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GENERATION OF DIOXOLENIUM AND OXTHIOLENIUM CATIONS AND THEIR CLEAVAGE IN STRONG MINERAL ACIDS.*[a,b]

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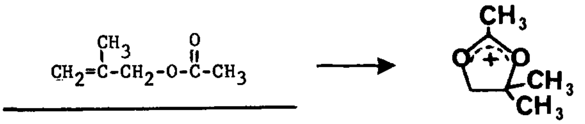
Since the first secondary and tertiary alkoxycarbonium ions were prepared by Meerwein, et al[1], further isolation, observation, and spectral studies of tertiary, secondary[2-6] and primary[7] examples have been reported including dioxolenium cations[3,6].

Alkoxycarbonium ions possess large gaseous stabilization energies compared to the methyl cation[8,9]. The stabilization energy of $CH_3OCH_2^+$ is 68 kcal compared to 35 kcal for $CH_3CH_2^+$[8]. Stable trialkylthiomethyl cations have also been reported[10-12].

We report the cyclization of allyl and methallyl esters and thiol esters to cyclic dioxolenium and oxthiolenium cations in strong proton acids. In 96, 80, and 60% H_2SO_4 and FSO_3H, methallylacetate, methallylcarbamate and methallylthiolacetate are quantitatively cyclized to the 2,4,4-trimethyldioxolenium cation (I) the 2-amino-4,4-dimethyldioxolenium cation (II), and the 2,5,5-trimethyloxthiolenium cation (III), respectively. Cyclization of allylacetate in 96% H_2SO_4 gave 30% of the 2,4-dimethyldioxolenium cation, IV, and 70% $CH_3COOH_2^+$. Ions I-IV were identified by their nmr spectra in acid (summarized in Table 1).**



$CH_2{=}\overset{\overset{\large CH_3}{|}}{C}{-}CH_2{-}O{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3$

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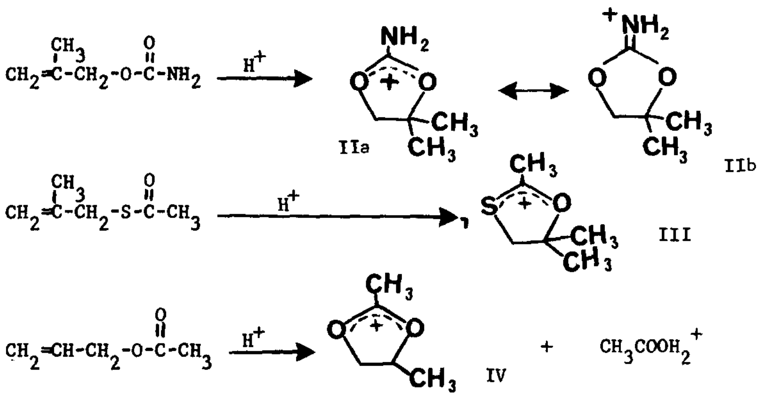
*(a) Acid Catalyzed Cyclization Reactions II. For paper I in this series see C. U. Pittman, Jr. and S. P. McManus, Chem. Comm., in press; (b) acknowledgment is made to the donors of the Petroleum Research Fund (Grant 3501-B to S. P. M.) administered by the American Chemical Society for partial support of this work.

**Nmr spectra were obtained on a Varian Associates HA-100 instrument. Spectra summarized in Table I were well resolved and devoid of impurity bands. Comparison of these spectra with those reported in ref. 2 and 3 serve to definitively establish their structure. Chemical shifts are relative to Tetramethylsilane in internal capilary tubes after making bulk susceptibility corrections.



Ions I, III, and IV decomposed to $CH_3COOH_2^+$ on heating in H_2SO_4 and D_2SO_4. The rate of cleavage is markedly facilitated as the acidity decreases.* In 96% H_2SO_4 ions I-IV were stable indefinitely at 30°C and for at least 20 minutes at 70°. At 120° cleavage of I is complete in 3 min., and III is 90% cleaved in 5 min. However, II, which, is stabilized by charge delocalization ($II_a \leftrightarrow II_b$)[3], is stable at 120° in 96% H_2SO_4. In 80% H_2SO_4, I is 75% cleaved at 66°C in 29 min. and rapidly destroyed at 120°C, but II is stable at 74° and only 20% cleaved after 6 min. at 122°. In 60% H_2SO_4, I is 100% cleaved within 5 min. and III is 47% gone after 6 min. at 66°.

Table I

H^1 Nuclear Magnetic Resonance Shifts of Ions I-IV in 96% H_2SO_4 (H_z downfield from TMS)[a]

Ion	Methyl at C-2	Methyls at C-4	Hydrogens at C-5
I	321	229	544
II	b	224	526
III	338	237	438
IV[c]	324	226 doublet J=6Hz	532 triplet J=9Hz 586 triplet J=9Hz

[a] Unless otherwise noted all bands were sharp singlets.
[b] The hydrogens on nitrogen appear as a rounded singlet at 872 Hz.
[c] The hydrogen at C-4 is a multiplet centered at 626 Hz.

Only one deuterium was incorporated into ions I-IV (at a C-4 methyl group) when they were generated in 96% D_2SO_4 (hydrogens at nitrogen completely exchanged in II).

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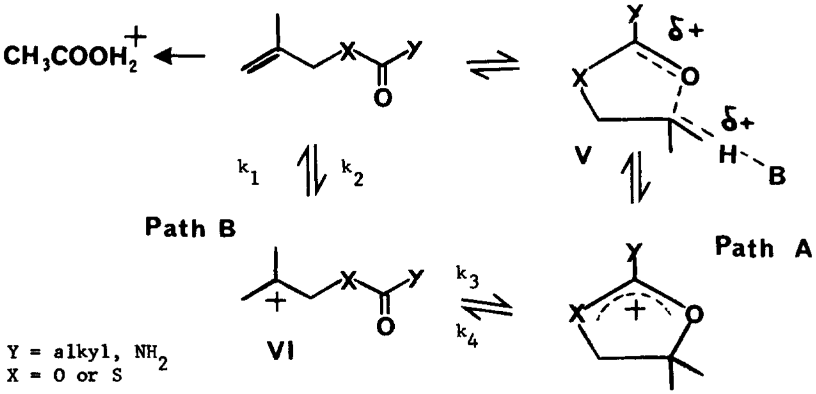
*The appearance of $CH_3COOH_2^+$ was followed by the growth of its CH_3 nmr band at 312 Hz downfield from TMS. When CH_3COOH was added to a solution of ion I or III prior to cleavage, the CH_3 group appeared as a sharp singlet at 312 Hz; its intensity increased during the course of fission. The addition of CH_3COOH to an H_2SO_4 solution of the cleavage products from I, III, or IV resulted in an increase in intensity of the then prominent 312 Hz band.

No further deuterium was incorporated into I-IV after 15 min. at 70°. Ion II incorporated no more deuterium after 2 min. at 128°. Thus, ions I-IV are not in equilibrium with their precursors. During cleavage of I and III to $CH_3COOD_2^+$ in both 96% (120°) or 65% (57°) D_2SO_4, no H-D exchange occurred in the fraction of ions remaining uncleaved at any time.[*] The $CH_3COOD_2^+$ formed, both in 96 and 65% D_2SO_4, incorporated no deuterium into the methyl group and resisted H-D exchange after 15 min. at 120°.

The dependence of cleavage rate on acidity and the incorporation of a single deuterium into ions I-IV on cyclization in 96% D_2SO_4 are in accord with cyclization (or ring opening) proceeding with oxygen neighboring group participation during protonation as represented by transition state V. Acceleration of the solvolysis rates of halides and sulfonates have previously been sited as evidence for carbonyl oxygen participation in related systems[13-16]. Winstein[16], for example, isolated cyclohexeneacetoxonium tetrafluoroborate.



Where Y = alkyl, NH_2
X = O or S

As acidity decreases, the H_2O activity sharply increases. Water could function as the base promoting the ring opening by path A. In path B constants k_3 and k_4 would be independent of acidity to a first approximation[**], but the rate of protonation will increase, and the rate of deprotonation of VI will decrease as acidity increases. Thus, a clear choice between paths A and B is not yet possible. However, invoking the intermediacy of VI requires that the activation energy leading to deprotonation of VI must be greater than that of its cyclization.

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[*] The area ratio of methyl, gem-dimethyl, and methylene nmr bands of ions I and III remained 3:6:2 throughout cleavage.

[**] In this intramolecular cyclization the relative solvation energies of VI compared to Ions I-IV and to the transition state between them in these highly ionic media should not change drastically.

We suggest that $CH_3COOH_2^+$ is generated by ring opening to the methallyl (or allyl) derivatives followed by A_{AL}-1 is fission.

Attempts to cyclize several acetates and benzoates of secondary allylic alcohols* in 96% H_2SO_4 in each case led to immediate quantitative cleavage. A_{AL}-1 fission of these esters would generate $CH_3COOH_2^+$ and secondary allylic carbonium ions which are unstable in 96% H_2SO_4 and cascade to complex mixture of cyclopentenyl cations.**

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*Included in this series were 3-acetoxy-pentene-1, 3-benzoyloxypentene-1, 3-acetoxy-2-methylpentene-1, and 2-acetoxy-2-methyl-2-pentene.

**Cyclopentenyl cations are rapidly generated from mono, di, and trisubstituted allylic carbonium ions in 96% H_2SO_4 (ref. 17, 18). The characteristic nmr pattern of a mixture of cyclopentenyl cations was observed in 96% H_2SO_4 after cleavage of ions I, II, IV and the esters in the footnote above.

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