tization of **1** produces **5** with a quantum yield equal to that of direct irradiation (*cf.* Table I). These observations clearly establish that **1** intersystem crosses to a triplet state which rearranges to the cyclopropyl ketone. The acetone results in Scheme I show that a characteristic triplet reaction of all three ketones is oxadi-π-methane rearrangement. Since addition of methyl groups decreases the amount of triplet product seen under direct irradiation and increases the amount of cyclobutanone, we conclude that these groups must be influencing the competition between isc and singlet 1,3-acyl shift.

The question immediately arises whether the decrease in the isc efficiency observed on introduction of methyl groups is due to a decrease in the rate of isc or to an increase in the rate of 1,3-acyl shift. Based on the following argument, we suggest that the rate of α-cleavage is markedly enhanced by α-methylation but we cannot rule out small changes in the isc rate. The total quantum yield of all processes (reaction, isc, and decay) originating from the singlet state is unity; that is, $\Phi_r^s + \Phi_{isc} + \Phi_d = 1$. In ketone **1** we know that Φ_{isc} is greater than 0.5 and that Φ_r^s is negligible because no 1,3-acyl shift product was detected. Thus Φ_d must be less than 0.5 and, from the definition[11] of Φ_d, the inequality $k_r^s + k_{isc} > k_d$ must be true. Assuming a detection limit of 2% for 1,3-acyl shift product in the direct reaction, the quantum yield for this product must be less than 0.02×0.15. The definition[11] of Φ_r^s then allows us to state that $k_{isc} + k_d > 332k_r^s$. Adding this inequality to the one derived above leads to the conclusion that $k_{isc} > 165k_r^s$ for ketone **1**. A similar argument obtains for compound **4** except that the absence of **9** in the direct irradiation shows the inefficiency of isc; in fact, Φ_{isc} must be less than 0.26.[12] It follows[11] that $k_r^s + k_d > 2.8k_{isc}$. Since Φ_r^s was measured for **4** as 0.24, we calculate that $k_{isc} + k_d = 3k_r^s$. Elimination of k_d between these equations shows that $k_{isc} < 1.1k_r^s$ for ketone **4**. Since liberal assumptions have been made throughout, it is apparent that the ratio of k_{isc} to k_r^s is at least 150 times greater for **1** than for **4**. Turro and Yang[13] have shown that α-alkylation causes only small changes in k_{isc} for alkanones and we have no reason to expect otherwise in the present case.[14,15] The variation in this ratio is therefore too great to be accounted for solely by differences in k_{isc}; an increase in k_r^s upon addition of α-methyl groups must be the most important factor.

The behavior of **1** resembles that of cyclohexanone[16] since both compounds intersystem cross and react from the triplet state; however, introduction of the double bond changes the characteristic triplet reaction from α-cleavage to oxadi-π-methane rearrangement. Ketone **4**, on the other hand, undergoes apparent α-cleavage from the singlet state, a reaction which is not generally observed in alkanones.[17] Since even singlet 2,2-dimethylcyclohexanone intersystem crosses before it reacts,[16] it appears that the double bond in **4** increases the rate of the 1,3-acyl shift reaction. If this reaction is concerted,[18] it occurs even though the proposed[1a] criterion of $\epsilon > 150$ is not met; on the other hand, if it proceeds by α-cleavage followed by allylic recombination, little stabilization of the incipient allyl radical should be available until after α-cleavage and bond rotation.[19]

Other explanations[1a,20] for the difference in photochemical behavior seen in **1**, **3**, and **4** might relate to variations in ϵ or differences in geometry. However, since both of these factors are similar[15] in all of the ketones, these explanations appear to be inadequate.[21]

(11) The quantum yield for any singlet process equals its rate divided by the sum of the rates for all singlet processes.

(12) This number is derived from the fact that the quantum yield of **9** under direct irradiation equals Φ_{isc} times the efficiency with which triplet 4 proceeds to product. The latter must be at least as high as the sensitized quantum yield of 9 (0.03). If 2% of **9** could be detected in the direct irradiation, its quantum yield would have to be less than 0.02×0.39.

(13) (a) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564 (1970); (b) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 6974 (1970).

(14) Photoelectron spectra for **1**, **3**, and **4** show that the π orbital lies about 0.5 eV above the n orbital in each case (K. N. Houk, unpublished results). Coupled with the similarity of the uv spectra,[15] this implies that introduction of methyl groups causes no change in the relative order of electronic states. Therefore no large difference in rate of isc is expected in these ketones.

(15) Uv data λ_{max}, nm (ϵ); **1** 285 (19); **3** 283 (70); **4** 278 (55).

(16) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

(17) *tert*-Butyl alkanones undergo some α-cleavage from the singlet state; *cf.* ref 13b and N. C. Yang, M. H. Hui, and S. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971).

(18) 1,3-Acyl shift in a ketone of general structure **2** proceeds stereospecifically; *cf.* ref 4b.

(19) The authors are grateful to Professor R. L. Cargill for stimulating discussion on this point.

(20) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971).

(21) A recent report by J. C. Hemminger, H. A. J. Carless, and E. K. C. Lee, [*J. Amer. Chem. Soc.*, **95**, 682 (1973)] shows that addition of α-methyl groups to cyclobutanone drastically reduces the singlet lifetime by enhancing α-cleavage, the same effect postulated in the present study.

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Synthetic Methods and Reactions. I. Selenium Tetrafluoride and Its Pyridine Complex. Convenient Fluorinating Agents for Fluorination of Ketones, Aldehydes, Amides, Alcohols, Carboxylic Acids, and Anhydrides

Sir:

We report that selenium tetrafluoride is a convenient fluorinating agent of general use, particularly suitable for replacement of hydroxyl and carbonyl groups by fluorine. Previously, this reagent was mentioned only in a patent[1] concerned with fluorination of some ketones. Selenium tetrafluoride has a suitable liquid range (bp 106°, mp −10°). It is soluble in halogenated solvents, such as methylene chloride or 1,1,2-trifluorotrichloroethane, in which fluorination can be carried out with ease in the liquid temperature range of the solvents, generally with yields of 70% or higher. Compared with

(1) P. W. Kent and K. R. Wood, British Patent, 1,136,075; *Chem. Abstr.*, 70, 88124 (1969).

Table I. Fluorination of Carbonyl Compounds with SeF_4

Carbonyl compound	Temp, °C	Reaction time, hr	Product	Bp, °C	% yield
Acetone[a]	20	1	2,2-Difluoropropane[c]	−7	78
Methyl ethyl ketone[a]	20	0.5	2,2-Difluorobutane[d]	30.8	75
Diethyl ketone[a]	20	0.5	3,3-Difluoropentane[e]	60.8	80
Cyclohexanone[b]	47	1	1,1-Difluorocyclohexane[c]	98	70
Adamantanone[b]	20	15	2,2-Difluoroadamantane	106 (mp)	100
Acetophenone[b]	47	6	1,1-Difluoro-1-phenylethane[f]	65 (40 mm)	65
Benzophenone[b]	40	2	Diphenyldifluoromethane[c]	174 (7.5 mm)	90
Cyclohexanecarboxyaldehyde[b]	−20	0.25	Difluoromethylcyclohexane[g]	125	85
Benzaldehyde[b]	20	1	α,α-Difluorotoluene[c]	6132	70
N,N-Dimethylbenzamide[b]	20	48	*N,N*-Dimethyl-α,α-difluorobenzamide[c]	70 (15 mm)	100

[a] Reaction was carried out with 1:1 mol ratio of carbonyl compounds:SeF_4 without solvent. [b] In $CF_2ClCFCl_2$ or CH_2Cl_2 solution with 1:1.2 ratio of reagents. [c] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960). [d] A. L. Henne, M. W. Renoll, and H. M. Leicester, *ibid.*, **61**, 938 (1939). [e] M. W. Renoll, *ibid.*, **64**, 1115 (1942). [f] K. Matsuda, J. A. Sedlak, J. S. Noland, and G. C. Gleckler, *J. Org. Chem.*, **27**, 4015 (1962). [g] F. Swarts, *Bull. Acad. Roy. Belg.*, 399 (1920).

Table II. Fluorination of Carboxylic Acids and Anhydrides with SeF_4–Pyridine[a]

Carboxylic acid (anhydride)	Acyl fluoride	Bp, °C	% yield
Formic acid[b]	Formyl fluoride	−29	25
Acetic acid[b]	Acetyl fluoride	20–21	80
Propionic acid[b]	Propionyl fluoride	42–44	85
Cyclohexanecarboxylic acid	Cyclohexanecarbonyl fluoride	80–81 (80 mm)	90
Benzoic acid	Benzoyl fluoride	154–155	95
Acetic anhydride[b]	Acetyl fluoride		90
Propionic anhydride[b]	Propionyl fluoride		85

[a] Reactions were generally carried out at room temperature. [b] Acyl fluorides were directly distilled out from the reaction mixture.

SF_4,[2] the reactions of SeF_4 can be carried out under milder conditions and at atmospheric pressure, in usual laboratory glass equipment, assuming the reagent is pure and anhydrous conditions are maintained.

Ketones and aldehydes give geminal difluorides in 65–100% yield, under very mild conditions (Table I).

$$R_2CO\ (RCHO) \xrightarrow{SeF_4} R_2CF_2\ (RCHF_2) + SeOF_2$$

A typical procedure is as follows. To a mixture of 15.5 g (0.1 mol) of SeF_4 and 125 ml of 1,1,2-trifluorotrichloroethane, 10 g (0.1 mol) of cyclohexanone dissolved in 100 ml of 1,1,2-trifluorotrichloroethane was added with stirring during 10 min at room temperature. The reaction continued for 50 min at reflux (47°). Then the solution was poured into ice water (at this stage excess SeF_4 and $SeOF_2$ formed were easily decomposed to selenious (fluoroselenious) acids). The organic layer was separated and dried over anhydrous Na_2SO_4. After removing the solvent, the product 1,1-difluorocyclohexane was isolated in 70% yield (bp 98°) and was analyzed by ir and nmr spectroscopy and by glc.

Carboxylic acids were also readily fluorinated by selenium tetrafluoride or even more conveniently by its complex formed with pyridine (see subsequent discussion).

$$RCOOH + SeF_4{\leftarrow}NC_5H_5 \longrightarrow RCOF + SeOF_2 + C_5H_5NHF$$

When carboxylic acid anhydrides were used in the reaction, 2 mol of acyl fluoride were formed for each mole of SeF_4. For the reaction of carboxylic acids and anhydrides the same procedure used for the reaction of alcohols was adapted. Table II summarizes the data for fluorination of carboxylic acids and anhydrides.

(2) (a) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960); (b) For a review see W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969.

Alcohols were found to react readily with SeF_4, but in some cases the more sensitive alkyl (arylalkyl, cycloalkyl) fluoride products were lost because of extensive rearrangement of polymerization due to HF formed in the reactions. In order to eliminate these unwanted side reactions, we found it advantageous to add 1 mol equiv of pyridine, which forms a liquid 1:1 donor–acceptor complex with SeF_4 (based on nmr studies the $C_5H_5N{\rightarrow}SeF_4$ complex is not ionic, resembling for example the BF_3 complex in its pmr spectrum and showing a singlet fluorine absorption at ϕ −20, only slightly deshielded from SeF_4 ϕ −27.5). It reacts selectively with alcohols, first forming alkoxyselenium trifluorides ($ROSeF_3$), which decompose upon heating to the corresponding alkyl fluorides.

$$ROH + SeF_4{\leftarrow}NC_5H_5 \longrightarrow F^-HN^+C_5H_5 + ROSeF_3 \longrightarrow RF + SeOF_2$$

Fluorination of alcohols with the SeF_4–pyridine complex gives no rearrangement except with susceptible systems, such as cyclopropylcarbinyl and isobutyl alcohol. Data on fluorination of alcohols are summarized in Table III.

A typical example of fluorination of alcohols is that of benzyl alcohol. Into the mixture of 15.5 g (0.1 mol) of SeF_4 and 100 ml of 1,1,2-trifluorotrichloroethane, 8 g (0.1 mol) of pyridine was added at 0°. Subsequently, 10.5 g (0.1 mol) of benzyl alcohol dissolved in 100 ml of 1,1,2-trifluorotrichloroethane was added to the stirred mixture at room temperature in 10 min. The reaction mixture was worked up as in the reaction of carbonyl compounds; 11 g of benzyl fluoride (bp 145°) was obtained, representing nearly 100% yield.

All yields reported in Tables I–III were based on isolated products, purified in the usual manner and

Table III. Fluorination of Alcohols with SeF_4–Pyridine

Alcohol	Alkyl fluoride	Bp, °C	% yield
Methyl[a]	Methyl	−78.5[b]	40
Ethyl[a]	Ethyl	−37.1[b]	58
Propyl	Propyl	−2.5[b]	50
Isopropyl	Isopropyl	−9.4[b]	60
Butyl	Butyl	32.5[c]	60
sec-Butyl	*sec*-Butyl	25.3[c]	65
Isobutyl	*tert*-Butyl	12.1[d]	65
2-Methyl-2-propyl	*tert*-Butyl		80
Pentyl	Pentyl	64.2[c]	60
Cyclopropyl	Cyclobutyl	34.0[e]	60
Cyclopropyl, phenylmethyl	Cyclopropyl, phenylmethyl	Dec[f]	56
	4-Phenylbuten-3-yl	Dec[f]	24
2-Cyclohexenyl	2-Cyclohexenyl	Dec[f]	90
1-Phenylcyclobutyl	1-Phenylcyclobutyl	Dec[f]	85
Benzyl	Benzyl	145[g]	100
α-Phenylethyl	α-Phenylethyl	46 (15 mm)[h]	100
β-Phenylethyl	β-Phenylethyl	55 (12 mm)[i]	100
α-Hydroxy-α-phenylacetophenone	α-Fluoro-α-phenylacetophenone	43[j] (mp)	100

[a] Reaction carried out without pyridine. [b] D. V. Grosse, R. C. Wachher, and C. B. Lin, *J. Phys. Chem.*, **44**, 275 (1942). [c] N. B. Chapman and J. C. Levy, *J. Chem. Soc.*, 1673 (1952). [d] V. Desreux, *Bull. Sci. Vog. Acad. Roy. Belg.*, **20**, 457 (1934). [e] M. Hanack and H. Eggensperger, *Chem. Ber.*, **96**, 1341 (1963). [f] These compounds decomposed at room temperature. [g] F. Cramer, K. Pawelzic, and F. W. Lichtentheler, *Chem. Ber.*, **91**, 1555 (1958). [h] K. Wiechert, C. Grueenert, and H. J. Preibisch, *Z. Chem.*, **8**, 64 (1968). [i] C. H. DuPuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2535 (1960). [j] R. F. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965).

analyzed by glc, as well by nmr (^1H and ^{19}F) and ir spectroscopy.

The needed selenium tetrafluoride for the reported fluorination reactions was found suitably prepared by converting selenium metal directly in better than 98% yield into SeF_4 by reaction with ClF_3 using SeF_4 itself as solvent for the reaction.

$$3Se + 4ClF_3 \longrightarrow 3SeF_4 + 2Cl_2$$

The reaction can be carried out in regular glass apparatus in dry nitrogen atmosphere by adjusting the rate of introduction of ClF_3 in relation to the addition of fresh selenium into the system such that exit gases consist only of chlorine. About 20 ml of SeF_4 (originally obtained by fluorination of selenium metal) was placed into the glass reaction vessel and about 2 g of selenium metal pellets was added. The mixture was stirred using a magnetic stirrer and ClF_3 was introduced below the surface of SeF_4 with such a rate that all the ClF_3 was absorbed and only chlorine gas was escaping the reaction vessel. The reaction mixture turned dark if ClF_3 was introduced too slowly, but as conversion proceeded it became almost colorless. At this time more selenium metal could be added and the introduction of ClF_3 continued. The reaction is fastest if the temperature of the reaction mixture is kept around 90°. Control of the temperature is maintained by the rate of introduction of ClF_3. Before distilling SeF_4 after completion of the reaction we made sure that there was only a small amount of ClF_3 dissolved in it,

$$3Se + 4ClF_3 \longrightarrow 3SeF_4 + 2Cl_2$$

since otherwise distillation could be dangerous. In a typical 8 hour run about 400 g of selenium metal could be reacted. Yield of pure SeF_4 obtained (bp 106°) was 98% based on selenium metal used.

Caution! All operation with ClF_3 must be carried out with great care as it is extremely reactive and will react vigorously with any organic material and moisture. All selenium compounds must be considered toxic and should be handled with according care. SeF_4 and $SeOF_2$ due to their low vapor pressure can be handled safely, particularly in solution, but are as all active fluorides, hydrolyzed with ease giving HF. All operation should be carried out in a well-vented hood.

We are also studying the utility of SeF_4 in other fluorination reactions and will report our results.

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Perfluoromethylenecyclopropane and 1-Trifluoromethyl-2,3,3-trifluorocyclopropene

Sir:

We report the synthesis of a new reactive fluoroolefin, perfluoromethylenecyclopropane (**1**). Reaction of 2,3-dichlorotetrafluoropropene[1] (1 mol) with hexafluoropropylene oxide[2] (1.8 mol) at 185° for 10 hr affords 1-(chlorodifluoromethyl)-1-chloro-2,2,3,3-tetrafluorocyclopropane (75% conversion, 94% yield), bp 58°,[3] which was dechlorinated with Zn in dioxane at 80–100° to afford a 20:1 mixture (70–75% yield) of **1** (bp 5–6°; ir 1818 cm^{-1} ($C{=}CF_2$); nmr (CCl_4) ϕ^* 57.3 (p, 2, J = 6.6 Hz), 135.2 (t, 4, J = 6.6 Hz)) and 1-trifluoromethyl-2,3,3-trifluorocyclopropene (**2**) (bp *ca.* 7°; ir 1889

1 **2**

(1) (a) J. E. Bissey, H. Goldwhite, and D. G. Roswell, *J. Org. Chem.*, **32**, 1542 (1967); (b) W. T. Miller, Jr., and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 4164 (1957).

(2) For examples of hexafluoropropylene oxide pyrolysis in the synthesis of fluorinated cyclopropanes, see P. B. Sargeant, *J. Org. Chem.*, **35**, 678 (1970).

(3) All compounds gave satisfactory combustion and/or mass spectral analyses. The products were unambiguously characterized by ^1H and ^{19}F nmr and ir in all cases.