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SYNTHETIC UTILITY OF 3-(PERFLUORO-1,1-DIMETHYLBUTYL)-1-PROPENE. PART. V*. REACTIONS OF 3-(PERFLUORO-1,1-DIMETHYLBUTYL)-1,2-EPOXYPROPANE WITH INORGANIC ANIONS, THIOUREA, AND GUANIDINE

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SUMMARY

The new branched polyfluoroaliphatic functional derivatives $R_FCH_2CH(OH)CH_2X$ [X = CN, N_3, $NH(C{=}NH)NH_2$], thiirane $R_FCH_2\overset{\frown}{CHCH_2}S$ sulphide $[R_FCH_2CH(OH)CH_2]_2S$, and allyl ether $R_FCH{=}CHCH_2{-}O{-}CH_2CH(OH)CH_2R_F$, where R_F = $CF_3CF_2CF_2(CF_3)_2C-$, were obtained in high yields by reacting epoxide $R_FCH_2\overset{\frown}{CHCH_2}O$ or its precursor $R_FCH_2\overset{\frown}{CHBrCH_2}OCOCH_3$ with KCN, NaN_3, guanidine, KSCN or thiourea, Na_2S, and KOH, respectively.

INTRODUCTION

Compounds containing perfluorinated aliphatic chain and reactive functional groups are valuable intermediates with many applications, particularly for the synthesis of fluorinated surfactants. In the first paper of this series [1] we had shown that the readily available 3-(perfluoro-1,1-dimethylbutyl)-1-propene, $CF_3CF_2CF_2(CF_3)_2CCH_2CH{=}CH_2$, may be easily converted to the corresponding epoxide and primary or secondary alcohols. Conversions to the carboxylic acids were also reported [2]. The epoxide, due to its high reactivity, is of particular interest

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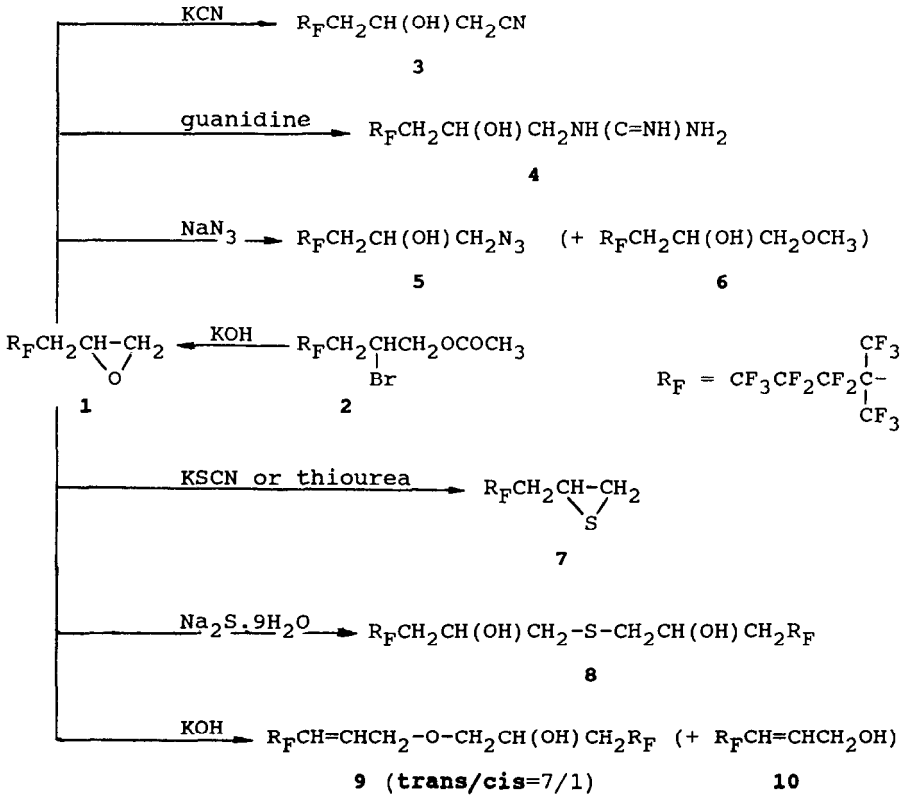
as an intermediate to other functional derivatives; thus, reactions with ammonia and amines led to a number of 2-hydroxy-3-perfluoroalkylpropylamines [3].

In the present paper we report further approaches to functional derivatives of the title alkene **via** epoxide **1** by treating the latter with inorganic anions, thiourea, and guanidine.

RESULTS AND DISCUSSION

The reactions (scheme below) were carried out using either epoxide **1** or its precursor, acetate **2**, as a substrate. In this second case, the epoxide was generated *in situ* by adding a sufficient amount of potassium hydroxide [1].

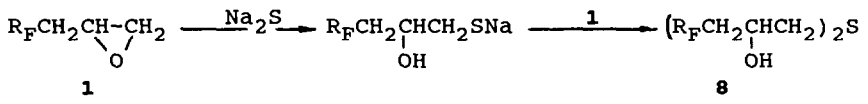


Scheme.

Two sets of experiments were conducted: in refluxing methanol (method **A**) and in a water-substrate catalytic two-phase system at 90 - 100°C (method **B**). The use of **1** or **2** as a substrate, had no practical effect on the results; in both cases comparable yields of products were obtained. The yields, however, strongly depended on the reaction system (Table 1).

The reactions with potassium cyanide and guanidine proceeded readily in methanol (method **A**) to give good yields of the oxirane ring opening products, 2-hydroxynitrile **3** and 2-hydroxyalkylguanidine **4**, respectively, but no reaction occurred in the two-phase system (method **B**), independently of a catalyst used (n-Bu_4NHSO_4, n-Bu_4NBr, Aliquot 336) or the reaction conditions. However, both substrates **1** and **2**, when treated with aqueous sodium azide, gave excellent yields of 2-hydroxyazide **5**, while in methanol predominant reaction was attack by the methoxide ion to give ether **6** [1] as the main product. This was in accord with the relative nucleophilicity of the azide and methoxide ions [4].

The reactions, either with potassium thiocyanate or thiourea, typically for oxiranes [5,6], led to the oxygen - sulphur exchange to give thiirane **7**. Compound **7** was obtained in high yields from the reactions conducted in methanol while with aqueous solutions of KSCN or thiourea the yields never exceeded 20% (large amounts of unreacted **1** were recovered), regardless of much prolonged reaction time. A similar behaviour was observed for the reactions of **1** or **2** with sodium sulphide. These reactions gave bis(2-hydroxyalkyl) sulphide **8** as the only product, even when large excess of sodium sulphide was used. That means that the thiolate, which should be formed as the primary product of the oxirane ring opening, reacts faster with epoxide **1** than does sodium sulphide.



1 **8**

The reaction of epoxide **1** with methanolic potassium hydroxide, as reported previously [1], resulted in attack by the

TABLE 1

Reactions of epoxide **1** and acetate **2** with nucleophiles

R_F = $CF_3CF_2CF_2C(CF_3)_2-$

Reagents	Product	Yield (%)[a] Method **A**	Yield (%)[a] Method **B**
1, KCN	$R_FCH_2CH(OH)CH_2CN$	89	tar[b]
2, KCN	**3**	80	tar[b]
1, guanidine	$R_FCH_2CH(OH)CH_2NH(C{=}NH)NH_2$	59	no reaction
2, guanidine	**4**	51	no reaction
1, NaN_3	$R_FCH_2CH(OH)CH_2N_3$	25[c]	90
2, NaN_3	**5**	23[c]	90
1, KSCN	$R_FCH_2CH(S)CH_2$ **7**	86	20[b]
2, KSCN		82	11[b]
1, thiourea	$R_FCH_2CH(S)CH_2$ **7**	82	15[b]
2, thiourea		87	15[b]
1, $Na_2S.9H_2O$	$R_FCH_2CH(OH)CH_2-S-CH_2CH(OH)CH_2R_F$ **8**	71	42[b]
2, $Na_2S.9H_2O$		86	40[b]
1, KOH	$R_FCH{=}CHCH_2-O-CH_2CH(OH)CH_2R_F$ **9**		84
2, KOH			80[d]

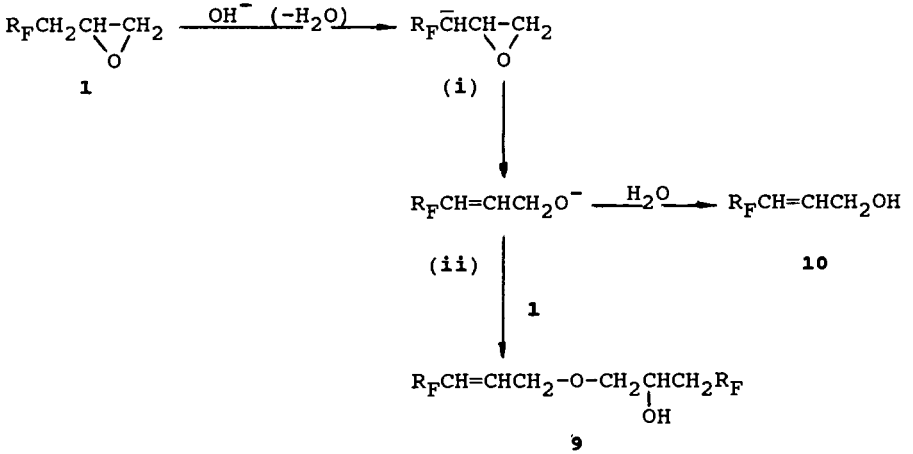
[a] Isolated yields in mole % of **1** or **2**.

[b] Large amount of the unreacted epoxide **1** remained.

[c] The main product (**ca.** 75%) was ether **6**.

[d] About 5% of allylic alcohol **10** (**trans**) was isolated.

methoxide ion to give hydroxy ether **6**. Treatment of **1** or **2** with concentrated aqueous potassium hydroxide gave allylic ether **9** (**trans/cis** = 7/1) as the main product, instead of the expected 1,2-diol, together with small amounts (1 - 5%) of 3-(perfluoroalkyl)allyl alcohol **10** (**trans** only). These reactions should be interpreted in terms of low nucleophilicity and high basicity of the hydroxide ion which abstracts a proton from the methylene group adjacent to the perfluoroalkyl substituent, rather than attacking the oxirane ring. The initially formed carbanion (**i**) rapidly rearranges to allyloxide ion (**ii**) which attacks epoxide **1** to give compound **9**. Protonation of (**ii**) gives alcohol **10**.



The above, rather unexpected, course of the reaction with aqueous potassium hydroxide indicates high acidity of protons of the exocyclic methylene group in **1**. Similarly, previously reported rearrangements of oxiranes to allyl alcohol required much stronger bases, Et_2NLi or R_2NAlEt_2 [7].

The molecular compositions of compounds **3** - **10** were obtained from elemental analyses (Table 2). The structures of the non-fluorinated parts of these compounds were confirmed by the high resolution ^1H NMR spectra (Table 3). The $-CH_2CHCH_2-$ fragments form characteristic ABXMN (or two ABX) spin systems; as-

TABLE 2

Physical properties and analyses of compounds **3** - **5** and **7** - **10**

Compnd. no.	B.P. ^{o}C(Torr)	IR (cm^{-1})	Analysis: found/(calculated), % C	H	F	N	S
3	118(0.8) m.p.58[a]	2295(ν_{CN}) 3470(ν_{OH})	29.8 (29.8)	1.3 (1.5)	61.4 (61.3)	3.5 (3.5)	
4[b]	m.p.168[c]	1645($\nu_{=NH}$) 1710($\nu_{C=N}$) 3150(ν_{NH}) 3470(ν_{OH})	27.6 (27.6)	2.4 (2.3)	56.5 (56.7)	9.5 (9.7)	
5	102(20)	2120(ν_{N}) 3470(ν_{OH})	25.8 (25.8)	1.6 (1.4)	58.8 (58.9)	9.9 (10.0)	
7	48(8)	3025(ν_{CSC})	27.4 (27.4)	1.2 (1.3)	62.9 (63.0)		8.3 (8.2)
8	128(0.2)	3420(ν_{OH})	27.6 (27.5)	1.6 (1.5)	62.7 (62.9)		4.0 (4.1)
9	100(0.6)	1680($\nu_{C=C}$) 3480(ν_{OH})	28.8 (28.7)	1.5 (1.3)	65.6 (65.7)		
10	35(0.6)	1680($\nu_{C=C}$) 3360(ν_{OH})	28.6 (28.7)	1.6 (1.3)	65.6 (65.7)		

[a] recrystallised from n-hexane.

[b] hydrochloride: m.p. 184 -186^{o}C, found: C, 25.5; H, 2.4; Cl, 7.5; F, 52.4; N, 9.0%. Calculated for $C_9H_{11}ClF_{13}ON_3$: C, 25.5; H, 2.4; Cl, 7.5; F, 52.4; N, 8.9%.

[c] recrystallised from ethanol.

TABLE 3

^{1}H NMR data for compounds **3** - **5** and **7** - **10**

R_F = $CF_3CF_2CF_2C(CF_3)_2$-

Compound	δ (ppm)*				Coupling const. (Hz)
	H(a)	H(b)	H(c)	OH	
1	2	3	4	5	6
a b c $R_FCH_2CHCH_2CN$ OH **3**	2.424(a) 2.609(a')	4.490	2.629,d	2.510	J(aa')=16.3 J(bc)=J(bc') =5.8
a b c $R_FCH_2CHCH_2NHC{=}NH$ OH NH_2 **4****	2.315(a) 2.412(a')	3.940	3.114(c) 3.130(c')	6.65,br	J(aa')=16.0 J(cc')=14.0
a b c $R_FCH_2CHCH_2N_3$ OH **5**	2.350(a) 2.450(a')	3.210	3.350	2.27,d	J(aa')=16.4 J(cc')=12.3 J(b-OH)=4.2
a b c $R_FCH_2CH(-CH_2)$ S **7**	2.120(a) 2.980(a')	3.110	2.300(c) 2.640(c')		J(aa')=15.7 J(cc')= 6.0

(continued)

TABLE 3 (cont.)

1	2	3	4	5	6
a b c $R_FCH_2CH(OH)CH_2$ S $R_FCH_2CH(OH)CH_2$ f e d **8**	2.380(af) 2.520(a'f')	4.18(b) 4.19(e)	2.590(c) 2.795(c') 2.670(d) 2.802(d')	2.75 2.86	J(aa')=16.3 J(cc')=14.0 J(dd')=14.0
a b c $R_FCH_2CHCH_2$ OH O $R_FCH{=}CHCH_2$ f e d **9 (trans)***	2.386(a) 2.420(a') 5.772(f),dt 6.333(e),dt	4.280	3.415(c) 3.456(c') 4.177(d),dd	1.550	J(aa')=16.2 J(cc')= 9.3 J(ef)=16.4 J(de)= 4.4 J(df)=ca.2
a b c $R_FCH{=}CHCH_2OH$ **10 (trans)**	5.86,d	6.44,dm	4.33,s	1.60,s	J(ab)=16.4

s - singlet, d - doublet, t - triplet, m - multiplet
br - broad

* In $CDCl_3$. Protons a, b, and c form ABXMN (or two ABX) spin systems. Centres of the signals related to internal TMS are quoted.

** In DMSO. The amine part of the molecule has been fully deuterated prior to the measurement.

*** For the **cis** isomer: δ(d) = 4.147,dd; δ(e) = 4.555,dt,
δ(f) = 6.152,dt ppm.
J(ef) = 6.3; J(de) = 4.2;
J(df) = ca. 1.5 Hz

signments of the chemical shifts and coupling constants were confirmed by computer simulations. The ^{19}F NMR spectra of the perfluoroalkyl group were within the range previously reported for fluorohydrocarbons $CF_3CF_2CF_2(CF_3)_2R$ and their derivatives [2,8]. The IR spectra (Table 2) exhibited absorptions characteristic for CN, NH, N_3, thiirane, OH, and C=C functions.

EXPERIMENTAL

Boiling and melting points are uncorrected. The NMR spectra were recorded with a Brucker 500 MHz instrument, and the IR spectra with a Beckmann Acculab.

Syntheses of 3-(perfluoro-1,1-dimethyl)-1,2-epoxypropane **1** and 3-(perfluoro-1,1-dimethylbutyl)-2-bromopropan-1-ol acetate **2*** were described previously [1].

General procedures

A. Reactions in methanol

Epoxide **1** (1.9 g, 5 mmoles) or acetate **2** (2.5 g, 5 mmoles; in this case 10 mmoles of potassium hydroxide was always added), methanol (5 - 10 ml), and a nucleophilic reagent** (10 mmoles) were refluxed for 3 - 4 hours. After the reaction, water was added (30 ml), the organic layer was separated, dissolved in diethyl ether (50 ml), the ether solution was washed with water (3 x 15 ml) and dried over anhydrous magnesium sulphate. Ether was removed under atmospheric pressure and the residue was vacuum distilled. Yields are given in Table 1, physical properties and analyses of products in Table 2.

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* A 5 to 1 mixture of **2** and its isomer, 3-(perfluoro-1,1-dimethylbutyl)-bromopropan-2-ol acetate was used.

** In the case of guanidine, free amine was liberated by adding guanidine hydrochloride (1 g, 10 mmoles) to methanolic solution of KOH (0.6 g, 11 mmoles). Potassium chloride was filtered off, then epoxide **1** or acetate **2** was added.

B. Two-phase reactions

Epoxide **1** (1.9 g, 5 mmoles) or acetate **2** (2.5 g, 5 mmoles and 10 mmoles of potassium hydroxide), nucleophilic reagent (10 mmoles), tetrabutylammonium hydrosulphate (0.1 g), and water (2.1 ml) were vigorously stirred at 90-100°C for 3 hours. The reaction mixture was diluted with water (30 ml) and worked up as described above. The results are summarised in Table 1.

ACKNOWLEDGMENT

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