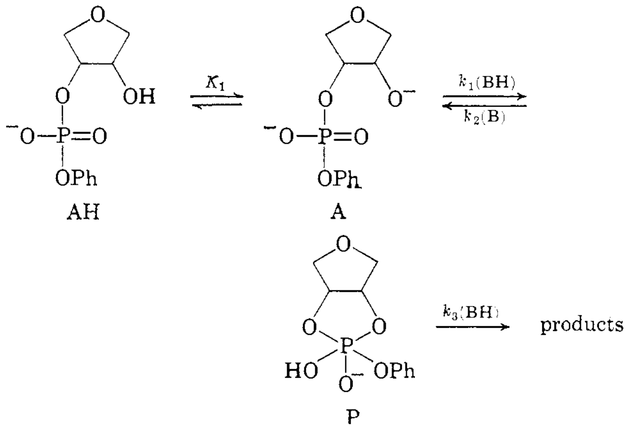
nucleophiles with respect to phosphorus;[13] (2) the *cis*-2-methoxy ester IV was completely unchanged under conditions that represented 70 half-lives for ester II; (3) the sterically hindered 2-methylimidazole also showed general species catalysis of the hydrolysis of II.

The many mechanisms that could fit our present data all involve some form of intermediate that can either return to starting material or go on to product; the partitioning is unsymmetrically catalyzed. One mechanism is presented here as an example only, and should not be taken literally. In this mechanism there is no necessity for the intermediate species to be pentacoordinate, though a phosphorane with finite lifetime is implicit in recent theories[14] concerned with the hydrolysis of cyclic phosphates and has been invoked as part of the mechanism of hydrolysis of ribonucleic acid by ribonuclease.[3,4] An alternative cyclic triester is considered by us to be an unlikely candidate.



In the pH range 7–9, A << AH, and the assumption of a steady-state concentration for P gives $k_{\text{cat}} = k_1k_3K_1a_H/(K_ak_2 + k_3a_H)K_a$, where K_a is the acid dissociation constant of the general acid, $k_{\text{cat}} = (k_{\text{obsd}} - k_{\text{hyd}})/$(free base), and k_{hyd} is the rate constant for hydrolysis at zero buffer concentration at that pH. If the value 13 is given to pK_1,[15] then for morpholine $k_1 = 29\ M^{-1}$ sec^{-1} and $k_2/k_3 = 0.33$.

The phenyl ester of *cis*-cyclopentane-1,2-diol monophosphate has also been synthesized and interestingly shows a hydroxide ion catalyzed rate of hydrolysis 80 times less than that of II, while the specific acid catalyzed rates are almost identical at pH 1.2.

Future research is directed toward achieving a more complete description of the mechanism of this reaction, its possible significance with respect to the action of ribonuclease, and the synthesis of polyfunctional molecules that may more efficiently catalyze the decomposition of II and related esters.

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Alkyldiazonium Cations. I. Direct Observation of the 2,2,2-Trifluoroethyldiazonium Ion

Sir:

We wish to report the first direct observation of a stable alkyldiazonium ion in which nitrogen is attached to sp^3 carbon. The ^{1}H and ^{19}F spectra of trifluoromethyldiazomethane in FSO_3H at −60° provide this evidence. Under these conditions the 2,2,2-trifluoroethyldiazonium ion is stable for at least 1 hr.

The alkyldiazonium ion has been postulated as a common intermediate species in the acid-catalyzed decomposition of diazo compounds and the nitrous acid deamination of aliphatic primary amines.[1] Evidence for the RN_2^+ intermediate has come from both rate data and product analysis studies. With bridgehead primary amines, both Curtin and Scherer have succeeded in trapping alkyldiazonium cations using the nitrosyl chloride route to produce RN_2^+.[2] However, vinyldiazonium cations could not be trapped by coupling with β-naphthol.[3]

In addition, a number of stable aliphatic diazonium ions have been reported recently.[4] However, each of these involves extensive stabilization through charge delocalization and nitrogen attached to an sp^2-hybridized carbon. These diazonium ions have been prepared by protonation of the corresponding diazo compounds. In each instance protonation was at a basic atom other than the α-carbon atom.

The great acid stability of diazo compounds, where loss of N_2 in the conjugate acid leads to unstable carbonium ions, is well known. Rate studies of the acid-catalyzed solvolyses of ethyl diazoacetate[5] and α-diazo sulfones[6] have demonstrated a protonation–deprotonation equilibrium preceding the rate determining loss of molecular nitrogen. The alkyldiazonium cation is clearly implicated as an important reaction intermediate. However, despite many attempts to obtain direct evidence for the alkyldiazonium ion in simple aliphatic systems, none had been found previously.

Slow addition of a solution of trifluoromethyldiazomethane[7] in chloroform-*d* to FSO_3H at −78° with good stirring gave a solution of the diazonium ion in the lower acid layer. Both ^{1}H and ^{19}F spectra were run at −60° on the FSO_3H solution. In each case absorptions corresponding to the presence of both the diazonium ion and the final reaction product, 2,2,2-trifluoroethyl fluorosulfate, were observed. Warming the solution to approximately −20° led to the vigorous evolution of a gas. Vapor density measurements showed that the evolved gas was nitrogen.

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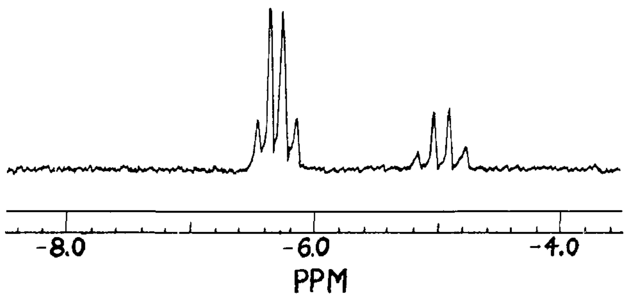

Figure 1. ^1H nmr spectrum of $CF_3CH_2N_2^+$ (and some $CF_3CH_2OSO_2F$) in FSO_3H at −60°.

$$CF_3CHN_2 \xrightarrow[-60°]{FSO_3H} CF_3CH_2N_2^+SO_3F^- \xrightarrow[-N_2]{\text{warming}} CF_3CH_2OSO_2F$$

Nmr spectra were recorded on a Varian Model A-60-A spectrometer and a Varian Model A56-60A spectrometer using TMS and fluorotrichloromethane, respectively, in capillary tubes as external references.

The ^1H nmr spectrum of trifluoromethyldiazomethane in FSO_3H at −60° (Figure 1) exhibits a quartet at −6.3 ppm, J_{HF} = 6.1 cps, which we assign to the 2,2,2-trifluoroethyldiazonium ion. There is also a smaller quartet at −5.0 ppm, J_{HF} = 7.5 cps, due to the presence of some 2,2,2-trifluoroethyl fluorosulfate[8] formed during the mixing and transferring processes.

After the evolution of nitrogen had been effected by warming the sample, the spectrum was again recorded at −60° (Figure 2). The quartet at −6.3 ppm has completely disappeared, while the quartet assigned to the reaction product at −5.0 ppm has grown in size.

Trifluoromethyldiazomethane itself shows a quartet in the ^1H spectrum at −4.6 ppm ($CDCl_3$), J_{HF} = 4.0 cps, and a doublet in the ^{19}F spectrum at +54.45 ppm ($CDCl_3$).

The ^{19}F nmr spectrum of trifluoromethyldiazomethane in FSO_3H at −60° complements the ^1H spectrum. It shows the diazonium ion as a triplet at +64.58 ppm, J_{HF} = 6.1 cps, and the fluorosulfate as a triplet of doublets at +75.76 ppm and a quartet at −36.98 ppm. We have assigned the −36.98-ppm quartet, J_{FF} = 2.5 cps, to the fluorine attached to sulfur and the +75.76-ppm pattern to the trifluoromethyl group. In the latter pattern the vicinal hydrogen–fluorine coupling, J_{HF} = 7.5 cps, is again apparent, and long-range fluorine–fluorine coupling,[9] J_{FF} = 2.5 cps, is seen as well. Again, warming and nitrogen evolution led to the disappearance of the +64.58 triplet assigned to the diazonium ion.

We find no evidence from the ^{19}F spectrum for the protonation of the diazo compound at the terminal nitrogen leading to the stable cationic species I under these conditions.[10]

$$CF_3CH{=}\overset{+}{N}{=}NH$$

I

The 2,2,2-trifluoroethyl fluorosulfate has been isolated from its FSO_3H solution by adding a 2,2,4-trimethylpentane solution of the diazo compound to FSO_3H at −78° and subsequently distilling the solution. Sodium fluoride was added to the distillation flask. The fluorosulfate was characterized by infrared and nmr spectra and elemental analysis. 2,2,2-Trifluoroethyl fluorosulfate, bp 81–82° (750 torr), has a quartet in its ^1H nmr spectrum (CCl_4) at −5.0 ppm, J_{HF} = 7.4 cps. Its infrared spectrum exhibits intense absorption peaks at 6.86, 7.8, 8.13, 8.46, 9.6, and 11.8 μ, which we have assigned to SO_2, CF_3, and SF absorptions.[11]

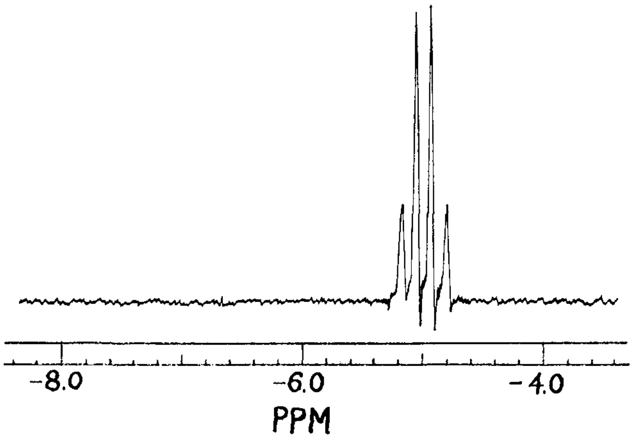

Figure 2. ^1H nmr spectrum of $CF_3CH_2OSO_2F$ in FSO_3H at −60°.

Anal.[12] Calcd for $C_2H_2F_4O_3S$: C, 13.19; H, 1.10; F, 41.74; S, 17.61. Found: C, 13.40; H, 1.20; F, 42.05; S, 17.90.

Preliminary deuterium exchange experiments have indicated that complete hydrogen exchange occurs in the perchloric acid catalyzed hydrolysis of trifluoromethyldiazomethane to 2,2,2-trifluoroethanol.

Further experiments testing the stability of simple alkyldiazonium ions in other systems are in progress.

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Stereochemistry of the Formation and Thermal Rearrangement of β-Ketosilanes

Sir:

We wish to report that β-ketosilanes on prolonged heating at temperatures of 80–175° are converted into