distilled under vacuum (Kugelrohr), bp 160–170 °C (0.002 mm). Separation of the diastereomers of **2a** was effected by careful chromatography on a silica gel column using benzene with an increasing amount of chloroform. The oxide **2a** was identical in all respects with that reported in the literature.[8] A series of experiments were performed in which the ratio of PPA to **1a** was reduced from 50 ml:1 g to 40 ml:1 g to 30 ml:1 g to give **2a** but this procedure only resulted in decreasing yield of **2a**. Lowering the temperature of cyclization gave *trans*-1-(1-propenyl)diphenylphosphine oxide (**4**) which was identical in all respects with that prepared earlier,[12] along with the starting **1a** and a polymeric product.

**1,2,3,4-Tetrahydro-4-methyl-1-phenylphosphinoline 1-Oxide (2b). Method A.** The phosphine oxide (**1b** or **1c**, 2 g, 7.81 mmol) was slowly added to 100 ml of 115% PPA at 180 °C and, when the addition was complete, a stirring period of 4 h followed. When cooled to 110 °C, the solution was poured into 500 ml of ice-water and stirring produced a homogeneous solution. Extraction ($HCCl_3$, five times with 60-ml portions) gave a clear organic solution which was dried ($CaCl_2$). The chloroform was evaporated under vacuum to give a viscous oil which, upon scratching, solidified. This solid **2b** was twice sublimed at 100 °C (0.005 mm) to give a pure crystalline compound (Table I).

**Method B. Base Hydrolysis of 1,2,3,4-Tetrahydro-4-methyl-1,1-diphenylphosphinolinium Hexafluorophosphate.** The phosphonium compound **6** (1 g, 2.2 mmol) was boiled for 12 h in 100 ml of methanol–water (4:1) containing 10 g of NaOH. The mixture was cooled and 150 ml of water was added. The water layer was extracted ($HCCl_3$) and, after drying ($CaCl_2$), the solvent was evaporated to give solid **2b** (0.5 g, 90%) which was sublimed. It was identical in all respects with that prepared by method A.

**3,3-Dimethyl-1-phenylphosphindoline 1-Oxide (2c).** In a procedure directly analogous to the preceding one, the reaction of phosphine oxide **1d** (2 g, 7.81 mmol) and 100 ml of PPA at 180 °C gave **2c** in a yield of 1.0 g (50%). Sublimation was carried out at 100 °C (0.005 mm) (Table I).

**1,2,3,4-Tetrahydro-4-4-dimethyl-1-phenylphosphindoline 1-Oxide (2d).** Reaction of the phosphine oxide **1e** (2 g, 7.4 mmol) and 100 ml of PPA at 160 °C gave **2d** in good yield, 0.8 g (40%) (Table I).

**Registry No.**—**1a**, 4141-48-4; **1b**, 16540-56-0; **1c**, 16958-43-3; **1d**, 4455-75-8; **1e**, 13303-61-2; **1f**, 13303-58-7; **1g**, 13303-57-6; *cis*-**2a**, 58191-09-6; *trans*-**2a**, 58191-10-9; *cis*-**2b**, 58191-11-0; *trans*-**2b**, 58191-12-1; **2c**, 58191-13-2; **2d**, 58191-14-3; **5**, 54230-12-5; 2-methyl-2-propen-1-ol, 513-42-8; diphenylphosphinous chloride, 1079-66-9; crotyl bromide, 4784-77-4; methyl diphenylphosphinite, 4020-99-9; 3-butenylphosphonium bromide, 16958-42-2.

## References and Notes

(1) We gratefully acknowledge support of this work by the USPHS, National Cancer Institute, Grant CA 11967.

(2) Research Associate, 1974–1975. Department of Chemistry, Faculty of Science, Ain-Shams University, Abbassia, Cairo, Egypt.

(3) F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1634 (1947).

(4) F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 4107 (1955).

(5) T. H. Chan and T. L. Wong, *Can. J. Chem.*, **49**, 530 (1971).

(6) Y. Kashman and O. Awerbouch, *Tetrahedron Lett.*, 3217 (1973).

(7) L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Am. Chem. Soc.*, **91**, 3308 (1969).

(8) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6205 (1971).

(9) M. P. Savage and S. Trippit, *J. Chem. Soc. C*, 1842 (1966).

(10) J. D. Martin and E. G. Griffin, *J. Org. Chem.*, **30**, 4034 (1965).

(11) We gratefully acknowledge the encouragement and generous sample of 115% PPA from Mr. J. P. Cassidy, FMC Corp., Inorganic Division. The 115% PPA used contained a minimum of 83.2% $P_2O_5$.

(12) F. J. Welch and H. J. Paxton, *J. Polym. Sci.*, 3439 (1965).

(13) W. R. Purdum, G. A. Dilbeck, and K. D. Berlin, *J. Org. Chem.*, **40**, 3763 (1975).

(14) G. A. Dilbeck, D. L. Morris, and K. D. Berlin, *J. Org. Chem.*, **40**, 1150 (1975).

(15) A similar situation has been observed in another phosphorinane system; see K. L. Marsi and R. T. Clark, *J. Am. Chem. Soc.*, **92**, 3791 (1970).

(16) (a) K. L. Marsi and J. E. Oberlander, *J. Am. Chem. Soc.*, **95**, 200 (1973); (b) J. W. Suggs and L. D. Freedman, *J. Org. Chem.*, **36**, 2566 (1971); (c) K. L. Marsi, *J. Am. Chem. Soc.*, **92**, 3791 (1970); (d) W. Egan, G. Chauviere, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970).

(17) J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961); E. Jonsson, *Ark. Kemi*, **26**, 357 (1967); P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 552 (1967); K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *ibid.*, 759 (1966); A. B. Foster, J. M. Druxbury, J. D. Inch, and J. M. Webber, *ibid.*, 881 (1967); A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *ibid.*, 1086 (1968).

(18) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 286 (1967); G. Marvel, *Annu. Rep. NMR Spectrosc.*, **5B**, 208 (1973).

(19) (a) K. L. Marsi, *J. Am. Chem. Soc.*, **91**, 4724 (1969). (b) A. Fitzgerald, G. D. Smith, C. N. Caughlan, K. L. Marsi, and F. B. Burns, *J. Org. Chem.*, in press. We thank Dr. Marsi for a preprint and permission to cite this work which is an x-ray analysis of *cis*-1-iodomethyl-3-methyl-1-phenylphospholanium iodide. Through this compound it was possible to correlate many phospholane systems including **8a**, **8b**, **9a**, and **9b**. (c) J. J. Breen, J. F. Engel, D. K. Myers, and L. D. Quin, *Phosphorus*, **2**, 55 (1972).

(20) E. E. Schweizer, J. G. Thompson, and T. A. Ulrich, *J. Org. Chem.*, **33**, 3082 (1968).

(21) K. L. Marsi, F. R. Burns, and R. T. Clark, *J. Org. Chem.*, **37**, 238 (1972). A private communication from Dr. Marsi has indicated that **12a** has the following properties: bp 120 °C (0.01 mm); $^1$H NMR ($DCCl_3$) $\delta$ 1.23 (C–$CH_3$) and (in $C_6H_6$) $\delta$ 0.853 (C–$CH_3$). Isomer **12b** has mp 60–61 °C; $^1$H NMR ($DCCl_3$) $\delta$ 0.776 (C–$CH_3$) and (in $C_6H_6$) $\delta$ 1.19 (C–$CH_3$).

---

# Direct Synthesis of Fluorinated Peroxides. IV. Addition of Pentafluorosulfur Peroxyhypochlorite to Alkenes

Michale J. Hopkinson, Nyal S. Walker, and Darryl D. DesMarteau*[1]

*Department of Chemistry, Kansas State University, Manhattan, Kansas 66506*

*Received October 29, 1975*

Pentafluorosulfur peroxyhypochlorite, $SF_5OOCl$, undergoes addition reactions with alkenes forming pentafluorosulfurperoxy derivatives in good yield. The additions are predominantly unidirectional and proceed by an electrophilic mechanism. Reactions with $C_2H_4$, $C_2F_4$, $C_2F_3Cl$, $CF_2CCl_2$, $CF_2CH_2$, and *cis*-CFHCFH occur readily below 0 °C, whereas $C_3F_6$, 2-$C_4F_6$, and c-$C_5F_8$ were unreactive under all conditions. With *cis*-CFHCFH the addition was stereospecific. The new peroxides are stable at 22 °C and have been characterized by their physical properties and ir and NMR spectra. Comparison of $SF_5OOCl$ reactions with those of the related compound $CF_3OOCl$ are discussed.

The systematic synthesis of fluorocarbon peroxides and the resultant change in their classification from isolated laboratory curiosities to a well-established class of compounds was made possible by the reagents $CF_3OOH$,[2] $CF_3OOCl$,[3] $CF_3OOF$,[4] and $CF_3OOOCF_3$.[5] It has been shown that the only available route at present to a variety of peroxides is their direct synthesis via reactions in which the $CF_3OO$ group is added to suitable substrates. In order to expand this interesting area of chemistry, the development of other reagents of the type $R_FOOX$ has been a

**Table I. Reactions of $SF_5OOCl$ with Alkenes**

| Registry no. | Alkene[a] | $SF_5OOCl$[a] | Conditions | $SF_5O$– products[b] | Registry no. |
|---|---|---|---|---|---|
| 74-85-1 | $C_2H_4$, 4.2 | 2.0 | 0.5 h, −78 °C | $SF_5OOCH_2CH_2Cl$, 58%;<br>$SF_5OCH_2CH_2Cl$, 25% | 58249-50-6 |
| 75-38-7 | $CH_2CF_2$, 4.6 | 2.0 | 5 h, −78 °C | $SF_5OOCF_2CH_2Cl$, 47%;<br>$SF_5OCF_2CH_2Cl$, 6% | 58249-51-7 |
| 1630-77-9 | *cis*-CHFCHF, 3.7 | 2.0 | 12 h, −78 to −20 °C | *erythro*-$SF_5OOCFHCFHCl$, 70%;<br>$SF_5O(CFHCFH)Cl$, 9% | 58267-74-6 |
| 116-14-3 | $C_2F_4$, 5.5 | 2.0 | 12 h, −78 °C | $SF_5OOCF_2CF_2Cl$, ~30%;<br>$SF_5OCF_2CF_2Cl$, <5%;<br>$SF_5OCF_2CF_2CF_2CF_2Cl$, ~10% | 58249-52-8 |
| 79-38-9 | $C_2F_3Cl$, 3.0 | 1.8 | 18 h, −95 °C | $SF_5OOCF_2CFCl_2$–<br>$SF_5OOCFClCF_2Cl$, ~8%;<br>$SF_5OCF_2CFCl_2$–<br>$SF_5OCFClCF_2Cl$, 23% | 58249-53-9<br>58249-54-0 |
| 79-35-6 | $CF_2CCl_2$, 4.3 | 2.5 | 18 h, −111 to −78 °C<br>and 12 h, −78 °C | $SF_5OOCF_2CCl_3$, ~4%;<br>$SF_5OOCCl_2CF_2Cl$, ~8%;<br>$SF_5OCF_2CCl_3$;[c] $SF_5OCCl_2CF_2CCl$[c] | 58249-55-1<br>58249-56-2 |
| 116-15-4 | $C_3F_6$, 4.7 | 2.0 | 8 days, −78 °C<br>2 days, 0 °C | No $SF_5O$– addition products | |
| 692-50-2 | 2-$C_4F_6$, 2.4 | 1.0 | 10 days, −78 °C<br>2 days, 0 °C | No $SF_5O$– addition products | |
| 559-40-0 | c-$C_5F_8$, 3.0 | 2.0 | 6 days, −78 °C<br>2 days, 0 °C | No $SF_5O$– addition products | |

[a] Amounts in millimoles. Registry no., 58249-49-3. [b] Yields are for purified products after GLC and are based on the amount of $SF_5OOCl$ added. [c] Yields not determined, but considerably greater than the yields of peroxide based on $^{19}F$ NMR and GLC.

major goal in our laboratories. The recent synthesis by us of $SF_5OOH$,[6,7] $SF_5OOCl$,[7] and $SF_5OOF$[7] now allows for the systematic preparation of pentafluorosulfur peroxides.

This paper is concerned with the reactions of $SF_5OOCl$ with olefins, and comparison with the similar reactions of $CF_3OOCl$.[3] The latter was shown to add to alkenes by an electrophilic mechanism. The additions were unidirectional in the case of unsymmetrical alkenes, and the direction of addition was easily predictable based on qualitative electrostatics. In one instance, the addition was shown to be stereospecific and most probably cis. The additions of $SF_5OOCl$ parallel those of $CF_3OOCl$ in most instances, but there are surprising differences.

## Experimental Section

**General.** All compounds were handled in Pyrex or stainless steel vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge or a precision Heise-Bourdon tube gauge. Infrared spectra were obtained on a Perkin-Elmer Model 180 or Model 337 spectrometer using a 10-cm path length glass cell fitted with silver chloride windows. NMR spectra were recorded on a Varian XL-100-15 spectrometer using ~80 mol % $CCl_3F$ solutions of the samples. Vapor pressures were determined by a static method employing the isotensiscope principle.[8] Equations describing vapor pressure as a function of temperature were obtained by a least-squares fit of the data. Volatile mixtures were separated by trap-to-trap distillation and by GLC using 41% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P. Chromatography was carried out at temperatures between 22 and 40 °C using a 1 ft × 0.375 in. ss column and gas injection.

**Reagents.** The olefins $C_2F_3Cl$, $CF_2CCl_2$, $CF_2CH_2$, *cis*-CHFCHF, $C_3F_6$, c-$C_5F_8$, and the acetylene 2-$C_4F_6$ were obtained from PCR Inc., $C_2H_4$ from Matheson Co., and $C_2F_4$ from the pyrolysis of Teflon.[9] The chloroperoxide, $SF_5OOCl$, was prepared by the literature method.[7]

**Reaction of $SF_5OOCl$ with Olefins.** All the reactions were carried out in 100-ml glass vessels fitted with glass–Teflon valves. The peroxide was prepared separately for each reaction and condensed into the bottom of the reaction vessel held at −196 °C. The olefin was condensed into the top portion of the bulb which was then placed in a low-temperature bath. The reaction was followed by the disappearance of the yellow color due to $SF_5OOCl$. In most cases the reactions were continued until a faint yellow color persisted, this color being due to a small amount of chlorine present. The products were collected in a −112 °C trap for the $C_2F_4$ and $C_2H_4$ reactions and a −78 °C trap for the others. These fractions were further separated by GLC. A variety of products were formed in the reactions including $SOF_4$, fluorinated, and fluorochlorinated olefins as well as $SF_5O$– and peroxide addition products. No effort was made to identify all the products. The ether and peroxy addition products, which usually formed the major part of the mixture, are reported in Table I.

*Although no explosions occurred during this work, fluorinated peroxides can detonate when subjected to thermal or mechanical shock. Precautions should be taken when handling these compounds. Pentafluorosulfur peroxyhypochlorite is especially reactive.*

The main identification of the ether products was by $^{19}F$ NMR and molecular weight. The ethers $SF_5OCH_2CH_2Cl$, $SF_5O(CF_2CFCl)Cl$, and $SF_5OCF_2CF_2Cl$[10,11] have been previously reported and nearly all others are currently being investigated by Fox and co-workers.[12]

In the reactions of $SF_5OOCl$ with $C_3F_6$, c-$C_5F_8$, and $CF_3C{\equiv}CCF_3$ no evidence was found for the formation of peroxides, the olefins remaining mostly unreacted even at 0 °C. In these cases decomposition products of $SF_5OOCl$ were observed together with unreacted olefin and a small amount of less volatile material, shown by $^{19}F$ NMR to contain no $SF_5$ groups.

$SF_5OOCH_2CH_2Cl$: bp 119.3 °C; mp (glassed at low temperature); mol wt 221.3 (calcd, 222.6); ir 2962 (w), 1442 (vw), 1371 (vw), 1308 (vw), 1254 (w), 1059 (vw), 974 (m sh), 915 (vs), 869 (vs), 785 (m), 767 (m), 730 (m), 685 (w), 605 (s), 585 cm$^{-1}$ (m); NMR $F^{A}SF^{B}_{4}OOCH^{C}_{2}\text{–}CH^{D}_{2}Cl$, $\phi^*_{A}$ −63.6, $\phi^*_{B}$ −45.6, $\delta_C$ 4.71, $\delta_D$ 3.90, $J_{AB} = 155.0$, $J_{AC} \simeq 0$, $J_{BC} = 0.9$, $J_{CD} = 6.0$ Hz; $\Delta H_{vapor} = 8.40$ kcal/mol, $\Delta S_{vapor} = 21.4$ eu; $\log P\ (mm) = 7.6968 - 1945.8/T + 21779/T^2$.

$SF_5OOCF_2CF_2Cl$: bp 61.4 °C; mp (glassed at low temperature); mol wt 290.7 (calcd, 294.4); ir 2502 (vw), 2400 (vw), 2350 (vw), 2290 (vw), 1668 (vw), 1615 (vw), 1509 (vw), 1484 (vw), 1356 (vw), 1312 (vw), 1263 (w), 1236 (m), 1208 (s), 1184 (s), 1117 (s), 980 (s), 931 (vs), 878 (vs), 842 (w), 824 (w), 800 (m), 734 (w), 680 (vw), 630 (w), 608 (s), 561 (w), 503 cm$^{-1}$ (vw); NMR $F^{A}SF^{B}_{4}\text{–}OOCF^{C}_{2}\text{–}CF^{D}_{2}Cl$, major $AB^4$ peak at $\phi^*$ −57.12, $\phi^*_{C}$ 93.87, $\phi^*_{D}$ 70.56, $J_{AC} < 1.0$, $J_{BC} \simeq 4.0$, $J_{CD} = 2.7$ Hz; $\Delta H_{vapor} = 8.17$ kcal/mol; $\Delta S_{vapor} = 24.4$ eu; $\log P\ (mm) = 8.2171 + 1785.6/T$.

$SF_5OOCF_2CH_2Cl$: bp 83.5 °C; mp (glassed at low temperature); mol wt 257.7 (calcd, 258.6); ir 2968 (w), 1431 (w), 1318 (m), 1271 (s), 1236 (s), 1134 (s), 1088 (s), 926 (vs), 874 (vs), 857 (m), 803 (w), 742 (w), 700 (vw), 678 (w), 639 (w), 606 (s), 594 (m), 552 cm$^{-1}$ (vw); NMR $F^{A}SF^{B}_{4}OOCF^{C}_{2}\text{–}CH^{D}_{2}Cl$, major $AB^4$ peak at $\phi^*$ −56.43, $\phi^*_{C}$ 83.66, $\delta_D$ 3.85, $J_{AC} = 0.8$, $J_{BC} = 4.0$, $J_{CD} = 8.2$ Hz; $\Delta H_{vapor} = 7.98$ kcal/mol; $\Delta S_{vapor} = 22.4$ eu; $\log P\ (mm) = 7.7692 - 1743.3/T$.

$SF_5OOCFHCFHCl$: bp 94.8 °C; mp (glassed at low temperatures); mol wt 257.4 (calcd, 258.5); ir 2968 (w), 1431 (w), 1318 (m), 1271 (s), 1236 (s), 1134 (s), 1088 (s), 926 (vs), 874 (vs), 857 (m), 803 (w), 742 (w), 700 (vw), 678 (w), 639 (w), 606 (s), 594 (m), 552 cm$^{-1}$ (vw); NMR $F^{A}SF^{B}_{4}OOCF^{C}H^{D}\text{–}CF^{E}H^{F}Cl$, major $AB^4$ peak at $\phi^*$

−57.50, $\phi^*_C$ 135.40, $\phi^*_E$ 152.98, $\delta_D$ 6.0, $\delta_F$ 6.2, $J_{AC} = 4.0$, $J_{BC} = 4.0$, $J_{CD} = 59.0$, $J_{CE} = 14.1$, $J_{CF} = 3.5$, $J_{DE} = 4.0$, $J_{DF} = 5.1$, $J_{EF} = 49.2$ Hz; $\Delta H_{vapor} = 8.93$ kcal/mol; $\Delta S_{vapor} = 24.3$ eu; log $P$ (mm) = $8.1976 - 1952.6/T$.

$SF_5OOCF_2CCl_3$: ir 1362 (m), 1243 (s), 1190 (s), 1175 (m), 1141 (s), 1082 (m), 928 (vs), 891 (s), 872 (vs), 853 (s), 834 (s), 789 (s), 729 (m), 652 (m), 605 (s), 558 cm$^{-1}$ (m); NMR $F^ASF^B_4OOCF^C_2\text{–}CCl_3$, major $AB^4$ peak at $\phi^*$ −57.47, $\phi^*_C$ 89.85.[13]

$SF_5OOCCl_2CF_2Cl$: ir 1236 (m), 1193 (s), 1180 (s), 1146 (m), 1071 (s), 1047 (s), 980 (s), 931 (vs), 872 (vs), 826 (s), 798 (s), 743 (m), 687 (m), 652 (m), 633 (w), 609 (s), 594 (s), 568 cm$^{-1}$ (m); NMR $F^ASF^B_4OOCCl_2\text{–}CF^C_2Cl$, major $AB^4$ peak at $\phi^*$ −58.74, $\phi^*_B$ 62.83.

$SF_5OOCF_2CFCl_2\text{–}SF_5OOCFClCF_2Cl$ (10/6 by NMR): mol wt 312.4 (calcd, 310.9); ir 1272 (m), 1240 (m), 1203 (s), 1175 (s), 1101 (s), 1044 (m), 985 (m), 931 (vs), 880 (vs), 810 (m), 770 (w), 745 (w), 731 (w), 722 (w), 655 (w), 608 (s), 592 (m), 560 cm$^{-1}$ (w); NMR $F^ASF^B_4OOCF^C_2\text{–}CF^DCl_2$ major $AB^4$ peak at $\phi^*$ −55.30, $\phi^*_C$ 91.85, $\phi^*_D$ 73.00, $J_{AC} < 1.0$, $J_{BC} \simeq 4.0$, $J_{CD} = 7.38$ Hz; $F^ASF^B_4OOCF^CClCF^D_2Cl$ major $AB^4$ peak at $\phi^*$ −57.23, $\phi^*_C$ 78.90, $\phi_D$ 66.42, $J_{AC} < 1.0$, $J_{BC} \simeq 4.0$, $J_{CD} = 6.75$ Hz.

## Results

The addition of $SF_5OOCl$ to several olefins proceeds readily at low temperatures to give varying yields of $SF_5OO$ peroxides, as well as significant amounts of $SF_5O$– ethers. The major $SF_5O_n$– products are given in Table I. The pentafluorosulfur ethers are presumably formed from the addition of $SF_5OCl$ to the olefin, the $SF_5OCl$ being the major decomposition product of the rather unstable $SF_5OOCl$. As observed previously with $CF_3OOCl$, $C_2F_4$ gave significant amounts of telemers or oligmers. These may also be formed in other reactions, but are probably too low in volatility to be observed by our methods. With $CF_2H_2$ and *cis*-CFHCFH, only one of two possible peroxide isomers is observed. Attempted reactions with $C_3F_6$, $CF_3C{\equiv}CCF_3$, and c-$C_5F_8$ were unsuccessful under conditions where reaction with the other olefins occurred readily. Temperatures higher than 0 °C could not be used in order to favor reaction, owing to the rapid decomposition of $SF_5OOCl$ at 22 °C.

The new peroxides are clear, volatile liquids and are thermally stable in glass at 22 °C. They are probably stable at considerably higher temperatures, with those having the highest chlorine or hydrogen content expected to be the least stable. Each of the new compounds is most readily identified by its $^{19}F$ NMR spectrum. All show characteristic $AB_4$ patterns for the pentafluorosulfur group with a $\phi^*$ value of approximately −55 for the B fluorines and $J_{AB}$ of ~150 Hz. Detailed analyses of the $AB_4$ spectra were not carried out in most cases because the exact $J_{AB}$, $\phi^*_A$, and $\phi^*_B$ values are unnecessary in order to establish the identity of the compounds. In those compounds containing carbon–fluorine and carbon–hydrogen bonds, the $^{19}F$ and $^1H$ spectra were as expected. For methylene fluorines adjacent to an $SF_5OO$ group, $J_{F\text{–}F^B}$ was observed to be ~4.0 Hz and $J_{FF^A} < 1.0$ Hz. For methylene protons, $J_{HF^B} < 1.0$ and $J_{HF^A} \simeq 0$ Hz.

The distinction between $SF_5OO$– and $SF_5O$– products is obvious from the magnitude of $J_{FF^A}$, $J_{FF^B}$, $J_{HF^A}$, and $J_{HF^B}$ coupling constants between the pentafluorosulfur fluorines and methylene protons and fluorines. For the ethers, these have values of approximately 2.0, 12.0, 1.0, and 4.0 Hz, respectively.[14] These coupling constants are thus approximately three times larger than for the peroxides, which is quite analogous to that situation in trifluoromethyl ethers and peroxides for the same coupling between $CF_3$.

The establishment of only a single isomer in the case of $SF_5OOCFHCFHCl$ was made by $^1H$ and $^{19}F$ NMR employing both homo- and heteronuclear decoupling. The magnitude of the vicinal $J_{HH}$ coupling suggests that the compound is the erythro isomer and thus the addition of $SF_5OOCl$ to *cis*-CFHCFH is cis.[3] The formation of two structural isomers in the reactions with $C_2F_3Cl$ and $CF_2CCl_2$ was obvious from the $^{19}F$ NMR of fluorine on carbon and in the case of $CF_2CCl_2$ the two isomers were easily separable by GLC.

Infrared spectra of the peroxides support the proposed structures, but are not especially characteristic in each case. All show three strong bonds for the $SF_5OO$– group in the region 915–931 and 869–880 cm$^{-1}$ assignable to $SF_5$–stretching and 605–608 cm$^{-1}$ (PQR) due to $SF_5$ deformation.[15]

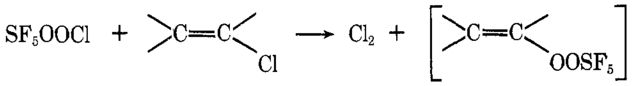
## Discussion

The addition of $SF_5OOCl$ to olefins significantly increases the number of pentafluorosulfurperoxyalkyl derivatives. Prior to this work, only one compound of this type was known, $CF_3OOSF_5$.[16] The latter was synthesized by a coupling reaction between $CF_3O\cdot$ and $SF_5O\cdot$ radicals. This type of reaction is responsible for only isolated examples of fluorinated peroxides and its generality has not been demonstrated. In contrast, this work clearly establishes the utility of reagents such as $SF_5OOCl$ in the direct synthesis of a variety of new peroxides. The different olefins employed in this work suggest a wide applicability for the reaction.

The mechanism for the reaction appears to be that for electrophilic addition of the positive chlorine of $SF_5OOCl$ followed by the addition of the $SF_5OO$ group. This might occur in two steps or in a concerted manner. As we have previously argued for the related reactions of $CF_3OOCl$ with olefins, a radical mechanism is unlikely owing to the lack of reactivity shown by $C_3F_6$ and c-$C_5F_8$. The latter are especially resistant to electrophilic additions but readily undergo free-radical additions. Furthermore, the stereospecific addition observed with *cis*-CFHCFH rules out a free-radical mechanism. The reactions of $CF_3OOCl$ and $SF_5OOCl$ are exactly analogous in the case of $C_2H_4$, $C_2F_4$, $CF_2CH_2$, *cis*-CFHCFH, $C_3F_6$, and c-$C_5F_8$. However, with $C_2F_3Cl$ and $CF_2CCl_2$, high yields of single isomeric peroxide were observed with $CF_3OOCl$, whereas $SF_5OOCl$ gives low yields of both possible structural isomers with these olefins. Initially, this was attributed to the poor control of experimental conditions, but repeated attempts under a variety of conditions always gave the same results: low yields and two isomers. There are many possible explanations for this, but we feel that the following has at least some evidence in its favor.

The two peroxyhypochlorites, $CF_3OOCl$ and $SF_5OOCl$, are the only known examples of compounds of this type and as such, very little is known regarding the nature of the oxygen–chlorine bond in these materials. However, in reactions which are based on the positive halogen character of the chlorine atoms, two factors would seem to be important. First, the electron density at chlorine may be different in the two materials owing to differences in the electronegativity of $CF_3$ and $SF_5$, and second, the oxygen–chlorine bond energy could vary significantly between the two materials. By comparison of $CF_3OSO_2F$[17] and $SF_5OSO_2F$,[18] it is possible to gain some idea of the relative electronegativity of $SF_5O$ and $CF_3O$ by comparing the average of the asymmetric and symmetric $SO_2$ stretching frequencies.[19] On this basis, $CF_3O$ is clearly more electronegative. A measure of the relative chlorine–oxygen bond strengths in the two compounds may be inferred from the difference in thermal stability between the two compounds.[20] Because $CF_3OOCl$ has a half-life at 22 °C of a few hours and $SF_5OOCl$ only a few minutes, the oxygen–chlorine bond in $CF_3OOCl$ may be stronger.

The above considerations could account for the difference in reaction of the two peroxyhypochlorites with $C_2F_3Cl$ and $CF_2CCl_2$. If $SF_5OOCl$ is less electrophilic, the selectivity and ease of addition with these olefins may decrease. If the oxygen–chlorine bond is weaker in $SF_5OOCl$, a side reaction of the type



may be thermodynamically and/or kinetically more favorable. Some evidence for latter was obtained by the reaction of $SF_5OOCl$ with $CH_3C(O)Cl$. The formation of $Cl_2$ and $CH_3C(O)OOSF_5$[21] occurred in high yield. There is at least some similarity between the carbon–chlorine bond in -C(O)Cl and >C=C–C and we believe the above side reaction takes place to give unstable peroxides as indicated, with a concomitant decrease in yield of the addition product.

**Acknowledgment.** The partial support of this work by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

## References and Notes

(1) Alfred P. Sloan Fellow, 1975–1977.
(2) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Am. Chem. Soc.*, **93**, 8882 (1971).
(3) N. S. Walker and D. D. DesMarteau, *J. Am. Chem. Soc.*, **97**, 13 (1975).
(4) F. A. Hohorst and D. D. DesMarteau, *J. Inorg. Nucl. Chem.*, H. H. Hyman Memorial Issue, in press.
(5) F. A. Hohorst, J. V. Paukstelis, and D. D. DesMarteau, *J. Org. Chem.*, **39**, 1298 (1974).
(6) D. D. DesMarteau, *J. Am. Chem. Soc.*, **94**, 8933 (1972).
(7) R. M. Hammaker and D. D. DesMarteau, in preparation.
(8) A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 897 (1910).
(9) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).
(10) L. R. Anderson, D. E. Young, D. E. Gould, R. Jurick-Hogen, D. Nuechterlein, and W. B. Fox, *J. Org. Chem.*, **35**, 3730 (1970); W. Maya, C. J. Shack, R. D. Wilson, and J. S. Muirhead, *Tetrahedron Lett.*, 3247 (1969).
(11) Some different, but related ethers have been obtained by reactions of $SF_5OF$: S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962); R. D. Place and S. M. Williamson, *J. Am. Chem. Soc.*, **90**, 2550 (1968).
(12) Private communication, W. B. Fox, Naval Research Laboratory, Washington, D.C.
(13) The $^{19}F$ NMR of this $CF_2$ group was not clearly resolved. It is a basic quintet of doublets but the lines are broadened and the pattern is asymmetric. This is not the case for the same ether derivative, and may reflect second-order effects caused by a restricted rotation about the carbon–oxygen bond in $SF_5OOCF_2CCl_3$. A similar but less pronounced effect was observed for $SF_5OOCF_2CFCl_2$ and $SF_5OOCFClCF_2Cl$. Here again, the ether derivatives showed well-resolved, symmetric patterns for the $-CFCl-$ and $-CF_2-$ groups.
(14) H. A. Carter and J. M. Shreeve, *Spectrochim. Acta, Part A*, **29**, 1321 (1973).
(15) See ref 10–12.
(16) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 909 (1963).
(17) W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960).
(18) H. J. Emeleus and K. J. Pacher, *J. Chem. Soc.*, 771 (1962).
(19) W. B. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).
(20) This is recognized as being a rather tenuous argument. Some other support for a weaker O–Cl bond in $SF_5OOCl$ comes from a comparison of the vibrational spectra of $CF_3OOCl$ and $SF_5OOCl$. Reference 7 and D. D. DesMarteau and R. M. Hammaker, to be published.
(21) M. J. Hopkinson and D. D. DesMarteau, *J. Fluorine Chem.*, in press.

---

# Pinacolyl Chloride Revisited. A Practical Synthesis

Miguel E. Alonso

*Centro de Petróleo y Química, Instituto Venezolano de Investigaciones Científicas, I.V.I.C.,*
*Apartado 1827, Caracas 101, Venezuela*

*Received October 27, 1975*

The synthesis of 3-methyl-2-chlorobutane in 90% yield and 3,3-dimethyl-2-chlorobutane (pinacolyl chloride) in 49% yield in which Wagner–Meerwein rearrangement products are completely absent is described. The method involves the displacement of the corresponding *p*-toluenesulfonyl esters with lithium chloride in dimethyl sulfoxide and hexamethylphosphoramide under moderate vacuum and temperature with concomitant evaporation of the chlorides produced. The application of several methods of halogenation to pinacolyl alcohol is discussed.

In connection with gas-phase kinetic studies pinacolyl chloride (8) was required in high purity. The tendency of this compound to rearrange under the conditions required for its synthesis is well known[1–4] and contaminants are usually difficult to separate. In fact, compound 8 and 2,3-dimethyl-2-chlorobutane (**10**), the Wagner–Meerwein rearrangement product of 8, differ in boiling point by only 1 °C.[4] The inherent steric hindrance of the secondary neopentylic carbon implies the use of rather harsh reaction conditions for bimolecular displacements to take place. Consequently significant quantities of olefins are generally produced.

These difficulties thwarted all efforts directed toward the synthesis of pinacolyl chloride until Whitmore[5] was able to obtain it by means of the chlorination of 2,2-dimethylbutane, albeit in poor yield.

Although 3,3-dimethyl-2-chlorobutane has been the subject of a limited number of studies,[3,6,28] the literature is exceedingly scant of reports about its synthesis. Addition of hydrogen chloride to 3,3-dimethylbut-1-ene[2,3] makes the task of isolation of 8 nearly impossible for practical purposes, for considerable amounts of **10** are produced. Similar results would arise from the chlorination of the corresponding hydrocarbon.[5] The halogenation of pinacolyl alcohol (**7a**) or some derivative thereof, though not devoid of obstacles, represented a more viable approach. In the present report an efficient synthesis of pinacolyl chloride free of compound **10** is described.

Treatment of carbinol **7a** with thionyl chloride in pyridine,[7,8] acetyl chloride, or phosphorus halides[9] furnished small quantities of 8 in admixture with several carbenium ion derived products. The use of phosphorus reagents of the triphenyl phosphite type appeared more promising. The reaction of triphenyl phosphite-benzyl chloride adduct[10] with 3-methylbutan-2-ol (**1a**), a model compound less prone to rearrange than **7a**, in dimethylformamide at room temperature gave a mixture of 2-chloro-3-methylbutane (**2**) and 2-chloro-2-methylbutane (**5**) in a 2:3 ratio. Analogously, pinacolyl alcohol yielded both chlorides 8 and **10**. This result is in consonance with the observed rearrangement during the halogenation of neopentyl alcohol.[11,12] Wiley et al.,[13] inter alia,[12] introduced the use of a