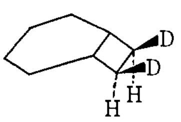
Stereochemistry of the Thermal Cyclobutane to Ethylene Reaction. Pyrolysis of 7,8-*cis*,*exo*-Dideuteriobicyclo[4.2.0]octane

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 $k(\text{rotations}) \gg k(\text{scission})$. 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



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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*.

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-

Table I. The Yields of Dimeric Product in the Gas-Phase Radiolysis of Alkylbenzenes

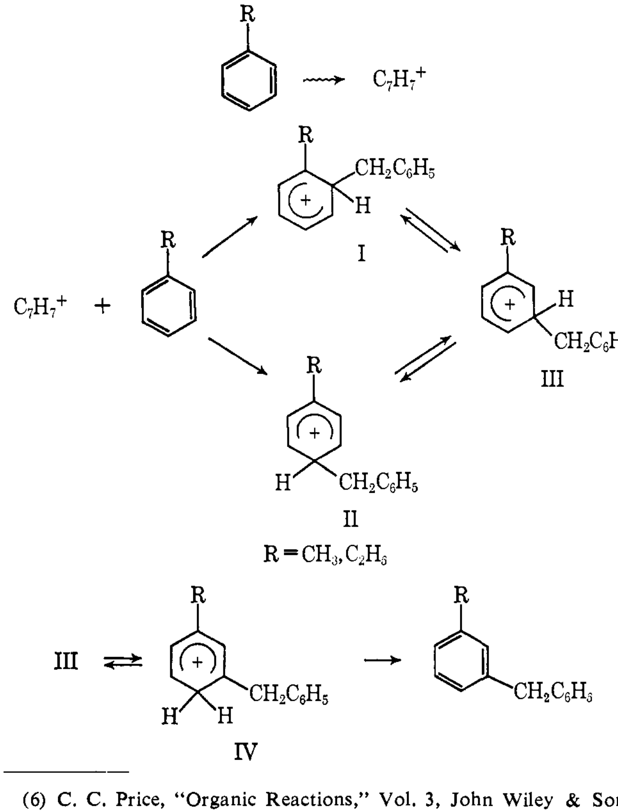
Alkylbenzene	Pressure, mm	Dimeric product	G	G^a with NO
Toluene	10.7	3-Methyldiphenylmethane	0.34	0.34
		2-Methyldiphenylmethane	0.05	0.05
		4-Methyldiphenylmethane	0.05	0.06
		Bibenzyl	0.03	0
Ethylbenzene[b]	4.7	3-Ethyldiphenylmethane	0.86	0.85
		2-Ethyldiphenylmethane	0.08	0.08
		4-Ethyldiphenylmethane	0.12	0.14
		Bibenzyl	0.05	0
m-Xylene[b]	5.0	3,5-Dimethyldiphenylmethane	0.28	0.30
		2,4-Dimethyldiphenylmethane	0.18	0.15
		2,6-Dimethyldiphenylmethane	0.02	0.01

[a] The mole ratio of added NO to alkylbenzene was about 0.10. [b] A few other dimeric products not shown in the table were also formed but in small yields.

carbon-atom ring structure on the basis of the isotope randomization observed in the mass spectra of labeled alkylbenzenes.[1] However, there is still the possibility of the existence of a benzyl-type ion if the tropylium ion is viewed as an unstable intermediate responsible for the skeletal rearrangement.[1] On the other hand it is reported in mass spectrometric studies of ion–molecule reactions in gaseous aromatic hydrocarbons that the $C_7H_7^+$ ion produced from toluene and xylenes adds to the neutral parent molecule to form a dimeric ion,[2,3] though the product formation of such an ionic reaction has not been investigated. During the course of our investigations of the gas-phase radiolysis of alkylbenzenes[4] the dimeric products have been observed to be formed by the ion–molecule reaction involving the $C_7H_7^+$ ion. This communication presents a study on the structure of the $C_7H_7^+$ ion and its reactivity with aromatic compounds.

Toluene, ethylbenzene, and *m*-xylene vapors were irradiated with ^{60}Co γ rays at room temperature and the dimeric products were analyzed gas chromatographically.[5] In all cases the corresponding benzylated alkylbenzenes were obtained as the main products. The G values were not appreciably affected with nitric oxide added as a radical scavenger, as shown in Table I, and it is indicated that the benzylation is a nonradical process. It seems most reasonable to conclude that these alkyldiphenylmethanes were formed by electrophilic substitution initiated by the attack of the $C_7H_7^+$ ion on the aromatic rings considering the following facts: (a) the $C_7H_7^+$ ion is a common reactive species formed in considerable yield by the irradiation of these alkylbenzenes; (b) aromatic compounds tend to be subject to electrophilic substitution.

In the cases of toluene and ethylbenzene the benzylated products exclusively consisted of those substituted at a *meta* position to the resident alkyl group, and for *m*-xylene 3,5-dimethyldiphenylmethane was most abundant; it was formed by benzylation at the position *meta* to both methyl groups (Table I). Alkyl groups are *ortho–para* directing in electrophilic aromatic substitutions. It has been shown that in Friedel–Crafts alkylations of alkylbenzenes the more vigorous the conditions, the greater is the tendency for the formation of abnormal *meta* derivatives.[6,7] The large proportion of *meta* isomer observed in Friedel–Crafts alkylation has been attributed to the formation and the isomerization of benzenonium ions (σ complexes) in the transition state, as reported in the HBr–AlBr$_3$ catalyzed isomerizations of dialkylbenzenes.[8] In view of these previous investigations in the liquid-phase catalytic reactions, the mechanism for the formation of the *m*-alkyldiphenylmethanes in the gas-phase radiolysis of toluene and ethylbenzene has been suggested as follows.



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(1) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 453.

(2) S. Wexler and R. P. Clow, *J. Am. Chem. Soc.*, **90**, 3940 (1968).

(3) A. Giardini-Guidoni and F. Zocchi, *Trans. Faraday Soc.*, **64**, 2342 (1968).

(4) Y. Yamamoto, S. Takamuku, and H. Sakurai, to be published.

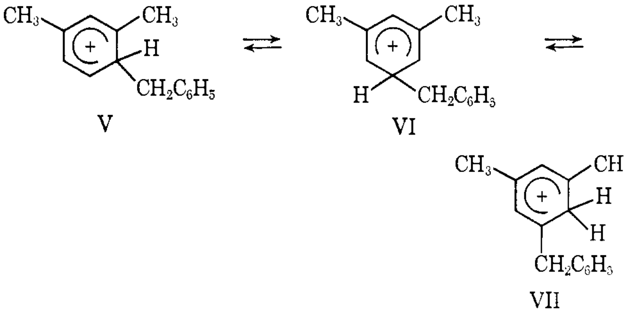
(5) The irradiations were carried out at dose rate 1.2×10^{15} eV/μmol hr and for analysis several kinds of columns, such as APL, Thermol-6000, SE-30, and mixed nitrates [W. W. Hanneman, C. F. Spencer, and J. F. Johnson, *Anal. Chem.*, **32**, 1386 (1960)], were used.

(6) C. C. Price, "Organic Reactions," Vol. 3, John Wiley & Sons, Inc., New York, N. Y., 1946, p 1.

(7) For example, in the benzylation of toluene at 25° the amount of *meta* isomer formed is reported to be 4.5% when AlCl$_3$–CH$_3$NO$_2$ and benzyl chloride are used as a catalyzer and a benzylating agent, respectively [G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962)], and to increase 21.1 to 45.7% with reaction times of 0.01–10 sec when GaBr$_3$ and benzyl bromide are used [H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3320 (1959)].

(8) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

In the case of *m*-xylene, where the $C_7H_7^+$ ion may predominantly attack at position 4 of the benzene ring because of steric hindrance at position 2 by two adjacent methyl groups, the similar isomerization of benzenonium ion has been proposed to be



The stabilization of these benzenonium ions which is caused through a resonance and inductive effect of alkyl groups may increase in the order IV $>$ I $\simeq$ II $>$ III, and VII $>$ V $>$ VI. Since the isomerizations from I and II to IV and from V to VII proceed *via* the most unstable ions (III and VI, respectively), these isomerizations may require activation energies. Thus, the isomerization is thought to occur easily in the gas phase where the benzenonium ions exist as free ions with excess vibrational energy. On the other hand, in the liquid-phase catalytic reactions the ions I, II, and V are stabilized by collisional deactivation and interaction with solvent and counterions and isomerize very poorly under mild reaction conditions. Of interest is the result indicating that electrophilic substitution of alkylbenzenes by free ions in the gas phase is thermodynamically controlled and predominantly leads to the formation of *meta* isomers. In the radiolysis of *m*-xylene, 2,4-dimethyldiphenylmethane was also formed in considerable yield (Table I).[9] This result can be ascribed to the fact that the benzenonium ion V is more stable than I and II because two methyl groups are attached to the electron-deficient carbon atoms.

In the radiolysis of these alkylbenzenes the products with seven-membered rings which would be expected to be formed through tropylium ions were not detected, and the reaction of the $C_7H_7^+$ ion produced the benzylated product as described above. Furthermore, the high reactivity of the $C_7H_7^+$ ion with aromatic compounds observed in the radiolysis suggests that the $C_7H_7^+$ ion leading to the formation of alkyldiphenylmethane might be a benzyl ion having a positively charged center rather than a tropylium ion in which the positive charge is distributed equally among the seven carbon atoms. On the basis of our experimental results it seemed reasonable to assume that a rapid variation of the structure between tropylium and benzyl ion occurs and benzyl ion reacts with aromatic compounds.

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[9] In the $AlCl_3$–CH_3NO_2 catalyzed benzylation of *m*-xylene with benzyl chloride the isomer distribution is 19.8% 2,6- and 80.2% 2,4-dimethyldiphenylmethane, but 3,5-dimethyldiphenylmethane is not detected [G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962)].

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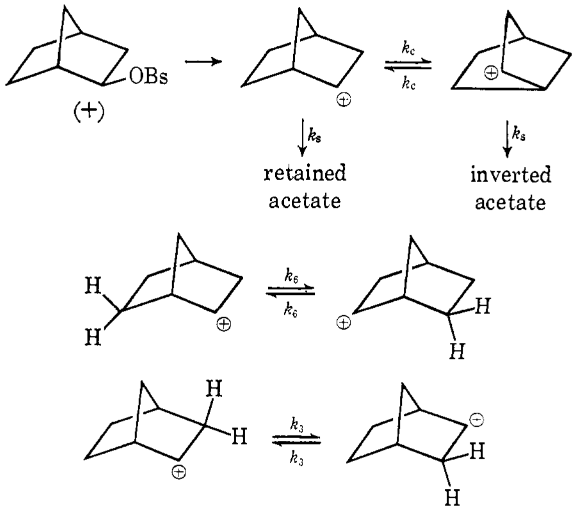
Ratio of the Rates of Solvent Attack and 3,2-Hydride Shift in the Norbornyl Cation[1]

Sir:

We have measured upper limits for the ratio k_s/k_3 (see Chart I for definitions) of the rates of solvent attack and 3,2-hydride shift for the norbornyl cation. Both π-route[2] and σ-route[2] acetolyses of the appropriate tosylates (I and II) were investigated. We find: k_s/k_3 (π route) $\leq$ 115; k_s/k_3 (σ route) $\leq$ 240. We became interested in this problem because of its importance to the calculation[3–5] that the rate (k_c) of Wagner–Meerwein rearrangement between classical norbornyl ions must approximate that of a molecular vibration. In one of the methods[3] by which k_c was estimated, the minimum ratio $(10^{8.8})$ for k_6/k_3 as determined by Saunders, Schleyer, and Olah[6] for "magic acid" was assumed also to be valid during the acetolysis of 2-*exo*-norbornyl tosylate. We questioned the validity of this assumption[3] because of the observation[7] that, whereas phenyl migrated much faster than hydrogen during solvolyses of 1,2,2-triarylethyl derivatives, these same materials, in "magic acid," exhibited only hydride shifts and no observable aryl migration.[8,9] As we pointed out[10] earlier, a carbon-14 label in the 4 position of the norbornyl ion A is unaffected either by carbon–carbon migration (k_c) or by 6,2-hydride shift (k_6).

Chart I



If we assume that there is no unprecedented side reaction,[11] then it is only through 3,2- or 7,1-hydride

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

[2] (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965, p 397; (b) S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

[3] Reference 2a, p 526.

[4] D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, 90, 1903 (1968).

[5] See also the book review by C. J. Collins, *ibid.*, **88**, 4117 (1966).

[6] M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

[7] C. J. Collins and W. A. Bonner, *ibid.*, **75**, 5372, 5379 (1953); **75**, 92, 99, 6725 (1955); **78**, 5587 (1956); C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

[8] G. A. Olah, C. U. Pittman, E. Namanworth, and M. B. Comisarow, *ibid.*, **88**, 5571 (1966).

[9] S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952), have also repeatedly called attention to the importance of environment in carbonium ion processes.

[10] See also C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967).