6	5·2 ± 1·3	0·53 ± 0·02
CPD (1 cm.)	14·4 ± 0·7	<0·9	0·55 ± 0·11
CPD (30 cm.), O_2 (2 cm.)	14·0 ± 1·4	5·8 ± 0·6	0·56 ± 0·06
CPD (4 cm.), Ne (76 cm.)	30·7 ± 2·8	<2·0	0·36 ± 0·03
CPD (3·8 cm.), O_2 (0·2 cm.), Ne (76 cm.) ..	16·0 ± 2·0	3·4 ± 0·5	0·36 ± 0·03
CPD (liquid, 25°)	19·1 ± 1·4	4·2 ± 0·9	c
CPD (solid, −195°)	21·3 ± 0·8	3·6 ± 0·3	c

[a] Errors indicate the standard deviations obtained from several experiments.

[b] Expressed as fraction of total ^{11}C atoms which react. The other major products, which with benzene and fulvene account for 70—80% of the volatile yield, are acetylene, vinylacetylene, diacetylene, and *cis-* and *trans*-hexa-1,3-dien-5-yne (ref. 3).

[c] The total volatile yields in the condensed phase were not determined. It may be assumed that the yield is about the same as in the CPD (30 cm.) sample. An analogous equivalence has been found in the ^{11}C–benzene studies (T. Rose, C. MacKay, and R. Wolfgang, *J. Amer. Chem. Soc.*, 1967, **89**, 1529).

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§ The compound thought to be benzvalene in refs. 8 and 9 was later proved to be fulvene (H. R. Ward, J. S. Wishnok, and P. Sherman, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 162; K. E. Wilzbach and L. Kaplan, *ibid.*, p. 1030).

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