

# Copper-catalyzed addition of perfluoroalkyl iodides to unsaturated alcohols and transformation of the addition products

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## Abstract

Iodoperfluoroalkyl alcohols  $R_FCH_2CHI(CR_2)_nOH$  ( $R_F = C_6F_{13}$ ;  $R = H, CH_3$ ;  $n = 1-3, 9$ ) have been readily prepared in high yield by the addition of perfluoroalkyl iodides  $R_FI$  to allylic and other unsaturated alcohols at 120 °C in the presence of a catalytic amount (10% mol) of metallic copper powder. The dibenzoyl peroxide-induced reaction gave lower yields of the addition products in most cases. The chemical changes of iodoperfluoroalkylated alcohols to epoxides and alcohols are described. A discussion of the by-products obtained and of the reaction mechanism is provided.

## Introduction

Additions of perfluoroalkyl iodides to unsaturated alcohols for the synthesis of iodoperfluoroalkyl alcohols have been mainly initiated by classical radical methods such as UV irradiation [1, 2], azonitriles [3–5] and organic peroxides [6]. In the case of allyl alcohol, the yields of the 1:1 adduct varied in the range of 50%–80%. Usually, however, long reaction times were necessary to obtain satisfactory yields of the products (e.g. irradiation of the reaction mixture with UV light for 14 d [1]). Recently, catalysis of the addition reaction by means of ruthenium carbonyl [7], tetrakis(triphenylphosphine)palladium [8] and tin(0) powder in the presence of copper or silver salts [9] has been reported as improving the yields of the 1:1 adducts. When the addition reaction was catalyzed by a palladium phosphine complex in the presence of base, direct synthesis of an epoxide was achieved in one step [10]. More recently, the palladium phosphine complex has been used for the preparation of fluorinated diols via the addition of perfluoroalkyl iodides to unsaturated diols [11].

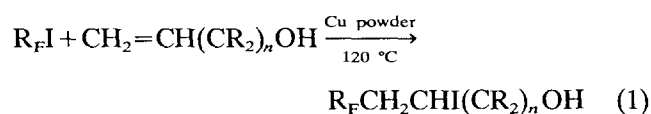
Perfluoroalkylated iodoalcohols have proved to be useful intermediates for the synthesis of perfluoroalkylated compounds. Considerable effort has been made in exploring a convenient synthetic route using novel

methods and reagents. Previous papers have documented that the addition of perfluoroalkyl iodides [12, 13] and iodofluoroacetates [14, 15] to olefins can be catalyzed by metallic copper.

The aim of the present study was to investigate the catalytic activity of metallic copper as a simple and cheap catalyst in the addition reactions of perfluoroalkyl iodides with unsaturated alcohols and to examine the transformation of the addition products into epoxides and alcohols.

## Results and discussion


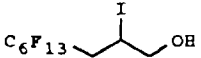
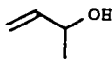
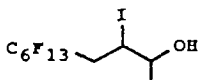
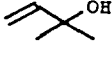
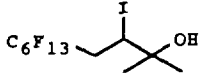
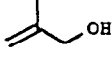
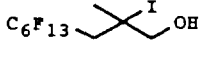
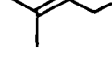
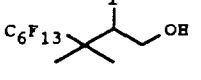
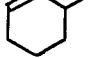
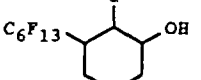
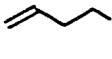
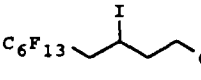
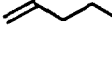
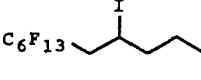
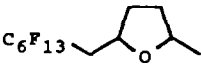
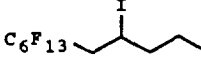
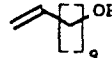
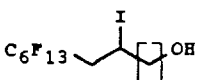
We have found that the addition of perfluoroalkyl iodides to a variety of unsaturated alcohols can be catalyzed efficiently by metallic powder (10% mol) giving 1:1 adducts according to eqn. (1). The additions were carried out at 120 °C in the absence of solvent. Additions initiated with dibenzoyl peroxide (2% mol) under the same reaction conditions were performed for comparison with the copper catalyst. The results obtained are summarized in Table 1.



( $R_F = C_6F_{13}$ ;  $R = H, CH_3$ ;  $n = 1-3, 9$ )

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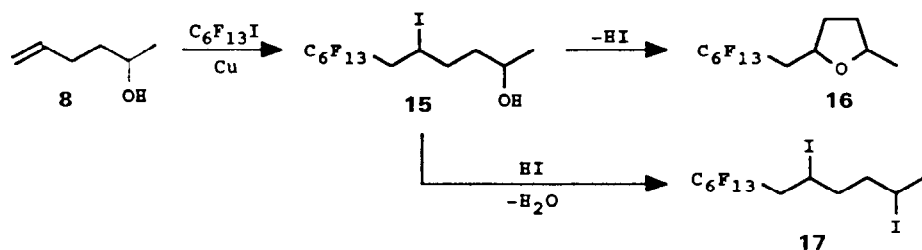
TABLE 1. Addition of perfluorohexyl iodide to unsaturated alcohols catalyzed by metallic copper or initiated by dibenzoyl peroxide at 120 °C

Alcohol	Product	Yield, % <sup>a</sup> (time, min)	
		Bz <sub>2</sub> O <sub>2</sub>	Cu
 (1)	 (10)	5 <sup>b</sup> (5)	76(120)
 (2)	 (11)	10 <sup>b</sup> (5)	78(105)
 (3)	 (12)	83(15)	83(60)
 (4)	 (13)	10 <sup>b</sup> (5)	48(60)
 (5)	 (14)	0 <sup>b</sup> (15)	0 <sup>b</sup> (60)
 (6)	 (15)	0 <sup>b</sup> (15)	0 <sup>b</sup> (60)
 (7)	 (16)	82(5)	63(90)
 (8)	 (15)	21.5(5)	37 <sup>b</sup> (30)
	 (16)	1.5 <sup>b</sup> (5)	25 <sup>b</sup> (30)
	 (17)	0 <sup>b</sup> (5)	5 <sup>b</sup> (30)
 (9)	 (18)	—	84(105)

<sup>a</sup>Isolated yields.<sup>b</sup>GC yields.

The copper-catalyzed addition of perfluorohexyl iodide to allylic alcohols **1–3**, 3-buten-1-ol (**7**) and 10-unden-1-ol (**9**) afforded the 1:1 adducts as the sole products in high yield (63%–84%). In the addition reaction with 5-hexen-2-ol (**8**) formation of three products was observed, i.e. the 1:1 adduct **15**, a cyclic product containing a tetrahydrofuran ring **16** and the diiodide **17**. A more detailed study revealed that the 1:1 adduct **15** was transformed to the tetrahydrofuran derivative **16** during the course of the reaction, evolving hydrogen

iodide as a by-product (Scheme 1). The diiodide **17** is considered to be formed by the substitution reaction of the hydroxy group of the 1:1 adduct **15** by nascent hydrogen iodide rather than by cleavage of the tetrahydrofuran derivative **16** with hydrogen iodide. This assumption resulted from an independent experiment in which no scission of the substituted tetrahydrofuran **16** was observed after heating it with hydroiodic acid, i.e. under conditions usually leading to scission of a tetrahydrofuran ring. No traces of the diiodide **17** were

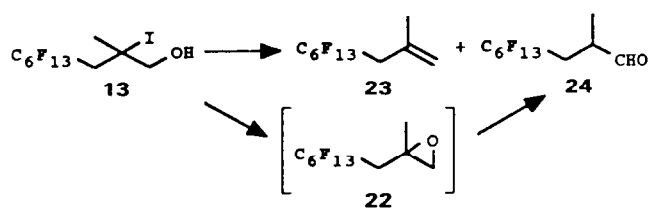


Scheme 1.

detected and the tetrahydrofuran derivative **16** was totally recovered after refluxing for 24 h with hydroiodic acid. The structure of the diiodide **17** was confirmed by GC analysis of an authentic sample prepared by the reaction of compound **15** with phosphorus(III) iodide. In order to obtain tetrahydrofuran derivative **16** as the main product, it was necessary to heat the reaction mixture for 7 h. The tetrahydrofuran derivative **16** was isolated in 60% yield.

The addition of perfluoroalkyl iodide to substituted or internal double bonds of unsaturated alcohols involved certain complications. The addition of perfluoroalkyl iodide to 2-methyl-2-propen-1-ol (**4**) afforded the 1:1 adduct **13** in moderate yield (48%). Because decomposition of the 1:1 adduct **13** into a complex mixture of products occurred, as a result of iodine being bonded to a tertiary carbon which readily leads to elimination reactions under the experimental conditions employed, reaction times longer than 1 h were not used. In order to prevent decomposition of the product **13**, the reaction time was limited to 1 h. A study of the decomposition, including heating the 1:1 adduct **13** with an excess of the copper powder, revealed that alkene **23** and aldehyde **24** were the main products of the decomposition (Scheme 2). There are two possible explanations for the formation of aldehyde **24**. Either it is formed by direct isomerization of the iodoalcohol **13** as in the palladium-catalyzed reaction [16] or acidic isomerization of the epoxide **22** occurs with nascent hydrogen iodide [17].

The addition of perfluoroalkyl iodide to 3,3-dimethyl-2-buten-1-ol (**5**) and 2-cyclohexen-1-ol (**6**) completely failed, both with the copper catalyst and dibenzoyl peroxide, presumably because of steric hindrance of the double bond.



Scheme 2.

The addition reactions initiated by dibenzoyl peroxide gave mixed results. Addition to allylic alcohols in high yield was only successfully accomplished with 2-methyl-3-buten-2-ol (**3**) (83%) and 3-buten-1-ol (**7**) (82%). Addition to other allylic alcohols (**1**, **2** and **4–6**) gave a low yield of the 1:1 adducts (0%–10%). Addition to 5-hexen-2-ol (**8**) afforded the desired 1:1 adduct **15** as the main product in a yield of 21.5% with only traces of the fluorinated tetrahydrofuran **16** being found, in contrast to the results with the metallic copper catalyst.

Generally, 1,2-haloalcohols are known to be good building blocks of great synthetic interest, because they can be used as important intermediates for further transformations. In particular, iodoalcohols R<sub>F</sub>CH<sub>2</sub>CHICH<sub>2</sub>OH (R<sub>F</sub> = C<sub>1</sub>–C<sub>8</sub>) have often been used as building blocks for the synthesis of epoxides [1, 2]. In order to investigate the possibility of cyclization with perfluoroalkylated epoxides, the iodoalcohols **10–13** were treated with powdered sodium hydroxide in diethyl ether at room temperature using a well-known procedure [18]. The results obtained are summarized in Table 2. A good yield of the epoxides (64%–80%) was obtained by transformation of iodoalcohols **10–12**. However, in the cyclization of iodoalcohol **13** only a low yield of epoxide **22** was obtained, because side reactions resulted in the formation of a complex product mixture composed of the epoxide **22**, the aldehyde **24** and a mixture of *cis*- and *trans*-perfluoroalkylated allylic alcohols **25**.

Iodoalcohols were also successfully transformed to perfluoroalkylated alcohols by reductive dehalogenation using tributylstannane. Contrary to the published procedure [5], we have found that reductive dehalogenation proceeds even at room temperature, and without the use of an initiator as is usually necessary for the successful reductive dehalogenation of organic chlorides or bromides [19]. Owing to the viscosity and immiscibility of both reactants (iodoalcohols and tributylstannane), it is recommended that the reaction mixture be heated to 80 °C in order to allow both reactants to react completely. Because of their immiscibility, perfluoroalkylated alcohols **26–30** and iodotributylstannane separate easily. Use of only a catalytic amount of tributylstannane in the presence of an excess of sodium tetrahydridoborate [20] was studied in order to avoid

TABLE 2. Transformation of iodoalcohols to epoxides

Alcohol	Product	Yield, % <sup>a</sup>
		75
		74
		64
		32
		18
		50

<sup>a</sup>Isolated yields. Conversion of iodoalcohols was quantitative.

the use of the stoichiometric amount of tributylstannane as a reductive agent. However, this procedure proved unsuccessful because, in addition to alcohols, epoxides as well as the products of dehydroiodination were found in the reaction mixture in various amounts. An alternative method for the reductive dehalogenation of iodoalcohols using nickel chloride hexahydrate in the presence of an excess of the zinc dust was also examined [14]. Using this procedure, iodoalcohol **18** was reductively dehalogenated to compound **31** in 76% yield. However, application of this method is limited to those iodoalcohols in which both functional groups are separated by more than one methylene group, otherwise side reactions produce olefin or epoxides. The results obtained are summarized in Table 3.

It may be concluded that the use of the metallic copper as the catalyst for the addition of perfluoroalkyl iodides to unsaturated alcohols is superior to dibenzoyl peroxide or UV initiation, giving good results even in those cases where other initiators failed to promote the addition. Copper is an example of a simple and inexpensive catalyst allowing a ready approach to iodoalcohols which could be potentially good basic building blocks for the syntheses of a number of compounds (perfluoroalkylated epoxides, tetrahydrofurans, olefins, etc.). The copper catalyst may also be convenient for large-scale syntheses where the use of transition metal complexes is expensive and the peroxide-induced initiation may be hazardous.

## Experimental

GC analysis was performed on a HP-5890A instrument fitted with a HP Ultra-1 capillary column. <sup>13</sup>C NMR spectra were recorded on a Varian XL-200 spectrometer with CDCl<sub>3</sub> as solvent. The NMR data obtained for various products are listed in Table 4.

### Materials

Perfluoroheptyl iodide (kindly supplied by Hoechst and Atochem), zinc powder, nickel chloride hexahydrate, copper powder (electrolytic, particle size 10–20 μm), allyl alcohol (Lachema, Brno), 3-buten-2-ol, 2-methyl-3-buten-2-ol, 2-methylpropen-1-ol, tributylstannane (Aldrich) and 3-buten-1-ol (Fluka) were used as obtained. 5-Hexen-2-ol and 10-undecen-1-ol were prepared from 5-hexen-2-one and ethyl undecenoate, respectively, by reduction with lithium aluminium hydride.

#### 2-Iodo-1-perfluoroheptyl-3-propanol (**10**)

A 10 ml glass ampoule was charged with 10 mmol of perfluoroheptyl iodide (4.5 g), 20 mmol of 2-propen-1-ol (1.2 g) and 1 mmol of fine copper powder (0.063 g). The reaction mixture was stirred at 120 °C for 120 min. After completion of the addition (GC), the reaction mixture was dissolved in 10 ml of diethyl ether, the catalyst filtered off, the solvent evaporated and the residue distilled under reduced pressure. Yield, 3.9 g (76%); b.p. 70–76 °C/2 Torr (m.p. 43–44 °C).

#### 2-Iodo-1-perfluoroheptyl-3-butanol (**11**)

A 10 ml glass ampoule was charged with 30 mmol of perfluoroheptyl iodide (4.5 g), 40 mmol of 3-buten-2-ol (2.5 g) and 3 mmol of fine copper powder (0.190 g). The reaction mixture was stirred at 120 °C for 105 min and then worked-up as for compound **10**. Yield, 12.3 g (78.5%); b.p. 75–78 °C/1.7 Torr.

#### 2-Iodo-1-perfluoroheptyl-3-methyl-3-butanol (**12**)

A 10 ml glass ampoule was charged with 10 mmol of perfluoroheptyl iodide (4.5 g), 10 mmol of 2-methyl-3-buten-2-ol (0.86 g) and 1 mmol of fine copper powder (0.063 g). The reaction mixture was stirred at 120 °C for 60 min and worked-up as for compound **10**. Yield, 4.4 g (83%); b.p. 80–85 °C/1.5 Torr.

#### 2-Iodo-1-perfluoroheptyl-2-methyl-3-propanol (**13**)

A 10 ml glass ampoule was charged with 10 mmol of perfluoroheptyl iodide (4.5 g), 20 mmol of 2-methyl-2-propen-1-ol (1.4 g) and 1 mmol of fine copper powder (0.063 g). The reaction mixture was stirred at 120 °C for 60 min and worked-up as for compound **10**. Yield, 2.5 g (48%); b.p. 80–85 °C/2 Torr.

TABLE 3. Reductive dehalogenation of iodoalcohols to alcohols

Iodoalcohol		Alcohol		Yield, % <sup>a</sup>
	(10)		(26)	86
	(11)		(27)	82
	(12)		(28)	67
	(13)		(29)	77
	(14)		(30)	82
	(18)		(31)	76

<sup>a</sup>Isolated yields. Conversion of iodoalcohols was quantitative.

#### 2-Iodo-1-perfluorohexyl-4-butanol (14)

A 10 ml glass ampoule was charged with 10 mmol of perfluorohexyl iodide (4.5 g), 12 mmol of 3-buten-1-ol (0.86 g) and 1 mmol of fine copper powder (0.063 g). The reaction mixture was stirred at 120 °C for 90 min and worked-up as for compound **10**. Yield, 3.3 g (63%); b.p. 83–88 °C/0.5 Torr (m.p. 49–50 °C).

#### 2-Iodo-1-perfluorohexyl-5-hexanol (15)

2-Iodo-1-perfluorohexyl-5-hexanol was prepared using dibenzoyl peroxide initiation of the addition of perfluorohexyl iodide to 5-hexen-2-ol (*vide infra*). Yield, 1.5 g (21%); b.p. 90–95 °C/1 Torr.

#### 2-(Perfluorohexylmethyl)-5-methyltetrahydrofuran (16)

A 10 ml glass ampoule was charged with 10 mmol of perfluorohexyl iodide (4.5 g), 10 mmol of 5-hexen-2-ol (1 g) and 1 mmol of fine copper powder (0.063 g). The reaction mixture was stirred at 120 °C for 420 min and worked-up as for compound **10**. Yield, 2.7 g (60%); b.p. 80–85 °C/20 Torr.

#### 2,5-Diiodo-1-perfluorohexylhexane (17)

A 2 ml ampoule was charged with 0.2 mmol of 2-iodo-1-perfluorohexyl-5-hexanol (110 mg), 0.2 mmol of red phosphorus (6 mg), 0.6 mmol iodine (76 mg) and 1 ml of dry benzene. The reaction mixture was stirred at 50 °C for 2 h, then washed with solutions of sodium carbonate and sodium thiosulphate and finally dried over magnesium sulphate. GC analysis showed that all

the iodoalcohol had reacted and that the diiodide was the sole product.

#### 2-Iodo-1-perfluorohexyl-11-undecanol (18)

A 10 ml glass ampoule was charged with 12 mmol perfluorohexyl iodide (4.5 g), 10 mmol of 10-undecen-1-ol (1.7 g) and 1 mmol of fine copper powder (0.063 g). The reaction mixture was stirred at 120 °C for 105 min and worked-up as for compound **10**. Yield, 5.2 g (84%); b.p. 128–135 °C/1 Torr.

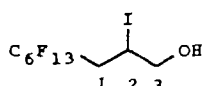
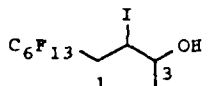
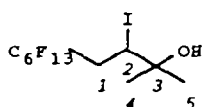
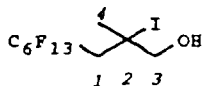
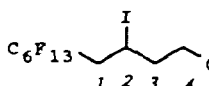
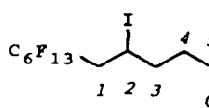
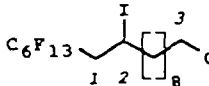
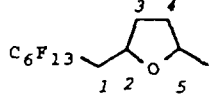
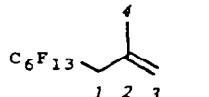
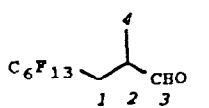
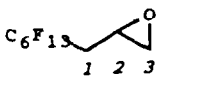
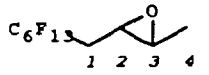
#### General procedure for the addition of perfluoroalkyl iodides to unsaturated alcohols initiated by dibenzoyl peroxide

A 10 ml glass ampoule was charged with 10 mmol of an unsaturated alcohol, 10 mmol of perfluorohexyl iodide (4.5 g) and 0.2 mmol of dibenzoyl peroxide (0.05 g). The reaction mixture was stirred at 120 °C. The reaction was stopped after the reaction mixture changed colour to violet–brown and was then analyzed by GC methods. The 1:1 adduct was isolated in the same way as for the case of the copper-catalyzed reactions.

#### Reaction of compound 13 with a stoichiometric amount of copper

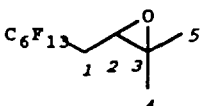
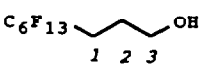
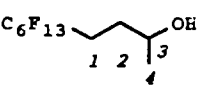
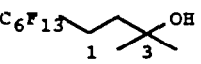
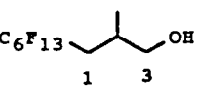
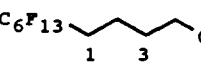
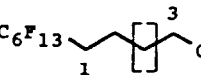
A 10 ml glass ampoule was charged with 5 mmol of iodoalcohol **13** (2.8 g) and 10 mmol of copper powder (0.630 g). The reaction mixture was stirred at 140–150 °C for 30 min (to obtain total conversion of the iodoalcohol). The reaction mixture was then dissolved in 10 ml of pentane. Unreacted copper powder salts

TABLE 4.  $^{13}\text{C}$  NMR spectra

Compound	Number of carbon atom					
	1	2	3	4	5	6
 $\text{C}_6\text{F}_{13}$	(10)	37.55, t, $^2J_{\text{CF}}=21$ Hz	21.70	67.96		
 $\text{C}_6\text{F}_{13}$	(11)	37.07, t, $^2J_{\text{CF}}=21$ Hz	29.71	69.50	20.59	
Two diastereoisomers (the minor one)		38.54, t, $^2J_{\text{CF}}=20.5$ Hz	31.70	70.73	24.77	
 $\text{C}_6\text{F}_{13}$	(12)	37.53 $^2J_{\text{CF}}=21.5$ Hz	31.89	72.53	26.43	+ 27.63
 $\text{C}_6\text{F}_{13}$	(13)	42.33, t, $^2J_{\text{CF}}=20$ Hz	47.98	74.01	31.04	
 $\text{C}_6\text{F}_{13}$	(14)	41.91, t, $^2J_{\text{CF}}=20.5$ Hz	16.59	42.38	62.54	
 $\text{C}_6\text{F}_{13}$	(15)	41.63, t, $^2J_{\text{CF}}=21.5$ Hz	20.22	36.74	38.77	67.94 23.18
Two diastereoisomers (the minor one)		41.63, t, $^2J_{\text{CF}}=21.5$ Hz	20.28	36.41	38.61	67.50 23.30
 $\text{C}_6\text{F}_{13}$	(18)	41.65, t, $^2J_{\text{CF}}=21$ Hz	20.76	62.85		
 $\text{C}_6\text{F}_{13}$	(16)	37.15, t, $^2J_{\text{CF}}=21$ Hz	72.17	33.71	32.52	75.56 21.30
Two diastereoisomers (the minor one)		36.91, t, $^2J_{\text{CF}}=21$ Hz	71.53	33.39	32.17	75.04 21.10
 $\text{C}_6\text{F}_{13}$	(23)	32.72, t, $^2J_{\text{CF}}=22.5$ Hz	134.20	118.80	23.30	
 $\text{C}_6\text{F}_{13}$	(24)	30.71, t, $^2J_{\text{CF}}=21.5$ Hz	39.36	200.65	14.46	
 $\text{C}_6\text{F}_{13}$	(19)	35.37, t, $^2J_{\text{CF}}=22$ Hz	44.77, t, $^3J_{\text{CF}}=5.8$ Hz	45.80		
 $\text{C}_6\text{F}_{13}$	(20)	30.69, t, $^2J_{\text{CF}}=21.5$ Hz	51.62	53.92	16.82	
Two diastereoisomers (the minor one)		34.92 $^2J_{\text{CF}}=22$ Hz	49.40	51.62	12.88	

(continued)

TABLE 4. (continued)

Compound	Number of carbon atom					
	1	2	3	4	5	6
 $C_6F_{13}$	(21)	31.85, t, $^2J_{CF}=21.4$ Hz	56.09, t, $^3J_{CF}=5$ Hz	57.87	18.65	+24.21
 $C_6F_{13}$	(25)	27.54, t $^2J_{CF}=22.5$ Hz	23.32	61.21		
 $C_6F_{13}$	(26)	27.36, t, $^2J_{CF}=22$ Hz	29.30, t, $^3J_{CF}=3.5$ Hz	66.91	23.70	
 $C_6F_{13}$	(27)	26.07, t, $^2J_{CF}=22$ Hz	33.33, t, $^3J_{CF}=3$ Hz	69.68	29.13	29.13
 $C_6F_{13}$	(28)	33.27, t, $^2J_{CF}=21.5$ Hz	29.51	67.11	17.19	
 $C_6F_{13}$	(29)	30.36, t, $^2J_{CF}=22$ Hz	16.77	31.87	62.00	
 $C_6F_{13}$	(30)	32.80, t, $^2J_{CF}=23.5$ Hz	20.07, t, $^3J_{CF}=4$ Hz	63.07		

were filtered off, the solvent was evaporated and the residue distilled under reduced pressure to give 1.3 g of product of b.p. 60–100 °C/105 Torr. GC–NMR analyses of the products showed that they were composed of 3-perfluorohexyl-2-methylpropene (**23**) (38%) and 3-perfluorohexyl-2-methylpropanal (**24**) (48%). The remainder (14%) was composed of a number of other products, none of which exceed 4% of the total amount of the mixture.

#### General procedure for the conversion of iodoalcohols to epoxides

A 100 ml flask was charged with 20 mmol of finely powdered sodium hydroxide (0.8 g), 50 ml of diethyl ether and 10 mmol of an iodoalcohol. The reaction mixture was stirred at room temperature until all the iodoalcohol had been converted to epoxide. To achieve a better progress for the reaction, it was found useful to add 10–15 glass balls (3-mm diameter) in order to break up the slurry of insoluble salts in the reaction mixture. The reaction mixture was filtered and diethyl ether was distilled off using a 30 cm Vigreux column. The residue was distilled under reduced pressure. The following products were obtained using this procedure: 1-perfluorohexyl-2,3-epoxypropane (**19**), 2.0 g (75%), b.p. 80–85 °C/140 Torr; 1-perfluorohexyl-2,3-epoxybutane (**20**), 2.1 g (74%), b.p. 100–103 °C/150 Torr; 1-

perfluorohexyl-2,3-epoxy-3-methylbutane (**21**), 1.9 g (64%), b.p. 87–90 °C/140 Torr; and 1-perfluorohexyl-2-methyl-2,3-epoxypropane (**22**).

The complex reaction mixture obtained was analyzed by GC methods. In order to assign the peak belonging to epoxide **22**, the reaction mixture was allowed to react with hydrochloric acid with which epoxides form chlorohydrins [21]. The peak disappearing after this reaction was assigned to epoxide **22**. Peaks corresponding to the aldehyde **24** and allylic alcohols **25** were assigned after comparison with authentic samples.

#### General procedure for reductive dehalogenation of perfluoroalkylated iodoalcohols

A 10 ml ampoule was charged with 5 mmol of perfluoroalkylated iodoalcohol and 6 mmol of tributylstannane (1.74 g) were added with stirring. The reaction mixture was heated to 80 °C for 30 min, then allowed to cool and left for 3 h until two immiscible layers were formed. The separated lower layer was distilled under reduced pressure. The following products were obtained using this procedure: 3-perfluorohexyl-1-propanol (**26**), 1.6 g (86%), b.p. 73–75 °C/10 Torr; 4-perfluorohexyl-2-butanol (**27**), 1.7 g (82%), b.p. 77–79 °C/12 Torr; 4-perfluorohexyl-2-methyl-2-butanol (**28**), 1.1 g (67%), b.p. 75–77 °C/10 Torr; 3-perfluorohexyl-2-methyl-1-propanol (**29**), 1.5 g (77%), b.p. 70–75 °C/

9 Torr; and 4-perfluorohexyl-1-butanol (**30**), 1.6 g (82%), b.p. 80–85 °C/11 Torr.

#### 11-Perfluorohexyl-1-undecanol (**31**)

A 25 ml flask equipped with a septum was charged with 10 mmol of the zinc powder (0.65 g) and 0.5 mmol of nickel chloride hexahydrate (0.12 g). The flask was washed with argon, then 10 ml of tetrahydrofuran and one drop of water were added. The mixture was stirred at room temperature for 30 min and then 5 mmol of 2-iodo-1-perfluorohexyl-11-undecanol (3.1 g) were added and stirring continued for 90 min. The reaction mixture was poured into an ammonium chloride solution and extracted three times with 40 ml of dichloromethane. The combined dichloromethane layers were washed with water and dried over magnesium sulfate. After evaporation of dichloromethane, the residue was distilled under reduced pressure to give 1.8 g of 11-perfluorohexyl-1-undecanol (76%), b.p. 110–115 °C/1 Torr.

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#### References

- 1 J.D. Park, F.F. Rogers and J.R. Lacher, *J. Org. Chem.*, **26** (1961) 2089.
- 2 L.D. Moore, *J. Chem. Eng. Data*, **9** (1964) 251.
- 3 M. Nagai, H. Shinkai, T. Kato, T. Wakatsu and S. Fukui, *Jpn. Kokai* **74 69 605**(1974); [*Chem. Abs.*, **81** (1974) 169 114y].
- 4 N.O. Brace and A.M. Mackenzie, *US Pat.* **3 083 224**(1963); [*Chem. Abs.*, **59** (1963) 5023f].
- 5 N.O. Brace, *J. Fluorine Chem.*, **20** (1983) 313.
- 6 A. Ohmori, N. Tomihashi, H. Inukai and Y. Shimizu, *Eur. Pat.* **138 091**(1985); [*Chem. Abs.*, **103** (1985) 106 434e].
- 7 T. Fuchikami and I. Ojima, *Tetrahedron Lett.*, **25** (1984) 303.
- 8 T. Ishihara, M. Kurobashi and Y. Okada, *Chem. Lett.*, (1986) 1895.
- 9 M. Kurobashi and T. Ishihara, *J. Fluorine Chem.*, **39** (1988) 299.
- 10 T. Fuchikami, Y. Shibata and H. Urata, *Chem. Lett.*, (1987) 521.
- 11 W. Qin and D.J. Burton, *J. Org. Chem.*, **58** (1993) 419.
- 12 Q.Y. Chen and Z.Y. Yang, *J. Fluorine Chem.*, **28** (1985) 399.
- 13 Q.Y. Chen, Z.Y. Yang and Y.B. He, *J. Fluorine Chem.*, **37** (1987) 171.
- 14 Z.Y. Yang and D.J. Burton, *J. Fluorine Chem.*, **45** (1989) 435.
- 15 Z.Y. Yang and D.J. Burton, *J. Org. Chem.*, **56** (1992) 5125.
- 16 H. Nagashima, K. Sato and J. Tsuji, *Tetrahedron Lett.*, **23** (1982) 3085.
- 17 *Houben-Weil, Sauerstoff Verbindungen I*, G. Thieme Verlag, Stuttgart, 1965, p. 435.
- 18 *Houben-Weil, Sauerstoff Verbindungen I*, G. Thieme Verlag, Stuttgart, 1965, p. 374.
- 19 W.J. Neumann, *Synthesis*, (1987) 665.
- 20 E.J. Corey and J.W. Suggs, *J. Org. Chem.*, **40** (1975) 2554.
- 21 M. Chini, P. Crotti, Ch. Gardelli and F. Macchia, *Tetrahedron*, **48** (1992) 3805.