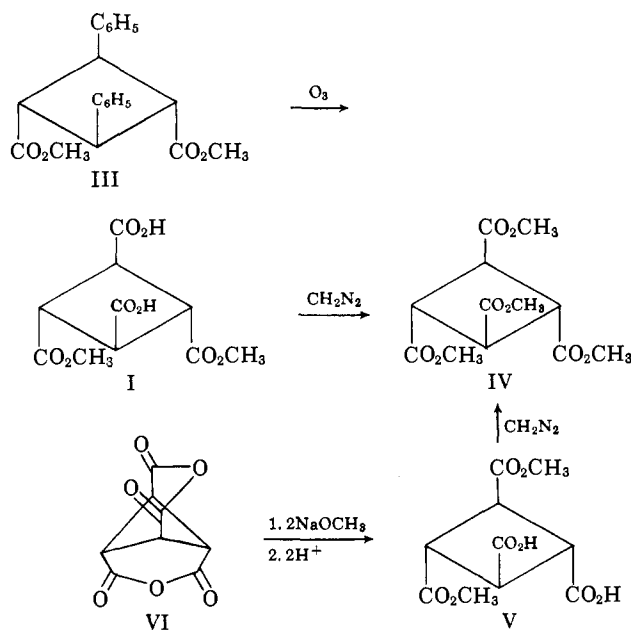


Although electrolysis of vicinal dicarboxylic acids often leads to olefins, the above reaction, to our knowledge, represents the first example of ring closure under Kolbe conditions.

The starting material, *trans,trans,trans*-1,3-dicarboxy-2,4-dicarbomethoxycyclobutane (I, m.p. 183–184°), was prepared by ozonolysis⁵ of the dimethyl ester III of ξ -truxillic acid. Confirmation of the structure of I was achieved by its conversion to the known *trans,trans,trans*-1,2,3,4-tetracarboxy-



cyclobutane (IV)⁶ upon treatment with diazomethane. It was established that the diacid diester was not identical with *trans,trans,trans*-1,2-dicarboxy-3,4-dicarbomethoxycyclobutane (V, m.p. 167–170°)⁷ by comparison of infrared spectra and mixture melting point determination. It is significant that V is the only other possible diester of "all-*trans*" 1,2,3,4-tetracarboxycyclobutane and was prepared by treating the "cage" dianhydride VI⁷ with 2 equiv. of sodium methoxide. All attempts to prepare I from VI by the addition of 1 equiv. of methanol, treatment with diazo-

Soc., **85**, 2529 (1963), (d) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.* (London), 144 (1964); (e) D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965); (f) R. B. Turner, P. Golbel, W. von E. Doering, and J. F. Coburn, Jr., *Tetrahedron Letters*, 997 (1965); (g) J. F. Coburn, Ph.D. Dissertation, Yale University, New Haven, Conn., 1963; W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).

(5) G. W. Griffin and D. F. Veber, *J. Am. Chem. Soc.*, **82**, 6417 (1960).

(6) G. W. Griffin, J. E. Basinski, and A. F. Velturo, *Tetrahedron Letters*, No. 3, 13 (1960).

(7) G. W. Griffin and R. B. Hager, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **7**, 901 (1962).

methane, and subsequent hydrolysis of the remaining anhydride linkage failed.

A solution of 1.0 g. of I in 40 ml. of anhydrous methanol containing 0.02 g. of sodium methoxide was electrolyzed (80 v., 0.8 amp.) between smooth platinum electrodes (2 × 3 cm.). The reaction chamber was cooled with ice during the course of the electrolysis, which was discontinued when the solution became basic (4 hr.). Most of the methanol was then removed under reduced pressure and autogenous temperature. The remaining yellow solution was gas chromatographed (220° and 15 p.s.i. of helium) on a 2 m. × 6 mm. glass column containing 30% silicone gum SE-30 on Chromosorb P (60/80 mesh). Under these conditions the 2,4-dicarbomethoxybicyclobutane (0.10 g., m.p. 83–85°) had a retention time of 8 min.

In view of the conditions of the reaction and the geometry of the system, it is inviting to propose a diradical mechanism in which the molecule is held in the vicinity of the electrode during oxidative bisdecarboxylation; however, a mechanism involving oxidation to a carbonium ion, subsequent lactonization, followed by loss of carbon dioxide, or alternatively a zwitterionic mechanism, cannot be excluded at this time.

Acknowledgments. The authors are indebted to the National Institutes of Health for support of this work.⁸

(8) A preliminary report of this work was presented at the Small Ring Symposium, University of Florida, Gainesville, Florida, May 14, 1965. Consistent analyses were obtained on all new compounds.

(9) Public Health Independent Postdoctoral Fellow (Fellowship No. 1-F2-GM-11,801-01 from the General Medical Sciences Division).

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Structure of Electron Impact Fragments. The C₄H₆O Cation from 2-Pyrone

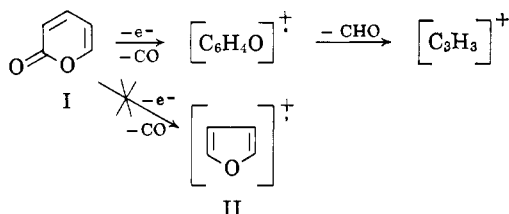
Sir:

Although substantial progress has been made in the interpretation of fragmentations of organic molecules under electron impact, the structure of cationic fragments can seldom be demonstrated. Consequently, fragment structures are often inferred from indirect evidence. For example, in the recent report¹ that the loss of carbon monoxide by coumarin upon electron impact yields a C₈H₆O radical cation, this ion was assigned a benzofuran structure because of the close

(1) C. S. Barnes and J. L. Ocolowitz, *Australian J. Chem.*, **17**, 975 (1964).

similarity between its subsequent fragmentation and that of the benzofuran molecular radical cation.² We wish to emphasize that structural conclusions so reached must be accepted cautiously.

As an instance where similar indirect evidence leads to a demonstrably erroneous conclusion, the electron impact fragmentation of 2-pyrone (I) is cited. 2-Pyrone, on electron impact, loses carbon monoxide^{3,4} to yield abundantly a C₄H₄O radical cation whose subsequent fragmentation leads to a mass spectrum similar to that of furan.⁵ From this, it could be inferred that the C₄H₄O radical cation has the furan structure II, for which a number of canonical resonance structures may be written. Most of these resonance structures place the positive charge on oxygen, a comparatively stable arrangement. It is generally accepted that the formation of stable oxonium ions plays an important role in controlling fragmentation processes^{6a,b}; therefore, *a priori*, II seems quite reasonable. However, deuterium labeling studies clearly show the C₄H₄O radical cation does not have structure II.⁷



In the mass spectrum of 2-pyrone, the most abundant fragment is a C₃H₃ cation⁸ formed either by loss of a formyl radical⁹ or by stepwise loss of carbon monoxide⁴ and a hydrogen atom from the C₄H₄O radical cation.

(2) While this assignment may be correct, it must be pointed out that the structure of the benzofuran radical cation is itself unknown.

(3) It appears likely that it is the carbonyl which is expelled. While no direct evidence of this is presently offered, there is ample precedent for it [J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963); C. Djerassi, *et al.*, *Tetrahedron*, **19**, 2247 (1963); P. Beak, T. H. Kinstle, and G. A. Carls, *J. Am. Chem. Soc.*, **86**, 3833 (1964)].

(4) The metastable peak for this transition is observed.

(5) The formation and subsequent fragmentation of a substantial amount of M-1 ion complicates somewhat the mass region of interest. However, the observation that all peaks in the furan spectrum are present in at least as great an intensity in the 2-pyrone spectrum and the exact correspondence of all furan metastable peaks (masses 22.4, 23.7, 25.8, 35.2, and 38.8) with those observed in the same region of the 2-pyrone spectrum is strong evidence for the similarity of fragmentation paths of the furan molecular ion and the C₄H₄O ion derived from 2-pyrone.

(6) (a) C. H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structural Elucidation of Natural Products by Mass Spectroscopy," Vol. 2, Holden-Day, Inc., San Francisco, Calif., 1964; (b) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p. 315.

(7) In a paper which has appeared since the completion of this work [H. Nakata, Y. Hirata, and A. Tatematsu, *Tetrahedron Letters*, No. 2, 123 (1965)] the claim is made that expulsion of carbon monoxide from the molecular ions of a number of substituted 2-pyrones results in furan-like ions. It is not, however, essential to invoke such ions to account for the fragmentation observed by these workers. In view of the present work, this assumption must be regarded as unwarranted.

(8) Presumably, this ion is the cyclopropenium cation [see F. W. McLafferty in "Determinations of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 93, and the paper by K. B. Wiberg, W. J. Bartley, and F. D. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962)].

(9) Although both the C₄H₄O and C₃H₃ ions give rise to intense peaks, the metastable peak for the transition between them is of rather low intensity. It should be noted, however, that a number of substituted 2-pyrones give rise to substituted cyclopropenium ions in a two-step process with both metastable peaks being easily observed (see Nakata, *et al.*⁷; W. H. Pirkle, unpublished work.).

Table I^a

<i>m/e</i>	Relative intensities (5% or greater)			
	Furan	2-Pyrone	2-Pyrone-3-d	2-Pyrone-6-d
97			79	52
96		72	19	
95		18		8
69			94	83
68	85	88		13
42	7.4	17	13	
41			39	50
40	13	32	100	59
39	100	100	31	100
38	14.5	24	14	42
37	8.3	13		34
29	13	13	12	7.0
28		8.2		17
27			5.0	15
26		7.3		8.4

^a Spectra were obtained at 70 e.v. in an Atlas CH 4 spectrometer.

Replacement of either the C-3 or the C-6 hydrogen in 2-pyrone by deuterium would lead, were structure II correct, to the same ion in both instances. The observation of gross differences in the distribution of deuterium among the fragments of these labeled pyrones¹⁰ indicates that the furan ion II is not an important contributor in the fragmentation of 2-pyrone. Moreover, it is obvious from Table I that C-3 deuterium is preferentially incorporated into the cyclopropenium ion while C-6 deuterium is preferentially excluded.

Reduction of ionizing voltage to the appearance potential of the three-carbon ion does not lead to label scrambling. Apparently, the C₄H₄O radical cation does not cyclize to generate a furan-like fragment even when formed with as little excess energy as possible.¹¹ Whether the C₄H₄O radical cation is acyclic or has closed to yield a formyl-substituted cyclopropene radical cation cannot be determined from the present experiment.¹² Moreover, the significance of the similarity between the mass spectra of furan and the C₄H₄O fragment cannot be stated with certainty. A possible inference is that the furan molecular radical cation is identical with the C₄H₄O fragment from 2-pyrone and hence no longer retains the furan ring.

(10) The synthesis of these specifically deuterated 2-pyrones will be published elsewhere.

(11) A referee has suggested that accurate appearance potentials of the furan molecular ion and the 2-pyrone C₄H₄O ion would be of interest. Unfortunately, accurate appearance potentials cannot yet be determined in this laboratory.

(12) A referee has suggested that the mass spectra of the two isomeric formylcyclopropenes would be a useful addition to the paper. However, these compounds are as yet unreported.

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Kinetic Evidence for 1,3-Diradicals from the Thermal Decomposition of 1-Pyrazolines

Sir:

We wish to present conclusive evidence for the formation of an intermediate in the thermal decomposition of 1-pyrazolines. The trimethylene diradical has been frequently postulated as an intermediate in the thermal