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Radiochemical addition of alcohols to perfluoro-2-alkenes

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Abstract

Radical addition of aliphatic alcohols to internal perfluorinated olefins has been studied. The process occurs non-stereoselectively to give equimolar mixtures of diastereoisomers in all cases.

Keywords: Radiochemical addition; Alcohols; Perfluoroalkenes

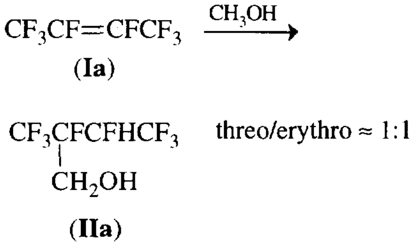
1. Introduction

Until now, the stereochemistry of addition to internal perfluorinated olefins has only been studied slightly. The free-radical addition of alcohols to perfluorinated cycloalkenes, initiated by γ-irradiation and resulting in mixtures of diastereoisomers, is known [1,2]; a preference for *trans* addition was reported in Ref. [2].

In order to study free-radical addition (*regio* and *stereo*) to higher perfluorinated olefins, we have investigated the interaction of three perfluoro-2-alkenes (**Ia–c**) with aliphatic alcohols under γ-irradiation. It should be noted that Japanese chemists have studied the radical addition (benzoyl peroxide-initiated) of alcohols and aldehydes to olefin **Ic**, but we failed to obtain the same adducts under the conditions reported [3].

2. Results and discussion

We have ascertained that internal perfluorinated olefins (**Ia–c**) add methanol readily in an alkyl trifuloroacetate solution or in the absence of solvent under γ-irradiation. However, in the latter case, the process occurs significantly more slowly than in the case when solvent is used. This is related to the very low mutual solubility of the starting reagents. In addition, prolonged irradiations can result in significant amounts of high molecular weight byproducts (their composition was not determined). Only one of the olefins studied, i.e. **Ic**, possesses a marked tendency to form such byproducts. Hardly any side products were observed for the lower alkenes, **Ia** and **Ib**. Thus, *trans*-perfluoro-2-butene gives monoadduct **IIa** in high yield. Product **IIa** is an equimolar mixture of diastereoisomers. The reaction of methanol with a 7:3 mixture of the *cis* and *trans* isomers of **Ia** afforded the same equimolar mixture of diastereoisomeric adducts **IIa** under γ-irradiation (Scheme 1).



$$\underset{\textbf{(Ia)}}{CF_3CF{=}CFCF_3} \xrightarrow{CH_3OH} \underset{\textbf{(IIa)}}{CF_3\underset{CH_2OH}{C}FCFHCF_3} \quad \text{threo/erythro} \approx 1{:}1$$

Scheme 1.

Note that no isomerization of the *trans* isomer **Ia** into the *cis* isomer or the reverse process was observed to any marked extent (±3%) over the same period of irradiation (ca. 6 h). (Two control tubes including no methanol were irradiated. One of them contained the pure *trans* isomer while the second contained a 7:3 mixture of the *trans* and *cis* isomers.)

The addition of methanol to the *trans* isomer of **Ib** proceeds non-regiospecifically to form a mixture of adducts **IIb** and **IIIb** in a 3:2 ratio (Scheme 2). Each of these adducts is an equimolar mixture of diastereoisomers.

The formation of two possible regioisomers (**IIb** and **IIIb**) in this process is likely to be explained by the insignificant difference in the size of the substituents (CF_3 and C_2F_5) around the multiple bond. Both position 2 and position 3 in the starting olefin **Ib** are sterically accessible to CH_2OH radical attack. Where there was a greater difference in the size of the substituents at the multiple bond in olefins of the type **I**, we expected that regioisomers of type **II** would predomi-

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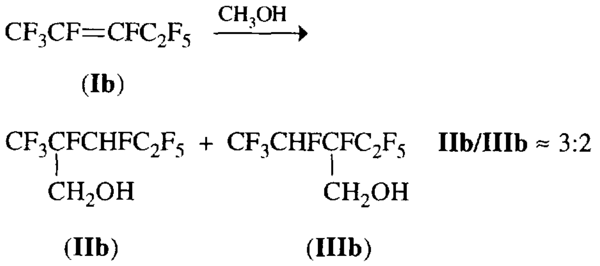
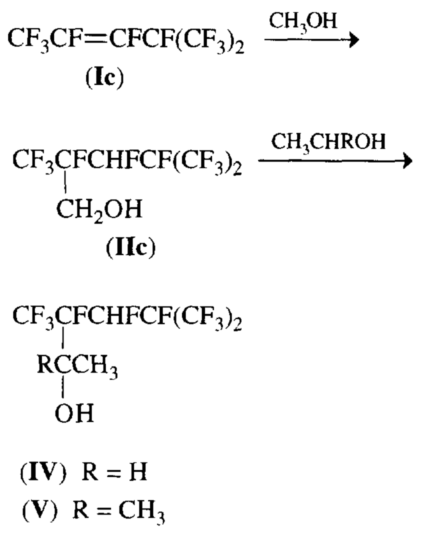
Table 1
Radical addition of alcohols to perfluoro-2-alkenes

Product	Solvent	Alcohol/olefin molar ratio	Dose (M rad h^{-1})	Conversion (%)	Yield (%)	Boiling point (°C/mmHg)	Analysis: Found/calculated (%)	
							C	H
IIa		2.0	25	84.7	84.7	117–119/760	25.92/25.86	1.97/1.72
Ib + IIIb		2.0	100	80.7	72.4	128–139/760	25.45/25.53	1.93/1.42
IIc		2.0	160	84.2	53.8	50–56/13	25.57/25.30	1.22/1.20
IIc	CF_3COOCH_3	1.2	23	33.3	65.0			
IIc	CF_3COOCH_3	1.3	65	66.7	51.6			
IIc	CF_3COOCH_3	1.4	65	74.5	59.0			
IIc	CF_3COOCH_3	3.1	65	81.0	72.3			
IIc	CF_3COOCH_3	4.0	65	91.7	76.6			
IIc	CF_3COOCH_3	5.0	30	74.0	57.6			
IIc	CF_3COOCH_3	10.0	30	92.4	63.0			
IV	$CF_3COOC_2H_5$	3.0	40	57.4	40.9	45–60/8	27.86/27.75	1.66/1.73
IV	$CF_3COOC_2H_5$	4.0	50	62.1	47.7			
IV	$CF_3COOC_2H_5$	5.0	50	67.4	60.1			
V		2.0	160	54.7	42.4	153–156/760	30.12/30.00	2.34/2.22



Scheme 2.



Scheme 3.

nate in the addition products. Actually, radiolysis of a mixture of CH_3OH and *trans*-perfluoro-4-methyl-2-pentene (**Ic**) or a solution of these in methyl trifluoroacetate resulted in the formation of only adduct **IIc** as an equimolar mixture of diastereoisomers.

Ethanol in ethyl trifluoroacetate and isopropanol in the absence of solvent add to olefin **Ic** regiospecifically under radiolysis conditions to give adducts **IV** and **V**, respectively. Compound **IV** is a mixture of four diastereoisomers while **V** is a mixture of two such isomers.

The assignments of the diastereoisomers to the *erythro* and *threo* series is a subject of a separate investigation.

3. Experimental details

A GUG-120 ^{60}Co γ-installation as an irradiation source was used. Dosimetry was implemented by the bichromate technique [4]. In all cases the dose was 1 M Rad h^{-1}. GLC analysis was conducted on a column packed with Chromosorb W using 20% dinonyl phthalate as the stationary phase.

3.1. General procedure

A mixture of olefin **I** and alcohol (or a solution of **I** and an alcohol in an appropriate solvent) was irradiated in a sealed glass tube. After irradiation, the tube was opened, the reaction mixture poured into dilute HCl, the organic layer separated and washed three times with water, and then dried over $CaCl_2$. The adducts were isolated by distillation (Table 1).

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