quenching of fluorenone triplets (6.5 kcal endothermic, $k = 1.1 \pm 0.2 \times 10^6$ sec^{-1}) and biacetyl triplets (5 kcal endothermic, $k = 8 \pm 2 \times 10^6$ sec^{-1}) with data[12] for *trans*-stilbene (a vertical[12] acceptor) quenching triplet sensitizers of comparable endothermicity. There the data indicate estimated rate constants of *ca.* 8×10^5 M^{-1} sec^{-1} for 6.5 kcal endothermicity and *ca.* 5×10^6 M^{-1} sec^{-1} for 5 kcal endothermicity, in close parallel to the values we observe.

Elimination of twisting of the α,β bond as a possible source of the kinetic isotope effects leaves the isotope effect on triplet excitation energy, known for ethylene and aromatic hydrocarbons,[13,14] as the odds-on candidate.[2] The origin of this isotope effect is somewhat obscure, though it must be related to changes in vibrational zero-point energy on going from S_0 to T_1[13c] (or S_1[14]). We have performed some calculations of zero-point energies related to the S_0–T_1 (or S_0–S_1) excitation of benzene and benzene-d_6 by use of a program devised by Boyd.[15] Reasonable changes in obvious force constants (C–C stretch and CC–CC torsion), with all C–H force constants kept constant, give isotope effects on the excitation energy that are only in the range of 10 cm^{-1}, more than an order of magnitude lower than the observed[13c,14] 200 cm^{-1}. We therefore believe that these isotope effects must reflect a significant change in some force constant directly associated with the C–H bond. Of the three possible local modes, the C–H out-of-plane bend seems more plausible than either the stretch or the in-plane bend. On this basis, the correlation of isotope effect with F_r follows logically (though not uniquely) from the expectation that this force constant at atom r will parallel total π-bond order at r ($= \sqrt{3} - F_r$) as a measure of resistance within the π system to out-of-plane deformation at that atom.

Acknowledgment. Acknowledgment is made to the National Science Foundation (Grant GP-14796) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 3031-A4), for financial support.

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Organic Fluorine Compounds. XXXII.[1] Protonated Fluoromethyl Alcohol

Sir:

Formation of fluoromethyl alcohol, **1** (FCH_2OH), from ethyl fluoroformate and from formyl fluoride was reported by Olah and Pavlath[2] in 1953. They were, however, unable to isolate and characterize the pure compound. Andreades and England[3] in 1961 prepared a number of highly fluorinated α-fluoro alcohols. Weinmayer[4] in 1963 studied the reaction of fluoroolefins with formaldehyde in hydrogen fluoride and suggested that a solution of paraformaldehyde in hydrogen fluoride contains an equilibrium of 25–30% fluoromethyl alcohol and 70–75% bis(fluoromethyl) ether. Olah and Tolgyesi[5] in 1964 reviewed the haloalkylation reactions and discussed the available literature on α-halo alcohols. The nature of solutions of paraformaldehyde in anhydrous HF, including nmr and other available data for this system, was discussed. It was pointed out that a polymeric fluorohydrin [$HO(CH_2O)_n$-CH_2F] is formed which reacts similarly to fluoromethyl alcohol under acid-catalyzed conditions. German and Knunyantz in a recent review article[6] discussed reactions of paraformaldehyde in hydrogen fluoride, with particular emphasis on their own earlier work in the field. Fluoromethyl alcohol recently aroused substantial theoretical interest as a model compound for *ab initio* calculations.[7]

We wish now to report the preparation of protonated fluoromethyl alcohol, **2**, through the reaction of formaldehyde with HF–SbF_5 and $HFSO_3$–SbF_5 in SO_2ClF solution and its nmr spectroscopic characterization in these superacid solutions.

When monomeric formaldehyde (generated by thermal depolymerization of paraformaldehyde) is dissolved in a 3:1 (v/v) HF–SbF_5 solution at −78° a white precipitate is formed (probably a polymeric formaldehyde product). This precipitate is partly dissolved when the temperature is increased to −40°. The clear supernatant consists of a saturated solution of fluoromethyl alcohol, **1**, in its stable protonated form **2**.

$$CH_2O + HF \longrightarrow \underset{\mathbf{1}}{FCH_2OH} \xrightarrow[SbF_6^-]{H^+} \underset{\mathbf{2}}{FCH_2OH_2^+\ SbF_6^-}$$

The pmr spectrum of **2** (Figure 1a) clearly demonstrates the structure. The methylene signal appearing at δ 6.15 (from capillary TMS) is a doublet ($J_{HF}^{gem} = 47.9$ Hz) of triplets $J_{HH}^{vic} = 4.9$ Hz). The OH_2 triplet ($J_{CH_2OH_2} = 4.9$ Hz) at δ 12.34 exhibits further splitting (1.7 Hz) due to the corresponding fluorine–proton vicinal coupling. The ^{19}F spectrum (Figure 1b) shows a triplet of triplets with the above-mentioned coupling constants. The fluorine chemical shift is ϕ 166.7 ppm (from CCl_3F), a value comparable with that obtained for FCH_2OCH_3 (ϕ 163.7).[8]

When formaldehyde is dissolved at −78° in 1:1 $HFSO_3$–SbF_5/SO_2ClF a stable solution of protonated formaldehyde, **3** (hydroxycarbonium ion),[9] is formed. Upon addition of fluoride ion (in the form of sodium

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[8] Prepared by the metathetic reaction of $ClCH_2OCH_3$ with HgF_2: δ_{CH_2} 4.69; δ_{CH_3} 3.02; $J_{HF}^{gem} = 57$ Hz; $J_{HF}^{vic} = 16$ Hz.

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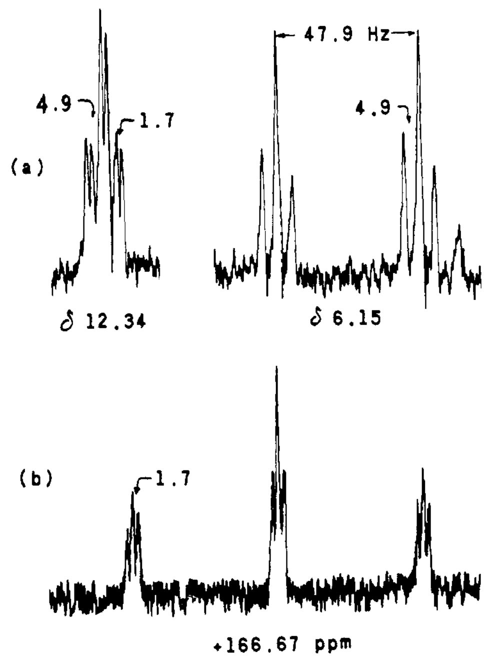

Figure 1. Nuclear magnetic resonance spectra of protonated fluoromethyl alcohol: (a) proton spectrum at 60 MHz; (b) fluorine spectrum at 56.4 MHz.

fluoride or hydrogen fluoride) at −78° protonated fluoromethyl alcohol, **2**, is obtained.

$$CH_2O \xrightarrow[SO_2ClF;\ -78^\circ]{HFSO_3\text{-}SbF_5} \underset{\mathbf{3}}{CH_2{=}OH^+ \longleftrightarrow {}^+CH_2OH} \xrightarrow[2.\ H^+]{1.\ F^-} \underset{\mathbf{2}}{FCH_2OH_2^+}$$

Ion **3** reacts through its hydroxycarbonium ion nature with fluoride ion giving fluoromethyl alcohol which then is protonated in the superacid medium.

$${}^+CH_2OH + F^- \longrightarrow \underset{\mathbf{1}}{FCH_2OH} \overset{H^+}{\rightleftharpoons} \underset{\mathbf{2}}{FCH_2OH_2^+}$$

When formaldehyde is dissolved in a 1:1 HF-SO_2ClF solution at −78°, the ^{19}F nmr spectrum shows the nearly exclusive presence of bis(fluoromethyl) ether, **4**, formed through the acid-catalyzed self-condensation of the initially produced fluoromethyl alcohol, **1**.

$$2CH_2O + 2HF \longrightarrow \underset{\mathbf{1}}{2FCH_2OH} \longrightarrow \underset{\mathbf{4}}{FCH_2OCH_2F} + H_2O$$

The self-condensation could involve the alkylation of fluoromethyl alcohol by the hydroxycarbonium ion and subsequent fluorination of the fluoromethyl hydroxymethyl ether by HF.[10]

$$FCH_2OH + {}^+CH_2OH \longrightarrow FCH_2OCH_2OH \xrightarrow{HF} FCH_2OCH_2F$$

The preparation of protonated fluoromethyl alcohol from protonated formaldehyde with fluoride ion seems to be the first direct experimental evidence of a stable protonated carbonyl intermediate reacting through its hydroxycarbonium ion nature and thus is in agreement with conclusions reached by ^1H and particularly ^{13}C nmr studies of the contribution of the hydroxycarbonium ion form in protonated formaldehyde. Fluoromethyl alcohol also represents a molecule of substantial interest as the parent compound of α-halo alcohols.

Whereas in its protonated form fluoromethyl alcohol is stable, the free alcohol readily loses HF to form formaldehyde and could not be isolated so far for direct studies. We are continuing our studies at lower temperatures, and are also investigating other halomethyl alcohols.

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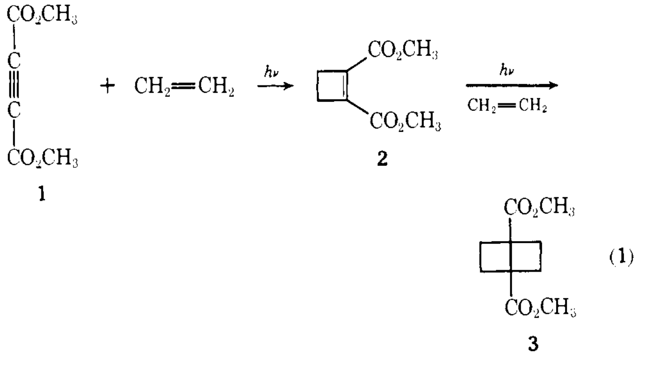
[10] The zinc chloride catalyzed condensation reaction of fluoromethyl alcohol with aromatic hydrocarbons was previously observed to produce diphenylmethane derivatives.[2] The reaction is also considered to involve hydroxymethylation of the aromatic followed by acid-catalyzed condensation of the benzyl alcohol.

Photochemistry of Acetylenes. I. The Photoaddition of Ethylene to Dimethyl Acetylenedicarboxylate

Sir:

Dimethyl acetylenedicarboxylate (**1**) has played an important role in organic synthesis because it undergoes a wide variety of thermal cycloaddition and conjugate addition reactions.[1] Very little is known, however, about its photochemistry. Dimethyl cyclooctatetraene-1,2-dicarboxylate is formed when **1** is irradiated in benzene solution.[2,3] Furthermore, when **1** is irradiated in cyclic ether solvents, products are formed which are the result of its alkylation by solvent *via* a free-radical mechanism.[4] We wish now to report the first example of the photochemical reaction of dimethyl acetylenedicarboxylate with two molecules of a simple olefin.[5]

It was expected that the photolysis of **1** in the presence of ethylene would lead to dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate (**3**) *via* two consecutive [2 + 2] cycloadditions to **1** and the intermediate dimethyl cyclobutene-1,2-dicarboxylate (**2**, eq 1). Direct irradiation of a 0.5% solution[6] of **1** in ethylene-saturated di-



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