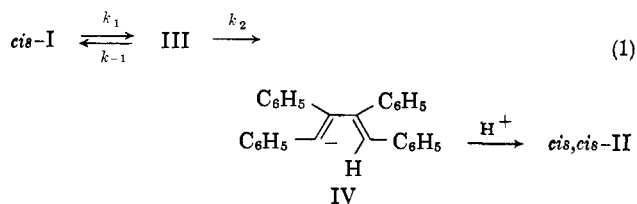


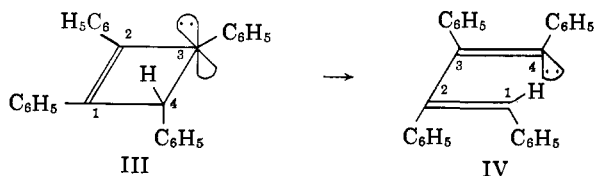
butene,^{5a} affords only *cis,cis*-II.¹² The rate constant at 24° in THF is $5 \times 10^{-5} \text{ sec.}^{-1}$, and $E_a = 21 \text{ kcal./mole.}^{13}$

It can now be demonstrated that, when *cis*-I undergoes reversible anion formation in dimethyl sulfoxide (DMSO), anion isomerization is competitive with anion protonation. A DMSO solution, 0.1 M in both *cis*-I and potassium *t*-butoxide, is completely isomerized to *cis,cis*-II in 15 min. at 24°. Since the rate of isomerization of *trans*-I is approximately the same in both DMSO and in THF (with or without added base) and is considerably slower than *cis*-I in DMSO with base, it is clear that the source of *cis,cis*-II is the anion III and not *trans*-I. In DMSO-*d*₆, *cis*-I with butoxide affords a mixture of approximately equivalent amounts of *cis*-I (*-d*₁ and *-d*₂) and *cis,cis*-II (*-d*₁ and *-d*₂) after 5 min., suggesting that k_{-1} and k_2 of eq. 1 are of comparable magnitude.¹⁴ To explain the absence of anion isom-



erization in THF (*i.e.*, k_2 is negligible) we propose that DMSO, with its unique ability to solvate cations, produces solvent-separated ion pairs of greatly increased reactivity relative to the stabilized ion pairs present in THF.

The conrotatory mechanism for cyclobutene isomerization¹⁵ is not readily applied in predicting the stereospecific isomerization of anion III, with its single sp_3 -hybridized center. The *cis* geometry at the butadienyl 1,2-bond is predictable from preferred eclipsing in the transition state of hydrogen, rather than phenyl, with the adjacent anionic π -lobe. The *cis* geometry at the 3,4-bond is less clear, but may be due to the minimum



movement necessary for the phenyl at C-3 in III to attain the configuration at C-4 in IV. Alternatively, the formation of *cis,cis*-II may be due to the stability of anion IV, which can exist in a quasi-five-membered ring sustained

(12) This rapid isomerization may explain why both Shechter^{4b} and Baker [W. Baker, J. W. Hilpern, and J. F. W. McOmie, *J. Chem. Soc.*, 479 (1961)] could only isolate *cis,cis*-II from reactions in which *trans*-I is a likely intermediate.

(13) The similarity between the rates and activation energies for I (*cis* and *trans*) and the *cis* and *trans* isomers of 1,2-diphenylbenzocyclobutene [R. Huisgen and H. Seidl, *Tetrahedron Letters*, 3381 (1964)] suggests that the rate of isomerization is primarily dependent on the allylic substituents.

(14) It is evident that solvent DMSO is serving as the proton source and that protonation is kinetically controlled. Cf. C. F. Price and W. H. Snyder, *J. Am. Chem. Soc.*, 83, 1773 (1961), who report kinetic control in the rearrangement of allylic ethers *via* their anions generated from butoxide in DMSO, and A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *ibid.*, 83, 3731 (1961), who demonstrate both kinetic control and solvent exchange with allylic olefins in this solvent-base system.

(15) R. B. Woodward and R. Hofmann, *ibid.*, 87, 395 (1965).

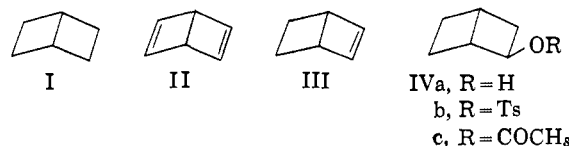
by hydrogen bonding of the relatively acidic proton to the ideally situated lone-pair orbital.

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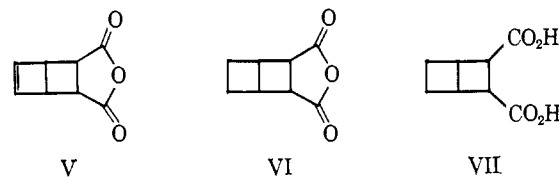
The Synthesis and Acetolysis of *exo*-Bicyclo[2.2.0]hex-2-yl Tosylate¹

Sir:

The synthesis of bicyclo[2.2.0]hexane² (I) and bicyclo[2.2.0]hexa-2,5-diene³ (II) have been reported. We now wish to report the synthesis of the remaining hydrocarbon in this series, bicyclo[2.2.0]hex-2-ene (III), its conversion to *exo*-bicyclo[2.2.0]hexan-2-ol (IVa), and the acetolysis of the tosylate of IVa (IVb).



Catalytic hydrogenation of the photoanhydride³ (V) of *cis*-1,2-dihydrophthalic anhydride gave bicyclo[2.2.0]hexane-2,3-dicarboxylic anhydride (VI),⁴ m.p. 84.5–86°, in 90% yield. Hydrolysis of VI gave bicyclo[2.2.0]hexane-2,3-dicarboxylic acid (VII), m.p. 152–156° (89%), which on oxidative bisdecarboxylation with lead tetraacetate in pyridine⁵ gave bicyclo[2.2.0]hex-2-ene (III, b.p. 43–48° (277 mm.)) in 30–38%



isolated yield.⁶

Hydrocarbon III gave a mass spectrometric molecular weight of 80 and exhibited a cracking pattern similar to cyclohexadiene. The n.m.r. spectrum of III (CCl₄ solution, TMS internal standard) exhibited olefinic proton resonance at τ 3.85, methine proton resonance centered at 6.83, and methylene proton resonance as absorption from 7.6 to 8.7, appearing in the expected ratio of 1:1:2.

Hydroboration⁷ of III and subsequent oxidation gave mainly *exo*-bicyclo[2.2.0]hexan-2-ol (IVa), b.p. 69–71° (12.5–13 mm.), n_D^{20} 1.4773, in 78% yield. The n.m.r. spectrum of IVa (neat, TMS internal standard)

(1) For the previous paper in this series on strained ring systems see R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, 86, 4866 (1964).

(2) (a) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, 24 (1960); (b) R. Srinivasan, *J. Am. Chem. Soc.*, 83, 4923 (1961); (c) C. E. Griffin, N. F. Hepfinger, and B. L. Shapiro, *ibid.*, 85, 2683 (1963).

(3) E. E. van Tamelen and S. P. Pappas, *ibid.*, 85, 3297 (1963).

(4) All new compounds have given satisfactory analyses.

(5) The conditions for the decarboxylation of VII are similar (reaction temperature 50–53°, time 1.5–2.5 hr.) to those reported for V.³ Oxidative decarboxylation of VI gives III in approximately 15% yield.

(6) V.p.c. analysis of the mixture before distillation indicated the yield of olefin III was 40–52%. At injection port temperatures above 150° some thermal isomerization of III was observed, and at 330° complete isomerization to 1,3-cyclohexadiene occurred.

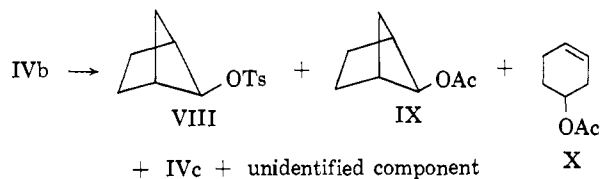
(7) G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 1 (1963).

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*-toluenesulfonfyl 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 $1.92 \pm 0.14 \times 10^{-4} \text{ sec.}^{-1}$ at 90° and $4.24 \pm 0.23 \times 10^{-5} \text{ sec.}^{-1}$ at 75° .^{10,11} Extrapolation to 25° gives $k = 9 \times 10^{-8} \text{ sec.}^{-1}$.

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*-toluenesulfonate⁸ (VIII) from the acetolysis mixture in 50% yield. The acetolysis rate constant for VIII is reported to be $5.82 \times 10^{-4} \text{ sec.}^{-1}$ at 164.2° ($9 \times 10^{-10} \text{ sec.}^{-1}$ 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 reported¹⁵ this question cannot be decided. An alternate consideration would be that this equilibrium

(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 $\Delta H^\ddagger = 24.7 \text{ kcal./mole}$ and $\Delta S^\ddagger = -8.2 \text{ e.u.}$ (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 reported¹² that X is a major product from the acetolysis of VIII. Further characterization of products was not made.

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.

(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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Received April 30, 1965

An Electrochemical Synthesis of a Bicyclobutane

Sir:

When *trans,trans,trans*-1,3-dicarboxy-2,4-dicarboxymethoxycyclobutane (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 5.78μ . 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

(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. Velturo, *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.*