fluoroxenate, $K_x(FXeO_3)_x$, by Hodgson and Ibers[6] has definitely shown the presence of polymers held together by xenon–fluorine bridges, where the Xe–F distance is somewhat greater than in the simple xenon fluorides but less than the sum of the van der Waals radii of xenon and fluorine. We find that mass spectrometric examination of the gases evolved when fluoroxenates are decomposed in concentrated H_2SO_4 shows Xe, O_2, and HF but no xenon compounds, as would be expected from the absence of primary Xe–F bonds in the fluoroxenates.

The stability and ease of preparation of haloxenates increases with decreasing atomic weight of the halogen: $CsFXeO_3 > CsClXeO_3{}^7 > CsBrXeO_3$, the cesium bromoxenate being the most difficult to prepare and to handle. We prepared this unstable compound from saturated cesium bromide solutions, at pH 9 at 0°. The solutions are quite unstable and caution should be exercised when preparing this compound.

Acknowledgments. The authors wish to thank the National Science Foundation (Contract GP 5045) for partial support of this project.

(6) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 326 (1969).

(7) B. Jaselskis, T. M. Spittler, and J. L. Huston, *J. Amer. Chem. Soc.*, **89**, 2770 (1967).

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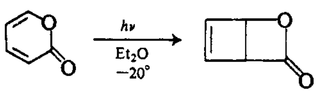
Flash Vacuum Pyrolysis. V. Cyclobutadiene[1]

Sir:

The chemistry of cyclobutadiene[2] and the corresponding theoretical calculations[3] of its properties have been of intense interest.[4] Here we report the results of some of our experiments on the characterization of cyclobutadiene by flash vacuum pyrolysis (FVP)[1] of photo-α-pyrone (**1**).[5]



2 **1**

1 was pyrolyzed at low pressures (~0.1 μ) and short contact times (~1 msec) in a quartz oven which was coupled directly into the ionization chamber of a mass spectrometer.[6] We found that (Figure 1) at temperatures up to 400° isomerization to α-pyrone occurred as shown by the increase of the parent mass (*m/e* 96) with increasing temperature and the decrease of the *m/e* 52 fragment, which is the base peak from **1** and a minor electronic fragment from α-pyrone.[7] Above 400°, the intensity of the *m/e* 52 fragment sharply increased and maximized at about 800°. Correspondingly, a less abundant signal due to a C_8H_8 (*m/e* 104) increased and maximized at about 800°. Thermal products having *m/e* 44, 78, 26, and 68 were also observed, but are not shown. These correspond to carbon dioxide, benzene, acetylene, and furan, respectively.

The appearance potential for *m/e* 52 (AP(52)) with the oven at 800° was at least 1.6 eV lower than AP(52) obtained at 20° (10.2 eV). The magnitude of the decrease in AP(52) with increasing temperature rules out vinylacetylene (IP 9.9 eV) and butatriene[8] (IP 9.4 eV)

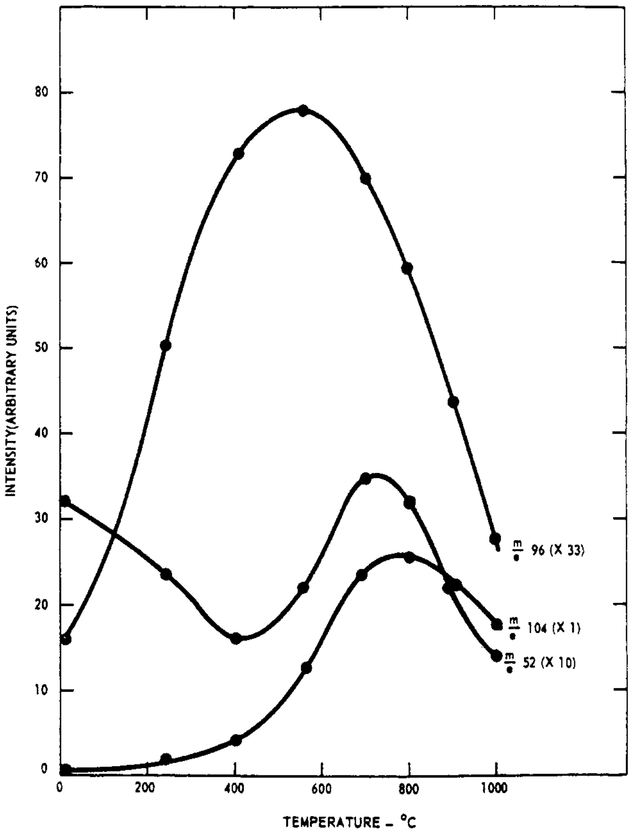


Figure 1. Photo α-pyrone (**1**) pyrolysis: intensity attenuations are indicated in parentheses. Electron bombardment spectrum obtained using 10.5 eV electrons.

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(1) Part IV: E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

(2) (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965); (b) M. A. Avram, I. G. Dinulescu, E. Marica, G. Matescu, E. Diam, and C. D. Nenitzescu, *Ber.*, **97**, 382 (1964), and references cited therein.

(3) (a) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952); (b) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965); (c) J. R. Hoyland, D. A. Berta, D. G. Brannon, W. B. Glenn, P. J. Green, and R. B. Simmons, *Proc. West Va. Acad. Sci.*, **37**, 238 (1965); (d) N. L. Allinger, C. Gilardeau, and L. W. Chow, *Tetrahedron*, **24**, 2401 (1968); (e) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(4) For review articles see: (a) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967; (b) R. Criegee, *Angew. Chem. Intern. Ed. Engl.*, **1**, 519 (1962); (c) G. Subrahonanyam, *J. Sci. Ind. Res.* (India), **26**, 158 (1967); (d) W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 43.

(5) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964). These authors discussed the use of **1** and analogous structures as potential cyclobutadiene sources.

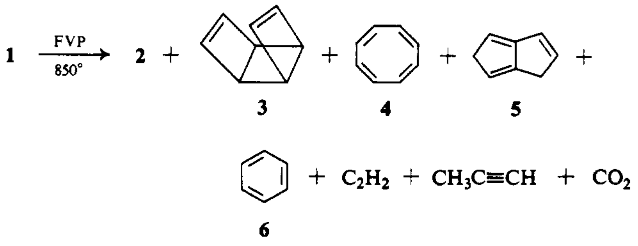
(6) P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, **49**, 5061 (1968).

(7) The partial mass spectrum for **1** at 20° using 50-eV electrons, *m/e* (relative intensity): 96 (0.9), 95 (3.3), 68 (31.4), 52 (100), 39 (90); for **2**: 96 (44.2), 95 (8.5), 68 (84.0), 52 (0.4), 39 (100). The mass spectral intensities reported for **1** in ref 5 are considerably different.

as major thermal products. α-Pyrone, which is the major thermal product, makes a negligible electronic or thermal contribution to the *m/e* 52 peak,[7] as does *syn*-tricyclo[4.2.0.0^{2,5}]octa-2,7-diene (**3**),[2b] cyclooctatetraene, benzene, and furan. Titration with methyl radicals[10] generated by copyrolysis of ethyl nitrite with **1** at 800° led to new signals at *m/e* 67 and 82 corresponding to *m/e* 52 plus one and two methyls, respectively; the latter is the more intense signal. A major signal at *m/e* 66, more intense than those at either *m/e* 67 or 82, was also observed and probably corresponds to hydrogen loss from the *m/e* 67 fragment.[11] Similarly, copyrolysis with allyl iodide resulted in signals corresponding to *m/e* 52 plus one and two iodines, one and two allyls, and one allyl with one iodine. Copyrolysis of **1** with both ethyl nitrite and allyl iodide gave additional signals corresponding to *m/e* 52 plus methyl and iodine (*m/e* 194) and methyl and allyl (*m/e* 108). Neither vinylacetylene nor butatriene reacted with allyl, methyl, or iodo radicals in the same way. Products from these radicals were not observed from photo-α-pyrone at temperatures below which the *m/e* 52 fragment is formed. Finally, copyrolysis of **1** with oxygen at 800° gave a product having *m/e* 84.

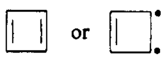
The temperature profile (Figure 1), appearance potential measurements, radical titration experiments, and reactivity with oxygen indicate that thermal *m/e* 52 is a reactive intermediate with diradical character. The following chemical experiments further elucidate its structure.

The pyrolysis of **1** was carried out at 845° and about 35 μ in the FVP apparatus previously described[12] where the pyrolysate is rapidly quenched at liquid nitrogen temperatures on the surface of a large dewar. The liquid products were determined by glpc using toluene as an internal standard and authentic reference compounds: α-pyrone (**2**, 60–67%), *syn*-tricyclo[4.2.0.0^{2,5}]-octa-2,7-diene (**3**, 3–6%),[2b] cyclooctatetraene (**4**, 0.5–1%), dihydropentalene[13] (**5**, 0.2–0.4%), benzene (2–3%), furan (<0.1%). The α-pyrone, *syn* dimer **3**, and benzene were also detected by nmr, and a quantitative nmr determination of **3** corresponded favorably to that obtained by glpc. Furthermore, no *anti*-tricyclo[4.2.0.0^{2,5}]octa-2,7-diene could be detected by nmr. The gaseous products consisted of carbon dioxide, acetylene, and methylacetylene on the basis of mass spectral, glpc, and nmr analyses (for the latter two products). Neither vinylacetylene nor other C_4H_4 products were detected.



Significantly, the *syn* dimer **3** must be formed after the pyrolysate exits from the oven since authentic **3** was completely converted to benzene, **4**, and **5** (approximate ratio 6:2:1, respectively) at the conditions of the photo-α-pyrone pyrolysis (850°, *ca.* 35 μ).[14] Furthermore, the ratio **6**/**3** was substantially increased when the photo-α-pyrone pyrolysate was allowed to pass through a 20-cm, baffled brass pipe before quenching at liquid nitrogen temperatures. Consequently, the gaseous dimerization of the short-lived C_4H_4 intermediate ($t_{1/2}$ *ca.* 10 msec at 35 μ) or dimerization on warm walls leads to different products than dimerization at low temperatures (on the quenching dewar).[15]

These data are best rationalized in terms of a cyclobutadiene (**7**) structure for the thermal *m/e* 52 fragment. The demonstrated formation of *syn* dimer **3** after the pyrolysate exits from the oven rules out any other precursor such as methylenecyclopropene (**8**), tetrahedrane (**9**), or other more unusual C_4H_4 isomers. Dimerization of any of these to **3** at the conditions of the rapid quenching requires rearrangements which are incompatible with the low reaction temperature. Furthermore, the radical and oxygen reactions of the thermal C_4H_4 intermediate are better rationalized in terms of **7**, especially if the ground state is triplet.[17] It is noteworthy that radical–molecule reactions at the conditions of the radical titration experiments have not been observed.[19] However, authentic methylenecyclopropene (**8**)[20] and tetrahedrane (**9**) have not been generated and investigated as yet.



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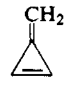

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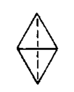

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To summarize, these data indicate that cyclobutadiene

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(8) We thank Dr. T. S. Krull for providing us with an authentic sample of butatriene. The lowest calculated ionization potential is 9.28 eV.[9]

(9) A. Streitwieser, *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

(10) S. Pignataro, A. Cassuto, and F. P. Lossing, *ibid.*, **89**, 3693 (1967).

(11) Apparently, tetramethylcyclobutadiene similarly reacts with methyl giving a diadduct and a monoadduct which loses hydrogen: P. S. Skell and R. J. Petersen, *ibid.*, **86**, 2530 (1964).

(12) E. Hedaya and D. W. McNeil, *ibid.*, **89**, 4213 (1967).

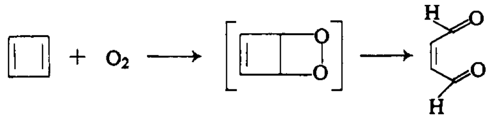
(13) This was prepared by pyrolysis of cyclooctatetraene on the basis of information supplied by Professor M. Jones: M. Jones, Jr., and L. O. Schwab, *ibid.*, **90**, 6549 (1968).

(14) Acetylene was the sole gaseous product.

(15) The flash photolysis of tricarbonylcyclobutadieneiron has been reported[16] to give a transient at *m/e* 52 having a lifetime of 1–2 msec, a transient *m/e* 104 dimer which is longer lived than the *m/e* 52 fragment, benzene, and acetylene. The differences with our results can be rationalized in terms of the different modes of formation of the *m/e* 52 fragment; even so they are comparable.

(16) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(17) In analogy with tetraphenylcyclobutadiene,[18] the reaction with O_2 is presumed to be



(18) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 2059 (1968).

(19) F. P. Lossing, private communication.

(20) The properties of substituted methylene cyclopropenes do not imply an extremely high order of reactivity for the parent compound: M. A. Battiste, *J. Amer. Chem. Soc.*, **86**, 942 (1964); W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); A. Kende, *Trans. N. Y. Acad. Sci.*, 981 (1966); I. Agranat, R. M. J. Loewenstein, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **90**, 3278 (1968).

is a reactive transient intermediate qualitatively comparable to species such as allyl or methyl with respect to dimerization or reaction with radicals, but which nevertheless has considerable stability compared to two acetylene molecules.[21] Its ionization potential is no higher than 8.6 eV and our best current value is 8.2 eV.

Acknowledgment. We acknowledge helpful discussions with F. P. Lossing concerning interpretation of the mass spectral data and Badische Anilin und Soda Fabrik for their generous gift of cyclooctatetraene.

[21] Empirically, molecules having bonds with dissociation energies of about 20 kcal or less will not survive our conditions at pyrolysis temperatures of about 800°. Also, most of the observed acetylene can be accounted for by a process other than $C_4H_4 \rightarrow 2C_2H_2$.

[22] Union Carbide Corporation Postdoctoral Fellow, 1967–1968.

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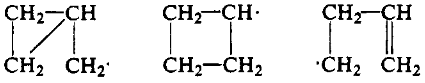
Homoallylic Rearrangement and Electron Spin Resonance of Cyclopropylcarbinyl Radicals

Sir:

Homoallylic rearrangements among cyclopropylcarbinyl (I), cyclobutyl (II), and allylcarbinyl (III) radicals and related systems have been extensively examined.[1] The problem is especially pertinent in view of the extremely facile rearrangement observed with the corresponding carbonium ions. In the latter case, the role of *nonclassical* carbonium ions has been the subject of considerable controversy.[2] The possibility of nonclassical free radicals in related systems has been considered,[3] and recently the 7-norbornenyl species has been presented as a nonclassical radical.[4]



I II III

Heretofore all discussions relating to the structure of these radicals have been based on inference from chemical studies. Direct observation of the electron spin resonance (esr) spectrum of these species would provide unequivocal evidence of their structure.

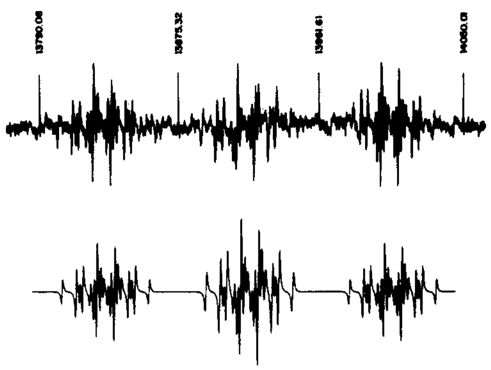


Figure 1. Esr spectrum of cyclopropylcarbinyl radical (−150°). The calculated spectrum includes second-order effects. The proton nmr frequency markers are in kilocycles per second.

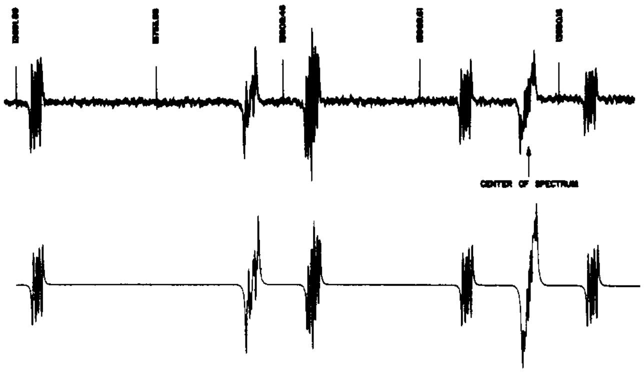
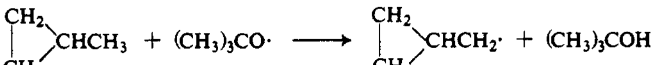


Figure 2. Experimental and calculated low-field halves of the esr spectrum of the allylcarbinyl radical showing second-order effects (−90°).

In this report we wish to present the esr spectrum of cyclopropylcarbinyl radicals in solution. A general method for the production of alkyl radicals from alkanes for esr studies, by the use of photochemically generated *t*-butoxy radicals from di-*t*-butyl peroxide, has been described previously.[5] *t*-Butoxy radicals react with methylcyclopropane by selective removal of one of the methyl hydrogens (eq 1).[6] The observed esr spectrum of the



(1)

resulting radical is highly dependent on the temperature. At temperatures less than −140°, the esr spectrum reproduced in Figure 1 was obtained. Between 0 and −100° the spectrum presented in Figure 2 was observed. At intermediate temperatures the esr spectrum consisted of a superposition of these two individual spectra. No exceptional line broadening was observed in these spectra to indicate the existence of any time-averaging phenomena.[7]

The esr spectrum presented in Figure 1 is clearly

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[1] (a) C. Walling, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 440 ff; (b) D. I. Davies and S. Cristol, *Advan. Free Radical Chem.*, **1**, 155 (1965); (c) J. C. Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Letters*, 4629 (1967); (d) M. Hanack and H. J. Schneider, *Forschr. Chem. Forsch.*, **8**, 554 (1967); (e) J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **90**, 295 (1968).

[2] (a) P. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) M. Hanack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967); (c) D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (d) P. von R. Schleyer and G. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966); (e) R. Moss and F. Shulman, *ibid.*, **90**, 2731 (1968); *Tetrahedron*, **24**, 2881 (1968); (f) K. B. Wiberg and G. Szelmies, *J. Am. Chem. Soc.*, **90**, 4195 (1968).

[3] (a) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 3051 (1967); **89**, 923, 934 (1967); (b) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, **89**, 3051 (1967).

[4] J. Warkentin and E. Sanford, *ibid.*, **90**, 1668 (1968).

[5] P. J. Krusic and J. K. Kochi, *ibid.*, **90**, 7155 (1968).

[6] Similarly, product studies of the free-radical chain chlorination of methylcyclopropane by *t*-butyl hypochlorite require that the methyl hydrogens be abstracted by *t*-butoxy radical [C. Walling and J. Fredericks, *ibid.*, **84**, 3327 (1962)].

[7] This does not include broadening due to restricted rotation.