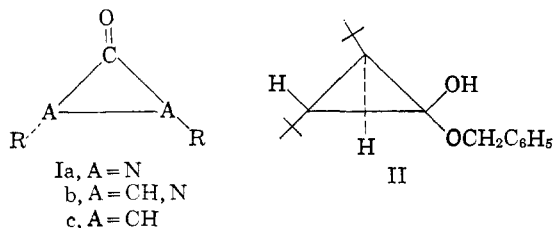


A Stable Cyclopropanone (*trans*-2,3-Di-*t*-butylcyclopropanone)

Sir:

Our investigations on diazacyclopropanones¹ (Ia) have provided a number of indications that the alkyl groups on nitrogen are not in the plane of the ring and that a substantial difference in stability exists between the ditertiary derivatives and those possessing smaller alkyl groups. Recently this has also been observed in the α -lactam series in the stability of 1,3-di-*t*-butylaziridinone (Ib).² Upon extension of this concept to cyclopropanones, we find that 2,3-di-*t*-butylcyclopropanone (Ic) may be prepared and is an isolable compound of moderate stability.³ We regard this finding with interest and feel that it may point the way to the preparation of other small-ring compounds which have heretofore appeared to be too unstable or reactive for isolation.

Reaction of α -bromodineopentyl ketone with the potassium salt of *p*-chlorophenyldimethylcarbinol results in the formation of 2,3-di-*t*-butylcyclopropanone in 20–40% yield: mp 24–26° (*Anal.* Calcd. for C₁₁H₂₀O: C, 78.51; H, 11.98. Found: C, 78.70, H, 12.08); carbonyl band in the infrared (CCl₄) at 1822 cm⁻¹; nmr (CCl₄) δ 0.96 (singlet, 18 H), 1.55 (singlet, 2 H); ultraviolet (isooctane) λ_{\max} 354 m μ (ϵ 33); major species in the mass spectrum at 70 ev: *m/e* (relative intensity), 168 (1.7, parent ion), 125 (75), 83 (100), 70 (90), 69 (91), 57 (90), 55 (90), 41 (90). The cyclopropanone is moderately stable in the absence of nucleophiles (50% destruction in 6 hr at 150° in carbon tetrachloride). It decomposes readily in air, but under anhydrous conditions is stable to oxygen. Chemical evidence in support of the cyclopropanone structure is found in catalytic hydrogenation with platinum in dioxane to dineopentyl ketone (45% yield) and in conversion by benzyl alcohol to a hemiketal (II, 65% yield): mp 102–103° (*Anal.* Calcd for C₁₈H₂₈O₂: C, 78.21; H, 10.2; mol wt, 276. Found: C, 78.04; H, 10.35; mol wt, 279 (osmometric)); infrared (CCl₄) hydroxyl at 3570 cm⁻¹, no carbonyl absorption, nmr (CCl₄) δ 0.97 and 1.02 (two sharp peaks of equal area; integrated area from δ 0.8 to 1.6 is 20 H, 9 for each of two different *t*-butyl groups and 2 for the cyclopropyl hydrogens), 2.8 (singlet, 1 H), 4.4–4.8 (AB quartet from the two magnetically nonequivalent benzylic hydrogens), 7.1 (singlet, 5 H). These nmr data permit



- (1) F. D. Greene and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964).
- (2) J. C. Sheehan and J. A. Beeson, *ibid.*, **89**, 362, 366 (1967).
- (3) See W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966), and references cited therein for information on cyclopropanones containing smaller substituents.
- (4) A direct indication of the intermediacy of the cyclopropanone under Favorskii conditions is seen in the buildup and disappearance of this band upon subjection of the bromo ketone to *t*-butoxide in *t*-butyl alcohol.

the assignment of *trans* stereochemistry to the two *t*-butyl groups of the cyclopropanone.

(5) James Flack Norris Fellow, 1966.

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Received December 19, 1966

Photolysis of Benzene Vapor at 1849 Å¹

Sir:

In two recent publications^{2,3} it has been suggested that benzvalene (the tricyclic valence isomer of benzene) is a major product of the photolysis of benzene vapor at 1849 Å. These suggestions were based upon the appearance of a highly structured ultraviolet absorption^{2,3} centered near 2400 Å and of a product² eluting near benzene in gas chromatography. Because of our interest⁴ in benzvalene and our desire to find a more efficient preparation than that afforded by the photolysis of liquid benzene at 2537 Å,⁵ we have reinvestigated the 1849-Å vapor photolysis. We find that benzvalene is not present in detectable quantities. Fulvene is the predominant volatile product and is responsible for the structure and most of the density of the optical absorption. Smaller amounts of other volatile products, however, make an appreciable contribution to the absorption.

In our studies, mixtures of benzene vapor (0.05 to 3 torr) and nitrogen (1 atm) in a 10-cm silica cell⁶ were irradiated with a mercury resonance lamp⁷ for 1 to 12 min at room temperature. The resulting absorption spectra were measured with a Cary Model 14 spectrophotometer against a benzene blank and corrected for nonvolatile absorption on the cell windows.⁸

A typical spectrum, obtained after 7% consumption of the benzene from an initial pressure of 2 torr, is shown as curve A of Figure 1. Spectra obtained at other benzene pressures and at conversions from 1 to 15% exhibit an identical fine structure. Curve A is almost indistinguishable from a spectrum reported by Shindo and Lipsky³ and is quite similar to that of Foote, *et al.*²

Gas chromatography of the photolysis mixtures on columns coated with didecyl phthalate, Apiezon L, and a polar Ucon show the presence of two reaction products eluting near benzene. (In the run corresponding to curve A the amounts of these products were 2.4 and 0.4% of the residual benzene.) The retention volumes of the major product are the same as those of

- (1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.
- (2) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 3698 (1966).
- (3) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).
- (4) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965), and subsequent publications.
- (5) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967).
- (6) A Pyrocell No. 2005, 10-cm cylindrical cell of S18-260 silica, to which inlet and outlet ports fitted with Teflon stopcocks were attached.
- (7) The Suprasil discharge tube, in the form of a flat helix, was placed 1 cm from one end of the cell.
- (8) Identical spectra were obtained when 2537-Å radiation was excluded (irradiated LiF filter⁹). No absorption at all was produced with 2537 Å alone (Corning 7910 filter).
- (9) J. L. Weeks, S. Gordon, and G. M. A. C. Meaburn, *Nature*, **191**, 1186 (1961).

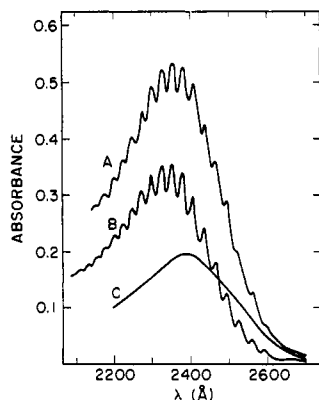


Figure 1. Ultraviolet absorption spectra: (A) benzene vapor irradiated at 1849 Å, vs. benzene blank; (B) fulvene vapor; (C) difference spectrum, A - B.

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 photoproduct 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 Å, spaced at intervals of $490 \pm 10 \text{ cm}^{-1}$ with a maximum absorption at 2350 Å. 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 ($\log \epsilon \sim 4.5$) and the position of maximum absorption (2500 Å 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 characteristic⁵ 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 corresponding⁵ to benzvalene. Even in the low-pressure runs, benzvalene equivalent to 1% of the fulvene would have been detected.¹⁴

(10) Fulvene was prepared^{5,11} by irradiation of benzene in the liquid phase at 2537 Å and purified by gas chromatography on polar Ucon. Its ultraviolet absorption spectrum in cyclohexane solution was identical with that¹² 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 Å.

Louis Kaplan, K. E. Wilzbach

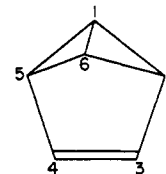
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Received December 22, 1966

Benzvalene, the Tricyclic Valence Isomer of Benzene¹

Sir:

We wish to report that benzvalene, tricyclo[3.1-



BENZVALENE

0.0^{2,6}]hex-3-ene, is formed by photolysis of benzene in the liquid phase at 2537 Å. It can be separated from photolysis mixtures by gas chromatography and re-aromatizes 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 Å 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.

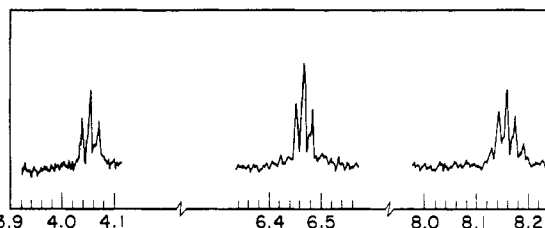


Figure 1. 100-Mc nmr spectrum of benzvalene.

Ultraviolet irradiation of liquid benzene has been reported¹⁰ 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 Å 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 formed¹² when benzene is photolyzed in the methanolic HCl and have been explained¹² 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

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

(2) H. G. Vfehe, 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).