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PHOTOCYCLOADDITION OF PERFLUOROALKANOIC ACID FLUORIDES TO PERFLUOROALKENES PERFLUOROETHEROXETANES*

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ABSTRACT

New perfluorooxetanes having one or more ether bonds in the substituents, were synthesized through the UV promoted cycloaddition between the appropriate acid fluorides and alkenes at atmospheric pressure. The selectivity of the synthesis was good provided that the olefin is used in adequate excess.

The thermal stability of the oxetanes is high and similar to that of known acyclic perfluoroethers. The presence of several isomers prevents crystallization even at very low temperatures : the only thermal phenomenon, below their boiling point, is the glass transition, whereas analogous oxetanes lacking an ether oxygen show sharp freezing points. The complexity of the isomeric mixture is also confirmed by the NMR spectra.

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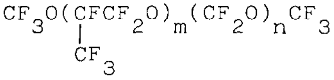
INTRODUCTION

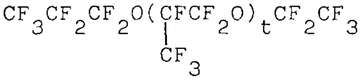
Fluids having the structure of perfluoroethers, particularly those with the character of polymers, are assuming larger and larger importance as working fluids in industry generally and particularly in electronics.

The products already marketed or under development are [1] :



$$CF_3O(CF(CF_3)CF_2O)_m(CF_2O)_nCF_3 \qquad (I)$$

$$CF_3O(CF_2CF_2O)_p(CF_2O)_qCF_3 \qquad (II)$$



$$CF_3CF_2CF_2O(CF(CF_3)CF_2O)_tCF_2CF_3 \qquad (III)$$

$$CF_3CF_2CF_2O(CF_2CF_2CF_2O)_wCF_2CF_3 \qquad (IV)$$

Perfluorooxetanes with perfluoroether groups as substituents were synthesized and their properties investigated with the aim of examining new classes of perfluoroethers.

RESULTS AND DISCUSSION

Experimental

The synthesis of the perfluoroether oxetanes was carried out by photocycloaddition of perfluorocarboxylic acid fluorides to perfluoroalkenes.

The experimental details are :

- quartz reactor with an optical path of 0.1 to 1.2 cm
- atmospheric pressure
- temperature as low as necessary to maintain the reagents liquid
- ultraviolet radiation source : a high pressure mercury lamp

The carboxylic acid fluorides tested were :

1) Hexafluoropropene oxide oligomers
2) Hexafluoropropene photooxidation derivatives
3) Perfluorooctanoic acid fluoride

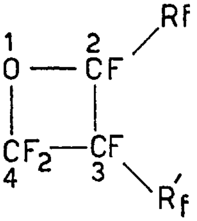
The alkenes tested were :

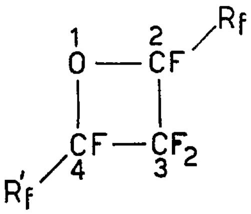
a) Hexafluoropropene
b) Perfluoroheptene-1
c) Perfluoropropylvinylether

Results

The reagents were coupled in such a way to ensure at least one ether bond in the final product.

The newly obtained oxetanes of formula :





are shown in Table 1.

TABLE 1

Perfluoroetheroxetanes by cycloaddition between R_fCOF and $R'_fCF{=}CF_2$

	REAGENTS		CONDITIONS			Optical	RESULTS				
	A R_f (mole)	B R'_f (mole)	Ratio A/B	Time (h)	Temp. (°C)	path (cm)	Conv. (%)	Selec (%)	MW	bp (°C)	Tg (°C)
1	$C_3F_7O\underset{\overset{\mid}{CF_3}}{C}F$ (0.72)	CF_3 (2.5)	1/3.5	100	-40	1.2	70	89	482	114	-138
2	$C_3F_7O(\underset{\overset{\mid}{CF_3}}{C}FCF_2O)\underset{\overset{\mid}{CF_3}}{C}F$ (0.63)	" (2.2)	1/3.5	134	-40	1.2	60.2	88	648	162	-119
3	$C_3F_7O(\underset{\overset{\mid}{CF_3}}{C}FCF_2O)_2\underset{\overset{\mid}{CF_3}}{C}F$ (0.27)	" (0.8)	1/3.0	30	-40	0.6	39.5	89	814	189	-107
4	$C_3F_7O\underset{\overset{\mid}{CF_3}}{C}F$ (0.02)	$n\text{-}C_5F_{11}$ (0.06)	1/3.2	15	20	0.1	99	-	682	168	-90
5	$n\text{-}C_7F_{15}$ (0.07)	C_3F_7O (0.28)	1/4	17	-30	0.2	85	86	682	180	-107
6	$C_3F_7O(\underset{\overset{\mid}{CF_3}}{C}FCF_2O)\underset{\overset{\mid}{CF_3}}{C}F$ (0.05)	" (0.20)	1/4	25	-30	0.2	92.7	72	764	187	-115
7	$CF_3O(CF_2\underset{\overset{\mid}{CF_3}}{C}FO)_{2.8}CF_2$ (0.10)	CF_3 (0.66)	1/6.6	24	-40	0.2	92.4	-	830	199	-117
8	$n\text{-}C_7F_{15}$ (0.16)	CF_3 (0.83	1/5.2	50	-40	0.3	72	91	566	158	mp -39

Compound 8 was prepared for comparison purposes only.

The yields were fairly satisfactory even although the lamp could give only a low emission in the range of maximum absorption of the carbonyl group (Fig. 1).

The selectivity of the synthesis was dependent on the ratio carboxylic acid fluoride/olefin : when it was lower than 1/3 the competitive photocoupling of the fluorides was low (Scheme 1).

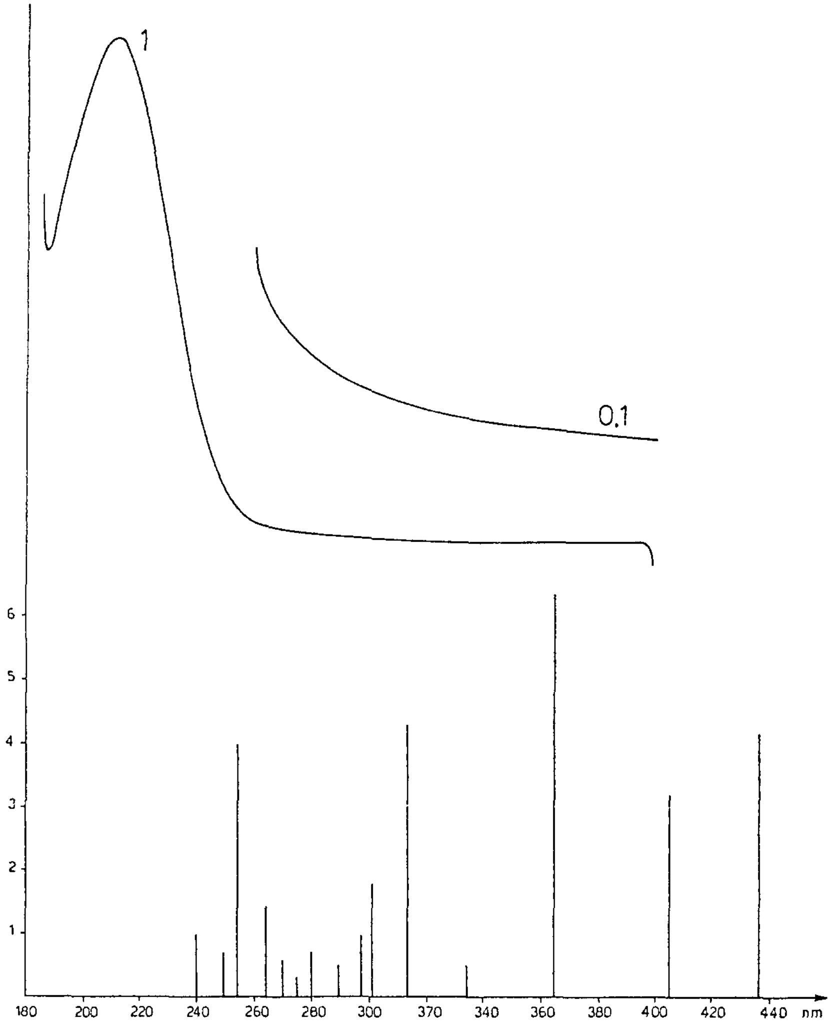
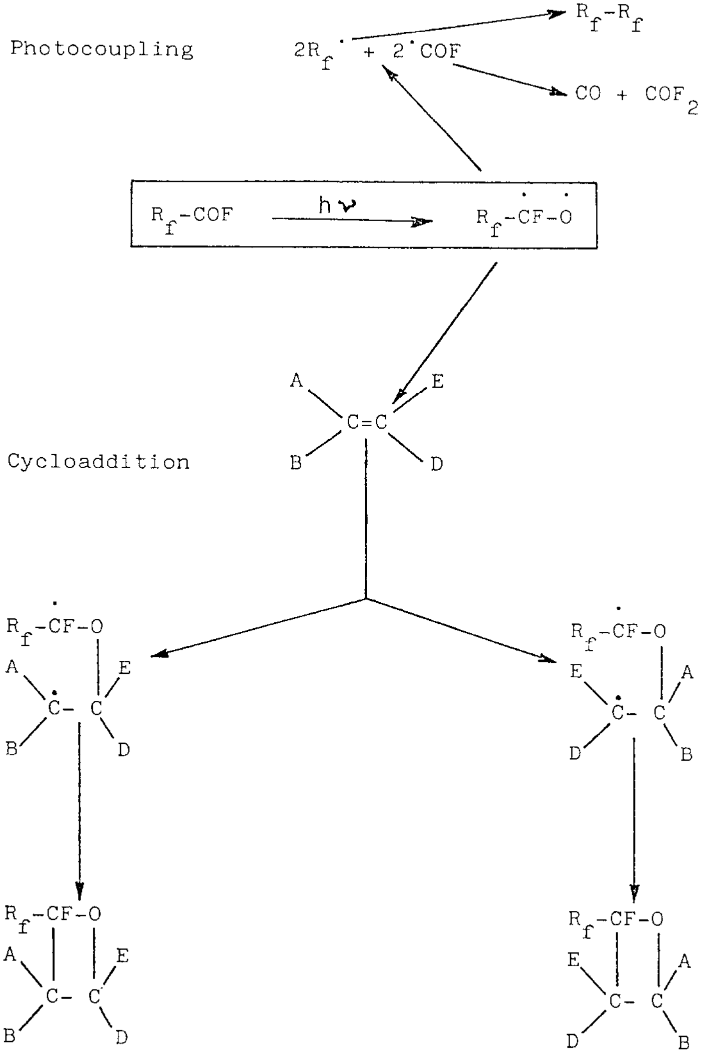


Fig. 1. UV spectrum of the carboxylic acid fluorides (a)compared with the lamp emission (b).

The perfluoroetheroxetanes are low viscosity liquids (η = 2.1 cSt, 20°C, for compound 2) with the density in the same range as that of the perfluoropolyethers (I) (IV) (d = 1.805 g/ml, 20°C, for compound 2). Their average boiling points are usually proportional to the MW. On the contrary compound 5, even



Scheme 1. Reactions of carboxylic acid fluorides promoted by UV radiation

though its molecular mass is the same as that of compound 4, boils 12°C higher. Compound 8 behaves similarly : both of them are characterized by unbranched substituents (Fig. 2).

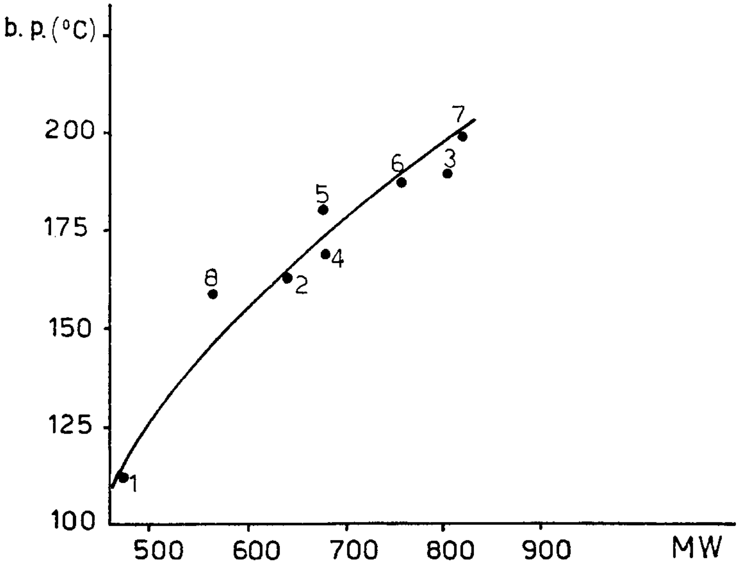


Fig. 2. Relationship between MW and bp.

The thermal stability of the perfluoroether oxetanes is good, even in air. Compound 2 can be heated in nitrogen up to 450°C with no decomposition: in air the onset of decomposition is at 400°C.

Discussion

The suggested mechanism of formation of the oxetanes involves the excitation of the carbonyl group followed by addition, probably in a stepwise mode, with oxygen first, to the unsaturated center of the olefin (Scheme 1) [2] .

The regioselectivity depends on the stability of the intermediate diradical. The carbon-carbon bond is preferably formed between the carbons giving the most highly stabilized radicals : the higher the stability, the higher is the yield of the corresponding product.

The photocycloaddition of carbonyl derivatives to electron poor alkenes is considered to be highly regiospecific and only 2,3-perfluoroalkyl disubstituted perfluorooxetanes were obtained [3] . However the oxetanes expected from the same pair of reagents can be either 2,3- and 2,4- disubstituted and each can exist in the cis or trans form. Furthermore, taking into account the presence of asymmetric centers, the synthesized perfluoroether oxetanes can include more than one species.

Hence the properties given should be those of mixtures. In general this is true for bulk properties (such as tendency to solidify) and the NMR and GC.

The thermoanalysis DSC does not indicate crystallization phenomena : at very low temperatures only second order transitions can be observed. In the homologous series 1, 2, 3 (compounds with increasing MW) the glass transition temperature (Tg) occurs at increasing temperatures. The oxetane 8, lacking ether bonds shows a sharp melting point at -39°C.

The NMR spectra are very complex (Fig. 3). From an examination of the spectra (Table 2) it is evident that the chemical shift e (175-190 ppm) is present only when R'_f is located in 3. However the expected integration ratios are not usually obtained. Only the reference oxetane 8 gives signals whose intensity is within the error limits of the instrument. In the other cases the difference is large (from 20% to 40%) leading to the conclusion that isomers 2,3 and 2,4 are present together. No information can be given for the oxetanes 5 and 6 which lack the signal e. The ring CF_2 group, which is possible

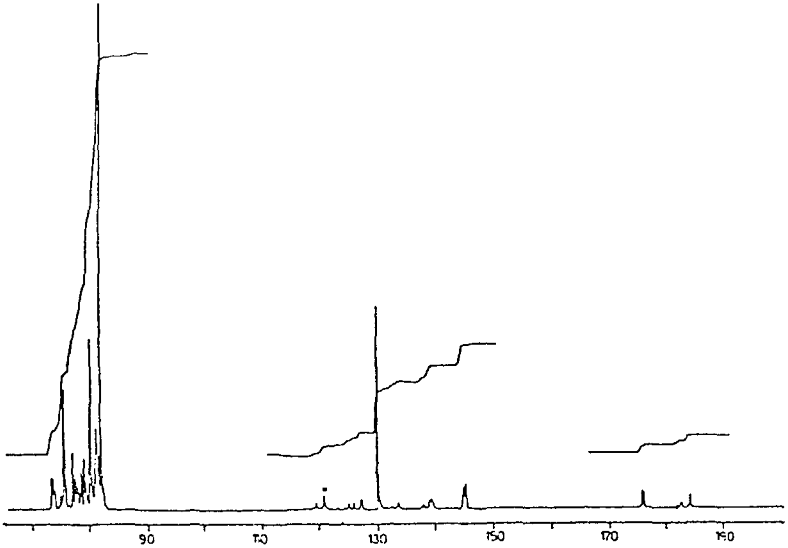
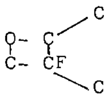


Fig. 3. ^{19}F NMR spectrum of compound 2 (Spectrometer Varian XL 200).

TABLE 2

^{19}F NMR Chemical Shifts of the perfluoroether oxetanes according to substituents

Ref.	Chemical shifts (or range) (CCl_3F)	Assignments	Oxetanes involved (*) according to the location of substituents	
			2,3-	2,4-
a	50	CF_3-O-	7	7
b	70-90	CF_3-C- $C-CF_2-O$	all	all
c	130	$C-CF_2-C$	all but 7	all
d	120-145	$C-\underset{\substack{\vert \\ C}}{C}F-O$	all	all
e	175-190		all but 5,6	none

(*) Reference number of Table 1.

TABLE 3

Distribution of perfluoroetheroxetane isomers

Compound	LOCATION (NMR)		MAIN PEAKS (GC, area %)			
	2,3	2,4				
1	71	29	9	40	26	25
2	79	21	6	34	49	11
3	60	40	9	43	48	
4 *	64	36	56	44		
5 *	100		40	50	8	2
6	100		2	89	9	
7 **	76	24				
8 *	93	7	66	34		

(*) The interpretation of the NMR is affected by the presence of some branched isomers in the reagents.

(**) GC interpretation was not possible since the carboxylic reagents were a mixture.

only for the 2,4 disubstitution, should increase the intensity of the signal c (130 ppm), but this has not been verified.

On the basis of what has been discussed and from the measurement of the intensities, the ratio between the two isomers was calculated (Table 3).

Gas-chromatography (Fomblin Y/Chromosorb) shows several badly defined peaks which confirm the complexity of the reaction products (Table 3).

We can conclude that, unlike the perfluoroalkyl oxetanes, the perfluoroetheroxetanes can be both 2,3 and 2,3/2,4 disubstituted.

Without entering into the electronic structure of the diradical intermediates [4], we can assume that the oxygen atoms close to the functional groups of the reagents play an important role in their stabilization.

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