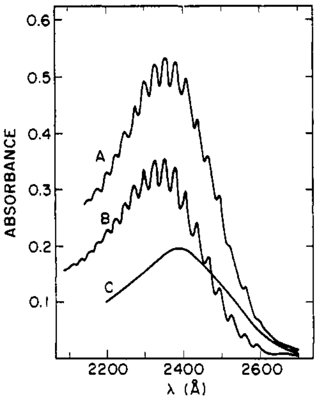

Figure 1. Ultraviolet absorption spectra: (A) benzene vapor irradiated at 1849 A, *vs.* benzene blank; (B) fulvene vapor; (C) difference spectrum, A − B.

fulvene.[10] The ultraviolet absorption of this product, eluted from a didecyl phthalate column and collected in cyclohexane, is also identical with that of fulvene.[12]

Conclusive evidence that fulvene is present in the photolysis mixture (even before chromatography) is provided by comparison of the photoproduced absorption with that of fulvene vapor. The spectrum of the latter, at the concentration of the major product in the experiment resulting in curve A, Figure 1, is shown as curve B. This spectrum shows a progression of 19 peaks between 2100 and 2600 A, spaced at intervals of 490 ± 10 cm^{-1} with a maximum absorption at 2350 A. The peaks in curve A fall at identical wavelengths.

Fulvene does not, however, account for all of the absorption in curve A. The difference spectrum is shown as curve C. Most of this absorption appears to be associated with the other product eluting near benzene. The magnitude of its extinction coefficient (log ϵ $\sim$4.5) and the position of maximum absorption (2500 A in cyclohexane solution) suggest that it may be an acyclic polyene, possibly 1,3-hexadiene-5-yne.[13]

Upon absorption of photolysis mixtures in acidic methanol, adduct formation characteristic[5] of benzvalene is not observed. Gas chromatograms of photolysis mixtures on a column coated with a mixture of didecyl phthalate and triethanolamine likewise show no peak corresponding[5] to benzvalene. Even in the low-pressure runs, benzvalene equivalent to 1% of the fulvene would have been detected.[14]

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(10) Fulvene was prepared[5,11] by irradiation of benzene in the liquid phase at 2537 A and purified by gas chromatography on polar Ucon. Its ultraviolet absorption spectrum in cyclohexane solution was identical with that[12] of synthetic fulvene. Its retention volume at 50°, relative to benzene, is 0.85 on didecyl phthalate, 0.80 on Apiezon L, and 0.89 on polar Ucon.

(11) H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

(12) H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

(13) K. K. Georgieff, W. T. Cave, and K. G. Blaikie, *J. Am. Chem. Soc.*, 76, 5494 (1954).

(14) NOTE ADDED IN PROOF. H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 162 (1967), also report fulvene to be the major product of the photolysis of benzene vapor at 1849 A.

Louis Kaplan, K. E. Wilzbach
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

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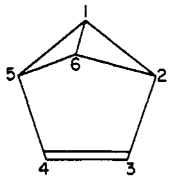
Benzvalene, the Tricyclic Valence Isomer of Benzene[1]

Sir:

We wish to report that benzvalene, tricyclo[3.1.0.0^{2,6}]hex-3-ene, is formed by photolysis of benzene in the liquid phase at 2537 A. It can be separated from photolysis mixtures by gas chromatography and rearomatizes only slowly at room temperature. It has been characterized by nmr spectroscopy and by methanolysis to known bicyclohexenyl ethers. Although two substituted benzvalenes have been reported,[2,3] benzvalene itself has not been observed previously. (Recent suggestions[4,5] that it is present in benzene vapor photolyzed at 1849 A have not been borne out.[6]) The only other known valence isomer of benzene, Dewar benzene,[7] has never been found[8,9] to be a photolysis product of benzene.



BENZVALENE

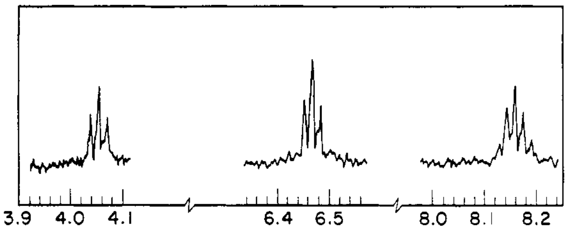


Figure 1. 100-Mc nmr spectrum of benzvalene.

Ultraviolet irradiation of liquid benzene has been reported[10] to give fulvene but no other benzene isomers. The presence of an additional isomer, however, is indicated by the observation that benzene, irradiated at 2537 A and subsequently treated with acidified methanol (0.2 vol. % HCl), yields two products identified by gas chromatography as methoxybicyclohexenes.[11,12] These products are not formed when fulvene is treated with this reagent. They *are* formed[12] when benzene is photolyzed in the methanolic HCl and have been explained[12] in terms of benzvalene-like intermediates.

Gas chromatography of irradiated benzene on a didecyl phthalate–triethanolamine column, from which fulvene does not elute, shows the presence of a product

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem.*, **76**, 922 (1964).

(3) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

(4) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *ibid.*, **88**, 3698 (1966).

(5) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

(6) L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **89**, 1030 (1967).

(7) E. E. van Tamelen and S. P. Pappas, *ibid.*, **85**, 3297 (1963).

(8) K. L. Kirk, Ph.D. Thesis, University of Wisconsin, 1964.

(9) I. Haller, *J. Am. Chem. Soc.*, **88**, 2070 (1966).

(10) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966), and references therein.

(11) 1-*endo*-Methoxy[3.1.0]bicyclohex-2-ene and a 4-methoxy isomer.

(12) L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **88**, 2881 (1966). Photolysis of benzene in methanolic HCl yields three products characterized by their nmr spectra as 4-*endo*(?)- 1-*endo*-, and 1-*exo*-methoxy[3.1.0]bicyclohex-2-ene. Their respective gas chromatographic retention volumes, at 60° relative to *o*-xylene, are 0.93, 0.72, and 0.60 on Carbowax 20M, and 1.14, 0.84, and 0.68 on poly-*m*-phenyl ether (5ring).

eluting shortly before benzene.[13] When this product is absorbed in isohexane and treated with methanolic HCl, the expected quantities of bicyclic ethers are obtained. The ultraviolet absorption spectrum of the isohexane solution exhibits no maximum above 2100 A but has a broad shoulder between 2200 and 2300 A ($\epsilon \sim 2500$). The known substituted benzvalenes have absorption maxima at 2320 A (ϵ 2500)[2] and 2350 A (ϵ 3500).[3] The ultraviolet absorption decreases with a half-time of about 10 days at room temperature; analysis by gas chromatography indicates that benzene is formed in an amount equivalent to the loss of photoproduct.

The 100-Mc nmr spectrum[14] of the product, shown in Figure 1, has three resonances of equal area: an unsymmetrical triplet (1.5- and 1.7-cps couplings) at τ 4.05, a symmetrical triplet (1.5-cps couplings) at τ 6.47, and a quintet (ΣJ = 6.2 cps) at τ 8.16. By decoupling at τ 8.16 both triplets are collapsed to narrow singlets. We can conceive of only two benzene isomers compatible with these results: benzvalene and 3-methylenetricyclo[2.1.0.0^{2,5}]pentane ("criss-cross fulvene"). Only benzvalene is in accord with the facile rearomatization of the photoproduct and its methanolysis to derivatives of bicyclo[3.1.0]hexene. Once the resonance at τ 4.05 is assigned to olefinic protons 3 and 4 in the benzvalene structure, it follows from symmetry considerations that the resonances at τ 6.47 and 8.16 must be assigned to protons 1,6 and 2,5, respectively.

A major problem in this work has been the achievement of concentrations of benzvalene high enough for nmr spectroscopy and preparative gas chromatography. The limiting concentration attainable by irradiation of liquid benzene at room temperature is only 0.01%. It increases with temperature, but is still less than 0.05% at 60°. Enrichment of the solutions by fractional freezing is practical, but we prefer to take advantage of the higher conversions which can be reached by irradiating solutions of the benzene in saturated hydrocarbons.[16] Use of hydrocarbon solvents which are either nonvolatile or more volatile than benzene permits the isolation of these more concentrated solutions by vacuum distillation. We have obtained[15] 1% solutions of benzvalene by irradiating dilute solutions of benzene in hexadecane at 65°.[17]

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[13] A 5 ft × 0.25 in. stainless steel column, packed with Chromosorb G coated with 5% didecyl phthalate and 1.25% triethanolamine, was used at room temperature with a helium flow of 100 cc/min. The retention volume of the product relative to benzene was 0.80. On columns coated with didecyl phthalate alone or with hexadecane, the product eluted very close to fulvene[6] and appeared to undergo some decomposition. On polar Ucon in a 12-ft copper column at 50° the product appeared to be completely converted to fulvene.

[14] Spectra were taken on a Varian HA-100 spectrometer (benzene lock); we thank Miss Gail Norman for these measurements. The sample, a 1% solution of benzvalene in benzene, was prepared as described in ref 15. The only other peaks observed in the spectrum were those of the benzene ^{13}C satellites and of the small amount of fulvene present.

[15] A solution of 0.2 ml of benzene in 25 ml of hexadecane, contained in a tube fitted with a Vycor 7910 well (light path 1.5 mm), was swept with N_2 and irradiated (6 min, 10^{21} quanta) at 65° with a mercury resonance lamp, Nester and Faust NFUV-300, operated at 2500 v. The benzene removed from the solvent on the vacuum line at room temperature contained 1% benzvalene and 0.1% fulvene, with only traces of other detectable contaminants.

[16] The limiting conversions increase steadily with dilution of the benzene, over at least a 100-fold range. It is interesting that fulvene formation is also increased by temperature and dilution and that similar limiting concentrations are reached. Fulvene is initially formed at a slower rate than benzvalene, in accord with the suggestion[10] that the latter is a precursor. When one quantum has been absorbed per molecule of benzene, the concentration of benzvalene has reached its limit, but that of fulvene is still low.

[17] NOTE ADDED IN PROOF. If the higher field nmr resonances were assigned in the reverse fashion, as suggested by a referee, the olefinic protons would have no couplings to adjacent or allylic cyclopropyl protons, in contrast to results found[8] for tri-*t*-butylbenzvalene.

K. E. Wilzbach, James S. Ritscher, Louis Kaplan
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

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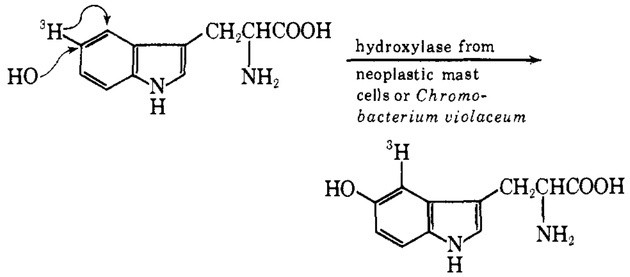
Selective Exchange of Nuclear Protons in Hydroxyindoles

Sir:

The enzymatic hydroxylation of tryptophan-5-^{3}H proceeds with over 90% retention of radioactivity and leads to 5-hydroxytryptophan-4-^{3}H.[1] This intramolecular shift during enzymatic hydroxylations has made necessary an investigation of the lability of tritium or deuterium in hydroxyindoles and their mechanism of tritiation, deuteration, and detritiation.



As the survey in Table I shows, the deuteration of hydroxyindoles under controlled conditions[2] is selective, as the nmr data indicate.[3]

5-Hydroxyindole, bufotenine, serotonin, and 5-hydroxytryptophan contain a characteristic peak for the 4-proton, a *meta*-coupled doublet (AB system) at 6.86–6.95 which disappeared after exchange with deuterium oxide, while the doublet of doublets (ABC system), belonging to the 6-proton, collapsed to an *ortho*-coupled doublet (BC system). Mass spectral data confirmed the *incorporation of one deuteron*, except in the case of the unsubstituted 5-hydroxyindole which also exchanged the 3-proton in accordance with previous observations.[4–6]

4-, 5-, 6-, or 7-hydroxyindoles partially exchange (70–100%) the 3-proton for deuterium after 16 hr at 60° in a much slower reaction than the exchange of the 4-proton in 5-hydroxyindole, which was complete in less than 3 hr. 6-Hydroxyindole exchanged the 3- and 7-protons (70–80%), while the 5-proton was stable (Table I).

The isomeric 4- and 7-hydroxyindoles exchanged only the 3-proton. Melatonin, a representative 5-methoxy-

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[1] J. Renson, J. Daly, H. Weissbach, B. Witkop, and S. Udenfriend, *Biochem. Biophys. Res. Commun.*, **5**, 504 (1966).

[2] The indole (0.2 mmole) was heated (60°) in a sealed tube under nitrogen with D_2O or T_2O, dimethylformamide (0.3 ml), and trimethylamine (20 μl) for 16 hr. Excess water or ethanol was added, the solution was treated with Norite and concentrated to dryness *in vacuo*, and the product was analyzed by mass spectrometry, nmr spectroscopy, and paper or thin-layer chromatography.

[3] *Cf.* L. A. Cohen, J. W. Daly, H. Kny, and B. Witkop, *J. Am. Chem. Soc.*, **82**, 2184 (1960).

[4] M. Koizumi, *Bull. Chem. Soc. Japan*, **14**, 453 (1939).

[5] R. L. Hinman and E. B. Whipple, *J. Am. Chem. Soc.*, **84**, 2534 (1962).

[6] R. A. Heacock, O. Hutzinger, B. D. Scott, J. W. Daly, and B. Witkop, *ibid.*, **85**, 1825 (1963).