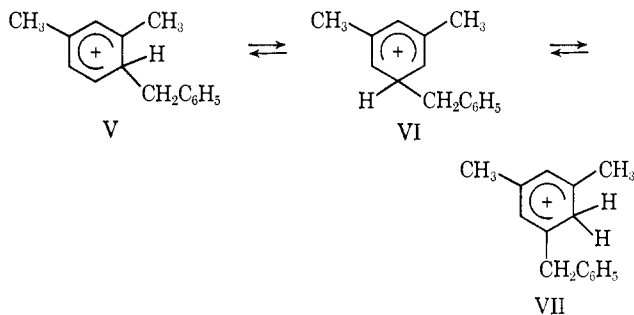


In the case of *m*-xylene, where the $C_7H_7^+$ ion may predominantly attack at position 4 of the benzene ring because of steric hindrance at position 2 by two adjacent methyl groups, the similar isomerization of benzenonium ion has been proposed to be



The stabilization of these benzenonium ions which is caused through a resonance and inductive effect of alkyl groups may increase in the order $IV > I \approx II > III$, 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.

(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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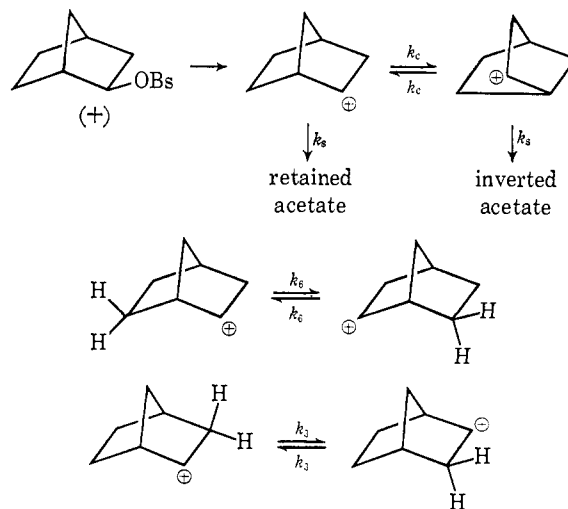
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Ratio of the Rates of Solvent Attack and 3,2-Hydride Shift in the Norbornyl Cation¹

Sir:

We have measured upper limits for the ratio k_6/k_3 (see Chart I for definitions) of the rates of solvent attack

Chart I



and 3,2-hydride shift for the norbornyl cation. Both π -route² and σ -route² acetolyses of the appropriate tosylates (I and II) were investigated. We find: k_6/k_3 (π route) ≤ 115 ; k_2/k_3 (σ route) ≤ 240 . We became interested in this problem because of its importance to the calculation³⁻⁵ that the rate (k_c) of Wagner-Meerwein rearrangement between classical norbornyl ions must approximate that of a molecular vibration. In one of the methods³ by which k_c was estimated, the minimum ratio ($10^{3.8}$) for k_6/k_3 as determined by Saunders, Schleyer, and Olah⁶ for "magic acid" was assumed also to be valid during the acetolysis of 2-*exo*-norbornyl tosylate. We questioned the validity of this assumption³ because of the observation⁷ 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 out¹⁰ 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).

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

(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).

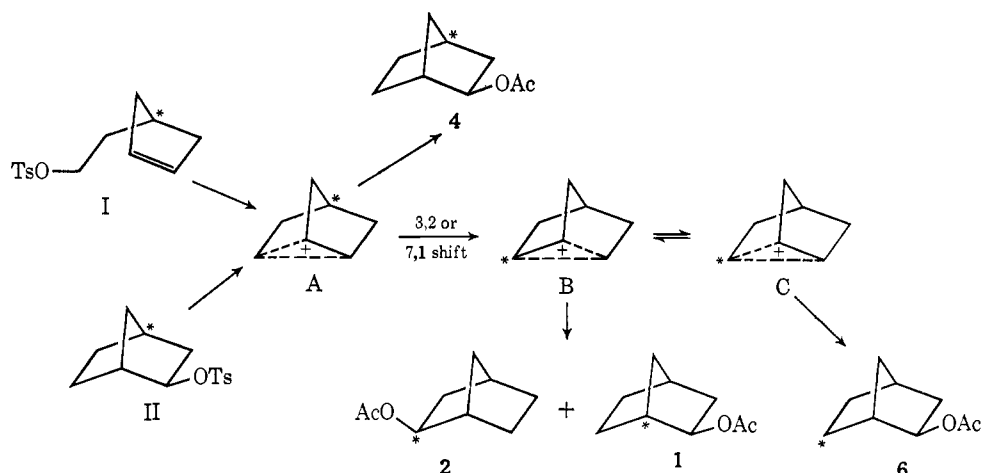
(7) C. J. Collins and W. A. Bonner, *ibid.*, **75**, 5372, 5379 (1953); **75**, 92, 99, 6725 (1955); **78**, 5587 (1956); C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959).

(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**, 2760 (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).

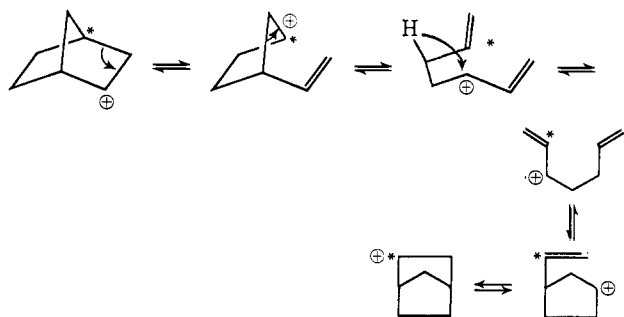
Chart II



shift that the carbon-14 can escape the 4 position (Chart II). We therefore prepared¹² and acetolyzed I (18.0 mCi of ¹⁴C/mol) in buffered acetic acid at 50.0 ± 0.2°. The product (1, 2, 4, 6) was reduced with lithium aluminum hydride to norborneol-¹⁴C which was oxidized to 2-norbornanone with pyridine-CrO₃.¹³ Addition of phenylmagnesium bromide afforded 2-*exo*-phenyl-2-norborneol, which was dehydrated to 2-phenyl-2-norbornene and oxidized to benzoic-¹⁴C acid, containing 0.33% of the original radioactivity. Another sample of the above norbornanone-¹⁴C was converted *via* the Grignard reaction to 2-*exo*-methyl-2-norborneol, which was dissolved in 97–98% formic acid; the solution was kept at 65° for 1 hr.¹⁴ The labeled 1-methyl-2-*exo*-norborneol obtained from the product was oxidized to the ketone, which was converted *via* Grignard reaction to 2-*exo*-phenyl-1-methyl-2-norborneol; on oxidation, benzoic-¹⁴C acid was obtained which was shown to have 0.52% of the original carbon-14.¹⁵

The results of repeated experiments are summarized in Chart III. The larger fraction of carbon-14 in C₁ with respect to C₂ is not unexpected,¹⁰ and will be explained in a subsequent paper.

(11) A referee has proposed the following scheme to explain our results.



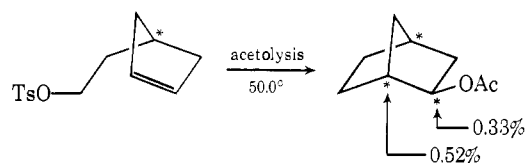
(12) The synthetic method was: *cis*-1,4-dichloro-2-butene through the disodiomalonic-2-¹⁴C ester synthesis to yield Δ³-cyclopentene-1-¹⁴C-carboxylic acid, which was converted by the Arndt-Eistert reaction and subsequent treatment with lithium aluminum hydride to 2-(Δ³-cyclopentenyl-1-¹⁴C)ethanol: K. Murdock and B. Angier, *J. Org. Chem.*, **27**, 2935 (1962).

(13) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(14) P. von R. Schleyer, *ibid.*, **89**, 3902 (1967).

(15) Isotopic purity of the benzoic-¹⁴C acid samples was established by the use of a Barber-Colman vapor phase chromatograph equipped with a radioactivity monitor.

Chart III



The product of π-route acetolysis, now containing a known fraction of its carbon-14 in positions 1 and 2, was converted to 2-*exo*-norbornyl tosylate, which was then acetolyzed. The product, 2-*exo*-norbornyl acetate, was reconverted to *exo*-norbornyl tosylate and reacetolyzed. This procedure was repeated until a total of four acetolysis cycles had been completed. Degradations of the acetolysis products after cycles 2 and 4 were carried out as for the product of π-route acetolysis, and the carbon-14 contents of position 2 were determined. The results are: after two cycles, 0.46% carbon-14 in C₂; after four cycles, 0.92% carbon-14 in C₂, 1.52% in C₁. These data not only demonstrate 3,2-hydride shift during σ-route acetolysis of II but also confirm the validity of the degradative method. The intramolecularity of the observed 3,2-hydride shift was demonstrated by repeating the reaction with tritium-labeled acetic acid (395 mCi/mol). There was no measurable fraction of tritium in the product. It can easily be shown that the ratio k_8/k_3 is given by the relation

$$\frac{k_8}{k_3} = \frac{\text{mole fraction of } ^{14}\text{C in 4 position}}{\text{mole fraction of } ^{14}\text{C in other positions}} - 1$$

from which the values given in the first paragraph were calculated. Since we know¹⁰ k_8/k_6 to be 1.55 ± 0.35, then k_6/k_3 for the acetolyses is no greater than 100–200, and not 10^{8.8} as has been estimated⁶ for “magic acid”.

(16) Oak Ridge Associated Universities Predoctoral Fellow. The results reported in this paper were taken from the Ph.D. dissertation of C. E. Harding.

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