Acknowledgment. This research was supported by National Institutes of Health Grant GM-15471.

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Received June 24, 1968

The Racemization of Sulfonium Salts. II. The Racemization of Substituted Benzylethylmethylsulfonium Perchlorates[1,2]

Sir:

Previously we reported that *t*-butylethylmethylsulfonium perchlorate racemizes faster than it undergoes solvolysis. The excess of loss of optical activity over solvolysis ($k_\alpha - k_t$) was interpreted as racemization involving an inversion of the sulfonium salt. Recently Mislow and Scartazzini reported[3] a study of 1-adamantylethylmethylsulfonium perchlorate in which they tested and confirmed our conclusion with regard to the inversion of sulfonium salts.

We now wish to report that similar behavior is observed with benzylethylmethylsulfonium perchlorate (I), *p*-nitrobenzylethylmethylsulfonium perchlorate (II), and phenacylethylmethylsulfonium perchlorate (III) and to present evidence that the racemization of *p*-methoxybenzylethylmethylsulfonium perchlorate (IV) is best interpreted by a different mechanism.

All the active salts were obtained by resolution of the corresponding (−)-dibenzoylhydrogentartrate salts followed by replacement of the dibenzoylhydrogentartrate ion by perchlorate. The salts had the following physical properties:[4] I, mp 34.5°, $[\alpha]^{25}\mathrm{D}$ −8.20° (*c* 3.0, methanol); II, mp 83.5–85°, $[\alpha]^{25}\mathrm{D}$ +7.6° (*c* 0.9, methanol); III, mp 144–144.5°, $[\alpha]^{25}\mathrm{D}$ −10.7° (*c* 0.88, methanol); IV, mp 79–81°, $[\alpha]^{25}\mathrm{D}$ −11.8° (*c* 0.62, methanol).

The relative rate constants for loss of optical activity, k_α, of I:II:III[5a,b] are 1:0.99:0.6 in solvent methanol at 70°. Compound I racemizes 38 times faster than it undergoes methanolysis. For methanolysis the relative rate constants,[5a,c] k_t, of I:II and I:III are 1:0.2 and 1:0.03 at 70 and 90°, respectively. These results are consistent with a scheme in which racemization is independent of solvolysis and racemization involves pyramidal inversion about the sulfur atom. The data show that electron-withdrawing groups have a negligible effect upon the inversion of sulfonium salts.

Markedly different behavior is exhibited by *p*-methoxybenzylethylmethylsulfonium perchlorate (IV). For methanolysis of IV the first-order rate constants, k_t, were 3.94×10^{-6} sec^{-1} and 203×10^{-6} sec^{-1} at 25 and 50°, respectively. At the same temperatures the polarimetric rate constants, k_α, were 6.59×10^{-6} sec^{-1} and 308×10^{-6} sec^{-1}, respectively. The ratio k_α/k_t is 1.5 at 50°. Compound IV undergoes solvolysis over three powers of ten faster than I in methanol at 50°. Racemization of IV ($k_\alpha - k_t$) is faster than I by a factor of ~15.

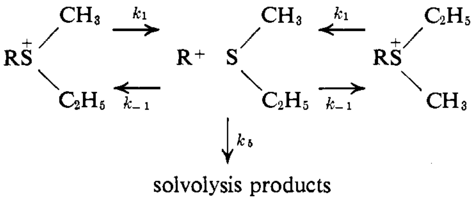
The increase in rate of racemization of IV relative to I is unexpected if pyramidal inversion is to account for the racemization of both sulfonium salts. It is difficult to rationalize the accelerative effect of the *p*-methoxy group in view of the fact that electron-withdrawing substituents have no significant effect upon the rate of inversion of sulfonium salts.

Two other processes might account for the racemization of IV. The first of the alternative reactions involves nucleophilic displacement on the primary benzylic carbon by ethyl sulfide, produced on the solvolysis of the sulfonium salts, as shown in eq 1.

$$\underset{\text{active}}{\mathrm{RCH_2\overset{+}{S}(CH_3)C_2H_5}} + \mathrm{CH_3SC_2H_5} \xrightarrow{k_2} \underset{\text{racemic}}{\mathrm{RCH_2\overset{+}{S}(CH_3)C_2H_5}} + \mathrm{CH_3SC_2H_5} \quad (1)$$

The addition of methyl ethyl sulfide speeds up the rate of loss of optical activity. The second-order rate constant, k_2, for reaction by eq 1 is 2.45×10^{-5} l. mol^{-1} sec^{-1} at 25°. Using this rate constant and the titrimetric and polarimetric rate constants the following conclusions can be reached. After 50% loss of optical activity, 34% of the sulfonium salt has undergone solvolysis. Of the unsolvolyzed salt 24.3% must be racemic. Only ~2% of the unsolvolyzed salt could have been racemized by the scheme shown in eq 1. At 50°, k_2 is 7.4×10^{-4} l. mol^{-1} sec^{-1}. After 50% loss of optical activity, 36.6% of the sulfonium salt has been solvolyzed and 21% of the unreacted salt is racemic; ~1.3% of the unreacted salt could have been racemized by the nucleophilic displacement reaction.[6] Hence, the principal pathway for racemization of IV must be some process other than that shown in eq 1.

Racemization of IV could also occur by carbon–sulfur bond heterolysis to yield an ion–neutral molecule pair which could react to give solvolysis products or return to racemic sulfonium salt as shown in eq 2.



(2)

While this reaction sequence does not account for the racemization of other sulfonium salts previously studied, it is a reasonable process in this case since the highly stabilized *p*-methoxybenzyl cation would be formed on bond heterolysis. This scheme would account for the acceleration of both the solvolysis and racemization reactions by the *p*-methoxy group.

We prepared *p*-methoxy-*m*-nitrobenzylethylmethylsulfonium perchlorate (V) to distinguish between racemization by pyramidal inversion and by the scheme shown in eq 2. Compound V was prepared from 4-hydroxy-3-nitrobenzyl alcohol[7] and had mp 137–138° and $[\alpha]^{27}\mathrm{D}$ +10.6 (*c* 2.93, acetone).

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[1] A portion of this material was presented before the Division of Organic Chemistry at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S20.

[2] For part I: D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88**, 4303 (1966).

[3] R. Scartazzini and K. Mislow, *Tetrahedron Letters*, 2719 (1967).

[4] All new compounds gave satisfactory analyses.

[5] (a) The sulfonium salts were 0.02–0.04 *M*. (b) The racemization of III was studied with 0.003 *M* $\mathrm{HClO_4}$ added to avoid complications due to ylide formation. (c) The solvolyses of I and II were carried out in the presence of *ca.* 0.08 *M* 2,6-lutidine.

[6] Similar behavior is observed for I and II. After 50% racemization *ca.* 0.1 and 0.02% of the racemization of I and II, respectively, could have resulted from the reaction shown in eq 1.

[7] J. B. Fishman, *J. Am. Chem. Soc.*, **42**, 2292 (1920).

If the racemization of IV involves pyramidal inversion, then there should be no significant difference in the value of $(k_\alpha - k_t)$ for compounds IV and V since electron-withdrawing groups have been shown to have no significant effect upon pyramidal inversion rates. The solvolysis of IV should be $\sim 10^3$ times faster than the solvolysis of V. In contrast, if eq 2 best describes the principal pathway for both solvolysis and racemization of IV, then both reactions by this pathway should be very much slower for V than IV. However, V should undergo pyramidal inversion at a rate comparable to the rates of inversion of I and II. The racemization of IV would be ~ 15 times faster than the racemization of V, and pyramidal inversion would represent the principal pathway for racemization of V. The latter type of behavior is observed experimentally. The rate constant for loss of optical activity, k_α, for V at 50° in solvent methanol is 7.0×10^{-6} sec^{-1}. This is very close to the k_α values of 6.5×10^{-6} sec^{-1} and 6.65×10^{-6} sec^{-1} for I and II, respectively, under the same conditions. At 90° the rate constant for methanolysis of V is 1.6×10^{-5} sec^{-1}, comparable to the value of 2.45×10^{-5} sec^{-1} for methanolysis of I at 90° obtained by extrapolation from data at lower temperatures.

We conclude that the principal pathway[8] for racemization of IV involves the sequence shown in eq 2. If dissociation to a free cation and ethyl methyl sulfide occurred prior to recombination, then a decrease in the rate of solvolysis of IV should be observed on the addition of ethyl methyl sulfide. At 50°, 0.05 *M* ethyl methyl sulfide has no effect on the rate constant for solvolysis. This observation requires the assignment of an ion–neutral molecule pair structure to the intermediate.

If this interpretation is correct, the racemization of IV represents the first example of the formation of an ion–neutral molecule pair and its return to covalent starting material in which the leaving group is not the same in structure as the solvent.[9] The formation and recombination of the ion–neutral molecule pair can be viewed as a reaction of the species within a solvent cage.[10]

The racemization of IV represents an example of the detection of bond heterolysis and return by racemization of an optically active leaving group. This process was first formally demonstrated[2,11] in the diastereoisomer interconversion which accompanies solvolysis of α-phenyl- and α-(p-methoxyphenyl)ethyl 2,6-dimethylbenzenesulfinates. Another example of this process has been reported by Fava and coworkers[12] in the racemization and rearrangement of optically active benzhydryl p-toluenesulfinate.

The racemization of optically active sulfonium and other "onium" salts should be a useful procedure for detecting bond heterolysis and return whenever this reaction is faster than all other processes which can result in racemization. For the sulfonium salts the formation of racemic starting material will require a simple rotation of the sulfide molecule relative to the carbonium ion within the solvent cage. The degree of rotation will depend on the detailed hybridization of the sulfide. The rotation will not require any further separation of the caged groups and should be energetically very facile. In this case k_1 would be a measure of the rate constant for carbon–sulfur bond heterolysis.

Acknowledgment. The authors wish to thank the National Research Council of Canada for financial support of this work.

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Received May 6, 1968

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[8] Racemization also occurs by pyramidal inversion and by nucleophilic displacement on carbon (eq 1). If the assumption is made that IV undergoes pyramidal inversion with a rate constant identical with that for the inversion of V, then $k_1 = 2.96 \times 10^{-4}$ sec^{-1} at 50° over the first 50% reaction; $\sim$46% of the intermediate returns to racemic sulfonium salt.

[9] E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

[10] S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).

[11] D. Darwish and R. A. McLaren, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, Abstracts, p 45-S.

[12] E. Ciuffarin, M. Isola, and A. Fava, *J. Am. Chem. Soc.*, 90, 3594 (1968). We wish to thank Professor Fava for a preprint of his paper.

[13] National Research Council of Canada Scholarship Holder, 1966–1968.

Ionic Chain Reactions in the Radiation-Sensitized Pyrolysis of Ethanol Vapor

Sir:

Two new types of ionic chain reaction have been found. They occur during the radiation-sensitized pyrolysis of ethanol vapor at 350°. One chain results in the conversion of ethanol to diethyl ether and water, while the other forms methanol and acetaldehyde from formaldehyde and ethanol.

The samples were irradiated with ^{60}Co γ rays to a dose of 1.3×10^{20} eV/g.

$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$

The *G* values of diethyl ether at *t*° in ethanol irradiated at a density of 0.66 g/l. are 1.1 (320°), 5.6 (350°), and 15.9 (375°). Water was also formed but its yield was not measured accurately. The yield of ether was unaffected by the presence of propylene (a free radical scavenger) or sulfur hexafluoride (an electron scavenger) but was decreased to $G = 0.3$ at 350° by the presence of 15 mole % of ammonia (a positive ion scavenger).

The proposed mechanism for ether formation is as follows

$$C_2H_5OH \xrightarrow{\rightsquigarrow} C_2H_5OH^+ + e^- \qquad (1)$$

$$C_2H_5OH^+ + C_2H_5OH \longrightarrow C_2H_5OH_2^+ + CH_3CHOH \qquad (2)$$

$$C_2H_5OH_2^+ + C_2H_5OH \rightleftarrows (C_2H_5OH)_2H^+ \qquad (3)$$

$$(C_2H_5OH)_2H^+ \longrightarrow (C_2H_5)_2OH^+ + H_2O \qquad (4)$$

$$(C_2H_5)_2OH^+ + C_2H_5OH \longrightarrow (C_2H_5)_2O + C_2H_5OH_2^+ \qquad (5)$$

$$(C_2H_5OH)_2H^+ + C_2H_5OH \rightleftarrows (C_2H_5OH)_3H^+ \qquad (6)$$

$$MH^+ + e^- \longrightarrow \text{neutralization} \qquad (7)$$

where MH^+ is any ion.

Charged molecular clusters, such as $(C_2H_5OH)_nH^+$, have been observed in several polar gases by mass spectrometry[1–4] and by ion cyclotron resonance spectrometry.[5] Reaction 4 and the equivalent reaction in metha-

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[1] P. K. Knewstubb and A. W. Tickner, *J. Chem. Phys.*, **38**, 464 (1963).

[2] P. Kebarle and A. M. Hogg, *ibid.*, **42**, 798 (1965).

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[5] J. M. S. Henis, *J. Am. Chem. Soc.*, **90**, 844 (1968).