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REACTIONS OF POLYFLUOROALKENES WITH ENOLATE ANIONS OF ALDEHYDES

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SUMMARY

Reactions of alkenes CF_2=CFX (X = Cl, CF_3) with aldehydes Ph(R)CHCHO (R = CH_3, Ph) and alkenes X-PhCF=$CFCF_3$ (X = H, p-NO_2) with diphenylacetaldehyde (R = Ph) in two-phase systems have been investigated. It has been found that these reactions proceed exclusively via the enolate form of anions of the aldehydes to give fluoroalkyl-vinyl ethers from alkenes CF_2=CFX, and divinyl ethers X-PhCF=$CFCF_3$.

INTRODUCTION

Anions generated from carbonyl compounds by abstraction of the α-hydrogen atom can be represented by two electronic arrangements: a carbanion, and an ion having the negative charge localised on the oxygen atom. Both types of anions were trapped in reactions with alkyl halides to give products of C-alkylation and O-alkylation, depending on the nature of the reagents and on the reaction conditions [1-3].

As a continuation of the studies of the reactions of polyfluoroalkenes with organic anions generated in catalytic two-phase systems [4] it was deemed of interest to look at the behaviour of mesomeric anions of aldehydes having α-hydrogen atoms. Phenylacetaldehyde, diphenylacetaldehyde, and 2-phenylpropionaldehyde were choosen as the precursors of the anions.

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RESULTS AND DISCUSSION

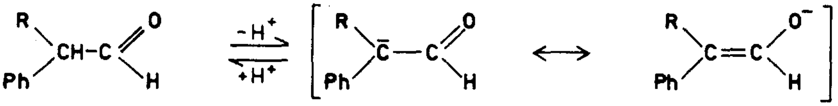
The reactions were conducted over the temperature range 35-70°C using two reaction systems:

system A - 50% aq. sodium hydroxide / benzene,

system B - solid potassium carbonate / dimethylformamide.

Tetra-n-butylammoniumhydrogensulphate (TBAH) was used as a phase-transfer catalyst.

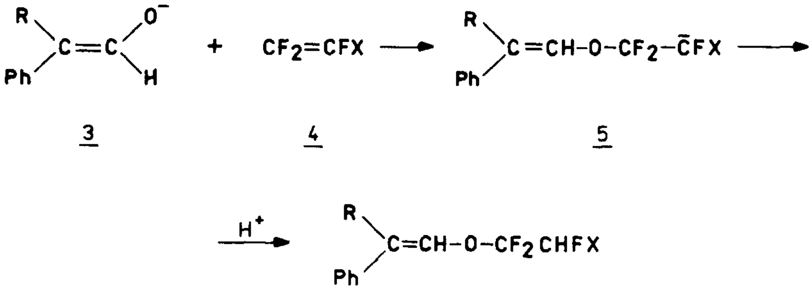
The attempted reactions with phenylacetaldehyde failed; the reaction mixture consisted of ca. 90% of the unreacted aldehyde and a number of minor components which could neither be isolated nor identified.



1 2 3

1a, 2a, 3a, R = CH_3

1b, 2b, 3b, R = Ph



3 4 5

6

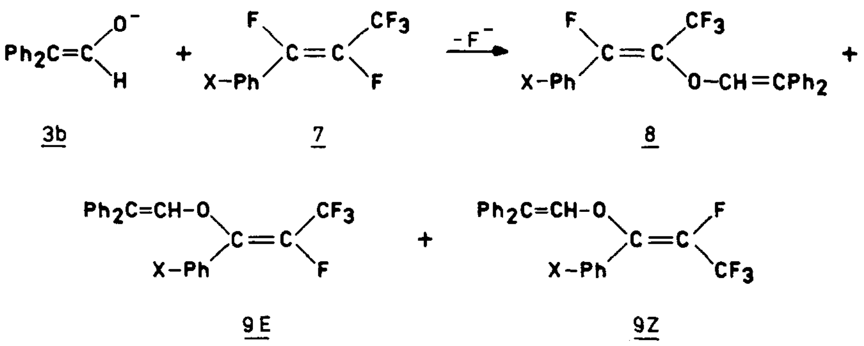
4a, X = Cl

4b, X = CF_3

	R	X
5a, 6a	CH_3	Cl
5b, 6b	CH_3	CF_3
5c, 6c	Ph	Cl
5d, 6d	Ph	CF_3

In contrast, 2-phenylpropionaldehyde 1a and diphenylacetaldehyde 1b reacted successfully with terminal fluoroalkenes 4a and 4b to give vinyl ethers 6a-d as the only isolable products together with the unreacted aldehydes and a tar-like material. These results have shown that the reactions involve exclusively enolate ions 3 and that the attack proceeds on the terminal CF_2 group of alkenes 4 followed by protonation of the intermediate carbanions 5. Neither products derived from the attack of carbanion-like form 2 nor products of the elimination of fluorine from 5 were found. Yields of ethers 6 were better in the case of the reactions with diphenylacetaldehyde 1b than for the reactions with 2-phenylpropionaldehyde 1a (Table 1) which could be interpreted in terms of the relative stabilities of the corresponding anions 3b and 3a.

The reactions of diphenylacetaldehyde 1b with 1-phenylpentafluoropropenes 7 (system B) also proceeded exclusively via enolate ion 3b.



7a, 8a, 9a, X=H ; 7b, 8b, X = p-NO_2

X	Products ratio*			Yield (mol %)
	8E	9E	9Z	
H	15	65	20	21
p-NO_2	100	—	—	35

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* Estimate from the integrated ^{19}F NMR spectra

TABLE 1

Yields, physical properties, and analyses of fluoroalkyl-vinyl ethers 6

$Ph(R)C{=}CH{-}O{-}CF_2CHFX$

Compound			B.p.	(C=C)	System A		System B		Elemental analysis			
					Temp.	Yield	Temp.	Yield	Found(calc.) (%)			
	R	X	(°C/torr)	(cm^{-1})	(°C)	(mol%)	(°C)	(mol%)	C	H	F	Cl
6a	CH_3	Cl	146-8/55	1650	50	30	50	29	52.9(52.7)	4.2(4.0)	22.5(22.7)	14.0(14.1)
6b	CH_3	CF_3	119-22/36	1635	70	25	50	27	50.9(50.7)	3.7(3.6)	39.8(40.1)	
6c	Ph	Cl	170-2/15	1675	50	61	35	68	61.6(61.5)	3.8(3.9)	18.4(18.2)	11.2(11.3)
6d	Ph	CF_3	159-60/18	1650	50	60	35	64	59.3(59.0)	3.6(3.5)	32.6(32.9)	

TABLE 2

^1H and ^{19}F NMR data for fluoroalkyl-vinyl ethers <u>6</u>, $Ph(R)C{=}\overset{a}{CH}{-}O{-}CF_2\overset{b}{CH}FX$

Compound			Chemical shifts, δ(ppm)*					Coupling constants (Hz)
	R	X	CH_3	H(a)	H(b)	CF_2**	F(b)	
<u>6a</u>^{x}	CH_3	Cl	1.78 s	6.66 s	5.80 dt	85.8	153.5 dt	$^2J(HF)=48.8$; $^3J(HF)=3.8$ and 4.4;
			1.98 s	6.84 s	5.98 dt	87.3		$^2J(FF)=152.0$; $^3J(FF)=13.0$
<u>6b</u>^{x}	CH_3	CF_3	1.90 s	6.70 s	4.75 dsx	not measured		$^2J(HF)=44.0$; $^3J(HF)=5.6$
			2.00 s	6.45 s	4.75 dsx			
<u>6c</u>	Ph	Cl		6.97 s	5.80 dt	85.9	153.8 dt	$^2J(HF)=48.0$; $^3J(HF)=4.1$;
						87.3		$^2J(FF)=144.0$; $^3J(FF)=12.0$
<u>6d</u>	Ph	CF_3^{xx}		7.00 s	4.65 dsx	80.1	212.7 dsx	$^2J(HF)=45.0$; $^3J(HF)=4.6$;
						82.3		$^2J(FF)=166.0$; $^3J(FF)=11.3$

s - singlet, d - doublet, t - triplet, sx - sextet

* From internal TMS for ^1H (positive downfield) and from internal CCl_3F for ^{19}F (positive upfield)

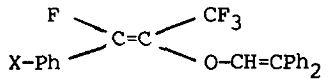
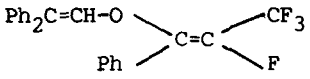
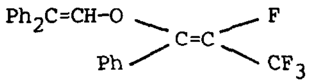
** AB patterns

^{x} A mixture of the E and Z isomers

^{xx} $\delta(CF_3)$ = 74.9 ppm (d, broad)

TABLE 3

^1H and ^{19}F NMR data for divinyl ethers 8 and 9

Compound		Chemical shifts, δ(ppm)*			$J(F-CF_3)$ (Hz)
		=CH-	=CF-	CF_3	
	8aE	6.28 s	129.3 q	64.4 d	29.3
	8bE	6.60 s	127.9 q	64.5 d	22.4
	9aE	6.46 s	159.6 q	64.6 d	9.8
	9aZ	6.53 s	150.3 q	65.0 d	13.4

s - singlet, d - doublet, q - quartet

* From internal TMS for ^1H (positive downfield) and from internal CCl_3F for ^{19}F (positive upfield).

Divinyl ethers 8a and 9a were formed by the attack of 3b on the C-2 carbon (bound to the CF_3 group) and on the benzylic carbon C-1 of alkene 7a, respectively. This is in accord with the earlier reported reactions [5-7] which have shown that 1-phenylpentafluoropropenes are susceptible to nucleophilic attack on both vinylic carbons C-1 and C-2.

The reaction of anion 3b with 1-(p-nitrophenyl)pentafluoropropene 7b gave exclusively product 8b of the attack on the C-2 carbon, thus showing strong polarisation of the double bond in 7b. Alkenes 7 are, in general, less reactive as compared to alkenes 4; total yields of products 8 and 9 did not exceed 35%.

Compounds 6 were isolated from the reaction mixtures by vacuum distillation and their boiling points and elemental analyses are given in Table 1. The ^1H and ^{19}F NMR spectra (Table 2) allowed these compounds to be unequivocally identified as fluoroalkyl-vinyl ethers.

Compounds 8 and 9 were separated from the tar by the column chromatography on silica-gel (8a, 9aE, and 9aZ were analysed as a mixture); the ^1H and ^{19}F NMR data are given in Table 3. The typical, large fluorine - CF_3 group coupling constants [8] identified both 8a and 8b as the isomers E. Analysis of the relative chemical shifts of numerous ethoxy-, alkyl-, and aminosubstituted 1-phenyltetrafluoropropenes [5-7] suggested structure 9 for compounds showing high field signals of the vinylic fluorines. The assignment of the E and Z forms for 9 was based on the relative magnitude of the F - CF_3 coupling constants [5-7].

EXPERIMENTAL

Boiling points were obtained by distillation and are uncorrected. NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer; chemical shifts are in ppm from internal CCl_3F for ^{19}F spectra (positive upfield) and from internal TMS for ^1H spectra (positive downfield). IR spectra were recorded with a Beckman Acculab spectrometer (film).

2-Phenylpropionaldehyde, diphenylacetaldehyde, chlorotrifluoroethylene, and hexafluoropropene were pure grade commercial reagents. 1-Phenylpentafluoropropene was prepared according to the procedure developed in this laboratory [9]; the E isomer of a 99 % purity was separated by distillation through a Büchi Fisher-type column. 1-(p-Nitrophenyl)pentafluoropropene (the E isomer) was obtained by nitration of 1-phenylpentafluoropropene [10] and fractional crystallisation.

Reactions of 2-phenylpropionaldehyde 1a and diphenylacetaldehyde 1b with chloro-trifluoroethylene 4a and with hexafluoropropene 4b

A. A mixture of the aldehyde (20 mmoles), benzene (10 ml), TBAH (0.07 g), and a concentrated (50%) aqueous solution of sodium hydroxide (6 ml) was warmed up to the required temperature (Table 1) and then, while vigorously stirring, the alkene was introduced from a gas-burette. When the equimolar amount of the alkene was reacted, the stirring was continued at the same temperature for 1 hour. The reaction mixture was diluted with water and extracted three times with benzene. The combined extracts were washed with dilute sulphuric acid followed by water and dried over anhydrous magnesium sulphate. The residue obtained after removal of the solvent was subjected to vacuum distillation to give products 6 as colourless oily liquids.

B. The alkene was introduced to a vigorously stirred mixture of the aldehyde (20 mmoles), dry potassium carbonate (4.6 g, 33 mmoles), TBAH (0.07 g), and dry dimethylformamide (5 ml) as in A. After completion of the reaction, water was added and the products were extracted with ether and isolated by distillation.

Reaction temperatures and yields are given in Table 1.

Reactions of diphenylacetaldehyde 1b with 1-phenylpentafluoropropenes 7a and 7b.

A mixture of aldehyde 1b (2 g, 10 mmoles), dry potassium carbonate (2.8 g, 20 mmoles), TBAH (0.05 g), and dimethylformamide (5 ml) was warmed up to the required temperature (70°C for 7a and 50°C for 7b) and, while vigorously stirring, the alkene (10 mmoles) was slowly added dropwise. The reaction was continued for 1 hour and then quenched by addition of water and an organic product was extracted with ether. Removal of the solvent and the unreacted aldehyde by vacuum distillation gave viscous oily liquids (1.5 g, 35% yield of 8b and 0.8 g, 21% yield of a mixture of 8a, 9aE, and 9aZ). Analytical samples were obtained by column chromatography on silica-gel using benzene as the eluent.

Analysis: Found for the mixture 8a and 9a: C, 72.1; H, 4.4; F, 19.4%. Calculated for $C_{23}H_{16}F_4O$: C, 71.9; H, 4.2; F, 19.8%. Found for 8b: C, 64.5; H, 3.7; F, 17.3; N, 3.1%. Calculated for $C_{23}H_{15}F_4NO_3$: C, 64.3; H, 3.7; F, 17.7; N, 3.3%.

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