Oxyfunctionalization of Hydrocarbons. 2. Ozonolysis of Alkylcarbenium Ions[1a]

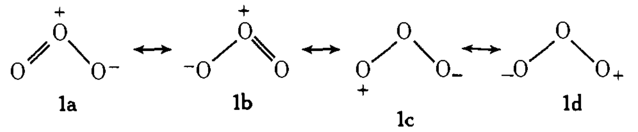
George A. Olah,* Norihiko Yoneda,[1b] and David G. Parker[1b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received August 25, 1975*

Abstract: The reaction of ozone with alkylcarbenium ions was investigated in magic acid–SO_2ClF solution. Products obtained were similar to those of the acid-catalyzed cleavage–rearrangement reactions of alkyl hydroperoxides. Experimental results indicate the reactions proceed via a nucleophilic quenching of the alkylcarbenium ion by ozone, followed by O_2 cleavage from the resulting trioxides with (apparent) simultaneous rearrangement to the corresponding carboxonium ions, which in turn can be hydrolyzed.

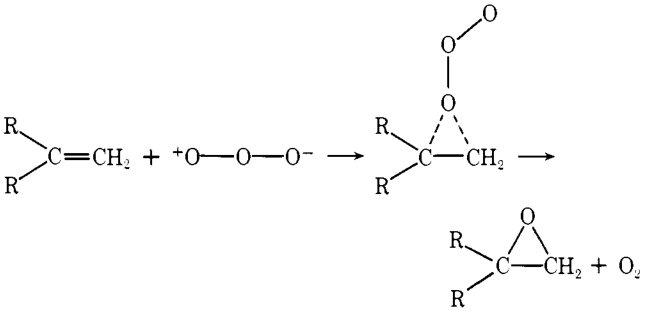
Introduction

Ozone has been shown by microwave spectroscopy to be the resonance hybrid of canonical structures **1a–d**.[2]

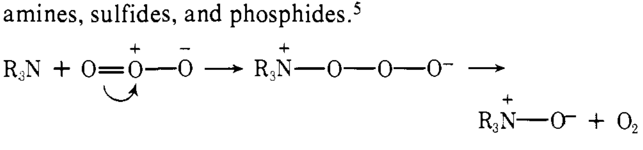

1a **1b** **1c** **1d**

Thus one might expect ozone to react as a 1,3-dipole, an electrophile, or a nucleophile. While it is thought that ozone reacts primarily as a 1,3-dipole toward alkenes, alkynes, and aromatics, initial electrophilic attack may be important. Wibault and co-workers found that typical Friedel–Crafts catalysts such as boron trifluoride or ferric chloride accelerated the rate of ozonation of aromatic compounds.[3]

The true electrophilic nature of ozone has been demonstrated in its reaction toward certain highly hindered olefins to yield epoxides.[4] Formation of an initial ozonide in these cases is restricted by steric crowding.

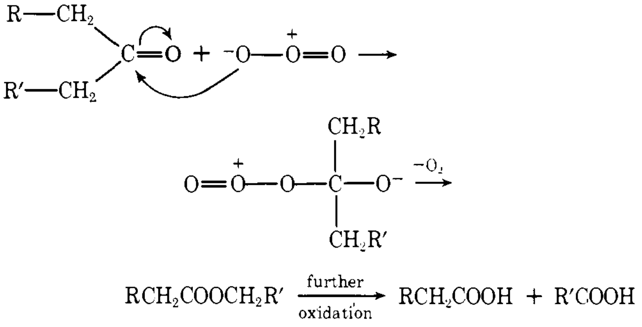


An initial electrophilic attack is also postulated for the reaction of ozone with nucleophilic compounds such as amines, sulfides, and phosphides.[5]

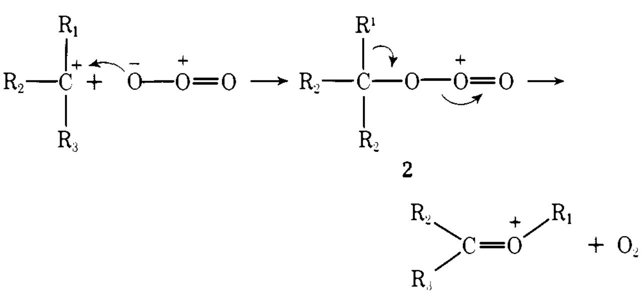


$$R_3N + O{=}\overset{+}{O}{-}\overset{-}{O} \longrightarrow R_3\overset{+}{N}{-}O{-}O{-}O^- \longrightarrow R_3\overset{+}{N}{-}O^- + O_2$$

Reactions of ozone as a nucleophile are less well documented.[6] The oxidation of ketones by ozone has been suggested to involve initial nucleophilic attack to produce an ester,[7] which undergoes further oxidation to yield carboxylic acids.



In continuation of our studies of oxygen functionalization of hydrocarbons, it was of interest to investigate the reaction of ozone toward carbenium ions. In such a system the initial attack by ozone should indeed be nucleophilic in nature, giving rise to an intermediate trioxide (**2**), which then would be anticipated to undergo alkyl group migration from carbon to oxygen with simultaneous cleavage of a molecule of oxygen, as in the acid-catalyzed rearrangement of hydroperoxides,[1,8] to give the corresponding carboxonium ion **3**.


2 **3**

The formation of such carboxonium ions from the acid-catalyzed rearrangement of tertiary alkyl hydroperoxides was reported in our preceding paper.

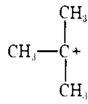
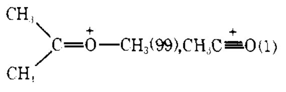
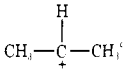
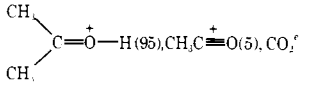
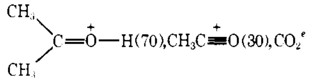
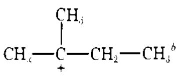
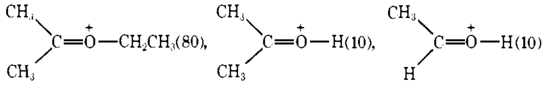
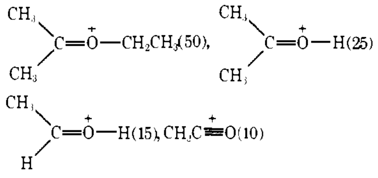
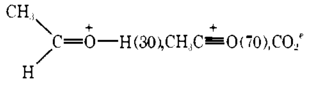
Results and Discussion

Trimethylcarbenium Ion (4). An SO_2ClF solution of **4** was prepared by adding an SO_2ClF solution of *tert*-butyl chloride to a well-stirred solution of magic acid (twofold excess) in SO_2ClF at dry ice–acetone temperature, ca. −78 °C. The ^1H NMR spectrum of the resultant solution indicated complete ionization of *tert*-butyl chloride to give **4**[9] as the sole organic species. Ozone was then bubbled through the solution, held at −78 °C for ~30 min. ^{13}C NMR and ^1H NMR analysis of the final reaction mixture was consistent with formation of the dimethylmethoxycarbenium ion (**5**). The reaction can be depicted as shown in Scheme I.

Dimethylethylcarbenium Ion (6). SO_2ClF solutions of **6**, prepared as described for the trimethylcarbenium ion, were treated with ozone at −78 and −30 °C.

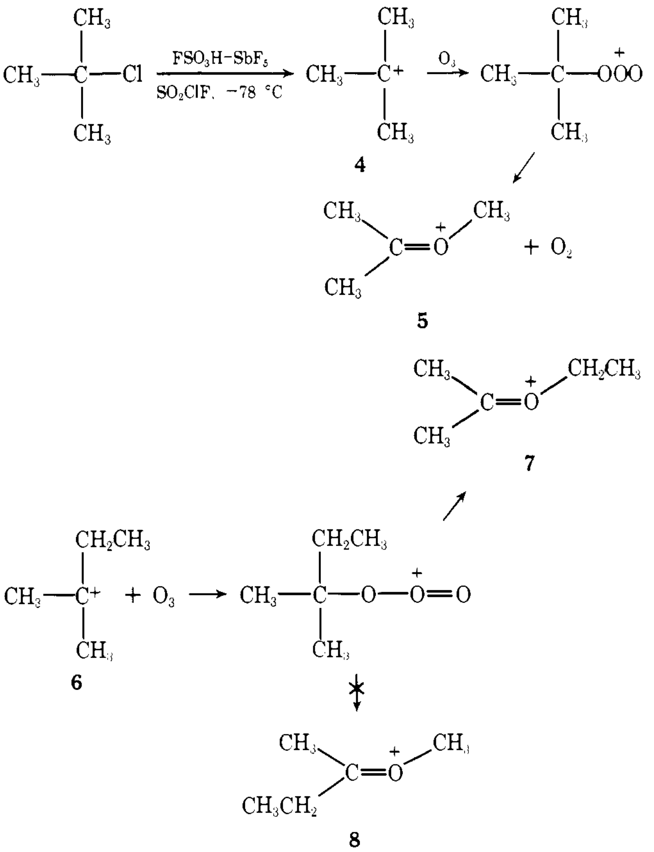
At −78 °C the main product (80%) was the carboxonium ion **7**.[1] No trace of ion **8**, which would arise from methyl migration, was detected. This observation is in agreement with the previously reported acid-catalyzed rearrangement of *tert*-amyl hydroperoxide.[1,8] In this system ethyl migration occurred to the total exclusion of methyl migration.

Table I. Products of Ozonolysis of Alkylcarbenium Ions

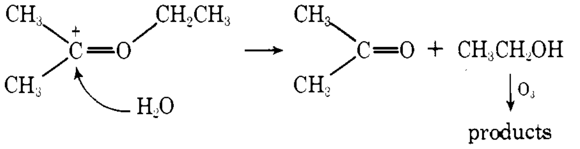
Carbenium ion	Reaction temp, °C	Conversion[a] of R^+, %	Product distribution (%)[a]
 $(CH_3)_3C^+$[b]	−78	55	 $(CH_3)_2C=\overset{+}{O}-CH_3$(99), $CH_3C\equiv\overset{+}{O}$(1)
 $CH_3-\overset{+}{C}H-CH_3$[c]	−78	85	 $(CH_3)_2C=\overset{+}{O}-H$(95), $CH_3C\equiv\overset{+}{O}$(5), CO_2[e]
	−30	99	 $(CH_3)_2C=\overset{+}{O}-H$(70), $CH_3C\equiv\overset{+}{O}$(30), CO_2[e]
 $CH_3-\overset{+}{C}(CH_3)-CH_2-CH_3$[b]	−78	50	 $(CH_3)_2C=\overset{+}{O}-CH_2CH_3$(80), $(CH_3)_2C=\overset{+}{O}-H$(10), $CH_3(H)C=\overset{+}{O}-H$(10)
	−30	80	 $(CH_3)_2C=\overset{+}{O}-CH_2CH_3$(50), $(CH_3)_2C=\overset{+}{O}-H$(25) $CH_3(H)C=\overset{+}{O}-H$(15), $CH_3C\equiv\overset{+}{O}$(10)
$\overset{\delta+}{CH_3CH_2F}\text{-}\overset{\delta-}{SbF_5}$[d]	−78	30	 $CH_3(H)C=\overset{+}{O}-H$(30), $CH_3C\equiv\overset{+}{O}$(70), CO_2[e]

[a] In all experiments, equal amounts of O_3 and R^+ were used. Conversion of starting material and product distribution were calculated from the ^1H NMR spectrum. [b] $RCl-FSO_3H-SbF_5-SO_2ClF$ solution. [c] $RCl-SbF_5-SO_2ClF$ solution. [d] SO_2 solution. [e] ^{13}C NMR spectrum of this solution indicated the presence of CO_2 (125 ppm).

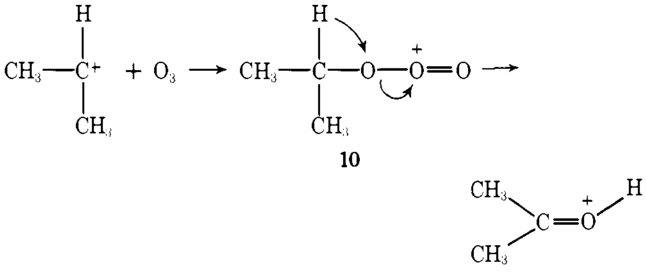
Scheme I



At −30 °C the yield of **7** decreased appreciably (product distributions for these reactions are shown in Table I). The secondary reaction products, namely acetone, acetaldehyde, and the acetylium ion, may well be derived from hydrolysis of **7** and reaction of ozone with the hydrolysis products (see also reaction with EtF–SbF_5), or possibly ozone reacts further with the intermediate carboxonium ion **7** to yield the observed secondary species. At this stage, we cannot speculate on the nature of such an attack. A discussion of these secondary reactions is presented later.

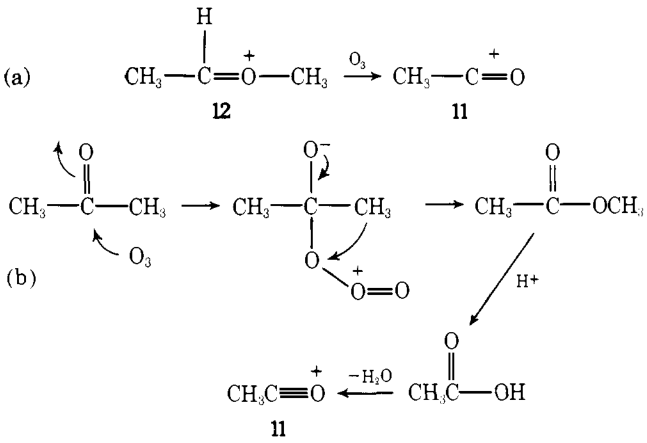


Dimethylcarbenium Ion (9). SO_2ClF solutions of **9** formed by the action of SbF_5 on isopropyl chloride were ozonolyzed at −78 and −30 °C. At −78 °C the predominant product was acetone (95%), observed in the ^1H NMR and ^{13}C NMR as a protonated species. This product arises from the anticipated proton migration in the intermediate trioxide **10** as with the analogous acid-catalyzed rearrangement reaction of isopropyl hydroperoxide.[8]



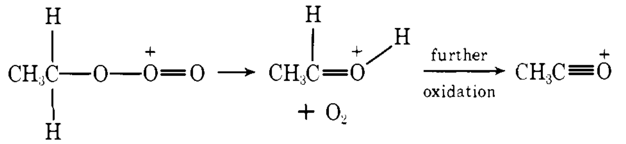
At −30 °C, however, a significant amount of the acetylium ion **11** (30%) was observed. Formation of **11** could arise from ozone attack on the carboxonium ion **12**, i.e., that derived from methyl migration in **10**, route a of Scheme II, or from an ozone-initiated Baeyer–Villiger type reaction of acetone, route b of Scheme II. If ozone was the active species in these oxidations, we would tend to favor route b or a related mechanism, since there are no examples of a methyl

Scheme II



group migration in analogous systems when an alternate migrating group is available. Furthermore, ozone reacts with ketones to yield carboxylic acids.[7] Acetic acid which would be derived from acetone is known to ionize in magic acid or SbF_5 solutions to give the acetylium ion.[10] It should be noted (Table I) that the isopropyl cation is more reactive toward ozone than the *tert*-butyl cation. This was confirmed in a competitive experiment in which equimolar amounts of the two cations were ozonolyzed. Complete ozonolysis of the isopropyl cation was effected before any noticeable reaction of the *tert*-butyl cation occurred. This reflects the greater reactivity of the isopropyl cation.[11]

Ethyl Fluoroantimonate. The intermediacy of the ethyl cation has been indicated for alkylating reactions involving the ethyl fluoride-SbF_5 complex.[12] We therefore thought that this complex might act as an incipient primary cation in its reaction toward ozone. When ozone was passed through a solution of ethyl fluoride in SbF_5-SO_2 (which shows equilibration through the $C_2H_5OSO^+$ ion), the reaction products obtained, i.e., acetaldehyde and the acetylium ion, are consistent with proton migration in the intermediate trioxide **13** which might arise from a nucleophilic attack by ozone on the ethyl cation. In this reaction a relative high yield of acetylium ion was observed.



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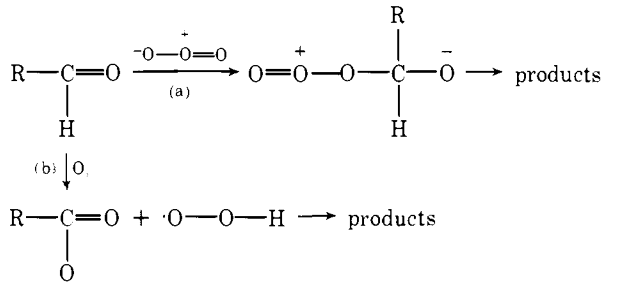
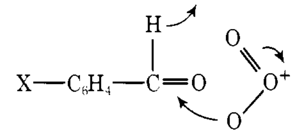
We depict the reaction of acetaldehyde to give the acetylium ion as "further oxidation", as we have no knowledge at this time of the nature of this process under the reaction conditions employed. However, aldehydes are known to yield carboxylic acids in reactions with ozone.[7,13] This will be discussed further subsequently. Thus acetaldehyde would yield acetic acid and, hence, the acetylium ion via ionization of acetic acid.[10]

We have, as discussed, examined the reaction of ozone toward tertiary, secondary, and incipient primary alkylcarbenium ions. In these reactions we believe that ozone is acting as a truly nucleophilic reagent. We have already mentioned that the ozonolysis reaction of ketones, in the absence of oxygen, was suggested to involve initial nucleophilic attack at the carbonyl carbon by ozone.[7] Aldehydes too in the absence of oxygen were believed to be attacked in a nucleophilic fashion by ozone (Scheme III, step a), whereas in the presence of oxygen, ozone was thought to initiate a radical reaction (step b) similar to that proposed by Schubert and Pease for alkane autoxidations.[14]

Scheme III



White and Bailey[13] strongly criticized these suggestions and found that for aromatic aldehydes reaction with ozone in the absence of oxygen gave results incompatible with a nucleophilic attack by ozone. The order of observed reactivity, *p*-nitrobenzaldehyde < benzaldehyde < anisaldehyde, is the opposite of what would be expected if a nucleophilic mechanism were operative, and their results are interpreted in favor of a 1,3-dipolar insertion reaction (**14**).



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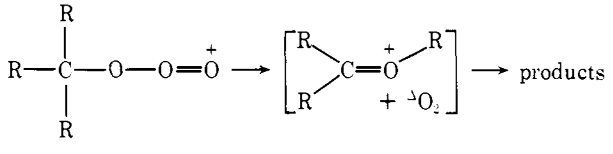
We therefore suggest that the reactions of alkylcarbenium ions with ozone studied in this work represent the first unambiguous example in which ozone reacts as a truly nucleophilic reactant.

In the reactions of ozone with alkylcarbenium ions, secondary reaction products were also observed (Table I).[15] We have suggested possible ways by which the primary product might react further with ozone to yield the secondary species. The suggestions are based on known reactions of ketones and aldehydes with ozone. However, when magic acid solutions of ethanol, acetaldehyde, or acetone were ozonolyzed, no formation of the acetyl cation or carbon dioxide could be detected, even at a reaction temperature of −10 °C. This seems to indicate that under the reaction conditions employed in the ozonolysis of alkylcarbenium ions, acetone and acetaldehyde formed are not further oxidized by ozone but by oxygen, which can be singlet oxygen liberated when the initial trioxide rearranges to yield a carboxonium ion. This suggestion is not unrealistic since singlet oxygen is known[16] to be an extremely reactive species.

The fact that the secondary products are obtained in reasonable yield (particularly for the reaction of ethyl fluoroantimonate) could suggest that the oxygen liberated from the trioxides is held in a "solvent cage" with the carboxonium ion. Some support for this comes from the observation that, for the reaction of **6**, increasing the relative molar amount of magic acid (which increases the viscosity of the solution) leads to higher yields of the secondary oxidation products.



We are currently investigating reactions of singlet oxygen with various substrates in superacids and will report our results subsequently.

Experimental Section

Preparation of Cations. Solutions of the trimethyl, and dimethyl, ethylcarbenium ions were prepared by adding 5 mmol of the corresponding halide in SO_2ClF to a 10-15-mmol solution of magic acid in SO_2ClF at −78 °C. A solution of the dimethylcarbenium ion was prepared by adding 5 mmol of isopropyl chloride in SO_2ClF to 15-20 mmol of SbF_5 in SO_2ClF at −78 °C.

^1H NMR spectra of the above solutions showed complete formation of the respective cation.

Ethyl fluoroantimonate complex was prepared, as described,[12] by passing ethyl fluoride through a 15-mmol solution of SbF_5 in SO_2 at −78 °C.

Ozonolysis. The solution of the alkylcarbenium ion to be ozonolyzed was placed in a 15-ml glass reaction tube, fitted with gas inlet and outlet tubes, which was held in a constant-temperature bath. Ozone (5–20 mmol) from a Welsbach T-816 generator was then passed through the solution. After addition of ozone, the solutions were flushed with nitrogen and transferred to ^1H NMR and ^{13}C NMR tubes for product analysis.

NMR Spectroscopy. ^1H NMR spectra were obtained on a Varian Associates Model A56/60-A spectrometer equipped with a variable-temperature probe. Chemical shifts were measured from external Me_4Si.

^{13}C NMR spectra were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad-band decoupler and variable-temperature probe. Operational parameters were as described previously.[1]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) (a) Part 1: G. A. Olah, D. G. Parker, N. Yoneda, and F. Pelizza, *J. Am. Chem. Soc.*, preceding article in this issue; (b) Postdoctoral fellows.

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(8) N. C. Deno, W. E. Billups, K. E. Kramer, and R. R. Lastomirsky, *J. Org. Chem.*, **35**, 3080 (1970).

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(15) In all final reaction solutions examined, varying amounts of CO_2 were detected.

(16) D. R. Kearns, *Chem. Rev.*, **75**, 395 (1975); C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).

Isotope Effects in Hydrogen Atom Transfers. IV. Alkyl Halides with Trialkyltin Hydrides

S. Kozuka and Edward S. Lewis*

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001.

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Abstract: Tritium isotope effects in the transfer of hydrogen atoms from tin to alkyl radicals are reported. Although the isotope effects generally increase as the new CH bond strength weakens, the correlation with bond strength is poor. All the isotope effects are quite small; with alkyl radicals k_H/k_T is in the range 2–3 at 80 °C, increasing to about 4 for benzylic radicals. There is poor agreement with the only published isotope effect on this reaction, and this discrepancy is discussed, with a careful search for possible errors.

The isotope effect in hydrogen atom transfer reactions is sensitive to the relative strengths of the breaking and forming bonds, reaching a maximum when these are roughly equal.[1a,2] This paper represents a study of the extent of this correlation in reaction 1, in which *Sn* represents alkylated tin, in our case either tributyltin or triphenyltin.[3]

$$R\cdot + \mathit{Sn}H \rightarrow RH + \mathit{Sn}\cdot \qquad (1)$$

The reaction is especially convenient because it is a step in the very general reduction of alkyl halides by tin hydrides (reaction 2),[4] and hence allows the study of any radical for

$$RX + \mathit{Sn}H \rightarrow RH + \mathit{Sn}X \qquad (2)$$

which the corresponding halide is available which does not follow some alternate reaction course with the tin hydrides. When the isotope effect is to be determined competitively, it is further necessary that the product RH be stable in the presence of the excess *Sn*H needed for competition, thus it should not contain double bonds, further reactive halogen, or carbonyl functions.

Isotope effects were determined by adding the alkyl halide to an excess (>2×) of the tin hydride in a solvent containing (as an initiator) azobisisobutyronitrile (AIBN) which was usually decomposed thermally, or in runs below 50 °C, photolytically. The isotope effect was calculated using eq 3[5] in which f is the fraction of hydride consumed,

$$k_H/k_T = \ln(1-f)/\ln(1-rf) \qquad (3)$$

and r is the ratio of the specific molar activity of the product RH to that of the reagent *Sn*H. The fraction f was established from the initial number of moles of the tin hydride, $\mathit{Sn}H_0$, and the initial number of moles of alkyl halide, RX_0, by the expression $f = RX_0/\mathit{Sn}H_0$. The results are presented in Table I.

The significance of these results is sensitive to their accuracy and we therefore discuss sources of error. A possible major source of error is the purity of *Sn*H and RH, and the estimation of f (eq 3) constitutes another. Impurities influence both the determination of r and of f. Both *Sn*H and RH were distilled before counting, and in most cases the purity was assayed by gas chromatography. Some samples of RH were purified by preparative scale GC, the others were checked for purity by analytical GC, and therefore nonradioactive contaminants can lead to very minor error only. Since the isotope effect is small, contamination of RH* by *Sn*H* below that detectable by gas chromatography will not introduce a detectable error, and there is no other high activity contaminant likely.