tion from alkanes by RSO_2 radicals can be expected to have an appreciable activation energy. Consequently, it is quite possible that with an increase of temperature, sulfinic acid formation shifts from the biradical to the hydrogen abstraction mechanism. In the systems in which this transition occurs a curvature of the Arrhenius plots of sulfinic acid formation should be observed. It should be noted that the square-root dependence of R_A/R_B on I_a, k_{20}, and β indicates that the conclusions reached by us are not limited by the values chosen for those parameters. It should also be pointed out that the increase of SO_2 concentration leads to the transition from the biradical to the hydrogen abstraction mechanism. This effect is due to the very efficient removal of R radicals by the reaction with SO_2 (reaction 21) that results in RSO_2 concentrations that are much higher than those of R. Thus it is quite possible that in systems where much SO_2 is present almost all the sulfinic acid will be formed by the hydrogen abstraction mechanism.

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Direct Synthesis of Fluorocarbon Peroxides. III. The Addition of Chloroperoxytrifluoromethane to Olefins

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Abstract: Chloroperoxytrifluoromethane, CF_3OOCl, undergoes addition reactions with olefins to yield trifluoromethylperoxy derivatives in high yield. The reactions are unidirectional and proceed by an electrophilic mechanism, in which the positive chlorine of CF_3OOCl adds to the carbon with the greatest number of hydrogens or the fewest fluorines. Reactions with C_2H_4, C_2F_4, C_2F_3Cl, CF_2CCl_2, CF_2CH_2, and *cis*-CFHCFH occur readily below 0°, whereas C_3F_6 and c-C_5F_8 were unreactive under all conditions tried. With *cis*-CFHCFH the reaction is stereospecific. The new peroxides exhibit high thermal stabilities and have been characterized by their physical properties and ir and nmr spectra.

Fluorocarbon peroxides can now be obtained in considerable number and variety by the direct addition of the CF_3OO group to suitable substrates. We have shown previously that the novel compounds, CF_3OOOCF_3,[1,2] CF_3OOH,[3-5] and CF_3OOF[6,7] are useful reagents for the direct synthesis of fluorocarbon peroxides, each having certain advantages in generating new peroxy derivatives. The reactions of CF_3OOH demonstrated thus far are polar in nature while those of CF_3OOOCF_3 and CF_3OOF are free radical. Chloroperoxytrifluoromethane, CF_3OOCl,[8] is also a potential reagent for the synthesis of CF_3OO derivatives. A brief, earlier report of some reactions of CF_3OOCl indicated, however, that reactions of CF_3OOCl probably proceeded by cleavage of the O-O bond. While it is likely that the O-O and O-Cl bonds in CF_3OOCl are of similar strengths, considering the utility of CF_3OCl[9,10] as a reagent for the synthesis of CF_3O derivatives and by analogy with the related compounds CF_3OOF and CF_3OF, it seemed reasonable to investigate CF_3OOCl as a potential source of new CF_3OO derivatives. In this paper we report the addition of CF_3OOCl to several olefins. In all cases involving ethylene and its chloro–fluoro derivatives, reaction proceeds readily at low temperatures to form peroxides which correspond to the simple addition of CF_3OOCl across the carbon–carbon double bond. Indeed, these reactions are quite analogous to the addition of CF_3OCl to olefins and are even more selective as no evidence was obtained for isomeric peroxides.

Experimental Section

General. All manipulations of volatile compounds were conducted in glass and stainless steel vacuum systems as previously described.[3] Quantities of reactants and products were measured by $n = PV/RT$, assuming ideal gas behavior or by direct weighing. Separation of volatile reaction mixtures was by trap-to-trap distillations and by glc using 49% halocarbon 11–21 polymer oil on acid washed Chromsorb P. Chromatography was carried out at appropriate temperatures between 22 and 45° using a 1 ft × ⅜ in. ss column for less volatile mixtures and a 10 ft × ⅜ in. ss column for mixtures boiling near or below room temperature. All glc separations employed gas injection.

^{19}F nmr spectra were obtained on 10 mol % solutions in $CFCl_3$ on a Varian XL-100-15 nmr spectrometer. Ir spectra were obtained on a Perkin-Elmer Model 180 or 337 spectrometer using 10-cm gas cells fitted with AgCl windows. Molecular weights were obtained by vapor density measurements using a Wallace and Tiernan differential pressure gauge. Vapor pressures were determined by the method of Kellogg and Cady[11] or by a static method employing the isotensiscope principle.[12] Data were analyzed by a computer assisted least-squares fit to both linear and quadratic equations and the ones agreeing most closely with the experimental data are reported.

Reagents. The olefins C_2F_3Cl, CF_2CCl_2, CF_2CH_2, *cis,trans*-CFHCHCl, C_3F_6, *cis*-CFHCFH and c-C_5F_8 were obtained from PCR Inc, C_2H_4 from Matheson Co., and C_2F_4 by the pyrolysis of Teflon.[13] Chloroperoxytrifluoromethane was prepared by two methods as follows. Method A. This preparation was essentially that of Ratcliffe, *et al.*, employing the low temperature reaction of CF_3OOH with ClF.[8] The CF_3OOH was obtained as previously described.[3] Method B. An alternate method for the preparation of CF_3OOCl consisted of the reaction of ClF with $CF_3OOC(O)F$ in presence of CsF at −78°. In a typical reaction, 7 mmol of each were condensed into a 75-cm^3 stainless steel reactor at −196° containing 15 g of dry, powdered CsF. The reactor was then held at −78° for 18 hr. Separation of the volatile products through traps at −125 and −196° gave an 88% yield of CF_3OOCl in the −125° trap contaminated with small amounts of $CF_3OOC(O)F$. The −196° trap contained COF_2 and small amounts of CF_3OCl, Cl_2, and CF_3OOCl. Under a variety of conditions, it was difficult to obtain CF_3OOCl completely free of $CF_3OOC(O)F$. In most cases the $CF_3OOC(O)F$ did not appear to be a serious contaminant for the reactions described in this paper. From this standpoint, method B is preferred for the preparation of CF_3OOCl because the intermediate 50-80% hydrolysis of $CF_3OOC(O)F$ to CF_3OOH is avoided. However, the purest CF_3OOCl is obtained by method A.

Reaction of CF_3OOCl with Olefins. All reactions between CF_3OOCl and olefins were carried out in 100-ml glass vessels fitted with glass–Teflon valves, by adding the olefin to CF_3OOCl held at −111°. In initial experiments the olefin was added in aliquots over a period of several hours until an excess of the olefin was present. The −111° bath was then allowed to warm slowly to −78° and maintained at this temperature for ~18 hr. The disappearance of the yellow color of the CF_3OOCl was found to be a satisfactory indication of complete reaction. If the yellow color of the CF_3OOCl was still noticeable after ~18 hr at −78°, the bath was allowed to warm slowly until the color disappeared or the temperature reached 0°. The products were then separated by collection in a −78° trap in the cases of CF_2CH_2, CF_2CFCl, CF_2CCl_2, *cis*-CFHCFH, and CFHCHCl and in a −111° trap with C_2H_4 and C_2F_4. These fractions were then separated by glc. In later experiments involving these reactions, the addition of the olefin in aliquots to the CF_3OOCl was found to be unnecessary. Condensing the CF_3OOCl into the bottom of the reactor held at −196°, followed by the olefin in the upper portion of the reactor and then warming to −111° and proceeding as above, was found to be satisfactory. However, the addition of the olefin in aliquots probably decreases the chances of an explosive reaction although only two such incidents were encountered in this work, both with *cis*-CFHCFH. A variety of products were usually formed in these reactions which usually included COF_2, O_2, chlorinated olefin and fluoro-chlorinated olefin epoxide, some CF_3OCl addition products, and the peroxides. No effort was made to identify all of the products formed in each reaction or their amounts. Since some CF_3O-ether products formed in each reaction were identical with those previously obtained by reactions of CF_3OCl with olefins, $CF_3OCH_2CH_2Cl$, $CF_3OCF_2CF_2Cl$, $CF_3OCF_2CH_2Cl$, and $CF_3OCF_2CFCl_2$ were identified by their characteristic ^{19}F nmr spectra.[9] In the reactions of CF_3OOCl with CF_2CCl_2 and CFHCHCl, the new ethers $CF_3OCF_2CCl_3$ and $CF_3OCFHCHCl_2$–$CF_3OCHClCFHCl$ were isolated and partially characterized.

In the reactions of CF_3OOCl with C_3F_6 and c-C_5F_8, no conclusive evidence could be found for the formation of the expected peroxides. The olefins were unreactive at −78° and at higher temperatures, up to 22°, the main products appeared to be unreacted olefin and decomposition products of CF_3OOCl. Small amounts of less volatile products were observed and these may have been the respective ethers formed with CF_3OCl, based on their ^{19}F nmr spectra. After a variety of attempts to isolate the peroxides with these olefins, it was concluded that these olefins simply would not undergo the hoped for addition, and the reactions were abandoned without further characterization. A summary of the reactions is given in Table I and data for the new compounds follow.

Table I. Peroxides from the Addition of CF_3OOCl to Olefins

Olefin[a]	CF_3OOCl[a]	Conditions[b]	Product, % yield[c]
C_2H_4, 4.8	1.1	2 hr, −111°	$CF_3OOCH_2CH_2Cl$, >50 $CF_3OCH_2CH_2Cl$, <10
C_2F_4, 3.3	2.7	37 hr, −111 to −75°	$CF_3OOCF_2CF_2Cl$,[d] 34 $CF_3OCF_2CF_2Cl$, 21
C_2F_3Cl, 3.0	1.0	21 hr, −78°	$CF_3OOCF_2CFCl_2$, >50 $CF_3OCF_2CFCl_2$, <10
CF_2CCl_2, 5.0	1.0	5 hr, −78°	$CF_3OOCF_2CCl_3$, >50 $CF_3OCF_2CCl_3$, <10
CF_2CH_2, 6.5	2.2	3 hr, −111 to −80°	$CF_3OOCF_2CH_2Cl$, >50 CF_3OCF_2Cl, 40
CFHCHCl, 2.2	2.1	33 hr, −111 to −0°	$CF_3OOCFHCHCl_2$, 75 $CF_3O(CFHCHCl)Cl$, 25
cis-CFHCFH, 1.2	1.1	11 hr, −111 to −35°	$CF_3OOCFHCFHCl$,[e] 40 $CF_3OCFHCFHCl$, 11
C_3F_6, 2.5	2.5	20 days, −78° 5 days, −17°	No peroxide[b]
c-C_5F_8, 2.1	2.1	16 days, 0°	No peroxide[b]

[a] Amounts in mmol. [b] Refer to text. [c] Exact yields were not determined in each case but yields of purified products were probably closer to 70% for those given as >50%. Values are based on the amount of CF_3OOCl used. [d] Another heavier fraction consisting of at least four components was obtained on glc and represented a 15% yield. These components were shown by ^{19}F nmr to contain predominantly CF_3O groups attached to CF_2–CF_2 groups with smaller amounts of CF_3OO groups similarly attached. The average molecular weight of this portion was 336, and these components are believed to be telemers of the type $CF_3O(CF_2)_nCl$ and $CF_3OO(CF_2)_nCl$. [e] The ether was characterized only by its molecular weight (found 184.0, calcd 183.5) and characteristic ^{19}F nmr of the CF_3O group at ϕ^* 60.7. A higher molecular weight portion was also observed but was not characterized.

$CF_3OOCH_2CH_2Cl$: bp 77.7; melting point forms a glass; mol wt 164.0, calcd 164.48; ir 3021 vw, 2980 w, 2932 vw, 2899 vw, 2862 vw, 2730 vw, 2505 vw, 2430 vw, 2145 vw, 2110 vw, 1460 w, 1436 w, 1371 w, 1266 s, 1230 vs, 1198 s, 1120 w, 1085 m, 1062 m, 1044 m, 988 m, 957 vw, 920 w, 852 vw, 833 vw, 770 m, 678 m, 618 w, 587 w, 460 vw; nmr ϕ^* 68.40 (t, CF_3OO), δ 4–5 (complex m, CH_2CH_2), $J_{FH} = 1.0$ Hz; $\Delta H_{vap} = 7.59$ kcal/mol; $\Delta S_{vap} = 21.6$ eu; $\log P(\text{mm}) = 5.7101 - 326.62/T - 23366/T^2$ (−15 to 47°).

$CF_3OOCF_2CF_2Cl$: bp 23.8; melting point forms a glass; mol wt 235.6, calcd 236.48; ir 2580 vw, 2520 vw, 2500 vw, 2460 vw, 2400 vw, 2370 vw, 2305 vw, 2240 vw, 2170 vw, 2140 vw, 2110 vw, 2050 vw, 1980 vw, 1620 vw, 1380 vw, 1328 m, 1294 vs, 1257 vs, 1200 s, 1188 s, 1168 vs, 1120 s, 1055 m, 985 s, 943 m, 925 m, 885 w, 848 m, 814 m, 750 vw, 685 w, 655 w, 610 w, 564 vw; nmr $CF_3{}^{A}OOCF_2{}^{B}CF_2{}^{C}Cl$ ϕ^* 68.69 ($CF_3{}^{A}OO$, t), 94.19 (q–t, $CF_2{}^{B}$), 70.54 (t, $CF_2{}^{C}$), $J_{AB} = 4.36$, $J_{BC} = 2.57$ Hz; $\Delta H_{vap} = 6.41$ kcal/mol; $\Delta S_{vap} = 21.6$ eu; $\log P(\text{mm}) = 6.9542 - 1019.2/T - 56609/T^2$ (−46 to 10°). This compound has been previously observed as a mixture with $CF_3OOCF_2ClCF_3$ in the reaction of CF_3OOF and C_2F_3Cl.[7]

$CF_3OOCF_2CFCl_2$: bp 56.6; melting point forms a glass; mol wt 250.3, calcd 252.96; ir 2568 vw, 2545 vw, 2514 vw, 2490 vw, 2465 vw, 2428 vw, 2368 vw, 2253 vw, 2198 vw, 2119 vw, 1984 vw, 1957 vw, 1710 vw, 1500 vw, 1462 vw, 1360 vw, 1300 m, 1272 s, 1244 s, 1218 s, 1200 m, 1151 s, 1103 m, 1040 w, 962 m, 920 s, 903 s, 866 m, 811 w, 790 m, 735 vw, 714 vw, 680 w, 652 vw, 598 w, 560 vw, 507 vw, 455 w; nmr $CF_3{}^{A}OOCF_2{}^{B}CF^{C}Cl_2$ ϕ^* 68.60 (t, $CF_3{}^{A}OO$), 92.15 (d–q, $CF_2{}^{B}$), 72.95 (t, CF^{C}), $J_{AB} = 4.4$, $J_{BC} = 7.0$ Hz; $\Delta H_{vap} = 7.40$ kcal/mol; $\Delta S_{vap} = 22.4$ eu; $\log P\ (\text{mm}) = 7.2902 - 1291.2/T - 53692/T^2$ (−35 to 35°).

$CF_3OOCF_2CCl_3$: bp 90.4° melting point forms a glass; mol wt 270.4, calcd 269.35; ir 2540 vw, 2500 vw, 2435 vw, 2395 vw, 2140 vw, 2095 vw, 1973 vw, 1630 vw, 1572 vw, 1486 vw, 1452 vw, 1381 vw, 1359 w, 1297 s, 1255 vs, 1206 s, 1190 s, 1169 m, 1136 s, 1034 m, 954 m, 890 s, 854 s, 835 s, 768 s, 679 m, 659 vw, 611 w, 599 m, 573 w, 555 w, 459 w; nmr ϕ^* 68.46 (t, CF_3OO), 90.17 (q, CF_2), $J_{F-F} = 4.4$ Hz; $\Delta H_{vap} = 8.00$ kcal/mol; $\Delta S_{vap} = 22.0$ eu; log P (mm) $= 7.2572 - 1433.5/T - 57330/T^2$ (0–62°).

$CF_3OCF_2CCl_3$: mol wt 253.0, calcd 253.35; nmr ϕ^* 56.5 (t, CF_3O), 85.1 (q, CF_2), $J_{F-F} = 9.6$ Hz.

$CF_3OOCF_2CH_2Cl$: bp 54.9; melting point forms a glass; mol wt 197.0, calcd 200.45; ir 2988 w, 2855 vw, 2535 vw, 2505 vw, 2462 vw, 2412 vw, 2155 vw, 2105 vw, 1436 m, 1325 m, 1274 s, 1238 s, 1210 s, 1132 s, 1089 s, 1031 w, 971 w, 963 w, 891 w, 861 w, 800 m, 765 w, 707 w, 670 m, 613 w, 579 w, 560 w, 531 vw, 450 vw; nmr ϕ^* 68.47 (t, CF_3OO), 84.07 (t–q, CF_2), δ 4.03 (t, CH_2Cl), $J_{F-F} =$ 4.4, $J_{F-H} = 8.4$ Hz; $\Delta H_{vap} = 8.18$ kcal/mol; $\Delta S_{vap} = 24.9$; log P (mm) $= 10.164 - 2991.1/T + 19746/T^2$ (−34 to 35°).

$CF_3OOCFHCHCl_2$: bp 92.1; melting point forms a glass; mol wt 217.5, calcd 216.93; ir 3003 w, 2510 vw, 2160 vw, 2115 vw, 1955 vw, 1930 vw, 1510 vw, 1490 vw, 1430 vw, 1358 vw, 1340 w, 1284 s, 1240 vs, 1225 sh, 1215 sh, 1100 m, 1063 s, 1012 w, 986 w, 938 vw, 928 vw, 883 w, 820 s, 789 w, 760 w, 690 w, 640 vw, 618 vw, 600 w, 580 sh; nmr $CF_3{}^AOOCF^BH^CCH^DCl_2$ ϕ^* 68.25 (t–d, $CF_3{}^AOO$), 129.99 (d–d–q, CF^B), $J_{AB} = 4.2$, $J_{AC} = 1.0$, $J_{BC} =$ 59.1, $J_{BD} = 4.1$ Hz; $\Delta H_{vap} = 8.36$ kcal/mol; $\Delta S_{vap} = 22.9$; log P (mm) $= 6.5274 - 836.08/T - 18114/T^2$ (−2 to 61°).

$CF_3O(CFHCHCl)Cl$: mol wt 202.5, calcd 200.93; nmr $CF_3{}^AOCF^BH^CCH^DCl_2$ ϕ^* 60.53 (d–d, $CF_3{}^A$), 129.08 (d–d–q, CF^B), $J_{AB} = 4.7$, $J_{AC} = 0.4$, $J_{BC} = 56.7$, $J_{BD} = 4.7$ Hz; *erythro*- and *threo*-$CF_3{}^AOCH^BClCH^CF^DCl$ ϕ^* 60.98 and 61.15 (d–d, $CF_3{}^AO$), 143.6 and 145.0 (d–d–q, CF^D), $J_{AB} = 0.9$, $J_{AD} = 0.4$, $J_{BD} = 4.0$ and 5.5, $J_{CD} = 50.0$ Hz, isomer ratio by ^{19}F nmr $CF_3OCFHCHCl_2$:$CF_3OCHClCFHCl$ 2.0:1.0 with equal amounts of erythro and threo.

erythro-$CF_3OOCFHCFHCl$: bp 62.1; mol wt 199.4, calcd 199.49; ir 2995 m, 2555 vw, 2510 w, 2475 w, 2450 vw, 2155 w, 2120 w, 1957 w, 1945 vw, 1928 w, 1890 w, 1850 w, 1834 vw, 1818 vw, 1650 vw, 1530 vw, 1480 vw, 1360 vw, 1340 w, 1280 vs, 1235 vs, 1215 sh, 1155 w, 1117 s, 1093 s, 1068 s, 1014 w, 933 w, 918 w, 877 w, 832 s, 772 m, 690 m, 653 vw, 607 m, 593 m, 500 vw, 475 w; nmr $CF_3{}^AOOCF^BH^CCF^DH^ECl$ ϕ^* 68.42 (d–d, $CF_3{}^AOO$), 135.4 (m, CF^BH), 153.2 (d–d, CF^DH), δ 6.06 (m, CFH^C), 6.34 (d–d, CFH^E), $J_{AB} = 3.9$, $J_{AC} = 1.0$, $J_{BC} = 58.4$, $J_{BD} = 3.9$, $J_{BE} =$ 13.3, $J_{DE} = 49.3$ Hz; $\Delta H_{vap} = 8.21$ kcal/mol; $\Delta S_{vap} = 24.5$ eu; log P (mm) $= 8.3064 - 1842.2/T + 7821.5/T^2$ (−18 to 35°).

Results and Discussions

Chloroperoxytrifluoromethane. Chloroperoxytrifluoromethane is one of two known examples of a compound containing an -OOCl group.[14] It is readily obtained by the reaction of trifluoromethyl hydroperoxide with ClF.[8]

$$CF_3OOH + ClF \xrightarrow{-111^\circ} CF_3OOCl + HF$$

An alternate method of synthesis is the reaction of fluorocarbonyl trifluoromethyl peroxide, $CF_3OOC(O)F$, with ClF in the presence of CsF.

$$CF_3OOC(O)F + ClF \xrightarrow{CsF} CF_3OOCl + COF_2$$

This latter method has the advantage of avoiding the intermediate preparation of CF_3OOH by the hydrolysis of $CF_3OOC(O)F$. With this method, it is in principle possible to prepare CF_3OOCl by a semicyclic process in which CO_2, F_2, Cl_2, and CO are the starting materials.

$$CO + F_2 \xrightarrow{AgF_2} COF_2$$

$$CO_2 + 2F_2 \xrightarrow{CsF} CF_2(OF)_2$$

$$CF_2(OF)_2 + 2COF_2 \xrightarrow{CsF} CF_3OF + CF_3OOC(O)F$$

$$Cl_2 + F_2 \longrightarrow 2ClF$$

$$CF_3OOC(O)F + ClF \xrightarrow{CsF} CF_3OOCl + COF_2$$

The synthesis of CF_3OOCl directly from $CF_3OOC(O)F$ and ClF in the presence of CsF is interesting when compared to the reaction of $CF_3OOC(O)F$ and F_2.[15] The latter reaction forms the stable fluoroxy compound CF_3OOCF_2OF corresponding to the simple CsF catalyzed addition of F_2 to the carbony group. Presumably the formation of CF_3OOCl employing ClF occurs by a similar route, in which the intermediate CF_3OOCF_2OCl is unstable, eliminating COF_2 to give the observed products.

The properties of CF_3OOCl were partially described by Ratcliffe and coworkers.[8] They reported CF_3OOCl to be stable for prolonged periods at 25° and to be chemically dissimilar to the related perfluoroalkyl hypochlorite. The very reasonable suggestion was made that CF_3OOCl might be primarily peroxidic in its reactions. We have found that CF_3OOCl has only limited stability at 25°, decomposing readily to CF_3OCl and O_2 as shown.

$$2CF_3OOCl \longrightarrow 2CF_3OCl + O_2$$

The half-life in the gas phase at 100 mm and 25° is only a few hours. It is possible that the decomposition is catalyzed by water and other impurities. However, in the same container, the CF_3OCl formed during decomposition is quite stable. Since CF_3OCl is very sensitive to water, we feel the observed decomposition is due to the thermal instability of CF_3OOCl, but a catalytic effect of substances other than water cannot be ruled out.

The reaction chemistry of CF_3OOCl should in principle be similar to CF_3OCl but the obvious alternative involving the primary cleavage of the O–O bond exists with CF_3OOCl. Earlier work suggested that the latter mode was possibly the dominant one, due to the failure to observe analogous reactions between CF_3OCl and CF_3OOCl with identical substrates.[8] However, the chemistry of the related molecules, CF_3OOH and CF_3OOF, do not involve primary cleavage of the O–O bond under mild conditions and it is reasonable that CF_3OOCl should be similar. In comparing CF_3OCl and CF_3OOCl there should be a difference in reactivity based on the degree to which the chlorine atoms are positively polarized. We have qualitatively shown that CF_3O- is more electronegative than CF_3OO- and therefore the greatest positive halogen character should be shown by CF_3OCl. However, the electronegativity of CF_3OO- is sufficiently large to render considerable positive character to the Cl and CF_3OOCl.

Reaction of CF_3OOCl with Olefins. Chloroperoxytrifluoromethane adds readily to olefins at low temperature to give high yields of new peroxides.

$$CF_3OOCl + R_1R_2C{=}CR_3R_4 \longrightarrow CF_3OOCR_1R_2CR_3R_4Cl$$

$$R_1R_2CCR_3R_4 = C_2H_4,\ C_2F_4,\ C_2F_3Cl,\ CF_2CH_2,\ CF_2CCl_2,\ CFHCHCl,\ cis\text{-}CFHCFH$$

In all cases involving unsymmetrical olefins, the addition is unidirectional and the positive chlorine adds to the carbon atom with the greatest number of hydrogens or the fewest fluorines.[16] In addition to the peroxides, significant amounts of the corresponding ethers are observed. These are probably formed by the addition of CF_3OCl to the olefin, the CF_3OCl arising from the decomposition of CF_3OOCl during the reaction. The new peroxides are readily identified by their ^{19}F nmr spectra. All show a characteristic resonance at about ϕ^* 69.0 which is readily assigned to the CF_3- groups.[1-7] The simple first-order spectra allow unambigious structural assignments in each case and confirm the presence of only one isomer. In the case of $CF_3OOCF_2CF_2Cl$ and $CF_3OOCF_2CFCl_2$ the $-CF_2Cl$ and $-CFCl_2$ groups show characteristic ^{35}Cl-^{37}Cl isotopic shifts of ~0.4 Hz providing further structural evidence.

The new peroxides are all colorless liquids with apparent high thermal stability. All are stable for prolonged periods in glass at 25° as both gases and liquids and none have shown any signs of explosive decomposition. They are unreactive at 25° toward water and do not readily oxidize aqueous KI or elemental Hg. We estimate that all are probably stable to at least 100° in the gas phase.

The reactivity of CF_3OOCl toward various olefins varies considerably. We were unable to observe reactions with C_3F_8 or c-C_5F_8 to form the expected peroxides up to 22° although very small amounts of ether products were observed. This points out a limitation of CF_3OOCl as a reagent in the formation of CF_3OO derivatives. The reactions must occur readily below 22° or the major product, if reaction does occur, will be the ether and not the peroxide because of the ready decomposition of CF_3OOCl. The reactivity of CF_3OOCl with olefins follows the order $C_2H_4 \geq CF_2CH_2 > CF_2CCl_2 > C_2F_3Cl > C_2F_4 \geq$ *cis*-CFHCFH $\geq$ CFCHCl $\gg C_3F_8 \geq$ c-C_5F_8. Consistent with this, 2-fluoropropene underwent reaction readily at −78° to give the expected product. The latter was not fully characterized but ^{19}F nmr of the impure product allowed large amounts of $CF_3OOCF(CH_3)CH_2Cl$. It is interesting to note that CF_3OCl has previously been shown to lack reactivity with 2-perfluorobutene and 2-perfluorobutyne, and, while reactions with olefins were predominantly unidirectional, isomers were observed in certain instances.[9] In this work, no evidence could be found for isomeric peroxides, but small amounts of the other possible ether isomer were observed in the case of C_2F_3Cl consistent with previous work. In the case of CFHCFCl considerable amounts of both isomers were observed for the ether product. These observations suggest that CF_3OOCl additions to olefins may be even more specific than those of CF_3OCl under similar conditions.

The mechanism of the addition of CF_3OOCl to olefins is of interest. Since the olefins employed are all susceptible to radical additions, some to electrophilic and others to nucleophilic additions, some difficulty arises in proposing a single mechanism and the possibility exits that different olefins may react with CF_3OOCl by different mechanisms. However, we believe the evidence obtained strongly suggests that the mechanism is that of electrophilic addition, involving the initial attack of the positively polarized chlorine of CF_3OOCl on the π-system of the olefin.

The initial indication that additions of CF_3OOCl to olefins proceeded in the above manner came from the failure to observe reaction with perfluoropropene and perfluorocyclopentene. Both of these olefins are very resistent to electrophilic additions but readily undergo both free radical and nucleophilic additions.[17,18] If either of these mechanisms were operative, there is no logical reason why they should not undergo additions with CF_3OOCl under the conditions used. Reactions with the related CF_3OOF,[7] which are free radical in nature, occur readily with both perfluoropropene and perfluorocyclopentene, suggesting that CF_3OOF and CF_3OOCl react by different mechanisms.

The unidirectional addition of CF_3OOCl to unsymmetrical olefins further suggests a polar addition mechanism. While free radical additions to olefins can sometimes be highly directional, with fluoroolefins the reactions are almost always bidirectional.[19] The single structural isomers observed with CF_2CH_2, CF_2CFCl, CF_2CCl_2, and CFHCHCl would seem unlikely for a free radical addition. In each case the nucleophile (CF_3OO-) attaches to the carbon of the original double bond which can form the better carbonium ion, exactly as expected for electrophilic addition. In contrast, the reaction of CF_3OOF with CF_2CFCl yields two structural isomers as expected for a free radical addition.

If the addition of CF_3OOCl to olefins is electrophilic, different olefins will vary in their reactivity, depending on the electron density of the π-system, and those olefins highly substituted with electronegative groups should be the least reactive. Of the olefins which were observed to undergo addition by CF_3OOCl, C_2H_4 would logically be expected to exhibit the highest reactivity and C_2F_4 the lowest. This is essentially what is observed, and, while quantitative rate data were not obtained, the observed relative rates of addition are consistent with this.

The above arguments suggest that the addition of CF_3OOCl to olefins proceeds by an electrophilic mechanism. However, in order to remove any remaining doubts about the mechanism and to determine if the reaction is stereospecific, the addition of CF_3OOCl to *cis*-1,2-difluoroethylene was carried out. If the addition is electrophilic and cis, the product $CF_3OOCFHCFHCl$ would be only the erythro isomer and if the addition is trans, the threo isomer. Using both ^{19}F and ^1H nmr with the aid of both hetro- and homonuclear spin decoupling, it was determined that only one isomer is present and thus the reaction is stereospecific. The fluorine decoupled ^1H nmr is a simple AB spin system consisting of two doublets with $J_{AB} = 5.2$ Hz.

The Karplus rule[20] predicts that the erythro isomer will have a larger vicinal coupling constant than the threo isomer. If both isomers of $CF_3OOCFHCFHCl$ were available, the assignment of each would be straightforward. However, since only one isomer is available, reference to related compounds must be used to make the assignment. The number of vicinal coupling constants assigned for both erythro and threo isomers of fluoroalkanes are small, but are in agreement with predictions that highly electronegative substituents will cause the average vicinal coupling constants to be small.[20,21] In the compounds *erythro*- and *threo*-$CF_3CHICHFCF_3$ and *erythro*- and *threo*-$CF_3CHBrCHFBr$, the vicinal coupling constants are 7.7, 1.8, 5.5, and 2.8 Hz, respectively.[22] The value of 5.2 Hz for $CF_3OOCFHCFHCl$ is indicative of the erythro isomer and therefore the reaction of CF_3OOCl with *cis*-CFHCFH most probably results in a cis addition.

In summary, the electrophilic addition of CF_3OOCl to olefins is a versatile new method for the synthesis of trifluoromethyl peroxides. It is probably the most generally applicable method yet for the synthesis of such compounds, and, combined with the stereospecificity of the reaction, CF_3OOCl offers considerable utility as a synthetic reagent in organic chemistry.

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Nitrosylmetalloporphyrins. II. Synthesis and Molecular Stereochemistry of Nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II)[1]

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Abstract: Nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II), ONFeTPP, is obtained by reductive nitrosylation of ClFeTPP. With a square-pyramidal coordination group, but with a bent Fe-N-O group, the ONFeTPP molecule has statistically required C_{4h} symmetry in an eightfold-disordered variant of a well-known structural type based on the tetragonal space group, $I4/m$. Cell data: a = 13.468 (9), c = 9.755 (8) Å; Z = 2; ρ_{calcd} = 1.31, ρ_{exptl} = 1.31 g/cm^3 at 20°. Intensity data for 951 independent reflections having $(\sin \theta)/\lambda \leq 0.725$ Å^{-1}, collected with graphite-monochromated Mo Kα radiation on a computer-controlled four-circle diffractomer, were used in the refinement of the statistically averaged structure. The final discrepancy indices were R_1 = 0.044 and R_2 = 0.061. Bond parameters in the porphinato core agree well with those observed in the other low-spin iron porphyrins. The displacement of the iron atom from the porphinato core (Ct ··· Fe) is 0.211 (5) Å; the displacement of the nitrosyl nitrogen atom (N_2) from the porphinato core is 1.928 (6) Å. The equatorial Fe-N_p bond length is 2.001 (3) Å, Fe-NO = 1.717 (7) Å. The FeN_2O angle is 149.2 (6)°.

Questions concerning the structure and bonding of the small molecules dioxygen, nitric oxide, and carbon monoxide coordinated to metalloporphyrins have been intensively investigated.[2] These compounds are of obvious interest in understanding the stereochemistry of iron porphyrins as it pertains to the biologically important hemoproteins. We have been investigating the reactions of nitric oxide with several metalloporphyrins and we report herein the preparation and structural characterization of one derivative, five-coordinate nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II), to be written as ONFeTPP. This molecule has been independently synthesized by Wayland and coworkers.[2d] The magnetic data are consistent with the formal description of low-spin iron(II) and neutral NO.

Salient features of the stereochemistry of this complex include the mode of nitrosyl coordination (a linear or bent FeNO moiety) and the magnitude of the out-of-plane displacement of the *low-spin* iron(II) atom from the mean porphinato plane. In contrast to the high-spin five-coordinate iron(II) and iron(III) porphyrins in which the requisite Fe-N_p (N_p = porphinato nitrogen) distance (≥2.07 Å) is too long to permit centering of the iron in the porphinato mean plane,[3] low-spin iron(II) porphyrins are expected to have Fe-N_p bond distances sufficiently short to allow centering of the metal in the porphyrin plane. Any observed out-of-plane displacement is then rationally attributed to minimizing the nonbonded contacts between the single axial ligand and atoms of the porphinato core. A comparison of the stereochemical parameters of ONFeTPP with those of ONCoTPP[1] and ONFeTPP(NMeIm)[4] (NMeIm = 1-methylimidazole) should allow the evaluation of changes in stereochemistry caused by the addition of one additional d electron or the coordination of a second axial ligand, respectively.

Experimental Section

Preparation of ONFeTPP. All reactions were carried out under argon using modified Schlenk tubes. ClFeTPP was prepared as previously described.[5] A solution of 0.2 g of ClFeTPP in 60 ml of chloroform was carefully degassed and 1 ml of dry pyridine was added to it. Nitric oxide, purified by passing through a KOH column, was bubbled into the solution for 20 min. Methanol, distilled from Mg, was added until crystals of ONFeTPP appeared. Filtration, under argon, gave lustrous purple crystals of ONFeTPP. *Anal.* Calcd for $FeC_{44}H_{28}N_5O$: C, 75.65; H, 4.04; N, 10.02. Found: C, 75.14; H, 4.10; N, 9.90.

Physical Data. The infrared spectrum of ONFeTPP was recorded on a Perkin-Elmer 457 spectrometer using a KBr pellet; the strong absorption at 1670 cm^{-1} was assigned as the NO stretching frequency. The mass spectrum, obtained on an AEI MS-9902 spectrometer, had prominent peaks at m/e 668 ($FeTPP^+$) and 30 (NO^+); the parent ion (m/e 698) was not observed. A sensitive test for piezoelectricity in the crystals, using a Geibe–Schiebe detector, was negative. The visible absorption spectrum of ONFeTPP in chloroform has peaks at 4050, 5370, and 6060 Å and a shoulder at 4750 Å. The extinction coefficients are 100 × 10^3, 8.7 × 10^3, 2.8 × 10^3, and 15 × 10^3 M^{-1} cm^{-1}, respectively. The visible absorption spectrum changes slowly on exposure to the atmosphere. The magnetic susceptibility, determined by the Evans method,[6] is 2.3 BM.

Crystallographic and X-Ray Data. Crystals of ONFeTPP suitable for X-ray study were grown by allowing anhydrous methanol to diffuse slowly into a chloroform solution of the porphyrin under