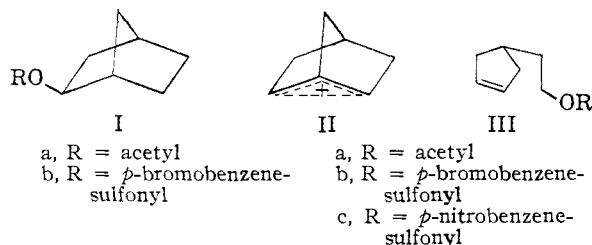


1,5 PARTICIPATION IN THE
SOLVOLYSIS OF β -(Δ^3 -CYCLOPENTENYL)-
ETHYL *p*-NITROBENZENESULFONATE

Sir:

Although acetolysis of norbornyl brosylate (Ib) has been shown to proceed through the non-classical carbonium ion (II)^{1,2} to *exo*-norbornyl acetate (Ia), a second possible product from ion II, β -(Δ^3 -cyclopentenyl)-ethyl acetate (IIIa), was not observed. For this reason, β -(Δ^3 -cyclopentenyl)-ethyl *p*-nitrobenzenesulfonate (IIIc) was prepared



and solvolyzed in acetic acid at reflux temperature. The sole product of this acetolysis was *exo*-norbornyl acetate (Ia), b.p. 80° (11 mm.), n_D^{26} 1.4563. Vapor phase chromatographic analysis³ indicated less than 0.5% of acetate IIIa. The product was characterized further by hydrolysis to *exo*-norborneol,⁴ m.p. 120–123°, and formation of the phenylurethan, m.p. 146–147°.

The required β -(Δ^3 -cyclopentenyl)-ethanol (III, R = H) was prepared as described by alkylation of ethyl cyanoacetate with Δ^3 -cyclopentenyl tosylate⁵ and afforded a 60% yield of ethyl α -cyano- α -(Δ^3 -cyclopentenyl)acetate,⁶ b.p. 143° (16 mm.), n_D^{25} 1.4584, N-benzylamide, m.p. 115–116°, which upon hydrolysis with 50% aqueous ethanolic potassium hydroxide produced Δ^3 -cyclopentenylmalonic acid, m.p. 149–150° dec., in 90% yield. Decarboxylation of the malonic acid in refluxing pyridine gave Δ^3 -cyclopentenylacetic acid, which without purification was reduced with lithium aluminum hydride to β -(Δ^3 -cyclopentenyl)-ethanol, b.p. 180–182°, n_D^{25} 1.4691, phenylurethan, m.p. 62–64.5°, *p*-nitrobenzenesulfonate (IIIc), m.p. 65–67°. Hydrogenation of the unsaturated alcohol yielded β -cyclopentylethanol,⁷ b.p. 79–82° (10 mm.), n_D^{25} 1.4559, *p*-nitrobenzenesulfonate, m.p. 74–75°.

Acetolysis of 0.04 M *p*-nitrobenzenesulfonate IIIc at 60° gave a first order titrimetric rate constant of 1.10×10^{-4} sec.⁻¹. This is about 95 times faster than the rate observed for acetolysis of β -cyclopentylethyl *p*-nitrobenzenesulfonate under the same conditions and indicates 1,5 participation of the double bond, presumably with formation of the non-classical structure II. Acetolysis of *p*-nitrobenzenesulfonate IIIc in 0.04 M sodium acetate in acetic acid also gave acetate Ia exclusively,

(1) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949); **74**, 1147 (1952); **74**, 1154 (1952).

(2) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

(3) Analysis was carried out with a 150 foot Golay "Ukon" column, 160°.

(4) Trace amounts of *endo* product were present as indicated by vapor phase chromatography.

(5) E. L. Allred, J. Sonnenberg and S. Winstein, *ibid.*, **81**, 5833 (1959); *J. Org. Chem.*, **25**, 26 (1960).

(6) Except where indicated, satisfactory analyses have been obtained for all new compounds.

(7) G. R. Yohe and R. Adams, *J. Am. Chem. Soc.*, **50**, 1505 (1928).

while acetolysis of *p*-bromobenzenesulfonate IIIb (an oil at room temperature) in acetic acid alone gave acetate Ia containing about 3% unsaturated acetate IIIa.³

Participation of the double bond with formation of the norbornyl structure gives additional information about the character of the non-classical carbonium ion. Aside from this inherent theoretical interest, the process provides a unique synthetic route to this, and possibly other, bicyclic systems.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN

RICHARD G. LAWTON

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REACTIONS OF ATOMIC CARBON
WITH SIMPLE HYDROCARBONS:
EVIDENCE FOR C-H BOND INSERTION¹

Sir:

The reactions of atomic carbon with hydrocarbons have been studied. A new method was employed in which a beam of C¹¹ ions in the Mev. energy range was produced by a nuclear reaction and passed through a foil into a chamber containing the hydrocarbon under study. The charge of this beam is governed by the resonance rule² which requires that it be neutral in the energy range where chemical reaction is possible. These considerations also suggest that the atoms probably are in their ground (triplet) state. Throughout this discussion it will be assumed that carbon reacts chemically in the triplet state as indicated by the resonance rule. However, reaction mechanisms similar to those postulated can be written for singlet carbon.

Only a trace quantity ($\sim 10^6$) of C atoms is used. The molecules in which they become incorporated are separated by gas chromatography and detected by a gas flow counter sensitive to the beta decay of the 20.5 minute C¹¹. A significant aspect of this method is that only small amounts of radiation energy are introduced into the system (< 0.01 ev./molecule). The products formed by C atom reaction thus are not likely to be modified by subsequent radiation induced reactions. The method is described in detail elsewhere.³

At present it is not known whether the products reported and the reactions discussed below are dependent on the kinetic energy of the carbon. This question is being investigated. Preliminary indications are that the major reactions undergone by thermal and high kinetic energy carbon atoms are qualitatively similar.

(1) Studies supported by the U. S. Atomic Energy Authority. The assistance of Dr. Mary Pandow and Mr. Paul Polak with these experiments is gratefully acknowledged. Contribution No. 1657 from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

(2) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, Oxford, 1952, p. 253.

(3) M. Pandow, Ph.D. thesis, Yale University, 1960. Material being prepared for publication in *J.A.C.S.*