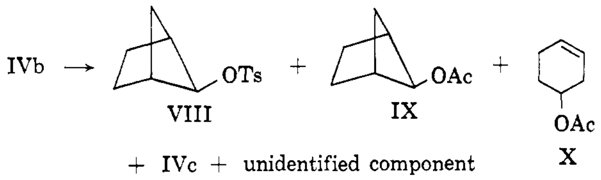
exhibited a singlet at τ 4.59 (hydroxyl), a triplet centered at 5.63 (C-2 methine), and continuous absorption from 7.0 to 8.4.

Conversion of IVa to the *p*-toluenesulfonate ester IVb was accomplished by reaction with *p*-toluenesulfonyl chloride in ether solution in the presence of potassium hydroxide.[8] Tosylate IVb, a colorless viscous liquid, was purified for acetolysis by successive molecular distillations (molecular weight by vapor pressure osmometer was 251). The infrared and n.m.r. spectra of the tosylate were consistent with those expected. The acetolysis rate constants for IVb, determined titrimetrically by the sealed ampoule technique,[9] were $1.92 \pm 0.14 \times 10^{-4}$ sec.$^{-1}$ at 90° and $4.24 \pm 0.23 \times 10^{-5}$ sec.$^{-1}$ at 75°.[10,11] Extrapolation to 25° gives $k = 9 \times 10^{-8}$ sec.$^{-1}$.

The infinity titer corresponds to reaction of $46.7 \pm 2.7\%$ of the IVb used with no observable change after ten half-lives. This observation is rationalized by ionization of IVb with ion pair return to a much more slowly solvolyzing tosylate. This was confirmed by the isolation of the isomeric *exo*-bicyclo[2.1.1]hex-5-yl *p*-toluenesulfonate[8] (VIII) from the acetolysis mixture in 50% yield. The acetolysis rate constant for VIII is reported to be 5.82×10^{-4} sec.$^{-1}$ at 164.2° (9×10^{-10} sec.$^{-1}$ at 25°).[12] The isomerization of the bicyclo[2.2.0]hexyl system (IVb) to the bicyclo[2.1.1]hexyl system (VIII) is expected by analogy with the thermal isomerization data for the parent hydrocarbons.[13]

The acetate mixture was composed of *exo*-bicyclo[2.1.1]hex-5-yl acetate (IX, 41%),[14] 4-cyclohexenyl acetate (X, 51%), *exo*-bicyclo[2.2.0]hex-2-yl acetate (IVc, 3%), and an as yet unidentified product (5%).



It was anticipated that an equilibrium between IVb and VIII favoring VIII *via* some carbonium ion intermediate would be observed in their acetolyses. This does not appear to be the case, but until a complete product study of the products from acetolysis of VIII is reported[15] this question cannot be decided. An alternate consideration would be that this equilibrium involves several carbonium ion intermediates and that acetic acid is interrupting the process at an early stage. Formolysis and ethanolysis studies may shed light on this proposal.

It should be noted that IVb undergoes acetolysis 100 times faster than VIII. It cannot be determined at this time whether this may mean some anchimeric assistance for IVb, or that IVb is normal and VIII is slow. Assistance would seem to be the better of the two explanations since the carbonium ion in the bicyclo[2.2.0]hexyl system would appear to be somewhat more strained than that derived from the bicyclo[2.1.1]hexyl system.

Work toward the synthesis of the *endo*-bicyclo[2.2.0]hexan-2-ol and solvolysis of its tosylate, as well as the preparation and chemistry of a variety of 2-substituted derivatives of this interesting hydrocarbon system, are presently underway.

Acknowledgment. The authors wish to express their gratitude to the National Science Foundation (NSF-G17430, GP-1916) for support of this research. We wish to thank Professor K. B. Wiberg for furnishing us with the infrared and n.m.r. spectra of *exo*- and *endo*-bicyclo[2.1.1]hexan-5-ols.

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(8) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

(9) S. Winstein, E. Grunwald, and L. Ingraham, *ibid.*, **70**, 821 (1948).

(10) The rate constants are the average of three independent runs at each temperature with no less than eight points taken for each run. The equation, $k = 2.303/t \log [(C_\infty - C_0)/(C_\infty - C_t)]$, where C_0 is concentration of ester reacted at time zero, C_t is concentration of ester reacted at time t, and C_∞ = the concentration of ester reacted after ten half-lives, was employed.

(11) The thermodynamic parameters for this acetolysis are $\Delta H^* = 24.7$ kcal./mole and $\Delta S^* = -8.2$ e.u. (75°).

(12) K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, **No. 20**, 1273 (1963).

(13) R. Srinivasan and A. A. Levi, *J. Am. Chem. Soc.*, **85**, 3363 (1963); C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964). The activation energy for thermal isomerization of the hydrocarbons to 1,5-hexadiene is 19 kcal. lower for bicyclo[2.2.0]hexane.

(14) The relative percentages of these acetates were determined by v.p.c. analysis. The peaks of the latter three acetates overlapped somewhat, so their relative amounts are approximate. Integration of the n.m.r. spectrum of the acetate mixture supports the v.p.c. data indicating the ratio of IX:X to be 7:11.

(15) It was reported[12] that X is a major product from the acetolysis of VIII. Further characterization of products was not made.

(16) This represents a portion of a dissertation to be presented by C. E. Reineke to the Graduate School of Kansas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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An Electrochemical Synthesis of a Bicyclobutane

Sir:

When *trans,trans,trans*-1,3-dicarboxy-2,4-dicarbomethoxycyclobutane (I) was electrolyzed under Kolbe conditions,[1] 2,4-dicarbomethoxybicyclobutane (II), assumed to be *cis*,[2] was the major product isolated. This structural assignment is supported by the infrared spectrum which showed a single carbonyl absorption band at 5.78 μ. No hydroxyl absorption was apparent, and the n.m.r. spectrum exhibited three peaks at τ 6.31, 7.35, and 8.42 in the apparent ratio 3:1:1, respectively. No signal due to vinyl protons was present, and the mass spectrum was also consistent.

Further evidence for this structure was obtained by catalytic hydrogenation of II (Adams' catalyst) to *cis*-1,3-dicarbomethoxycyclobutane,[3] dimethyl adipate, and dimethyl α-methylglutarate, formed in the ratio 15:1:21. It should be noted that a trace of the dimethyl β-methylglutarate may have escaped detection. These results are not inconsistent with previous hydrogenation data reported for other bicyclobutyl systems.[4]

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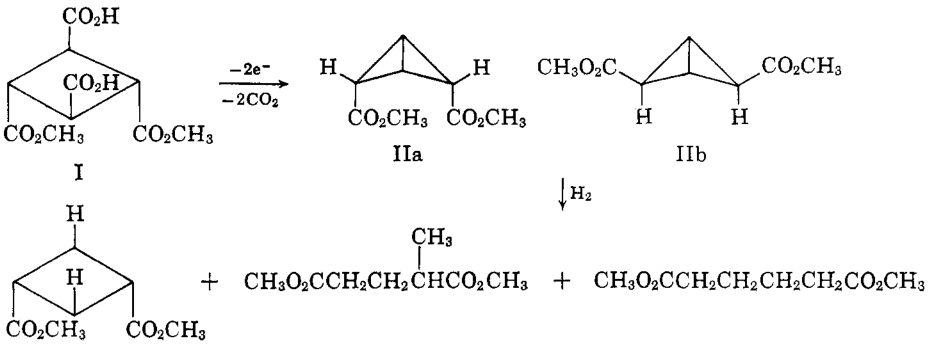
(1) For recent reviews on the Kolbe electrolysis see: (a) B. C. L. Weedon, *Advan. Org. Chem. Methods Results*, **1**, 1 (1960); (b) G. W. Thiessen, *Record Chem. Progr.*, **21**, 243 (1960).

(2) Although it should be noted that two *cis* stereo modifications may exist (the *syn* form, IIa, and the *anti* form, IIb), only one product has been isolated to date and characterized as a bicyclobutane. Variable temperature n.m.r. studies are in progress.

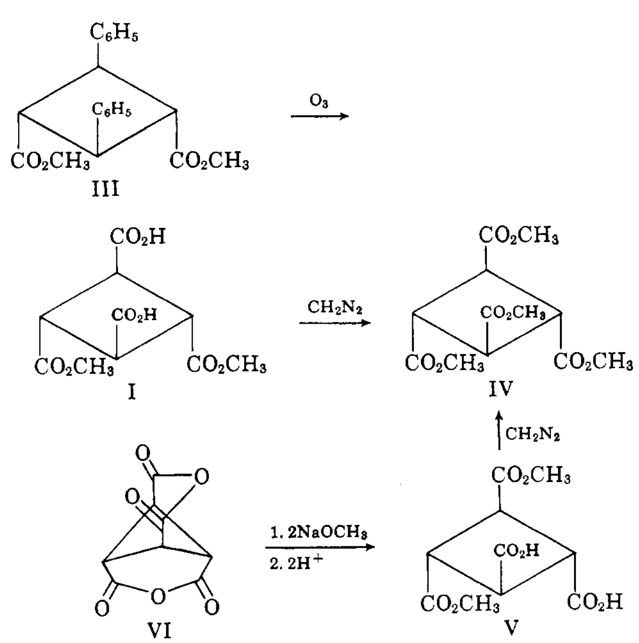
(3) G. W. Griffin and A. F. Vellturo, *J. Org. Chem.*, **26**, 5183 (1961).

(4) (a) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959); (b) K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters*, 2173 (1963); (c) D. M. Lemal, F. Menger, and G. W. Clark, *J. Am. Chem.*



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 ozonolysis[5] 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-tetracarbomethoxycyclobutane (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 VI[7] with 2 equiv. of sodium methoxide. All attempts to prepare I from VI by the addition of 1 equiv. of methanol, treatment with diazomethane, 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]

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. Vellturo, *Tetrahedron Letters*, No. 3, 13 (1960).

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

(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 C_4H_4O 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 report[1] that the loss of carbon monoxide by coumarin upon electron impact yields a C_8H_6O radical cation, this ion was assigned a benzofuran structure because of the close

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