

818 cm^{-1} . The nmr spectrum showed a doublet centered at τ 8.57 (3 H, $J = 6$ cps, CH_3) and a multiplet at approximately τ 5.28 (1 H, CHO).

When the methylhexahydrobenzofuran was set aside with access of moist air, it slowly became more viscous, the infrared spectrum showed hydroxyl absorption, and, on distillation, 2-(2'-hydroxypropyl)cyclohexanone was obtained (identified by infrared and nmr spectra); a resinous residue remained.

cis-2-Methyloctahydrobenzofuran (8).—2-Methyl-2,3,4,5,6,7-hexahydrobenzofuran in ethyl acetate was shaken with hydrogen at 1-atm pressure in the presence of reduced platinum oxide. Absorption of hydrogen was rapid and ceased after the uptake of 1 mole of hydrogen. Removal of the catalyst, and distillation gave, in quantitative yield, *cis*-2-methyloctahydrobenzofuran, bp 70–71° (20 mm), n_D^{25} 1.4570 [lit.⁸ bp 63° (16 mm), n_D^{25} 1.4548].

The infrared spectrum was identical with that of an authentic sample. The nmr spectrum showed a sharp doublet centered at τ 8.71 (3 H, $J = 6$ cps, CH_3) and a broad multiplet at approximately τ 6.1 (2 H, CHOCH). There was no indication of other peaks which could be attributed to methyl protons, and the material, therefore, probably consists of a single isomer since Cantor and Tarbell⁸ record the presence of two methyl doublets in the spectrum of material considered to be a mixture of diastereoisomers. Gas chromatography (15-ft column, 4% Dow 11 on Chromosorb G, 100°) showed only one peak, thereby establishing the fact that the material was free of the *trans* isomer.

Registry No.—1, 10198-26-2; 2, 10198-27-3; 3, 2402-57-5; 4, 10198-28-4; 5, 10198-29-5; 6, 6126-52-9; 7, 10198-31-9; 8, 10198-32-0; acetyl derivative of 2, 10198-33-1.

Concerning the Structure of the $(\text{C}_4\text{H}_4\text{O})^+$ Ion from the Electron Impact Induced Fragmentation of 2-Pyrone

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One of the fundamental and most difficult problems in mass spectrometric investigations is the assignment of structures to the various ions encountered. A classic attack on this problem has resulted in the elucidation of the structure of C_7H_7^+ ion by S. Meyerson and co-workers.^{1b}

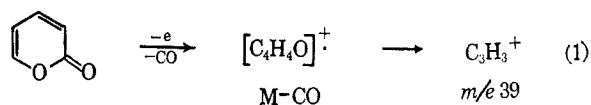
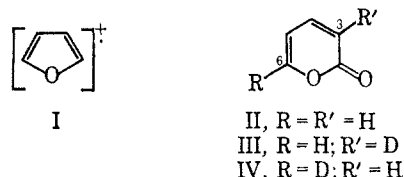
For want of positive structural evidence, many workers simply assign ionic structures which correspond to well known energy minimization criteria used in the ground state (*e.g.*, tertiary carbonium ions > secondary > primary). Another common practice may be termed the "external standard method."² The latter

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(2) For applications of this procedure, see (a) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); (b) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **17**, 975 (1964); (c) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. II, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 29; (d) P. Funke, K. G. Das, and A. K. Bose, *J. Am. Chem. Soc.*, **86**, 2527 (1964); (e) K. G. Das, P. T. Funke, and A. K. Bose, *ibid.*, 3729 (1964); (f) P. Brown and C. Djerassi, *ibid.*, **88**, 2469 (1966); (g) G. Spitteller and M. Spitteller-Friedman, *Monatsh. Chem.*, **93**, 1395 (1962); (h) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963); (i) J. M. Wilson, M. Ohashi, H. Budzikiewicz, C. Djerassi, S. Itô, and T. Nozoe, *Tetrahedron*, **19**, 2247 (1963); (j) C. E. Brion and L. D. Hall, *J. Am. Chem. Soc.*, **88**, 3661 (1966).

involves making a qualitative correlation between peaks of lower m/e values than a fragment ion, with peaks derived from a standard molecular ion of identical elemental composition. The observation of such a correspondence often prompts the claim that the fragment ion and the molecular ion (assumed to be unarranged) possess the same structure.

The "external standard method" has found wide use in the assignment of structure to ions formed by direct loss of carbon monoxide from various aromatic systems on electron impact.^{2a-c,g-i} Recently, the application of this technique in the assignment of a cyclic furan structure (I) to the M-CO species produced in the fragmentation of 2-pyrones (reaction 1) has been questioned and rejected.³ Pirkle has proposed³ that if a cyclic furan radical ion (I) were an intermediate in



the fragmentation of 2-pyrone (II), the distinction between carbon atoms three and six would be lost. Therefore, specific deuteration at C-3 (III) and C-6 (IV) would lead to the same isotopic distribution in peaks derived from the proposed furan intermediate I, *i.e.*, mainly m/e 39, which is the base peak in the spectrum of both furan and 2-pyrone. The spectra of 3-*d*-2-pyrone (III) and 6-*d*-2-pyrone (IV) were obtained,³ and in the former the m/e 39 peak is preferentially shifted to m/e 40, while in the latter the m/e 39 peak largely remains unshifted. It was, therefore, concluded³ that the $\text{C}_4\text{H}_4\text{O}$ radical ion cannot have a furan structure (I).

We wish to show in this communication that the intermediacy of furan radical ion I is still an open question in these systems, since the differences of isotopic distribution in the mass spectra of III and IV can equally well be explained by multiple⁴ pathways to m/e 39.

In fact, a second pathway which does not proceed through the intermediacy of an $[\text{M}-\text{CO}]^+$ ion has been clearly demonstrated⁵ in the mass spectral fragmentation of various substituted 2-pyrones. This process (reaction 2) is supported⁶ by the presence of an appropriate metastable peak, and involves specific loss of the C-6 substituent⁶ in the first step ($\text{V} \rightarrow \text{aa}$). Exactly the same situation obtains in the mass spectra of deuterium labeled 2-pyrones,³ since III exhibits only an $\text{M} - 1$ ion, while IV shows solely an $\text{M} - 2$ ion. These results strongly suggest that formation of C_3H_3^+ (m/e 39) in 2-pyrone proceeds at least in part *via* the C-6 cleavage pathway (reaction 2). Since

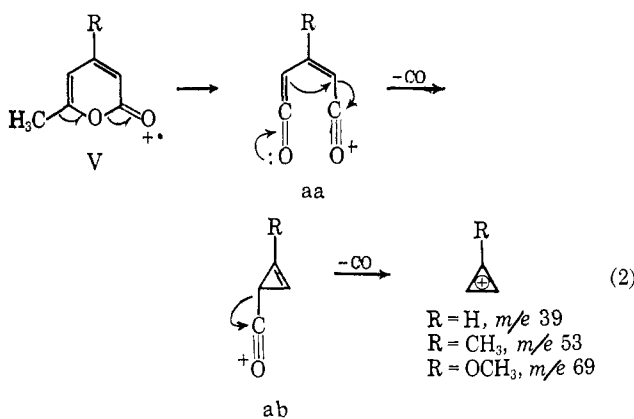
(3) W. H. Pirkle, *ibid.*, **87**, 3022 (1965).

(4) We should point out that in principle the demonstration of more than one pathway to m/e 39 in itself invalidates the conclusions drawn in ref 3.

(5) H. Nakata, Y. Hirata, and A. Tatematsu, *Tetrahedron Letters*, 123 (1965).

(6) H. Budzikiewicz, J. I. Brauman, and C. Djerassi [*Tetrahedron*, **21**, 1855 (1965)] report the mass spectrum of 4-methoxy-6-phenyl-2-pyrone, which also suffers characteristic cleavage of the 6-phenyl substituent.

$C_3H_3^+$ is demonstrably produced by at least two processes, as shown above, the observation of gross differences in the distribution of deuterium among the fragments of these labeled 2-pyrone (III, IV) does not constitute evidence for the presence or absence of a furan intermediate (I) in the electron impact induced decarbonylation reaction.



To be more specific, Pirkle's data³ clearly show that approximately 37% of the $m/e 39$ peak moves to $m/e 40$ in the spectrum of IV. This information permits estimation of an upper limit for the C-6 cleavage mechanism (reaction 2) of 63%, which could be lower because of other competing processes involving loss of deuterium from C-6 which may be operative. The published data³ also show that at least 94% of $m/e 39$ is shifted to $m/e 40$ in III. This interesting fact still does not exclude a furan intermediate (I),⁷ since this species could be generated in rearranged form, with C-3 (or C-4) arising from C-3 of 2-pyrone.

Registry No.—II, 504-31-4.

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(7) The similarity of the mass spectra of furan (I) and 2-pyrone (II) below $m/e 68^+$ and especially the correspondence of the metastable peak shapes⁸ (determined in this laboratory on an Atlas CH-4 mass spectrometer) leaves little doubt that the major ions of mass 68 in the spectra of I and II are identical, but of as yet unknown structure.

(8) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966).

The Synthesis of Perfluoroisobutylene from Perfluoropropylene

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A simple and excellent preparation of bis(trifluoromethyl)ketene from perfluoroisobutylene has recently

been disclosed by England and Krespan.¹ The facile preparation and novel reactions of this compound make inevitable a greatly increased interest in its chemistry and prompt the publication of this Note, which describes an improved preparation of perfluoroisobutylene developed some years ago. The preparation utilizes perfluoropropylene rather than the more expensive perfluorocyclobutene or the less convenient tetrafluoroethylene, gives higher yields and conversions than other reported methods,²⁻⁴ involves no elaborate apparatus or handling of gases boiling below -80° , and is a continuous process suitable for any quantity of materials. Although the reaction pathway may be complex, the main over-all reaction is merely the conversion of four molecules of C_3F_6 to three molecules of $i-C_4F_8$. The method has been used several times on an approximately 1-mole scale, with yields of 71-95% and conversions of 47-57%. The exact results obtained apparently depend to some extent on the flow rate, higher rates giving higher conversions but lower yields. No detailed study of the side products has been made but they presumably resemble those found in other pyrolytic preparations of $i-C_4F_8$ and also include an appreciable quantity of C_2F_6 . Fractionation of the crude product through a 1-ft, low-temperature column packed with metal helices gives perfluoroisobutylene of at least 95% chromatographic purity.

Perfluoro-*t*-butyl iodide can be made in fair yield by catalyzed addition of the elements of iodine monofluoride⁵ to perfluoroisobutylene, provided the reaction time is sufficiently extended; reaction for 60 hr at 130° gave $(CF_3)_3CI$ in 69% yield and 37% conversion. The iodide is a very volatile solid, mp 81° (sealed tube), and is stable indefinitely if protected from light, a sample having been stored without gross decomposition for four years at room temperature.

Experimental Section

Perfluoroisobutylene is extremely toxic and all reactions involving handling of this gas should be done in a well-ventilated area.

Perfluoroisobutylene by Pyrolysis of Perfluoropropylene.—An unpacked nickel tube (12 in. \times 1 in) connected to a large trap cooled in a Dry Ice-acetone bath was continuously evacuated while being heated in a Hoskins tube furnace. The vacuum was broken with dry nitrogen and 105 g of C_3F_6 was passed through the tube over a period of 24 hr at a temperature of $750 \pm 10^\circ$. The system was flushed with dry nitrogen and the crude product (103 g) fractionated to give 3 g of overhead (Dry Ice condenser), 50 g of reclaimed C_3F_6 plus side products (bp -30 to -2°), and 52 g of $i-C_4F_8$, boiling almost completely at $6-8^\circ$. The infrared spectrum of the product agreed with that published⁶ and a gas chromatogram indicated a purity of at least 95%. The conversion, based on weight of C_3F_6 admitted, was 50% and the yield, neglecting impurities in the recovered C_2F_6 , was 95%. In another run, 155 g of C_3F_6 passed through a similar tube at $750 \pm 10^\circ$ over 13 hr gave 30 g of recovered C_3F_6 [bp -39 to -23° (630 mm)] and 89 g of perfluoroisobutylene [bp -3 to $+1^\circ$ (630 mm)]; these figures represent a 71% yield and a 57% conversion.

(1) D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 4019 (1965); **88**, 5582 (1966).

(2) A. T. Morse, P. B. Ayscough, and L. C. Leitch, *Can. J. Chem.*, **33**, 453 (1955).

(3) M. Hauptschein, A. H. Fainberg, and M. Braid, *J. Am. Chem. Soc.*, **80**, 842 (1958).

(4) W. H. Pearlson and L. J. Hals, U. S. Patent 2,617,836 (1952).

(5) M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2383 (1961).

(6) D. G. Weiblen in "Fluorine Chemistry," Vol. 2, J. H. Simons Ed., Academic Press, Inc., New York, N. Y., 1954, p 477.