Communications to the Editor

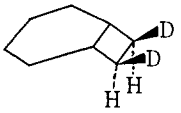
Stereochemistry of the Thermal Cyclobutane to Ethylene Reaction. Pyrolysis of 7,8-*cis*,*exo*-Dideuteriobicyclo[4.2.0]octane

Sir:

The kinetics and stereochemistry of the thermal fragmentation of cyclobutanes to pairs of ethylenic products have been interpreted in terms of an intermediate tetramethylene diradical.[1] The lifetime of the intermediate and the stereochemistry of the products derived from the diradical are determined by the relative rates of several competing processes. The diradical formulation can encompass all stereochemical results respecting an ethylenic product ranging from complete preservation of the geometrical relationships existing in the cyclobutane precursor, when the second C–C bond cleavage converting the diradical to products is much faster than rotations about C–C bonds, all the way to the thermodynamically determined mixture of ethylenic isomers corresponding to the difference in activation energy for the processes leading from the intermediate to *cis* or *trans* products, when k(rotations) $\gg$ k(scission). The general acceptance of the tetramethylene diradical hypothesis may be traced to its versatility and the absence of conflicting experimental facts.

Orbital symmetry theory applied to the cyclobutane fragmentation gives $[\sigma_s{}^2 + \sigma_a{}^2]$ as an allowed designation and predicts that, if the process is "concerted," the stereochemical relationships at three of the four carbons of the cyclobutane will be retained in the products.[2]

We have studied the stereochemistry of the pyrolysis of 7,8-*cis*,*exo*-dideuterio-*cis*-bicyclo[4.2.0]octane (**1**), a system giving predominantly ethylene rather than 1,7-octadiene, and assumed constrained to give *cis*-cyclohexene and thus to force the antarafacial role upon the ethylenic moiety in the "concerted" mechanism. Reduction of bicyclo[4.2.0]oct-7-ene[3] with dideuteriodiimide[4,5] gave the labeled cyclobutane **1**. This substrate was pyrolyzed for varying times at ≤ 1 mm and 450° in sealed tubes and the 1,2-dideuterioethylene produced was transferred on a vacuum line to a gas infrared cell. The relative intensities of the vibrational band absorptions for the *cis* (843 cm^{-1}) and *trans* (987 cm^{-1}) isomers of 1,2-dideuterioethylene[6] in the product compared with the relative intensities of the same bands observed for a thermodynamically controlled mixture of *cis*- and *trans*-1,2-dideuterioethylene[7] indicated that the proportion of *trans* isomer formed was larger than the thermodynamic value by a 1.309 ± 0.004 to 1 ratio. Assuming a 50:50 mixture at equilibrium, this ratio implies 57 ± 1% *trans* isomer in the pyrolysis mixture. Control experiments in which bicyclo[4.2.0]octane[8] was pyrolyzed in the presence of *trans*-1,2-dideuterioethylene[9] showed that *cis–trans* isomerization of 1,2-dideuterioethylene under the reaction conditions was negligible. When **1** was pyrolyzed at 500° in a flow reactor with nitrogen as the carrier, the 1,2-dideuterioethylene produced was 62 ± 3% *trans*.



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These results, demonstrating *trans*-1,2-dideuterioethylene as the major isomer from the pyrolysis of **1**, show that the predominant portion of the reaction occurs in a stereochemical sense incompatible with both the tetramethylene diradical hypothesis and the completely stereoselective antarafacial elimination of ethylene predicted through orbital symmetry theory.

The first published account of a cyclobutane pyrolysis in a system having stereochemical properties sufficient to test for the stereochemistry of both ethylenic products, a recent communication on the thermal decomposition of 6,7-dimethylbicyclo[3.2.0]heptanes,[10] led to evidence "strongly in favor of a biradical intermediate." It may be that here, as in the 7-substituted bicyclo[3.2.0]hept-2-ene systems studied by Berson and coworkers,[11] methyl substituents are not merely geometrical markers but effective disrupters of stereochemical norms.

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[1] See H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966), and H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969), for references.

[2] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and unpublished.

[3] R. H. S. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).

[4] E. J. Corey, D. J. Pasto, and W. L. Mock, *ibid.*, **83**, 2957 (1961); *cf.* the *exo* addition of deuteriodiimide to norbornadienes and bicyclo-[2.1.0]pent-2-ene: W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **89**, 410 (1967); P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969).

[5] From hydrazine hydrate-d_6 (Merck Sharp and Dohme of Canada Ltd., Montreal) in C_2H_5OD.

[6] B. L. Crawford, J. E. Lancaster, and R. G. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953).

[7] Prepared by the hydrogen sulfide catalyzed isomerization of the *trans* isomer at 450°, following a most helpful suggestion of Professor B. S. Rabinovitch.

[8] Prepared by hydrogenation of bicyclo[4.2.0]oct-7-ene over Pt; satisfactory analyses were obtained.

[9] W. I. Patterson and V. du Vigneaud, *J. Biol. Chem.*, **123**, 327 (1938).

[10] A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969).

[11] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967); J. A. Berson, comment at the 21st National Organic Chemistry Symposium, Salt Lake City, Utah, June 15–19, 1969.

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Structure and Reactivity of Organic Ions in Gas-Phase Radiolysis. I. The $C_7H_7^+$ Ion from Toluene, Ethylbenzene, and *m*-Xylene

Sir:

It is well known that in the mass spectra of simple alkylbenzenes such as toluene, ethylbenzene, and xylenes the most abundant ion is $C_7H_7^+$ in common with these compounds. The $C_7H_7^+$ ion has been suggested to be a tropylium ion having a symmetrical seven-