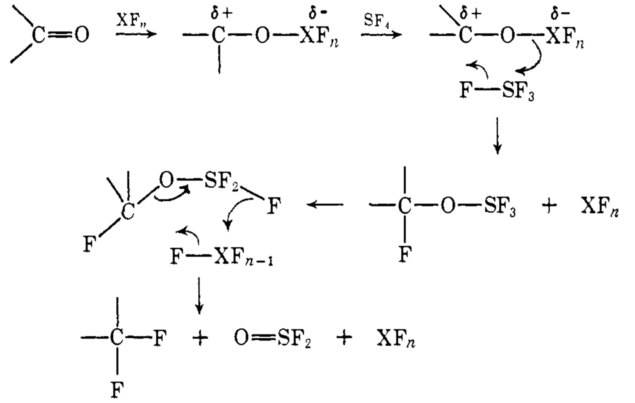
Isolation of an Alkoxysulfur Trifluoride[1]

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]

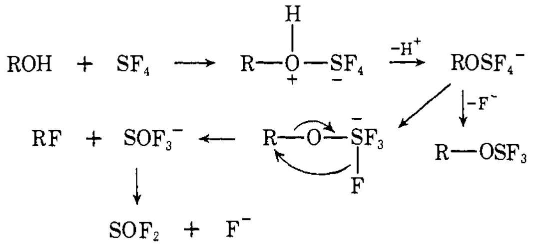
Temp, °C	Time, hr	Yields, % (R = F(NO$_2$)$_2$CCH$_2$–)		
		RF	ROSF$_3$	ROSO$_2$R
25	20	25	28.4	14.5
100	20	29.6	9.3[b]	. . .[c]
25	3.5	Trace	21.6	35.7

[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 S$_N$i 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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[3] D. G. Martin, *Ann. N. Y. Acad. Sci.*, **145**, 161 (1967).

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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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[1] This work was supported by the National Science Foundation (GP-6555X) and the National Institutes of Health (GM-14134).

[2] B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 1730 (1967).

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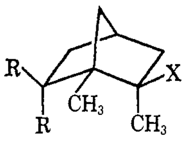
γ-isotope effect would be insignificant (as for the *endo* isomer) if ionization were unassisted and involved a classical transition state.

We wish to report that we have put this assumption to the test by examining the γ-isotope effect in an *exo*-norbornyl system which is known to involve unassisted ionization. In this work we have compared the rates of solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (Ia-OPNB)[4] and the 6,6-dideuterio ester (Ib-OPNB) in 90% aqueous acetone. It has been shown[5] that under these conditions I undergoes unassisted ionization, at least in part, to give the asymmetric classical carbonium ion.



Ia, R = H
b, R = D

The 6,6-dideuterated tertiary system Ib was prepared by the π route[6] as follows. Reduction of methyl 3,4-dimethyl-Δ^3-cyclopentenylacetate with LiAlD$_4$ gave 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethanol-1,1-d_2 which was converted[6] to 1,2-dimethyl-*exo*-2-norbornanol-6,6-d_2 (Ib-OH). The *p*-nitrobenzoate derivative,[4] Ib-OPNB, contained 1.98 atoms of deuterium per molecule. Hydride shifts that result in scrambling of the deuterium atoms in the synthesis[7] and solvolysis[2,3] of the parent norbornyl system are not involved in this tertiary system.

Three independent comparisons of the rates of solvolysis of the undeuterated (Ia-OPNB) and dideuterated (Ib-OPNB) esters are presented in Table I. In each case the esters were solvolyzed simultaneously. The initial concentrations were the same and solvent was taken from the same batch. Reactions were followed from 20 to 70% completion by titration, and in each comparison points for the two experiments were taken at the same times.

Table I. First-Order Rate Constants and Isotope Effects (k_H/k_D) for Solvolysis of Undeuterated and 6,6-Dideuterated 1,2-Dimethyl-*exo*-norbornyl *p*-Nitrobenzoate in 90% Aqueous Acetone at 78.47°

Ester (I-OPNB)[a]	$k \times 10^4$ [b] min^{-1}	k_H/k_D[c]
6,6-Dideuterated[d]	7.34 ± 0.05	1.02 ± 0.01
Undeuterated	7.47 ± 0.02	
6,6-Dideuterated[d]	7.31 ± 0.03	1.02 ± 0.01
Undeuterated	7.47 ± 0.02	
6,6-Dideuterated[d]	7.33 ± 0.04	1.02 ± 0.01
Undeuterated	7.47 ± 0.03	

[a] Initial concentration 0.030 *M* for each experiment. [b] Each value is the average, and average deviation, of eight point-by-point determinations of the rate constant between 20 and 70% reaction. [c] Uncertainties determined from limiting values of the rate constants. [d] Substrate contained 1.98 atoms of deuterium per molecule.

These results show that the γ-isotope effect for two C-6 deuterium atoms in the tertiary *exo*-norbornyl system is barely detectable; this is in sharp contrast to the remarkable isotope effect for one deuterium atom in the parent *exo*-norbornyl system (k_H/k_D = 1.02 *vs.* 1.10).[8] This striking difference cannot be attributed simply to the change from a secondary brosylate to a tertiary *p*-nitrobenzoate or to the change in solvent and temperature because the β-deuterium isotope effect for acetolysis of 3,3-d_2-*endo*-norbornyl brosylate (k_H/k_D = 1.26)[9a] is very similar to that for solvolysis of *exo*- or *endo*-3,3-d_2-2-methyl-2-norbornyl *p*-nitrobenzoate in 70% acetone (k_H/k_D = 1.30).[9b] Also, typical β-deuterium isotope effects have been observed for solvolysis of *exo*- and *endo*-2-phenyl-2-norbornyl *p*-nitrobenzoate in aqueous dioxane.[10]

The present results show that the γ-isotope effect for unassisted ionization in an *exo*-norbornyl system is small, as previously assumed,[2,3] and support the view that the large γ-isotope effect for solvolysis of the parent *exo*-norbornyl system[8] is a manifestation of assisted ionization.

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[8] In the parent *exo*-norbornyl system the γ-isotope effect is the same for *exo* and *endo* deuterium at C-6[2,3] and there is evidence[7] that these effects are additive, in which case the γ-isotope effect for the 6,6-d_2-*exo*-norbornyl system is $k_H/k_D \sim (1.10)^2 \sim 1.21$.

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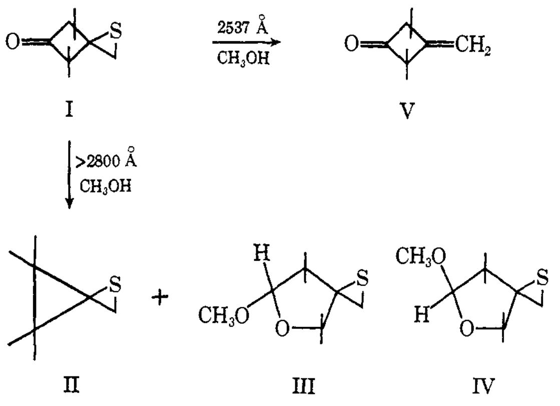
Wavelength Effect in Photolysis of 4,4,6,6-Tetramethyl-1-thiaspiro[2.3]hexan-5-one

Sir:

We have found that the photochemistry of 4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-5-one (I)[1] displays a remarkable dependence on the wavelength of the exciting light (Scheme I).

Scheme I



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[1] I was prepared by treatment of 2,2,4,4-tetramethyl-3-thio-1,3-cyclobutanedione with diazomethane at 0° in ether; white, crystalline solid, mp 84.5–85.5°; ir (CCl$_4$) 1708 cm^{-1} (s); nmr (CDCl$_3$) δ (ppm) 2.55 (s, 2 H), 1.12 (s, 6 H), and 1.18 (s, 6 H). A more detailed account of the preparation and reactions of I will appear in a forthcoming paper.