Reaction of (Ic) in AcOH at 20°C. The yellow solid which separated was extracted with hot toluene. Insoluble (IIIb) was crystallized from 50% ethanol, and identified by composition with an authentic sample [2]. Evaporation of the toluene solution gave (IVc), which was further crystallized from ethanol. The residue obtained by evaporating the acetic acid filtrate was treated with 50% alcohol to give a further quantity of (IVc). The aqueous-alcoholic solution was evaporated, and the residue extracted with hot benzene. The benzene extracts were evaporated, the residue dissolved in a small amount of acetone, and the solution cooled to give $CH_3CONHCH(C_2H_5)CONHC_3H_7$ (VII), purified by repeated freezing-out from acetone.

Reaction of (Id) in Boiling Benzene. The residue after removal of the benzene was dissolved in alcohol. The (IVd) which separated was recrystallized from pyridine, and washed on the filter with cold alcohol.

Reaction of (Id) in AcOH at 20°C. The residue after distillation of the AcOH was diluted with acetone, and the (VI) which separated was purified by reprecipitation from acetone with water.

Reaction of (Ie) in Ether. The solid which separated from the ether solution was treated with hot ethanol. The insoluble (IVe) was washed on the filter with ethanol. The residue after removal of the ethanol was treated with toluene to give (IIIc). A further quantity of (IIIc) was obtained by evaporating the ethereal mother liquors.

Reaction of (Ie) in Benzene at 20°C. The residue after removal of the benzene was treated with hot ethanol to give (IVe) and (IIIc), isolated as described above.

CONCLUSIONS

1. Fully substituted bisoxazolylalkylamines react with maleimide as azadienes, giving the products of 1,4-addition to one of the oxazole rings. In acetic acid, these adducts are cleaved to give a mixture of β-hydroxy- and β-aminopyridines.

2. Bisoxazolylalkylamines which are unsubstituted in the 4,4'-positions react with maleimide to give β-hydroxy and β-aminopyridines in all reaction solvents.

LITERATURE CITED

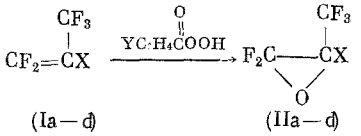
1. G. Ya. Kondrat'eva, M. A. Aitzhanova, V. S. Bogdanov, and O. S. Chizhov, Izv. Akad. Nauk SSSR, Ser. Khim., 1313 (1979).
2. G. Ya. Kondrat'eva and Huang Chih-heng, Dokl. Akad. Nauk SSSR, 141, 628 (1961).

EPOXIDATION OF HIGHLY ELECTROPHILIC UNSATURATED FLUORINE-CONTAINING COMPOUNDS BY PERACIDS

A. A. Kadyrov, E. M. Rokhlin, and I. L. Knunyants

UDC 542.91:547.367'161:547.58-39

It has previously been shown [1, 2] that methyl perfluoromethacrylate (Ia) is epoxidized by percarboxylic acids (PA) to give the glycidyl ether (IIa). It would appear that this reaction could be extended to other derivatives of perfluoromethacrylic acid, namely the ethyl ester (Ib) and the dimethylamide (Ic), and to the perfluoroisopropenylphosphonate ester (Id).



(Ia—d) (IIa—d)

X = COOMe (a), COOEt (b), $CONMe_2$ (c), $PO(OMe)_2$ (d), Y = *m*-Cl, *p*-MeOCO.

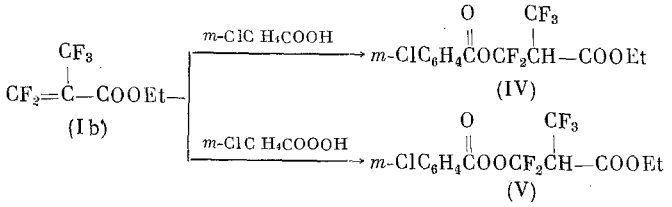
A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2344-2347, October, 1982. Original article submitted February 12, 1982.

0568-5230/82/3110-2063$07.50

Epoxidation of (I) is readily effected in ether, diglyme, and THF*; methylene chloride, the usual solvent for the Prilezhaev reaction, is unsuitable in this case. In contrast to the usual Prilezhaev reaction [3], in this instance PA appear to function as nucleophiles, since the highly electrophilic unsaturated compounds (Ia-d) are epoxidized with particular ease. Perfluoroisobutylene also reacts with PA to give the α-oxide, but the reaction proceeds less readily than with the ester [1, 2]. The even less electrophilic perfluoropropylene fails to react with PA even under more severe conditions.†

Epoxidation of (I) was accompanied by side reactions. Thus, in the reaction of (Ib) with m-ClC_6H_4COOOH, in addition to the glycidyl ether (IIb), there were obtained ethyl α-hydrohexafluoroisobutyrate $(CF_3)_2CHCOOEt$ (III), and the adduct (IV), formed by addition of m-chlorobenzoic acid to (Ib) (cf. [6]). The ^{19}F NMR spectrum of the reaction mixture showed signals attributable to a similar adduct of m-chloroperbenzoic acid (V)



Despite the occurrence of side reactions, the reaction of highly electrophilic unsaturated fluoro-compounds with PA can be used for the preparation of some difficultly accessible fluorinated α-oxides, which can be used to synthesize a variety of organofluorine compounds (see, e.g., [7]).

EXPERIMENTAL

PMR spectra were obtained on a Perkin-Elmer R-32 instrument (^1H 90 and ^{19}F 84.6 MHz), from the external standards TMS and CF_3COOH. IR spectra were recorded on a UR-20 instrument as thin layers. Mass spectra were obtained by E. I. Mysov on a Varian MAT CH-8 spectrometer (ionizing electron energy 70 eV); shown are m/z, intensities in %, and suggested assignments.

Ethyl α-Trifluoromethyl-β,β-difluoroglycidate (IIb). To a solution of 9.9 g of 85% m-ClC_6H_4COOOH in 30 ml of absolute ether was added dropwise with stirring (20 min, 0-5°C) 9.8 g of ethyl perfluoromethacrylate (Ib). After 2 h, a sample was withdrawn from the reaction mixture, and the solid filtered off. The filtrate contained, in addition to the ester (IIb), ethyl α-hydrohexafluoroisobutyrate (III), ethyl α-trifluoromethyl-β,β-difluoro-β-(m-chlorobenzoyl)hydroxypropionate (IV), and ethyl α-trifluoromethyl-β,β-difluoro-β-(m-chlorobenzoyl)peroxypropionate (V). ^{19}F NMR spectrum of (III): −12.7 d (CF_3), J_{CF_3-H} = 7.3 Hz; (IV): − 13.2 d.t. (CF_3), −7.1 m (CF_2, center of the AB region of the $ABMX_3$ system), $J_{CH_3-CF_2}$ = 10, J_{CF_3-H} = 8 Hz; (V): −13.5 d.t. (CF_3), −0.2 m (CF_2, center of the AB region of the $ABMX_3$ system), $J_{CF_3-CF_2}$ = 9.6, J_{CF_3-H} = 7.9 Hz.

Volatile products were removed from the reaction mixture in vacuo (∿1 mm, ∿20°C) and collected in a trap (−78°C), and ether was removed from the distillate. The residue (6.5 g) contained 92% of (IIb) and 8% of (III) (GLC and NMR). The yield of pure (IIb) was 6.0 g (55%). Redistillation gave the glycidyl ether (IIb) containing 6% of hexafluoroisobutyric ester, bp 97.98°C. Mass spectrum: 220, 0.5, M^+; 175, 23, $M^+ - EtO$; 147.54, $C_3F_5O^+$; 97, 35, $C_2F_3O^+$; 69,100, CF_3^+. Found: C 31.7; H 2.59; F 42.5%. $C_6H_{10}F_5O_3$. Calculated: C 32.7; H 2.29; F 43.2%.

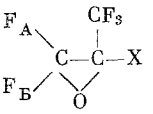
The glycidyl ether (IIb) was also obtained by reacting the perfluoromethacrylate ester (Ib) with m-ClC_6H_4COOOH in THF or diglyme; when the reaction was carried out in CH_2Cl_2 under the same conditions, no (IIb) was formed.

Ethyl α-Trifluoromethyl-β,β-difluoro-β-(m-chlorobenzoyl)hydroxypropionate (IV). To 0.5 g of ethyl perfluoromethacrylate (Ib) was added with cooling a solution of 0.5 g of m-ClC_6H_4-COOH in 1 ml of THF over 1.5 h (∿20°C) to give a solution of ester (IV). ^{19}F NMR spectrum −13.8 d.t. (CF_3), −7.8 and −6.8, AB system with further splitting into a d.q. (CF_2),

*These solvents, which are capable of breaking intramolecular hydrogen bonds in the PA molecule, usually retard the Prilezhaev reaction [3-5].

†Similarly, perfluorocyclobutene, the allenes $(CF_3)_2C=C=C(CF_3)_2$, $(CF_3)_2C=C=C(COOEt)_2$, and the ether $(CF_3)_2C=CFOMe$ could not be epoxidized.

TABLE 1. ^{19}F NMR Spectra of Fluorinated α-Oxides (IIb-d)



Compound	X	Chemical shift, δ, ppm			J, Hz		
		CF_3	F_A	F_B	CF_3-F_A	CF_3-F_B	F_A-F_B
(IIb)	COOEt	−8,4	+33,2	+31,4	10,7	2,6	42,3
(IIc) *	$CONMe_2$						
1st conformer		−8,6	+36,8	+30,2	10,7	1,7	47,0
2nd conformer		−7,6	+32,7	+29,1	11,9	~1	47,0
(IId)	$PO(OMe)_2$†	−9,8	+32,0	+27,9	17,4	2,6	46,2

*At −30°C.

†J_{CF_3-P} = 1.4, J_{F_A-P} = 9.4, J_{F_B-P} = 14.1 Hz.

$J_{gem-F-F}$ = 158, $J_{CF_3-CF_2}$ = 9.8, J_{CF_3-H} = 8.0, J_{CF_2-H} = 9.8 Hz.

α-Trifluoromethyl-β,β-Difluoroglycidic Acid Diethylamide (IIc). To a solution of 5.0 g of 85% m-ClC_6H_4COOH in 13 ml of dry ether was added slowly with stirring (∿−10°C) 5.7 g of perfluoromethyacrylic acid dimethylamide (Ic), and the mixture was gradually warmed to ∿20°C. After 2 h at this temperature the ether was distilled off in vacuo (∿20 mm), followed by the amide (IIc) (0.01 mm). Redistillation afforded 1.8 g (30%) of the amide (IIc), bp 68°C (34 mm). PMR spectrum: 2.96 s and 3.08 s (Me_2N). The ^{19}F NMR spectrum at −30°C showed the presence of two conformers (see Table 1). At +36°C, the ^{19}F NMR spectrum showed unresolved multiplets for the CF_3 groups (−8.1) and CF_2 (+29, +32, and +36). IR spectrum: 1510 (oxide ring), 1680 and 1695 cm^{-1} (CO). Mass spectrum: 219, 30, M^+; 200, 1, M^+-F; 161, 7, $M^+-2F-HF$ or $M^+-CH_2-CO_2$(?); 159, 3, $C_3F_5CO^+$; 150, 3, M^+-CF_3; 138, 10, $Me_2NCF_2CO_2^+$; 110, 10, $Me_2NCF_2O^+$; 72, 100, Me_2NCO^+; 60, 30, CF_3^+. Found: C 33.0; H 3.04; F 42.1; N 6.1%. $C_6H_6F_5NO_2$. Calculated: C 32.9; H 2.76; F 43.3; N 6.4%.

Dimethyl α,β-Epoxypentafluoropropyl-2-phosphonate (IId). To a suspension of 8.6 g of 65% p-$MeOCOC_6H_4COOOH$ [8] in 25 ml of dry ether was added slowly at −5°C 8.9 g of dimethyl pentafluoroisopropenylphosphonate (Id) [9]. The mixture was warmed gradually to ∿20°C, and after 3.5 h the ether was distilled off. Distillation of the filtrate gave 6.1 g of a mixture boiling at ∿45°C (0.05 mm), containing ∿75% of (IId), significant amounts of $(CF_3)_2CMePO(OMe)_2$ [9, 10] [present as an impurity in the starting material (Id)], and $(CF_3)_2CHPO(OMe)_2$ [10], together with starting material (Id) (^{19}F NMR). Yield of pure (IId), ∿4.7 g (∿60%). Redistillation afforded 90% (IId), bp 69°C (11 mm). PMR spectrum: 3.97 d (Me), J_{Me-P} = 11.2 Hz. Mass spectrum: 237, 1.5, M^+-F; 159, 2, M^+-CF_3-CO; 128, 4, $M^+-CF_3-CO-MeO$; 109, 100, $(MeO)_2PO^+$; 98, 48, $M^+-CF_3-CO-MeO-CH_2O$; 93, 14, C_3F_3; 79, 22, $MeOPHO^+$; 69, 14, CF_3^+. Found: C 22.8; H 2.29; F 37.8%. $C_5H_6F_5O_4P$. Calculated: C 23.4; H 2.36; F 37.1%.

Action of Peracids on Perfluoroisobutylene and Perfluoropropylene. A mixture of 2.50 g of 89% p-$MeOCOC_6H_4COOOH$, 2.60 g of perfluoroisobutylene, and 3.31 g of dry monoglyme was kept for ∿14 h in a sealed ampul (∿20°C). Volatile fractions (∿3 g) were removed in vacuo (∿20 mm, ∿20°C). These contained perfluoroisobutylene, monohydroperfluoroisobutane $(CF_3)_3CH$, and perfluoroisobutylene oxide (^{19}F NMR, molar ratio ∿1:1:1), together with a considerable amount of monoglyme. Perfluoropropylene was unchanged on heating with p-$MeOCOC_6H_4COOH$ in monoglyme (60°C, 7 h).

The authors thank G. S. Bylina for the gift of a sample of p-methoxycarbonylperbenzoic acid.

CONCLUSIONS

Derivatives of perfluoromethacrylic and perfluoroisopropenylphosphonic acids, together with perfluoroisobutylene, are readily peroxidized by aromatic peracids in ether solvents. The order of the changes in the reactivity of olefins indicates a reversal of the mechanism of the Prilezhaev reaction, peracids functioning as nucleophiles in their reactions with highly electrophilic unsaturated compounds.

LITERATURE CITED

1. Yu. V. Zeifman, E. M. Rokhlin, U. Utebaev, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 226, 1337 (1976).
2. U. Utebaev, Dissertation, Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow (1975).
3. E. N. Prilezhaeva, The Prilezhaev Reaction. Electrophilic Oxidation [in Russian], Nauka, Moscow (1974).
4. R. G. Makitra and Ya. I. Pirig, Zh. Fiz. Khim., 52, 785 (1978).
5. J. Skerjanc, A. Regent, and B. Plesničar, Chem. Commun., 1007 (1980).
6. U. Utebaev, E. M. Rokhlin, and É. P. Lur'e, Izv. Akad. Nauk SSSR, Ser. Khim., 142 (1976).
7. A. A. Kadyrov, E. M. Rokhlin, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2653 (1981).
8. G. S. Bylina, U. M. Dzhemilev, N. S. Vostrikov, G. A. Tolstikov, A. M. Moiseenkov, A. V. Semenovskii, and S. S. Shabanov, Izv. Akad. Nauk SSSR, Ser. Khim., 447 (1978).
9. A. A. Kadyrov and E. M. Rokhlin, Izv. Akad. Nauk SSSR, Ser. Khim., 2583 (1981).
10. W. J. Middleton and W. H. Sharkey, J. Org. Chem., 30, 1384 (1965).

FLUORINATED ENETHIOLS*

R. A. Bekker, V. Ya. Popkova, and I. L. Knunyants

UDC 542.91:547.367'161

The closest analog of the well-studied keto–enol system is the enethiol–thione system. However, studies of prototropy in the latter system are extremely difficult [3-6] as a result of the instability of both forms, and their liability to undergo interconversion both in the presence of a variety of reagents, and also spontaneously, with the consequence that studies of this problem contain numerous contradictions and erroneous data [7].

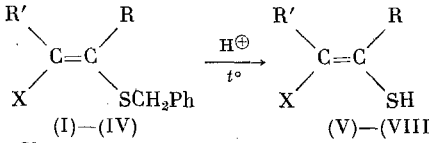
The introduction of fluorine atoms and perfluoroalkyl groups usually confers high kinetic stability on unstable enols [8], and it was therefore to be expected that perfluorinated enethiols would be more stable, and hence more convenient for study.

Perfluorinated enethiols have hitherto been unknown. Radical addition of H_2S to acetylenes [9] affords only hydrogen-containing analogs, which polymerize on storage. Their conversion into the corresponding thiocarbonyl compounds was not reported in [9].

$$R{-}C{\equiv}C{-}R' + H_2S \rightarrow RCH{=}\underset{\displaystyle SH}{\underset{|}{C}}{-}R'$$

$R = R' = CF_3$ (a) $R = CF_3$, $R' = H$ (b).

We have developed a general method for the preparation of perfluorinated enethiols of the aliphatic and alicyclic series which involves heating perfluoroalkenyl(cycloalkenyl) benzyl sulfides with fluorosulfuric or sulfuric acid, with the simultaneous removal of volatile products. Thus, enethiols (I)-(IV) affords the enethiols (V)-(VIII), which are stable compounds which remain unchanged on storage



(I)–(IV) (V)–(VIII)

$R = R' = CF_3$, X = Cl (I), (V); R, R' = $-(-CF_2-)_2-$, X = F (II), (VI);
R, R' = $-(-CF_2-)_3-$, X = CF_3 (III), (VII); R, R' = $-(-CF_2-)_4-$, X = Cl (IV), (VIII).

Acid hydrolysis of benzyl or tert-butyl perfluoro(1-ethyl-2-methyl-1-propenyl) sulfide (IXa, b) under similar conditions gives a mixture consisting of the enethiol (X) (86.3%) and

*For previous communications, see [1, 2].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2347-2354. October, 1982. Original article submitted February 9, 1982.

 0568-5230/82/3110-2066$07.50