through a vacuum jacketed Vigreux column (300 × 15 mm). The residual liquid (ca. 50 ml) was transferred to a smaller flask and fractional distillation was continued to yield a fraction bp 75–75.9 °C, 13.14 g. NMR spectra of this fraction indicated the presence of water (1 wt %), ether (6 wt %), and trifluoroacetone (4 wt %, as hemiacetal and hydrate); crude yield 62%, $\alpha^{25}\mathrm{D}$ (neat, uncorrected) 1.990. Redistillation afforded a sample with the following properties: bp 75.8–76.2 °C (726 mm); $n^{25}\mathrm{D}$ 1.3135; $d_4{}^{25}$ 1.259; $\alpha^{25}\mathrm{D}$ (neat) 2.165 [lit.[12] bp 77.7–77.9 °C (752 mm); $n^{25}\mathrm{D}$ 1.3130; $d_4{}^{25}$ 1.263; $\alpha^{25}\mathrm{D}$ −7.14].

Reduction by the procedure described above at various temperatures gave the following crude yields and enantiomeric excess values: −78 °C, 26%, 9.1% ee; −10 °C, 61%, 13.3% ee; 25 °C, 62%, 30% ee.

1,1,1-Trifluoroacetone-^{18}*O*. 1,1,1-Trifluoroacetone (9.5 g, 85 mmol) was distilled into a cooled 50-ml two-necked flask equipped with a dry ice condenser, drying tube, stir bar, and serum cap. Water (1.58 g, 50 atom % ^{18}O, 83 mmol) was added dropwise via a syringe. The first droplets of water added solidified. These were allowed to melt to globules of water on the surface, and a mildly exothermic reaction commenced. Crystallization started after addition of about 1.0 ml of labeled water, but continued addition caused solution and gentle refluxing. The system continued to reflux for about 15 min after addition of the last portion and then rapidly solidified to a mass of prisms. The solid was warmed to room temperature and volatiles were collected in a small trap cooled in dry ice–acetone. Less than 0.1 ml of volatile material was collected during a 3-h period. A vacuum jacketed Claisen-Vigreux still was attached to the reaction flask, sulfuric acid (0.5 ml, 96 wt %) was added, and the reaction mixture was heated to reflux. Distillate (7.0 ml, 8.8 g, bp 22–24 °C) was collected in a dry ice cooled graduated receiving tube. A mass spectrum indicated ca. 25% ^{18}O incorporation.

1,1,1-Trifluoro-2-propanol-^{18}*O*. 1,1,1-Trifluoroacetone-^{18}*O* (8.59 g, 76.4 mmol, ca. 25% ^{18}O) was slowly distilled into a stirred and cooled (−40 °C) 100-ml round-bottom flask containing a suspension of lithium aluminum hydride (1.53 g, 40 mmol) in 35 ml of diglyme (freshly distilled at 20 mm from $\mathrm{LiAlH_4}$). The reaction flask was equipped with a dry ice condenser, serum cap, and stir bar. The reaction mixture was then brought to room temperature with the dry ice condenser charged and maintained during a 3-h period. Twelve hours later, the reaction mixture was treated with 25 ml of dry diethylene glycol. A vacuum jacketed Claisen-Vigreux still was attached and the labeled alcohol was distilled directly from the quenched reaction mixture to yield 6.99 g (5.8 ml, bp 74.5–78 °C) and 1.10 g (bp 78–120 °C). NMR analysis indicated that the first fraction was 95.6 wt % alcohol (76.4% yield) with diglyme the principal impurity. Preliminary mass spectral analysis indicated ca. 25% ^{18}O incorporation.

***p*-Toluenesulfonates of 1,1,1-Trifluoro-2-propanols.** The following procedure is representative. (+)-1,1,1-Trifluoro-2-propanol (10.1 g, 88 mmol, $\alpha^{25}\mathrm{D}$ +1.101) was added slowly via a syringe to a cold (−7 °C), magnetically stirred solution of dry pyridine (60 ml) and *p*-toluenesulfonyl chloride (16.0 g, 84 mmol). The resulting mixture was stored in the freezer (−20 °C) for 2 weeks. The extent of conversion was monitored by NMR spectroscopy. The tosylate was isolated in the usual way, and purified by vacuum distillation to yield (−)-1,1,1-trifluoro-2-propyl tosylate, 13.1 g (56%), bp 97.5 °C (1 mm), $\alpha^{20}\mathrm{D}$ −4.024, $n^{25}\mathrm{D}$ 1.4165. Unlabeled and ^{18}O-labeled tosylates were prepared by similar means in 50 and 80% isolated yields, respectively. NMR spectra and refractive indices were identical.

Solvolysis of 1,1,1-Trifluoro-2-propyl *p*-Toluenesulfonate-*ether*-^{18}*O*. A sample of the ^{18}O-labeled tosylate (0.4618 g, 1.72 mmol) was transferred to a 10-ml volumetric flask and 98 wt % sulfuric acid was added to the mark. The resulting solution was double sealed and held at 25 °C until the reaction was about 80% complete. The reaction mixture was quenched by pouring it on 80 g of crushed ice with magnetic stirring and external cooling, and the resulting acidic solution was neutralized with ca. 20 ml of 50% sodium hydroxide solution by dropwise addition with stirring and cooling so that the temperature did not exceed 15 °C. The solution was adjusted to pH 9, additional water was added to dissolve precipitated sodium sulfate, and the aqueous suspension was extracted with three 10-ml portions of methylene chloride. Thirty-seven milligrams of tosylate was recovered from the methylene chloride extracts. The NMR and mass spectra were identical with those of starting material.

The aqueous solution containing sodium sulfate, sodium 1,1,1-trifluoro-2-propyl sulfate, and sodium *p*-toluenesulfonate was rotary evaporated (temperature less than 35 °C) to yield a crystalline mass that was more thoroughly dried at the oil pump (1 mm, 25 °C, 24 h). The mixture of salts was triturated with two 15-ml portions of refluxing anhydrous methanol and the methanol filtrate evaporated to yield 0.97 g of hydrated crystalline residue. The NMR spectrum ($\mathrm{D_2O}$) indicated a mole ratio sodium 1,1,1-trifluoro-2-propyl sulfate:sodium *p*-toluenesulfonate of 0.95:1.0.

Samples of unlabeled and chiral 1,1,1-trifluoro-2-propyl tosylate were solvolyzed in an identical manner. Products were isolated by the procedure described with similar results. Samples of 1,1,1-trifluoro-2-propyl hydrogen sulfate were prepared by direct esterification of labeled and chiral samples of 1,1,1-trifluoro-2-propanol with 98% sulfuric acid. The alkyl hydrogen sulfate was isolated as the sodium salt and purified by the method described above.

Hydrolyses of Sodium 1,1,1-Trifluoro-2-propyl Sulfates in Moist Ether. The procedure used is based on the known method most recently discussed by Groen and Kochansky.[13] The following is representative. The mixed salts, sodium (−)-1,1,1-trifluoro-2-propyl sulfate and sodium *p*-toluenesulfonate (4.68 g, 11.4 mmol of sulfate ester), obtained via steps ABD (Scheme I) were mixed with anhydrous ether (65 ml), water (0.5 ml), and 10% sulfuric acid (0.1 ml). The mixture was heated at reflux for 60 min and then titrated with standard base; 10.4 mequiv was consumed, 91% yield. The ether layer was separated. The aqueous layer was saturated with sodium sulfate and then extracted twice with ether. The combined, dried (sodium sulfate) ether layers were concentrated by distillation and the residue was distilled with the use of a one-piece vacuum-jacketed Vigreux microstill to yield 0.625 g, bp 72–76 °C, plus 0.200 g of hold-up in the still. NMR analysis indicated that the distilled fraction was 78.7 wt % alcohol (38%), contaminated with water and some ether. Rotation measurements and density measurements were made with this sample dissolved in 95% ethanol. A calibration chart was constructed with the use of standard solutions containing known amounts of the starting alcohol 1 in 95% ethanol. The observed rotations could then be converted to comparable specific rotations.

Samples of 1-^{18}*O* obtained via steps ABDE and CDE were purified by GLC (Carbowax 20M) and analyzed by mass spectrometry. The intense $\mathrm{CF_3CO^+H}$ ion was used for these measurements.

Registry No.—(+)-**1**, 17628-73-8; (−)-**2**, 58219-97-9; (−)-**3**, 58219-98-0; (−)-**4**, 58219-99-1; *p*-toluenesulfonyl chloride, 95-59-9; sulfuric acid, 7664-93-9.

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HMO Calculation of the First Transition Energy of the Seleninium Cation and Its Benzologs[1]

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The uv spectra of the seleninium cation and its benzologs are very similar to those of their analogues in the thiapyr-

Table I. Regression Lines ($\tilde{\nu} = a\Delta m + b$) for Various Sets of Parameters h_{Se} and k_{C-Se}

h_{Se}	k_{C-Se}	a	b	S_ν, kcm^{-1}
0.9	0.6	27.06	−3.30	0.663
0.9	0.7	24.43	−2.15	0.658
0.9	0.8	22.15	−1.03	0.772
1.0	0.6	28.08	−4.13	0.836
1.0	0.7	25.54	−3.09	0.624
1.0	0.8	23.15	−1.90	0.675
1.1	0.6	28.71	−4.54	1.092
1.1	0.7	26.48	−3.83	0.698
1.1	0.8	24.06	−2.65	0.629
1.1	0.9	21.84	−1.37	0.714
1.2	0.8	24.88	−3.29	0.647
1.2	0.9	22.60	−1.99	0.662

Table II. Wavenumbers of the Longest Wavelength Electronic Bands and HMO Transition Energies (Δm) Based on Optimum Parameters (h_{Se} = 1.0, k_{C-Se} = 0.7)

Compd	$\tilde{\nu}$, kcm^{-1} [a]	Δm (β)
I	33.8	1.439
II	24.2	1.081
III	24.6	1.036
IV	18.2	0.823
V	21.3	0.974
VI	22.4	0.995
VII	22.5	1.033
VIII	21.7	0.962
IX	22.7	1.022

[a] All spectra were measured in H_2SO_4 (96%): I,[2a] 263 nm (log ϵ 3.92), 296 (3.60); II;[6] III;[7] IV,[8] 253 (3.97), 282 (4.87), 389 (4.44), 517 (3.64), 549 (3.57); V–VIII;[2e] IX.[2c]

ylium series, apart from a bathochromic shift attributable to the change in the heteroatom.[2a–e]

The present paper examines the longest wavelength uv spectrum band (assigned as the first $\pi \rightarrow \pi^*$ transition) of the only nine seleninium salts so far synthesized (Figure 1).

In the case of seleninium itself (I) (C_{2v} point group), this transition is $^1A_1 \rightarrow {}^1B_2^*$, which is allowed in the molecular plane and is perpendicular to the C_2 axis; in that of 9-selenaxanthylium (IV) (same point group), it is $^1A_1 \rightarrow {}^1A_1^*$, which is admitted parallel to the twofold axis. The other seven cations belong to the C_S group, whose first $\pi \rightarrow \pi^*$ transitions are $^1A' \rightarrow {}^1A'^*$; these are permitted in the molecular plane.

An attempt was made to relate the wavenumbers ($\tilde{\nu}$, kcm^{-1}) of these bands for all nine compounds, and the HMO transitions energies from the highest occupied (m) to the first virtual (m + 1) orbital, in accordance with the following formula (I)

$$h\nu = E_{m+1} - E_m$$

where

$$E_j = \alpha_c + \chi_j\beta_{cc}$$

This gives II

$$\tilde{\nu} = \Delta m \frac{\beta_{cc}}{hc}$$

with

$$\chi_{m+1} - \chi_m = \Delta m$$

Equation II represents a straight line with slope β_{cc}/hc and zero intercept.

The least-squares method was therefore used to determine a regression line in the form

$$\tilde{\nu} = a\Delta m + b$$

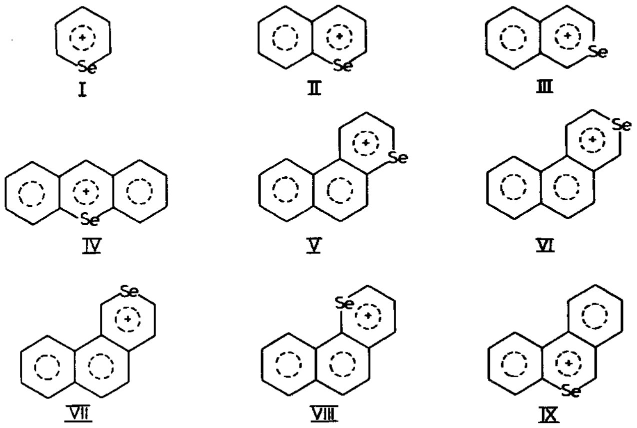

Figure 1.

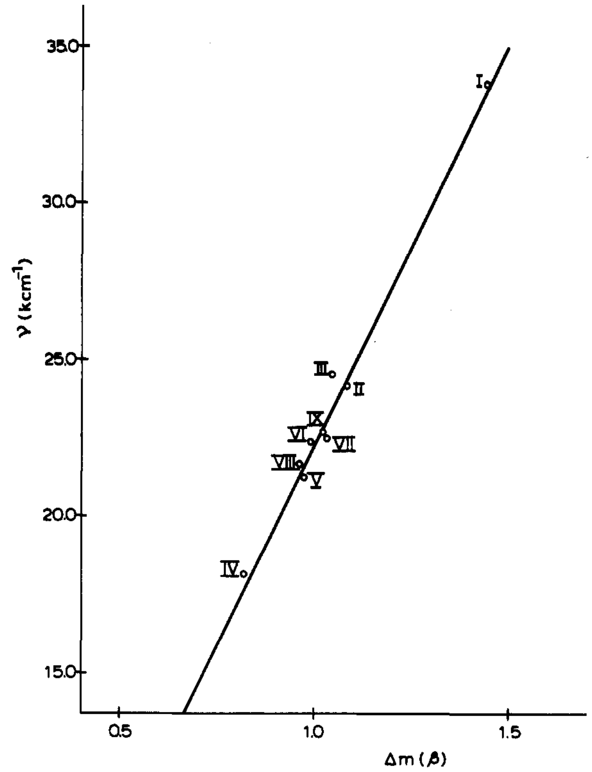

Figure 2. Final regression line of seleninium cations I–IX, correlating the longest wavelength uv spectrum bands with the $m \rightarrow m + 1$ HMO transition energies based on the parameters h_{Se} = 1.0 and k_{C-Se} = 0.7. Correlation coefficient r = 0.991; standard deviation $S_{\tilde{\nu}}$ = 0.624 kcm^{-1}.

For each h_{Se} and k_{C-Se} set, HMO gives a set of transition energies Δm (in β units), corresponding to a straight line with a given standard deviation (S_ν). The best regression line and parameters for the relation could thus be identified. Table I shows the regression line constants and standard deviations for a number of h_{Se} and k_{C-Se} values in the ranges 0.7–1.2 and 0.5–0.9, respectively. The best fit was obtained with h_{Se} = 1.0 and k_{C-Se} = 0.7 (values near those of sulfur[3a,b]), yielding a regression line $\tilde{\nu} = 25.54\Delta m - 3.09$, standard deviation S_ν = 0.624, and correlation coefficient r = 0.991 (Figure 2). The data for this fit are shown in Table II.

The failure of this line to pass through the point of origin, often noted in other aromatic and heteroaromatic series,[3a,4a–d] is attributable to the approximative nature of the HMO method.[5]

Our results support assignment of the longest uv band for these cations to the lowest $\pi \rightarrow \pi^*$ transition.

As suggested by Boyd and Singer,[4c] the fact that different slope values are observed for different series of compounds indicates that β_{cc} is an empiric quantity, rather than the constant required by eq II. This is yet another result of the many approximations used in the HMO method.

It is debatable whether Hückel's method can be applied to charged systems.[9] Its use here for a class of very similar compounds can, however, be justified by the linear relation between the HMO energies for the $m \rightarrow m + 1$ transition and the SCF–CI energies for the essentially similar transition observed for the thiapyrylium series.[10]

A more elaborate method is now being applied in the investigation of the electronic transitions of these nine cations.

Registry No.—I, 2567-17-1; II, 2567-18-2; III, 10352-19-9; IV, 2749-61-3; V, 53391-12-1; VI, 53391-14-3; VII, 53391-16-5; VIII, 53391-18-7; IX, 3541-46-6.

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Photooxidation of Benzophenone Oxime and Derivatives

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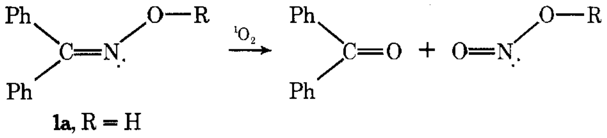
Singlet oxygen, generated by dye photosensitization of ground state triplet oxygen or by chemical reactions, has been shown to undergo a variety of reactions with organic compounds.[2] One of the more interesting of these reactions has been the [2 + 2] cycloaddition of singlet oxygen to electron-rich olefins, giving 1,2-dioxetanes which subsequently cleave to carbonyl products.[2,3] We have found that singlet oxygen reacts with benzophenone oxime and derivatives to give benzophenone and nitrite (Scheme I). To our knowledge, this represents the first report of a reaction of singlet oxygen with a π bond other than a C═C double bond.

Scheme I. Photooxidation of Benzophenone Oxime Derivatives



1a, R = H
b, R = CH$_3$
c, R = :$^-$

Photooxidations were carried out in methanol solution, using rose bengal as sensitizer, keeping the solution saturated with oxygen, and irradiating with a 500-W projector bulb. Appropriate blank experiments indicated that the dye, the oxygen, and the light were all necessary for the photooxidation reaction. Further evidence that these are singlet oxygen reactions was the observation of specific quenching by 1,4-diazabicyclo[2.2.2]octane (Dabco), a singlet oxygen quencher.[4] Photooxidation of benzophenone oxime (**1a**), benzophenone oxime *O*-methyl ether (**1b**), or benzophenone oximate anion (**1c**) yielded benzophenone as the only product observable by gas chromatography. Benzophenone was isolated and characterized from the photooxidation of **1c**. The presence of nitrite ion was also detected in the photooxidations of **1a** and **1c**.

The addition of 2-methyl-2-butene, a singlet oxygen acceptor, decreased the rate of photooxidations. The rate of disappearance of 2-methyl-2-butene was taken to be 1.3 × 10^6 M^{-1} s^{-1}, using the reported relative reactivity[2] and the reported lifetime of singlet oxygen in methanol.[5] The rate of appearance of benzophenone from **1a**, **1b**, or **1c**, compared to the disappearance of 2-methyl-2-butene, thus allowed the absolute reactivities of the oxime derivatives to be determined (Table I). The order of reactivity is what would be expected for reaction with an electrophilic reagent such as singlet oxygen—reactivity is enhanced by electron donation to the π bond.[2]

Table I. Reaction Rate Constants for Singlet Oxygen Reactions

Substrate	Rate constant, M^{-1} s^{-1}	Substrate	Rate constant, M^{-1} s^{-1}
2-Methyl-2-butene	1.3×10^6	**1a**	7.7×10^4
1c	3.4×10^5	Acetone oxime	$<1 \times 10^4$
1b	2.0×10^5		

While we have obtained no direct evidence for a dioxetane intermediate in this reaction, we consider it highly probable, based upon analogies with similar reactions which involve cleavage of an electron-rich π bond by singlet oxygen.[2]

Experimental Section

Materials. Benzophenone oxime (**1a**) was prepared from benzophenone and hydroxylamine hydrochloride, mp 138–141 °C (lit. 142 °C).[6] Benzophenone oximate anion (**1c**) was prepared from **1a** and sodium in ether solution.[7] Benzophenone oxime *O*-methyl ether (**1b**) was prepared by refluxing **1c** with methyl iodide in ether solution, mp 97.5–100 °C (lit. 102 °C).[8] Acetone oxime was prepared from acetone and hydroxylamine hydrochloride, mp 54–57 °C (lit. 60–61 °C).[9] Dabco was from Eastman and was used as received.

Photooxidation Procedure. The light source was a 500-W quartz–iodine projector bulb (G.E. FBG), contained in a water-jacketed well and also cooled by air. A yellow glass filter was used to eliminate short-wavelength light (OD >2 for λ <390 nm). The sample to be irradiated was contained in a test tube cooled in ice in a clear Dewar flask, and was within several inches of the light source. Oxygen was presaturated with solvent and bubbled slowly into the reaction solution. Oxygen bubbling continued for 5 min before the light was turned on.

A typical reaction solution contained 1 × 10^{-4} M rose bengal as sensitizer and 0.1 M substrate in methanol solvent. Aliquots were removed at intervals and analyzed by GC, using a Hewlett-Packard Model 700 with a 6 ft × 0.125 in. column packed with 10% UC-W98. Benzophenone was the only product detectable as the photooxidation proceeded. By temperature programming, the disappearance of the oxime (**1a**) or the *O*-methyl ether (**1b**) could also be observed.