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RADICAL ADDITIONS TO 1,2-DICHLORODIFLUOROETHENE

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SUMMARY

Fluorine containing alcohols, esters and ethers have been obtained by peroxide induced radical addition of alcohols, esters and ethers to 1,2-dichlorodifluoroethene.

The influence of the kind and amount of the peroxide has been studied and the reactivity of alcohols, esters and ethers compared.

INTRODUCTION

Partly fluorinated alcohols, esters and ethers are intermediate products for the synthesis of fluorinated alkenes and these compounds are potentially interesting for use as comonomers in fluorinated polymers.

The synthesis of addition products of alcohols and their derivatives to 1,2-dichlorodifluoroethene has been reported previously to occur by means of γ-radiation [1, 2]. Consequently, use of this class of compound in synthesis has not been developed beyond laboratory scale.

The present work reports a simple method that is applicable to the synthesis of these adducts. It is well known [3-5] that organic peroxides induce radical additions of alcohols, esters and ethers to many fluoroolefins, but no reference has been found concerning 1,2-dichlorodifluoroethene.

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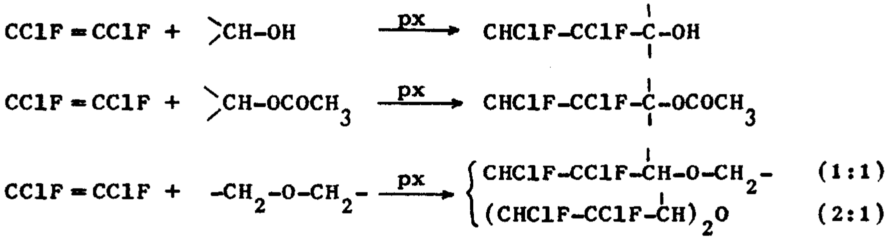
The general reactions involved are:



$$\mathrm{CClF{=}CClF} + \;{>}\mathrm{CH{-}OH} \xrightarrow{px} \mathrm{CHClF{-}CClF{-}}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{{-}OH}$$

$$\mathrm{CClF{=}CClF} + \;{>}\mathrm{CH{-}OCOCH_3} \xrightarrow{px} \mathrm{CHClF{-}CClF{-}}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{{-}OCOCH_3}$$

$$\mathrm{CClF{=}CClF} + \mathrm{{-}CH_2{-}O{-}CH_2{-}} \xrightarrow{px} \left\{\begin{array}{ll} \mathrm{CHClF{-}CClF{-}}\overset{|}{\mathrm{C}}\mathrm{H{-}O{-}CH_2{-}} & (1{:}1) \\ (\mathrm{CHClF{-}CClF{-}}\overset{|}{\mathrm{C}}\mathrm{H})_2\mathrm{O} & (2{:}1) \end{array}\right.$$

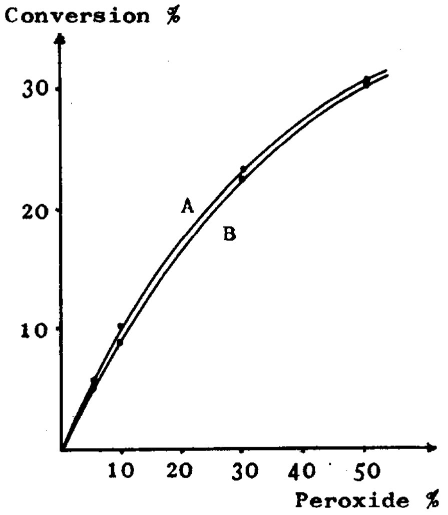
RESULTS AND DISCUSSION

The influence of the kind and amount of the peroxide and the different reactivity of the reactants have been investigated in more details.

Influence of the peroxide

In the most common radical additions to fluoroolefins the peroxide is added in small amount; in contrast, however, 1,2-(dichlorodifluoroethene needs a large amount of peroxide (up to 50% mol based on the olefin) in order to obtain reasonable conversions of the olefin as shown in Figures 1 and 2. The yields of the reaction of the olefin with alcohols and esters are almost quantitative, while in the reaction with ethers some by-products are formed, as will be discussed later.

The large amount of the peroxide which is needed for the reaction and the low conversions which are obtained can be attributed to the low reactivity of 1,2-dichlorodifluoroethene in comparison with other fluoroolefins. For example, in similar reaction conditions, hexafluoropropene reacts with methanol in 60-70% conversion in the presence of very low concentration of di-t-butylperoxide or di-benzoylperoxide [3,5] . This is probably due to the steric interference of the bulky chlorine atoms on both the carbon atoms of the olefin.



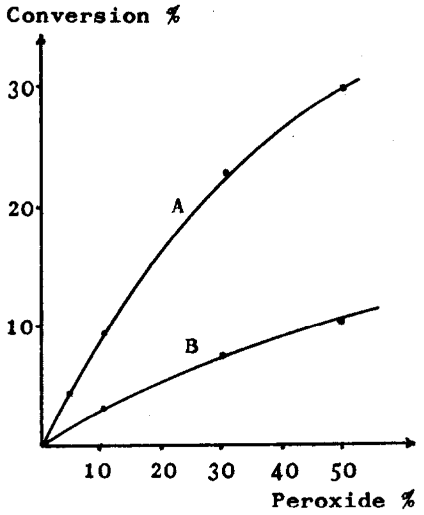


Fig.1. A: CClF=CClF + i-PrOH with di-t-butylperoxide, 150°C/5hr
B: CClF=CClF + THF with di-t-butylperoxide, 150°C/5hr

Fig.2. A: CClF=CClF + THF with di-benzoylperoxide, 115°C/5hr
B: CClF=CClF + i-PrOH with di-benzoylperoxide, 115°C/5hr

Different peroxides have been tested:

- di-benzoylperoxide (Peroximon BP *)
- di-tert-butylperoxide (Peroximon DB *)
- 3,3,5-trimethyl-1,1-di(tert-butylperoxy)cyclohexane (Trigonox 29 **).

The reactions with Peroximon DB and Trigonox 29 have been carried out at the temperature at which the half-life time of the peroxide is one hour (150 °C for Peroximon DB; 115 °C for Trigonox 29) in order to get similar radical concentration. The reactions with Peroximon BP have been carried out at 115 °C (half-life time: 5 min) because LaZerte [3] has reported that this is the optimum temperature for this kind of reaction.

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* Montefluos Trade mark

** AKZO Trade mark

Table 1 shows that conversions in ether and ester additions are independent of the kind of the peroxide, while conversions in alcohol additions are strongly dependent on the peroxide used.

TABLE 1

The addition of tetrahydrofuran, i-propanol and ethyl acetate to CClF=CClF [a]

Reactant	Peroxide	Temp. °C	Conv. % [b]
Tetrahydrofuran	Peroximon BP	115	30
Tetrahydrofuran	Peroximon DB	150	30
Tetrahydrofuran	Trigonox 29	115	30
i.Propanol	Peroximon BP	115	10
i.Propanol	Peroximon DB	150	30
i.Propanol	Trigonox 29	115	30
Ethyl acetate	Peroximon BP	115	20
Ethyl acetate	Peroximon DB	150	20
Ethyl acetate	Trigonox 29	115	20

[a] Molar ratio reactant / olefin = 9/1
Molar ratio olefin / peroxide = 2/1
Reaction time: 5 hr

[b] Based on olefin

Addition of alcohols, esters and ethers to CClF=CClF

The addition of alcohols, esters and ethers to 1,2-dichlorodifluoroethene has been examined. The results, physical properties and analyses of the products are shown in Tables 2 - 3.

TABLE 2

The addition of alcohols and esters to CClF=CClF [a]

Reactant	Addition product[b]	Conv.[c] %	B.p. °C/mmHg	Carbon %		Hydrogen %		Chlorine %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Methanol	$R{-}CH_2OH$	10	75/40	21.9	21.8	2.4	2.3	42.7	42.5
Ethanol	$R{-}CH(CH_3)OH$	15	65/20	27.0	27.2	3.4	3.3	39.3	39.2
Propanol	$R{-}CH(C_2H_5)OH$	17	80/20	31.2	31.2	4.2	4.0	36.5	36.5
i-Propanol	$R{-}C(CH_3)_2OH$	30	71/20	31.2	31.3	4.2	4.1	36.5	35.9
Methyl acetate	$R{-}CH_2{-}OCOCH_3$	14	74/45	29.1	29.0	2.9	2.9	34.0	34.2
Ethyl acetate	$R{-}CH(CH_3)OCOCH_3$	20	95/45	32.7	32.5	3.6	3.8	31.8	31.8
i-Propyl acetate	$R{-}C(CH_3)_2OCOCH_3$	4	86/20	35.9	36.0	4.3	4.3	29.9	29.4

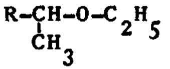
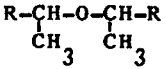
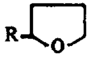
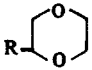
[a] Reactions with Peroximon DB, 150°C/5 hr
Molar ratio reactant/olefin = 9/1
Molar ratio olefin/peroxide = 2/1

[b] R = CHClF-CClF-

[c] Based on olefin

TABLE 3

The addition of ethers to $CClF{=}CClF$[a]

Reactant	Addition product[b]	Conv.[c] %	B.p. °C/mmHg	Carbon % Calcd.	Carbon % Found	Hydrogen % Calcd.	Hydrogen % Found	Chlorine % Calcd.	Chlorine % Found
Diethyl ether	 $R{-}\underset{CH_3}{CH}{-}O{-}C_2H_5$ (1:1)	8	90/80	34.9	34.8	4.8	4.7	34.0	33.4
	 $R{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}R$ (2:1)	20	135/20	28.4	28.5	3.0	3.0	41.4	41.3
Diisopropyl ether	no reaction								
Tetrahydrofuran		30	115/60	35.3	35.3	3.9	3.8	34.3	34.8
1,4-Dioxane		20	125/60	32.7	32.5	3.6	3.5	31.8	31.5

[a] Reactions with Peroximon DB, 150 °C / 5 hr
Molar ratio reactant/olefin = 9/1
Molar ratio olefin/peroxide = 2/1

[b] R = $CHClF{-}CClF{-}$

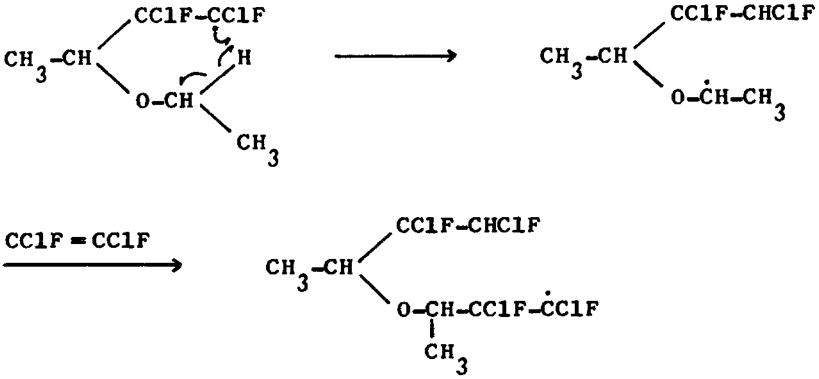
[c] Based on olefin

The addition of esters occurs only on the alcoholic moiety of the molecule because of the stabilization of the alkoxy radicals. The order of reactivity of alcohols is consistent with the stabilization of the intermediate α-hydroxyalkyl radicals as follows:

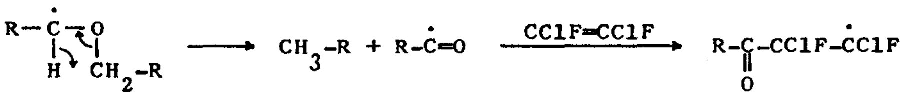
$$(CH_3)_2\dot{C}\text{-}OH > CH_3\text{-}CH_2\text{-}\dot{C}H\text{-}OH \sim CH_3\text{-}\dot{C}H\text{-}OH > \dot{C}H_2\text{-}OH$$

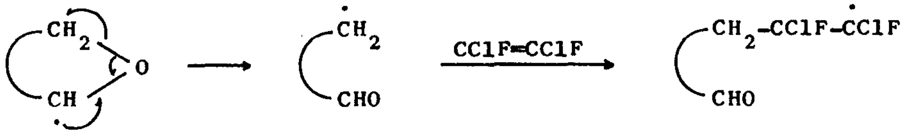
Methyl and ethyl acetate follow the order of reactivity discussed before, while the reactivity of i-propyl acetate decreases. In the same conditions diisopropyl ether gives no reaction. This decrease of reactivity of i-propyl group in the order i-propanol > i-propyl acetate > diisopropyl ether is likely due to the steric hindrance on the reaction centre.

Diethyl ether gives preferentially 2:1 adduct instead of 1:1 adduct with an intramolecular mechanism:



Cyclic ethers give only 1:1 adducts; this behaviour can be explained by the stiffness of the heterocyclic ring with respect to the linear chain. Both cyclic and acyclic ethers form small amounts of some carbonyl compounds as by-products by cleavage of the intermediate radicals, according to the following intramolecular mechanism [2] :





The structures of the products were determined by the proton and fluorine NMR spectra. Some NMR data are reported in Table 4. The reaction products have two or three asymmetric carbon atoms and the enantiomeric couples have been evidenced by two-dimensional NMR COSY techniques. Details of our studies on NMR analysis of these compounds will be the subject of future publication.

CONCLUSION

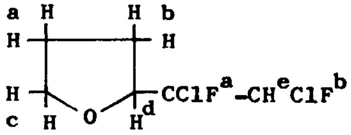
This work has pointed out that radical addition of esters, alcohols and ethers to 1,2-dichlorodifluoroethene can occur in the presence of peroxides; therefore, these reactions could be carried out in an industrial scale.

The conversions of these reactions are low, but the high selectivities allow easy recovery of the olefin.

Our results also indicate that formation of telomeric compounds, such as $H(CClF{-}CClF)_n\overset{|}{\underset{|}{C}}{-}O{-}$, does not occur under our experimental conditions, while telomers are formed in analogous reactions with other fluoroolefins as $CF_2{=}CF_2$ and $CF_2{=}CClF$ [6, 7, 8] .

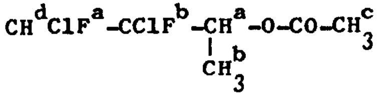
TABLE 4

^{1}H and ^{19}F NMR data

Compound	Chem. shifts (ppm)		Coupling constants (Hz)
	H^a	1.9	
	H^b	2.1	
	H^c	3.8	
	H^d	4.4	
	H^e	6.3	$J^2(F-H) = 48.0$ $J^3(F-H) < 0.8$
1st enantiomeric couple	F^a	141.4	$J^3(F-F) = 22.2$
	F^b	149.8	
	H^e	6.4	$J^2(F-H) = 48.0$ $J^3(F-H) = 2.6$
2nd enantiomeric couple	F^a	135.4	$J^3(F-F) = 17.3$
	F^b	151.8	
	H^e	6.5	$J^2(F-H) = 50.8$ $J^3(F-H) = 4.3$
3th enantiomeric couple	F^a	139.1	$J^3(F-F) = 19.1$
	F^b	157.5	
	H^e	6.6	$J^2(F-H) = 47.8$ $J^3(F-H) < 0.8$
4th enantiomeric couple	F^a	137.9	$J^3(F-F) = 17.5$
	F^b	145.7	

(Continued overleaf)

TABLE 4 (cont.)

Compound		Chem. shifts (ppm)	Coupling constants (Hz)
 $CH^dClF^a-CClF^b-CH^a(CH_3^b)-O-CO-CH_3^c$	H^a	5.4	
	CH_3^b	1.8	
	CH_3^c	2.1	
1st enantiomeric couple	H^d	6.8	$J^2(F-H) = 47.0$
	F^a	147.3	$J^3(F-F) = 19.3$
	F^b	129.4	
2nd enantiomeric couple	H^d	6.8	$J^2(F-H) = 48.9$
	F^a	149.5	$J^3(F-F) = 19.0$
	F^b	129.4	
3th enantiomeric couple	H^d	6.8	$J^2(F-H) = 47.4$
	F^a	143.0	$J^3(F-F) = 19.1$
	F^b	131.6	
4th enantiomeric couple	H^d	6.8	$J^2(F-H) = 46.7$
	F^a	145.9	$J^3(F-F) = 19.1$
	F^b	131.6	

CH^aClF^a–$CClF^b$–$C(CH_3)_2OH$	CH_3	1.4		
	OH	4.9		
	H^a	6.8	$J^2(F\text{-}H) = 48.0$	$J^3(F\text{-}H) = 11.0$
1st enantiomeric couple	F^a	138.4	$J^3(F\text{-}F) = 17.7$	
	F^b	130.4		
	H^a	7.0	$J^2(F\text{-}H) = 47.8$	$J^3(F\text{-}H) = 0.8$
2nd enantiomeric couple	F^a	136.5	$J^3(F\text{-}F) = 25.8$	
	F^b	122.3		

EXPERIMENTAL

Materials

1,2-dichlorodifluoroethene has been prepared by dechlorination of 1,1,2,2-tetrachloro-1,2-difluoroethane with zinc dust in dimethylsulfoxide. The peroxides have been supplied by AKZO and Montefluos.

Apparatus

The addition reactions have been carried out in a 500 ml stainless steel AISI 316 oscillating autoclave.

^{1}H and ^{19}F NMR spectra have been recorded using a Varian XL-200 spectrometer operating for ^{19}F at 188.22 MHz.

Gas-mass spectra have been recorded using a Varian CH-7A spectrometer.

Procedure

All radical additions have been carried out with a concentration ratio olefin/reactant = 1/9.

The autoclave was charged with a mixture of reactant and peroxide and then cooled in an ice bath before the olefin was added. After sealing, the autoclave was shaken for 5 hours at 115°C (for Peroximon BP and Trigonox 29) or at 150°C (for Peroximon DB). The products were purified by fractional distillation and olefin was easily recovered.

All products were characterized by infrared spectral analysis, ^{1}H and ^{19}F NMR spectroscopy and mass spectrometry-g.l.c.

ACKNOWLEDGEMENT

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