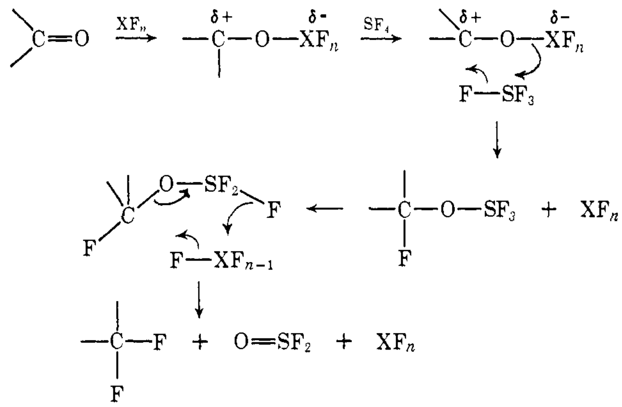
Isolation of an Alkoxysulfur Trifluoride[1]

Sir:

The discovery[2] that sulfur tetrafluoride is a selective reagent for replacing carbonyl and hydroxyl groups by fluorine has provided an extremely useful synthetic tool, and several review articles have been written on the subject.[3-6] The hydroxyl reactions were postulated to take place by elimination of HF to give $ROSF_3$ intermediates which then undergo an internal displacement.[5] Scheme I was proposed for the carbonyl reactions, which were found to be catalyzed by Lewis acids.[2] Several modifications of this pathway were subsequently discussed in order to account for the acceleration of the reaction by substantial amounts of hydrofluoric acid, but in each case alkoxysulfur trifluoride intermediates were invoked.[7] Such intermediates have not previously been isolated.

Scheme I



Extending the sulfur tetrafluoride reaction of β-nitro alcohols[8] to the newly available[9,10] 2-fluoro-2,2-dinitroethanol has now yielded 2-fluoro-2,2-dinitroethoxysulfur trifluoride, bp 38° (0.5 mm), as well as 2-fluoro-2,2-dinitroethyl sulfite, bp 90° (0.025 mm), and 1,2-difluoro-1,1-dinitroethane, bp 26° (10 mm). Each of the compounds gave satisfactory elemental analyses and ir and nmr spectra. The fluorine nmr spectrum of 2-fluoro-2,2-dinitroethoxysulfur trifluoride showed a singlet at ϕ^* +109.8 (CF) and a multiplet at ϕ^* −62.6 (SF), whereas that of 1,2-difluoro-1,1-dinitroethane showed a multiplet at ϕ^* 112.3 for $FC(NO_2)_2$– and a triplet of doublets (J_{HF} = 45 cps, J_{FF} = 17 cps) for FCH_2. 2-Fluoro-2,2-dinitroethoxysulfur trifluoride is a colorless liquid which is readily hydrolyzed by atmospheric moisture and slowly etches glass containers. The effect of reaction conditions on isolated yields is summarized in Table I. The fact that similar yields of 1,2-difluoro-1,1-dinitroethane were obtained at 25 and 100° under otherwise identical conditions is difficult to explain on the basis of mechanisms involving 2-fluoro-2,2-dinitroethoxysulfur trifluoride as an intermediate.

Table I. Reaction of 2-Fluoro-2,2-dinitroethanol with Sulfur Tetrafluoride[a]

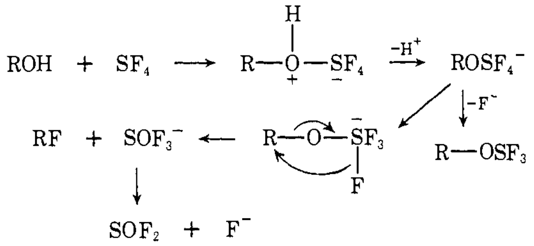
Temp, °C	Time, hr	Yields, % (R = $F(NO_2)_2CCH_2$–) RF	$ROSF_3$	$ROSO_2R$
25	20	25	28.4	14.5
100	20	29.6	9.3[b]	. . .[c]
25	3.5	Trace	21.6	35.7

[a] Mole ratio of SF_4 to alcohol used was 3.6:1. [b] Reduced yield attributed to water washing in work-up. [c] Not determined.

An inert solvent would be expected to have little effect on an uncatalyzed SNi reaction. Consequently, solutions of the trifluoride in methylene chloride and in benzene were heated at 100° for 20 hr in sealed nmr tubes. After this heating period, spectra showed the presence of some starting material as well as 2-fluoro-2,2-dinitroethyl sulfite and 2-fluoro-2,2-dinitroethanol. The trifluoride was immiscible with liquid anhydrous HF, and the addition of ether to promote solubility did not yield 1,2-difluoro-1,1-dinitroethane.

Although these preliminary results suggest that the trifluoride is not an intermediate in the formation of 1,2-difluoro-1,1-dinitroethane, additional control experiments are obviously needed. The mechanism of the reaction of this highly electronegatively substituted alcohol may not be typical of SF_4 reactions. Scheme II shows a possible mechanism in which the alkoxysulfur trifluoride is not a direct intermediate in the formation of a CF bond.

Scheme II



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On γ-Deuterium Isotope Effects in Norbornyl Systems[1]

Sir:

Either an *exo* or an *endo* deuterium atom at C-6 in the 2-norbornyl system results in a secondary isotope effect of $k_H/k_D \sim 1.10$ for acetolysis[2,3] or ethanolysis[2] of the *exo* brosylate. The isotope effect is insignificant for solvolysis of the *endo* brosylate.

The extraordinarily large γ-isotope effect for the *exo*-2-norbornyl system has been interpreted in terms of a bridged or nonclassical transition state.[2,3] This interpretation is based on the implicit assumption that the

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