## 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

I II III

a, R = acetyl
b, R = p-bromobenzene-
sulfonyl

a, R = acetyl
b, R = p-bromobenzene-
sulfonyl
c, R = p-nitrobenzene-
sulfonyl
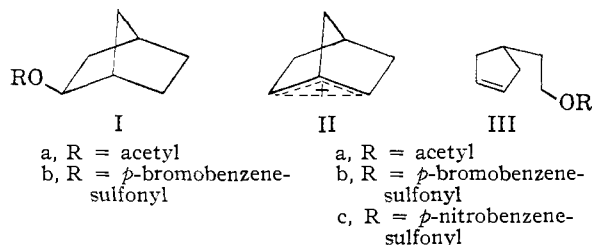
and solvolyzed in acetic acid at reflux temperature. The sole product of this acetolysis was exo-norbornyl acetate (Ia), b.p. 80°(11 mm.), n^{25}D 1.4563. Vapor phase chromatographic analysis[3] indicated less than 0.5% of acetate IIIa. The product was characterized further by hydrolysis to exo-norborneol,[4] 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 tosylate[5] and afforded a 60% yield of ethyl α-cyano-α-(Δ^3-cyclopentenyl)acetate,[6] b.p. 143° (16 mm.), n^{25}D 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^{25}D 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^{25}D 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,

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

(3) Analysis was carried out with a 150 foot Golay "Ukon" column, 180°.

(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).

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REACTIONS OF ATOMIC CARBON WITH SIMPLE HYDROCARBONS: EVIDENCE FOR C-H BOND INSERTION[1]

Sir:

The reactions of atomic carbon with hydrocarbons have been studied. A new method was employed in which a beam of C^{11} 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 rule[2] 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 C^{11}. 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. 1057 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.
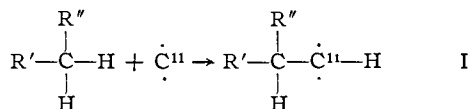
TABLE I

PRODUCTS OF REACTION OF ATOMIC CARBON WITH ALKANES

All yields are % total volatile activity as determined by passing an aliquot of the sample directly through the counter. ~2% O_2 was present in all samples to minimize radiation induced reduction of unsaturated hydrocarbon products, and to act as a scavenger for C atoms[4] and for radicals. Blanks denote that the product was undetected, having a yield of $\lesssim 1\%$. Cyclopropane and the butene-2's were also sought and have a yield of $\lesssim 1\%$.

|	Reacting molecule			
	CH₄	C₂H₆	C₃H₈	cyclo-C₃H₆
Carbon monoxide	26.8	25.2	19.0	15.0
Methane	1.5	<2	<2	<2
Ethane	3.1	<2	2.0	
Ethylene	28.0	19.5	12.1	
Acetylene	30.0	32.7	29.5	65.5
Propane		5.1	.7	
Propene		5.0	.6	
Allene			1.4 ⎫	
Propyne			2.7 ⎬	2.3
Isobutane			2.0	
n-Butane			3.9	
Isobutene			2.4	
Butene-1			3.0	
Butadiene-1,3			1.2	7.4

Table I gives some of the significant products observed in several saturated hydrocarbons. The most striking result is the high yield of acetylene. This has been observed in each of the ten hydrocarbons of varying structure and bond type that we have investigated. This high yield is explained readily if C–H bond insertion is assumed. Suf-


$$R'-\underset{\underset{H}{|}}{\overset{\overset{R''}{|}}{C}}-H + \overset{\bullet}{\underset{\bullet}{C}}{}^{11} \rightarrow R'-\underset{\underset{H}{|}}{\overset{\overset{R''}{|}}{C}}-\overset{\bullet}{C}{}^{11}-H \qquad I$$

ficient energy may be made available by this insertion to rupture two C–C bonds directly where the spin conservation rule is obeyed.

$$R'-\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}-\overset{\bullet}{C}{}^{11}-H \rightarrow R'\cdot + R\cdot + HC\equiv C^{11}H \qquad II$$
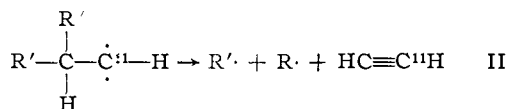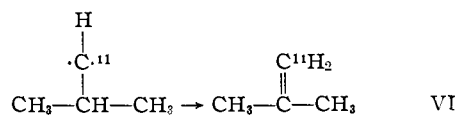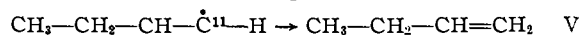
Alternatively the carbene produced in reaction I may be collisionally de-excited to the singlet state. When this happens the molecule would immediately decompose by reaction II or by reaction III (which has a lower energy requirement)

$$R'-\underset{\underset{H}{|}}{\overset{\overset{R''}{|}}{C}}-C^{11}-H \rightarrow R'-R'' + HC\equiv C^{11}H \qquad III$$
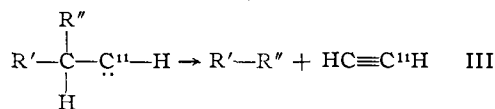
There are several specific points supporting this mechanism: (1) It is difficult to conceive of any mechanism other than insertion of C or CH into a C–H bond which would yield acetylene from methane. (2) The carbene intermediate formed by C atom insertion may decompose in other ways which do not yield acetylene (discussed below). However, with cyclopropane decomposition to acetylene should be particularly favored because stable products can be formed by simple electronic rearrangement with little nuclear motion
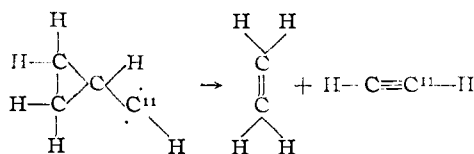
This is true only of the carbene formed by insertion into cyclopropane. Experimentally cyclopropane yields about twice as much acetylene as any of nine other hydrocarbons we have studied. Acetylene formation from cyclopropane is also significantly greater than that from cyclobutane. (3) Products present in smaller yield than acetylene can result from more complex modes of rearrangement of the intermediate carbene. For example in the reaction with propane sufficient energy is available to yield ethylene, propylene, allene, methylacetylene, and butadiene, all of which are observed. (4) The small yields of butenes-1 and isobutene from propane are interesting. These may result from deactivation of the intermediate carbenes without decomposition

$$CH_3-CH_2-CH-\overset{\bullet}{C}{}^{11}-H \rightarrow CH_3-CH_2-CH=CH_2 \qquad V$$

$$CH_3-\underset{\underset{\overset{|}{\cdot}C^{11}}{|}}{\overset{\overset{H}{|}}{CH}}-CH_3 \rightarrow CH_3-\overset{\overset{C^{11}H_2}{\|}}{C}-CH_3 \qquad VI$$

By these considerations most of the products may be rationalized. The yields of built-up saturates are in exception.[5] Such products are significant but are never the major yields. They may be formed by the reactions of the CH_2 radical[6] which in turn arises from H atom pick-up by the carbon atom.

(4) M. Pandow, et al., J. Inorg. and Nuclear Chem., 14, 153 (1960).

(5) Previously observed by A. Wolf and C. MacKay and W. F. Libby: see A. Wolf, Angew. Chemie, 71, 237 (1959).

(6) W. Doering and H. Prinzbach, Tetrahedron, 6, 24 (1959).

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THE PHOTOLYSIS OF ORGANIC NITRITES. III. OXIDATIVE FISSION OF CARBON–CARBON SINGLE BONDS IN α-OXYGENATED ALCOHOLS[1]

Sir:

A recent paper by a group of Japanese workers[2] describes the preparation of 3,3,21,21-bis-(ethylenedioxy)-5-pregnen-20β-ol (Ia) by means of a Mattox–Kendall rearrangement of Compound S, and then reduction. Since this compound appeared to be a promising starting material for the synthesis of 18-oxygenated substances related to aldosterone via the irradiation of 20-nitrites,[3a,b,c] it was converted to its nitrite (Ib) by treatment with

(1) Paper II of this series: C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto and D. H. R. Barton, J. Am. Chem. Soc., 83, 1771 (1961).

(2) K. Tsuda, N. Ikekawa and S. Nozoe, Chem. Pharm. Bull. (Japan), 7, 519 (1959).

(3) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, J. Am. Chem. Soc., 82, 2640 (1960); (b) D. H. R. Barton and J. M. Beaton, ibid., 82, 2641 (1960); (c) A. L. Nussbaum, F. E. Carlon, E. P. Oliveto, E. Townley, P. Kabasakalian and D. H. R. Barton, ibid., 82, 2973 (1960).