Nemours and Rohm and Haas Corporations, and technically assisted by R. L. Thrift and L. Brodsky.

[10] National Science Foundation Predoctoral Fellow, 1966–1968; Public Health Service Predoctoral Fellow, 1968–1969.

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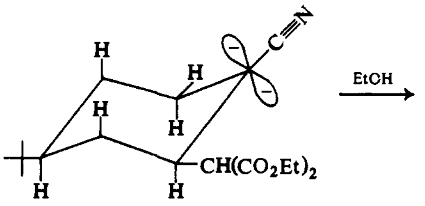
The Stereochemistry of Protonation of 2-Substituted Cyclohexyl Anions

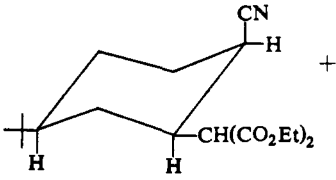
Sir:

There has been much discussion recently concerning the stereochemistry of C-protonation of nitronates and nitronic acids and of the ketonization of exocyclic enolates derived from ketones and esters,[1-4] but no concensus has been reached. We report some results in this area which throw light on the subject.

The addition of diethyl sodiomalonate in ethanol to 4-*t*-butyl-1-cyanocyclohexene *under conditions of kinetic control* gives mainly the *cis* product II together with some of the thermodynamically more stable *trans* isomer III.[5] Protonation of the intermediate delocalized anion I has, therefore, taken place from the equatorial side which, according to Zimmerman,[6] is the least hindered. It should be pointed out that, the nitrile group being linear, it would not be likely to give rise to any appreciable $A^{(1,3)}$ strain[1] in I, and that, in any event, the presence of the equatorial 4-*t*-butyl group in addition to the equatorial malonate group ensures that no chair–chair interconversion[1] can occur.

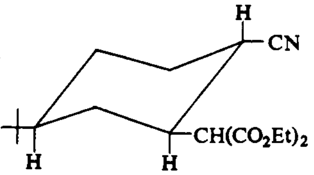


I



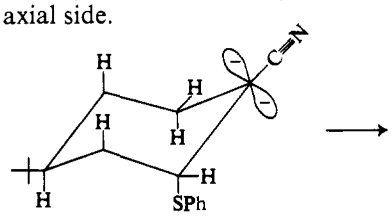
II

+

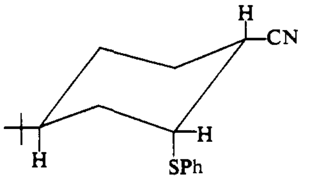


III

The addition of thiophenoxide ion to 4-*t*-butyl-1-cyanocyclohexene in ethanol gave a mixture of adducts: IV, mp 55–55.5°, and V,[7] bp 138–140° (0.1 mm), in which the thiophenoxy group was axial.[8] Under conditions of thermodynamic control (90 hr) the equilibrium mixture contained IV and V in the ratio 1.97:1. Under conditions of kinetic control (16 hr) the adducts were formed in the ratio of IV:V = 52.5:1; *i.e.*, IV was the main product of kinetic control of the protonation as well as the thermodynamically more stable isomer. Clearly, protonation of the intermediate anion VI in this case takes place more readily from the axial side, which is readily understood, as pointed out by Johnson and Malhotra,[1] in terms of the greater steric hindrance by the axial 2 substituent to the approach of the proton donor from the equatorial side than by the 3 and 5 axial protons to its approach from the axial side.

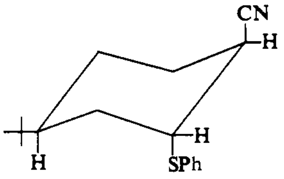


VI



IV

+



V

The situation in which the 1 substituent can give rise to $A^{(1,3)}$ strain with an equatorial 2 substituent, *but in which relief of such a strain by chair–chair interconversion is not possible*, was examined next. The addition of diethyl sodiomalonate in alcohol solution to ethyl 4-*t*-butylcyclohexene-1-carboxylate gave the intermediate enolate anion VII which, under conditions of kinetic control, gave VIII, mp 50.5–51.5°, and IX, bp 128° (0.05 mm), with VIII predominating.[9] Under thermodynamic control IX was the main product, as expected. Once again, approach from the equatorial side at C-1 appears to be the least hindered for the small proton donors (EtOH or CH_3CO_2H)[10] used in this work in spite of the presence of a bulky equatorial group at C-2.[11]

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[1] F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5495 (1965); S. K. Malhotra and F. J. Johnson, *ibid.*, **87**, 5493 (1965); F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

[2] F. G. Bordwell and M. M. Vestling, *J. Am. Chem. Soc.*, **89**, 3906 (1967).

[3] H. E. Zimmerman and P. S. Mariano, *ibid.*, **90**, 6091 (1968), and references cited therein.

[4] R. J. Sundberg and P. A. Bukowick, *J. Org. Chem.*, **33**, 4098 (1968).

[5] R. A. Abramovitch and D. L. Struble, *Tetrahedron*, **24**, 357 (1968); *Tetrahedron Letters*, 289 (1966).

[6] H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

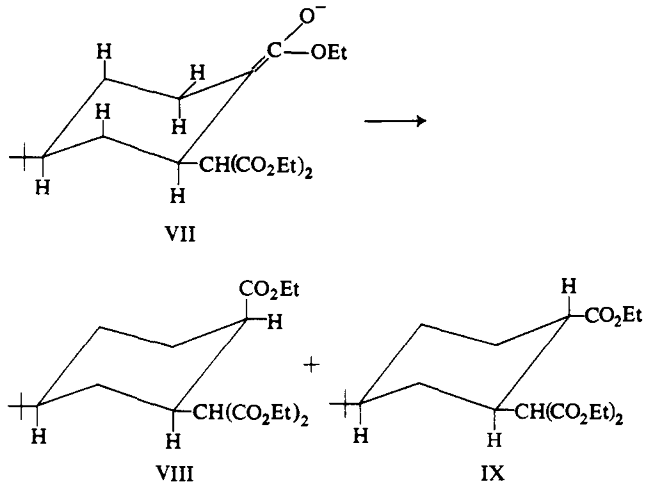
[7] Satisfactory analyses and infrared, nmr, and mass spectral data were obtained for all the new compounds reported.

[8] R. A. Abramovitch, M. M. Rogić, and N. Venkateswaran, in preparation.

[9] When a solution of diethyl malonate (2 mol), ethyl 4-*t*-butylcyclohexene-1-carboxylate (2 mol), and sodium ethoxide (1 mol) in ethanol was kept at room temperature for 2 weeks only VIII was formed. When a relatively smaller amount of olefin was used (1.36 mol) the ratio of VIII to IX was 2.2:1. Equilibration of either VIII or IX with NaOEt in boiling EtOH gave a mixture of VIII and IX in the ratio of 1:5.2–7 (a considerable amount of reversal of the Michael addition was also observed with both isomers). The structures of VIII and IX were confirmed by their conversion under mild conditions to the corresponding known[5] *cis*- and *trans*-4-*t*-butyl-2-carboxymethylcyclohexanecarboxylic acids.

[10] A direct proton transfer from the equatorial malonate residue in I and VII is stereochemically unlikely. A referee has pointed out, however, that a solvent-mediated transfer of a proton from the malonate residue involving a six-membered-ring transition state may take place. It has been previously shown that ethanol is a much better proton donor than diethyl malonate in this reaction.[5]

[11] Any flattening of the cyclohexane ring from the chair conformation would tend to make approach from the axial side easier and from the equatorial side more difficult since it would increase the dihedral angle between the group at C-1 and the axial protons at C-3 and C-5 but decrease the angle between the carbethoxyl group and the axial protons at C-2 and C-6.



VII

VIII

IX

The above results appear to bridge the opposing views[1-4] and upholds the general hypothesis of least hindered approach[3] in such protonations.

Acknowledgment. Part of this work was supported by the Defence Research Board of Canada whom we thank.

[12] To whom inquiries should be addressed at the University of Alabama.

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Kinetic Evidence for a Bishomocyclobutenium Dication[1]

Sir:

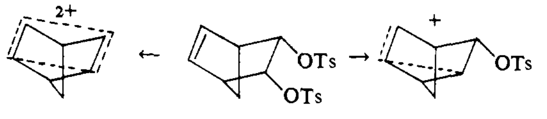
Dicarbonium ions have been recognized in structurally diverse situations.[2] A particularly elusive member of this class has been the cyclobutenium or cyclobutadiene dication (I). This ion was expected to be relatively stable, since it conforms to the Hückel rule ($n = 0$) and is isoelectronic with the known cyclopropenium ion (II).[3]


I


II

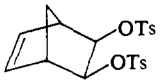
Because of the forced proximity of the charges, the stability of I is undoubtedly less than that of II, although the apparent success of several derivative syntheses[4] confirms the presence of some special stability for the cyclobutenium structure.

We wish to report kinetic evidence from the acetolysis of the conformationally rigid ditosylate of *exo-cis*-bicyclo[2.2.1]hept-5-ene-2,3-diol (III) that may implicate rapid loss of both tosylate groups to form a bishomocyclobutenium dication (IV). In the past,[5] two tosylate or brosylate groups in a molecule have been observed to undergo independent, stepwise solvolysis. Such a pathway for III would lead by way of homoallylic participation to ion V, which would absorb a molecule of solvent to form an acetoxy tosylate intermediate (in acetolysis) before losing the second tosylate group.

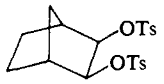


IV III V

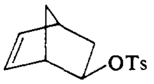
The essential kinetic argument involves comparison of the rates of the saturated and unsaturated mono- and ditosylates (III, VI–VIII). The double bond in monotosylates is known to be rate retarding, despite homoallylic assistance.[6] The second tosylate group is known to cause considerable rate retardation in a stepwise reaction, since the first-formed carbonium ion is destabilized by the remaining electron-withdrawing tosylate group.[5] If III were to lose both tosylate groups to form a cyclobutenium-stabilized dicarbonium ion (IV), the double bond would necessarily be rate enhancing (VI/III) and the second tosylate group would be much less rate retarding (VII/III).



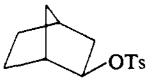
III



VI



VII



VIII

We have prepared[7] III and VI–VIII and measured their solvolysis rates by the usual titrimetric methods in buffered (KOAc) acetic acid in duplicate or triplicate at each of three or four temperatures. The rates and activation parameters at 75° are given in Table I. The rate-

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[1] This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (PRF 2970-A 4, 5), and by the National Science Foundation.

[2] H. Hart, T. Sulzberg, R. H. Schwendeman, and R. H. Young, *Tetrahedron Lett.*, 1337 (1967); I. S. Akhrem, E. I. Fedin, B. A. Kvasov, and M. E. Vol'pin, *ibid.*, 5265 (1967); H. Volz and M. J. Volz de Lecea, *ibid.*, 4675 (1966); C. U. Pittman, Jr., *ibid.*, 3619 (1967); J. S. McKechnie and I. C. Paul, *J. Am. Chem. Soc.*, **89**, 5482 (1967); B. E. Fleischfresser, W. J. Cheng, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 2172 (1968); D. M. Brouwer, *Chem. Commun.*, 515 (1967).

[3] R. Breslow, J. T. Groves, and G. Ryan, *J. Am. Chem. Soc.*, **89**, 5048 (1967); D. G. Farnum, G. Mehta, and R. G. Silberman, *ibid.*, **89**, 5048 (1967).

[4] D. G. Farnum and B. Webster, *ibid.*, **85**, 3502 (1963); H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); H.-E. Sprenger and W. Ziegenbein, *Angew. Chem. Intern. Ed. Engl.*, **7**, 530 (1968); also see M. H. Benn, T. S. Sorenson, and A. M. Hogg, *Chem. Commun.*, 574 (1967), for mass spectral evidence.

[5] S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 816 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948); A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **81**, 1650 (1959); A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).

[6] The subject has been discussed by M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 672 (1967).

[7] The unsaturated diol was prepared from bicyclo[2.2.1]heptadiene according to the procedure of Y. F. Shealy and J. D. Clayton, *J. Am. Chem. Soc.*, **88**, 3885 (1966). We thank Dr. Shealy for sending us the experimental details. An nmr analysis of the *exo-cis* and *endo-cis* isomers leaves no doubt concerning the stereochemistry of the product (M. C. Thorpe, private communication). The unsaturated monoalcohol was synthesized by the method of S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2733 (1966). Hydrogenation of these materials yielded the saturated compounds. All the tosylates were crystalline and pure by our analytical techniques.