Journal of Fluorine Chemistry, 21 (1982) 201--219

Received: March 5, 1982

NUCLEOPHILIC REACTIONS OF FLUOROOLEFINS. II. REGIOSELECTIVITY AND ELIMINATION-ADDITION COMPETITION IN THE REACTION OF 1-PHENYLPENTAFLUOROPROPENES WITH SODIUM ETHOXIDE

Wojciech DMOWSKI

Institute of Organic Chemistry, Polish Academy of Sciences, 00-961 Warsaw (Poland)

SUMMARY

1-Phenylpentafluoropropene and its para-substituted analogs 1 are susceptible to nucleophilic attack at both vinylic carbon atoms C-1 and C-2. They react with ethanolic sodium ethoxide to give predominantly substitution products, 1-ethoxy-1-phenyltetrafluoropropenes 2 and 2-ethoxy-1-phenyltetrafluoropropenes 3, with only little formation of adducts, viz. 2-ethoxy-1H-1-phenylpentafluoropropanes 4. Alkenes 1, where the para-substituent X = H,Cl,and CF_3 give additionally 1,2-diethoxy-1-phenyltrifluoropropenes 5 and, where X = CF_3 also 2,2-diethoxy-1H-1-phenyltetrafluoropropane 6. Overall regioselectivity of nucleophilic attack of the ethoxide ion on alkenes 1 exhibits the Hammett type correlation with σ_p values of substituents X: CH_3O and CH_3 groups favour the attack on the vinylic carbon C-1, while CF_3 and Cl substituents direct the attack on the C-2 carbon of alkenes 1. The E and Z isomers of 1-ethoxy and 1,2-diethoxy substituted alkenes 2 and 5 were formed in comparable amounts, while the E isomers of 2-ethoxy substituted alkenes 3 were always formed with a 93 - 97 % selectivity.

0022-1139/82/0000-0000/$02.75

INTRODUCTION

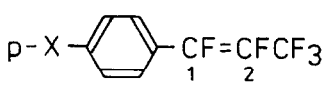
Results of our earlier work [1] , which concern reactions of 1-(2-tetrahydrofuryl)pentafluoropropene with a number of sodium alkoxides in parent alcohol solutions, stimulated further studies on the influence of substituents R in alkenes of the type $RCF{=}CFR_f$ on the direction of their reactions with nucleophiles. This paper discusses results of detailed studies on the reactions of ethanolic sodium ethoxide with 1-phenylpentafluoropropene (R=phenyl, $R_f{=}CF_3$) and p-substituted 1-phenylpentafluoropropenes 1a-e, which were prepared in this Laboratory in high yields [2] . Although, compounds 1a and 1e were previously reported to react with lithium diethylamide to give 1- and 2-substituted alkenes [3] , the authors claim that alkenes 1 do not react with sodium or potassium alkoxides. Since those reactions were carried out in an aprotic medium, nothing is known about a competition between substitution and addition.

RESULTS

In spite of the earlier statement [3] , 1-phenylpentafluoropropenes 1a-e reacted successfully with concentrated ethanolic sodium ethoxide at 80° to give complex mixtures of products. The conversion was very high and it can be seen (Table 1) from a decrease of the reaction time required for completing these reactions that the reactivities of alkenes 1a-e increase gradually with the electronegativity of p-substituents X .

The reaction mixtures were found to consist of compounds which arose from nucleophilic attack of ethoxide ion on either carbon atom C-1 or C-2 and also on both vinylic carbons of the reactant alkenes 1 .

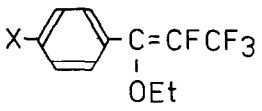
Substrates:



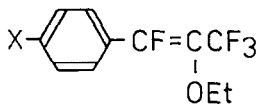
1

a: X = CH_3O d: X = Cl
b: X = CH_3 e: X = CF_3
c: X = H

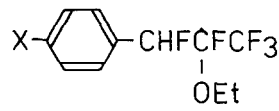
Products of the reaction of 1 with EtONa/EtOH:



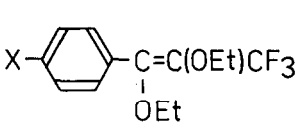
2a-e



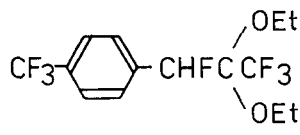
3a-e



4a-d



5c-e



6

The attack on the C-1 carbon of alkenes 1a-e resulted exclusively in replacing fluorine by the ethoxy group to give isomers Z and E of 1-ethoxy-1-phenyltetrafluoropropenes 2a-e. Similarly, the attack on the C-2 carbon led mostly to a substitution of fluorine to give 2-ethoxy-1-phenyltetrafluoropropenes 3a-e. In the case of alkenes 1a-d small amounts of saturated ethers 4a-d, formed by an addition of ethanol across the double bond of the reactant alkenes, were also obtained. In the case of more reactive alkenes 1c-e a replacement of both vinylic fluorines occured to some extent and gave isomers Z and E of 1,2--diethoxy-1-phenyltrifluoropropenes 5c-e. Unlike alkenes 1a-d, alkene 1e did not afford adduct 4e, but adduct 6 was formed with resonable yield.

Distribution of reaction products 2 - 6 and the ratio of their isomers in raw reaction mixtures are given in Table 1. The reaction products were provisionally identified as their mixtures by the ^{19}F and ^{1}H NMR spectrometry and the GLC-MS analyses but because of overlaping of some NMR signals and GLC peaks this identification was not certain and it was difficult to determine the contents of individual compounds. The reaction mixtures were divided by simple distillation into two fractions: lower boiling fractions containing compounds 2,3,and 4 and higher boiling fractions which consisted of the Z and E isomers of compounds 5. The former fractions were

TABLE 1

Reactions of 1-phenylpentafluoropropenes 1 with sodium ethoxide in ethanol[a].

Substrate XPhCF=CFCF$_3$[b]		Reaction time[c]	Conversion of 1	Product distribution									
				2		3		4	5		6		
no.	X	hrs.	%[d]	%	Z/E	%	Z/E	%	%	Z/E	%		
1a	CH_3O	18	77	77.8	10/12	18.7	2/98	3.5					
1b	CH_3	16	91	55.8	13/10	36.2	3/97	8.0					
1c	H	14	99	40.1	15/10	46.1	4/96	9.7	4.1	10/32			
1d	Cl	6	96	20.1	36/10	60.3	3/97	7.7	11.3	10/22			
1e	CF_3	3	96	6.0	36/10	59.3	7/93		23.6	10/10	11.1		

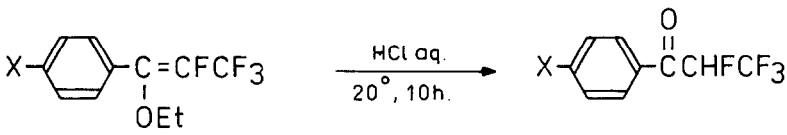
[a] 0.05 mole 1, 0.15 mole Na, and 60 ml EtOH were used in each experiment

[b] Z/E = 1/4 approximately

[c] all reactions were carried out at 80°

[d] based on GLC analysis of the crude reaction mixtures

treated with concentrated hydrochloric acid at 20° under which conditions the ethoxy groups of 1-ethoxyalkenes 2 were hydrolised quantitatively to give ketones 7, whereas 2-ethoxyalkenes 3 and adducts 4 remained unaffected.



2a-d 7a-d (100%)

In this manner, the total number of individual substances (inclusive of the Z and E isomers) were reduced by one and further, the GLC retentions of ketones 7 were different from those of the original compounds enough to determine the contents of all components in the resultant mixtures and thereafter their preparative GLC isolation and full identification. A mixture obtained from alkene 1e was simple enough to be separated directly without hydrolysis. However, products 5e(Z) and 6 appeared as one GLC peak and they were identified and determined from the NMR spectra, only.

Physical properties and analyses of compounds 2,3,4, and 5 are given in Table 2 and of compounds 7 in Table 3. Infrared spectra of tetrafluoropropiophenones 7 exhibited two absorptions for the carbonyl group. Since NMR spectra (Table 5) showed no evidence for the presence of the enol form of these compounds, the above behaviour should be attributed to the Fermi effect.

Comparison of chemical shifts of the CF_3 groups and vinylic fluorines in the ^{19}F NMR spectra of compounds 2 (Table 4) with chemical shifts of the corresponding signals of 1-alkoxy-1-(2-tetrahydrofuryl)tetrafluoropropenes previously reported [1], allowed us to assign appropriate signals to the Z and E isomers of compounds 2. Similarly assigment of the CF_3 group signals to the Z and E forms of compounds 5 (Table 4) was based on a comparison of chemical shifts of these signals with the corresponding signals of compounds 3. In all cases signals due to the CF_3 groups and vinylic fluorines (if present) of the E forms appeared characteristically at slightly higher field than

TABLE 2

Physical properties and analyses of compounds 2 - 5 .

Compd.[a]	B.p. °C	ν(C=C) cm^{-1}	$M^{+\cdot}$ m/e(rel.int.)[b]	Found (%)				Calculated (%)			
				C	H	F	Cl	C	H	F	Cl
2e		1690	302(14)	47.7	3.1	44.0		47.7	3.0	44.0	
3a			264(37)	54.8	4.6	28.6		54.5	4.6	28.8	
3b	226-227	1670	248(88)	57.9	4.8	30.7		58.1	4.9	30.6	
3c	200	1672	234(48)	56.2	4.2	32.5		56.4	4.3	32.5	
3d	229-230	1670	268,270(54,18)	49.2	3.3	29.3	13.1	49.2	3.4	28.3	13.2
3e	207	1675	302(26)	47.7	3.2	44.1		47.7	3.0	44.0	
4b			268(15)	53.8	4.9	35.7		53.7	4.9	35.4	
4c	193-197		254(5)	51.9	4.5	37.1		52.0	4.4	37.4	
4d	225-226		288,290(15,5)	45.6	3.3	32.8	12.2	45.8	3.5	32.9	12.3
5c		1655	260(100)	59.9	5.6	21.9		60.0	5.8	21.9	
5d	ca.240	1655	294,296(93,30)	53.1	4.7	19.2	12.2	53.0	4.8	19.3	12.0
5e		1660	328(18)	50.9	4.3	35.0		51.2	4.3	34.7	

[a] compounds 2a - 2d, 4a, and 6 were not isolated; only GLC-MS and NMR identification

[b] the most intense peaks were used as datum base; $[M-C_2H_4]^+$ for compounds 2 and 3, $[XPhCHF]^+$ for compounds 4, and $[M-C_4H_9]^+$ for compounds 5.

TABLE 3

Physical properties and analyses of tetrafluoropropiophenones 7 .

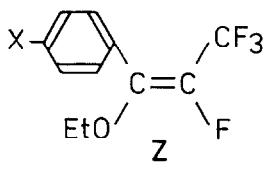
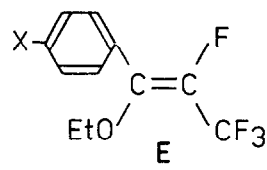
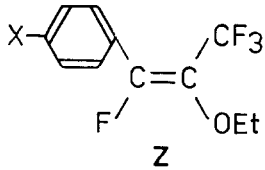
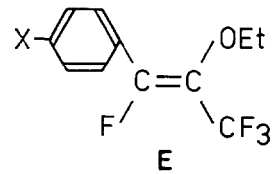
Compd.	M.p. °C	ν(C=O)[a] cm^{-1}	M$^{+\cdot}$ m/e(rel.int.)[b]	Found (%)				Calculated (%)			
				C	H	F	Cl	C	H	F	Cl
7a	38-39	1698 1680	236(19)	50.7	3.3	32.4		50.9	3.4	32.2	
7b	36-37	1705 1685	220(9)	54.6	3.5	34.5		54.6	3.7	34.5	
7c	40-41	1712 1692	206(2)	52.3	2.8	36.9		52.4	2.9	36.9	
7d	64-65	1712 1695	240(10) 242(3)	44.7	1.9	31.6	14.6	44.9	2.1	31.6	14.7

[a] in CCl_4

[b] the most intense peak $[XPhCO]^+$ was used as datum base.

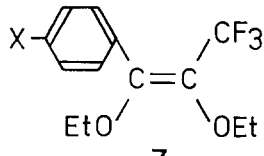
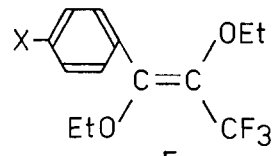
TABLE 4

^{19}F NMR data of compounds 2,3, and 5 [a].

Compound no.	X	Ø(CF_3) ppm	Ø(F) ppm	J(F-CF_3) Hz	Ø(CF_3) ppm	Ø(F) ppm	J(F-CF_3) Hz
		 Z			 E		
2a	CH_3O	63.8	155.8	12.6	65.8	164.0	10.0
2b	CH_3	64.0	155.8	12.8	66.0	163.3	10.0
2c	H	64.0	156.0	12.7	66.2	163.3	9.6
2d	Cl	64.1	154.5	12.7	66.1	161.7	10.0
2e	CF_3	64.3 Ø(CF_3Ph)=63.3	154.5	12.6	64.4 Ø(CF_3Ph)=63.7		10.0
		 Z			 E		
3a	CH_3O				63.7	131.9	21.6
3b	CH_3	64.0		8.8	64.1	132.5	22.5
3c	H	64.0		9.4	64.1	132.0	21.9
3d	Cl	64.2		8.8	64.3	134.1	22.8
3e	CF_3	64.2		8.8	64.3 Ø(CF_3Ph)=61.2	131.5	22.2

(continued on facing page)

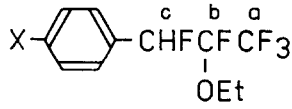
TABLE 4 (Continued)

	 Z	 E
5c	62.7	63.8
5d	62.6	63.8
5e	63.5 $\phi(CF_3Ph)$=62.6	$\phi(CF_3Ph)$=63.4

a) Chemical shifts are related to internal CCl_3F, positive upfield. The CF_3 group signals of compounds 2 and 3 appeared as doublets, and of compounds 5 as singlets. Signals of vinylic fluorines appeared as quartets.

TABLE 5

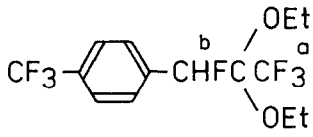
^{19}F and ^{1}H NMR data of compounds 4, 6, and 7 [a].

Compound		$\phi(CF_3)$	$\phi(F)$	$\phi(CHF)$ $\delta(C\underline{H}F)$	Coupling constant, J
no.	X	ppm	ppm	ppm	Hz
					Two diastereoisomers
4a	CH_3O	76.7(d) 78.3(d)			F_aF_c = 10.7
4b	CH_3	76.9(d)	135.4(d)	192.8(dqn)	F_cH_c = 44.0 F_aF_c=F_bF_c=11.0
		78.6(d)	146.3	192.6(dqn)	F_cH_c = 44.0 F_aF_c=F_bF_c=13.2

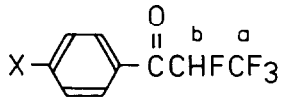
(continued overleaf)

TABLE 5 (continued)

		77.1(d)	135.0(d)	194.0(dqn)	F_cH_c=44.5, F_bH_c=3.5
4c	H			5.5(dd)	F_aF_c=F_bF_c= 10.6
		78.6(d)	146.0(dd)	193.2(dqn)	F_cH_c=45.6, F_bH_c=16.0
				5.4(dd)	F_aF_c= F_bF_c= 13.2
		77.1(d)	135.1(d)	195.0(dqn)	F_cH_c=45.6, F_bH_c=3.3
4d	Cl			5.6(dd)	F_aF_c= F_bF_c= 10.6
		78.7(d)	147.0(dd)	195.0(dqn)	F_cH_c=45.0, F_bH_c=16.0
				5.5(dd)	F_aF_c= F_bF_c= 13.0



6	73.6(d)		194.0(dq)	F_bH_b = 46.2
	ϕ(CF_3Ph)=64.4		5.6(d)	F_bF_a = 11.0



7a	CH_3O	75.0(dd)		199.1(dq)	F_bH_b=46.9, F_bF_a=12.6
				5.5(dq)	F_aH_b = 6.6
7b	CH_3	74.9(dd)		199.7(dq)	F_bH_b=46.1, F_bF_a=12.7
				5.7(dq)	F_aH_b = 6.8
7c	H	75.1(dd)		201.2(dq)	F_bH_b=46.0, F_bF_a=12.5
				5.7(dq)	F_aH_b = 6.6

(continued on facing page)

TABLE 5 (continued)

7d	Cl	74.9(dd)	199.1(dq)	F_bH_b=46.9, F_bF_a=12.5
			5.6(dq)	F_aH_b = 6.7

d = doublet, q = quartet, qn = quintet

a) Chemical shifts are related to internal CCl_3F (positive upfield) for ^{19}F and to internal TMS (positive downfield) for ^{1}H .

those for the Z forms. Compounds 3 were subjected to NMR investigations (Table 4) as mixtures of the E and Z isomers so, signals due to vinylic fluorines of the low abundant isomers Z (2 - 7%) were to weak to be detected.

It is worth pointing out that the ^{19}F NMR signals of the CF_3 groups bonded to sp^2 (Table 4) and sp^3 (Table 5) carbon atoms appeared characteristically within the regions of 62-65 ppm and 73-79 ppm, respectively.

DISCUSSION

Regioselectivity of the attack of the ethoxide ion

The ratios of 1-ethoxy and 2-ethoxysubstituted products 2 and 3 (Table 1) were found to be strongly dependent on the ring substituents X. Substituents which donate electrons to the aromatic system, like methoxy and methyl groups, favour the attack of the ethoxide ion on vinylic carbon C-1 while electron withdrawing substituents, like chlorine and the CF_3 group, direct the attack to vinylic carbon C-2.

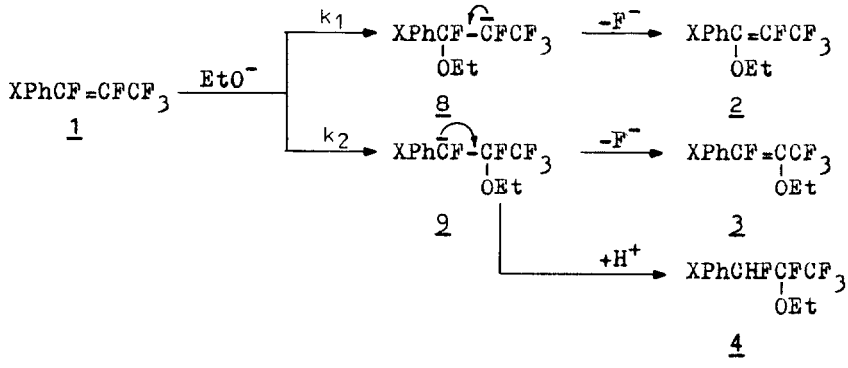
The tendency to form 1,2-disubstituted products 5 also increases with the electronegativity of the ring substituents X. It was evidenced by monitoring the course of the reaction by GLC, that 1,2-diethoxyalkenes 5 were formed mostly at the expense of 2-ethoxyalkenes 3 initially formed. This last result and also the fact that adducts 4 and 6 were

formed by the attack on vinylic position 2 allowed us to determine the overall regioselectivities of the attack of the ethoxide ion on 1-phenylpentafluoropropenes 1. They are shown in Table 6.

TABLE 6
Regioselectivity of the attack of ethoxide ion on 1-phenylpentafluoropropenes 1.

Substrate		% of the attack at:		C-2/C-1
no.	X	C-1	C-2	ratio
1a	CH_3O	77.8	22.2	0.285
1b	CH_3	55.8	44.2	0.792
1c	H	40.1	59.9	1.494
1d	Cl	20.7	79.3	3.831
1e	CF_3	6.0	94.0	15.666

Results of a number of works [5,6,7] including our earlier observations [1] suggest that in nucleophilic reactions of fluoroalkenes, unsaturated products are formed directly from intermediate carbanions via elimination of fluoride ion (tetrahedral mechanism) rather then by a subsequent dehydrofluorination of saturated products formed by protonating these carbanions. Thus, the main course of the reaction of 1-phenylpentafluoropropenes 1 with sodium ethoxide in ethanol must proceed as follows:



From kinetic studies on reactions of gem-difluoroalkenes of general formula $PhCR{=}CF_2$, when R = CF_3, CF_2Cl, CF_2H and CF_3CF_2, with sodium alkoxides in parent alcohol solutions, Koch and co-workers [7] concluded that the rate determinig step in these reactions is the attack of alkoxide ion on the alkene to generate a carbanion intermediate. Since fluoride ion is a better leaving group than are alkoxide ions [8], formation of such intermediates must be irreversible.

The above experimental evidence suggests that the orientation in the reaction of 1-phenylpentafluoropropenes 1 with ethoxide ion is controlled kinetically and may be interpreted in terms of the relative susceptibility of the reactive centres C-1 and C-2 to the nucleophilic attack, rather than of the stability of the possible carbanion intermediates 8 and 9. Then, the C-2/C-1 ratios (Table 6) are ratios of the rate constants k_2 and k_1 for the formation of carbanions 9 and 8*. Figure 1 represents a plot of $\log k_2/k_1$ versus σ_p values [9] of substituents X, according to the equation:

$$\log k_2/k_1 = (\rho_2 - \rho_1)\,\sigma_p + \log k_2^o/k_1^o$$

where: k_1 and k_2 are rate constants for the reaction of ethoxide ion with any alkene 1 at carbons C-1 and C-2,
k_1^o and k_2^o are the corresponding rate constants for the reactions of ethoxide ion with alkene 1c, where X = H,
ρ_1 and ρ_2 are rection constants for the reactions of ethoxide ion with a set of alkenes 1 at carbons C-1 and C-2, respectively.

---

* For two competitive irreversible reactions of the same order with respect to each of the substrates the ratio of concentration of products is determined by the ratio of the corresponding rate constants of these reations independently of the reaction order, reaction time, and the initial concentration of the substrates [4].

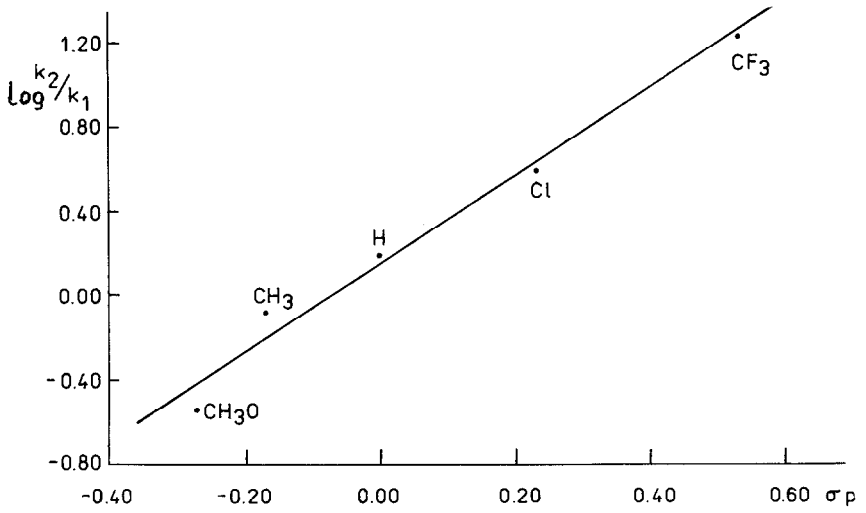


FIG. 1. Correlation between relative rates of the ethoxide ion attack on carbons C-2 and C-1 in 1-phenylpentafluoropropenes 1 and σ_p constants of the benzene ring substituents X of these compounds.

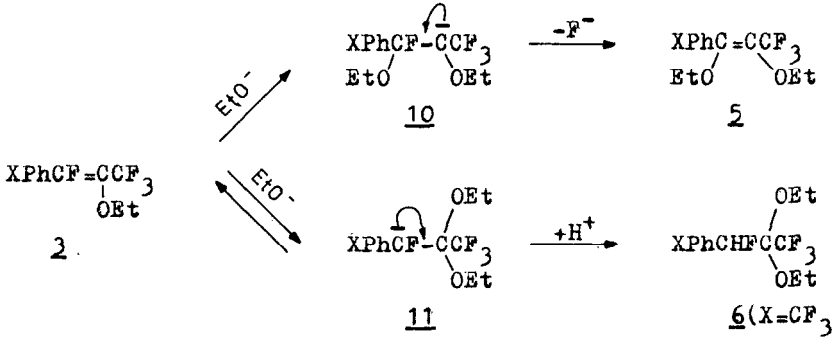
The plot indicates good correlation for all substituents so, it may be concluded that the orientation of the attack of ethoxide ion on 1-phenylpentafluoropropenes 1 is a linear function of the sum of resonance and field effects of the benzene ring substituents X of these compounds.

In these reactions, a difference of constant ρ_1 and ρ_2 values ($\rho_2 - \rho_1$ = ca.2) is a measure of the relative sensitivity of the reactive centres C-1 and C-2 to the influence of the benzene ring substituents X.

In the reactions of alkenes 1 with sodium ethoxide, the attack on the vinylic carbon C-2 is more favoured than in the corresponding reactions with lithium diethylamide reported by by Nguyen et al. [3] . In the latter reactions the C-2/C-1 ratio was 8/92 for alkene 1c and 50/50 for alkene 1e. A reasonable explanation of these results seems to be that steric factors play an important role in the reactions with lithium diethylamide but they are less important or negligible in the

reactions with the ethoxide ion; possibly, the benzene ring causes less steric blockage for the nucleophilic attack than does the trifluoromethyl group.

A subsequent attack of ethoxide ion on 2-ethoxy-1-phenyltetrafluoropropenes 3 (and probably also on 1-ethoxy-1-phenyltetrafluoropropenes 2) led in most cases exclusively to 1,2-diethoxyalkenes 5. A small yield of 2,2-diethoxy substituted compound 6 was obtained only from alkene 3e, where X is trifluoromethyl group.These facts can be explained on the bases of presumed properties of the intermediate carbanions involved. Only vic-diethoxy carbanions 10 are capable of stabilising themselves by the irreversible loss of fluoride ion to give 1,2-diethoxyalkenes 5. Gem-diethoxy carbanions 11 must be, in general, unstable and they are in an equilibrium with substrates 3 and only in the case when strong electron withdrawing substituent X is present in the phenyl system are they stable enough to react with a proton from a solvent to give saturated 2,2-diethoxy compounds.



Formation of unsaturated products in the reactions of 1-phenylpentafluoropropenes 1 with sodium ethoxide showed a different stereochemistry for the reactions at carbons C-1 and C-2. The E and Z isomers of 1-ethoxy substituted alkenes 2 were essentially formed in comparable amounts, but the ratio of isomers of 2-ethoxy substituted alkenes 3 were within the range of 2/98 to 7/93 in favour of isomers E (Table 1). Since, in these reactions formation of products is controlled kinetically, the ratio of isomers must be influenced by the conformational stability of the reactive intermediate involved.

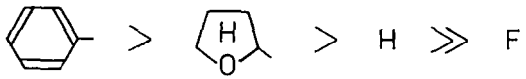
However, the analysis of the Newman projections of carbanions 8 and 9 gives no satisfactory explanation to the high stereosectivity of substitution on vinylic carbon C-2 as compared with substitution on carbon C-1. Stereoselectivity in nucleophilic reactions of 1-phenylpentafluoropropenes will be discussed in more detail in a later paper.

Elimination-addition competition

In the reactions of 1-phenylpentafluoropropenes 1 with ethanolic sodium ethoxide saturated compounds were formed as very minor products; they arose exclusively from the attack of ethoxide ion on vinylic carbon C-2 (Table 1, compounds 4). No adducts were formed from the attack on carbon C-1 bearing the phenyl substituent. These are rather surprising results as compared to the analogous reactions with 1-(2-tetrahydrofuryl)-pentafluoropropene and 1H-pentafluoropropene previously reported [1], which gave the corresponding 1-ethoxy-2H-adducts with 11 and 25 % yields, respectively.

Total lack of adducts of the type $PhCF(OEt)CHFCF_3$ from the reactions of alkenes 1 with ethanolic sodium ethoxide can be attributed to a particularly high ability of carbanions 8 to eject a fluoride ion from a position α to the phenyl substituent, which in turn can be due to the mesomeric influence of this substituent weakening the adjacent carbon - fluorine bond. High rate of fluoride ion elimination from carbanions 8 gives no chance for competitive protonation to proceed.

Koch et al. [7] assigned an order of leaving group ability for a fluoride ion from various environments. It may be concluded that this ability is inversely proportional to the strength of a carbon-fluorine bond which is going to break. Results of the present and earlier work [1] give an order of leaving group ability for a fluoride ion from carbanions of the type $RCF(OEt)\bar{C}FCF_3$ (carbanions 8) depending on the nature of substituents R as follows:



Formation of adducts 4 in the present reactions, via carbanions 9, has been preceded by the formation of adducts $PhCHFCF_2OEt$, $PhCHClCF_2OEt$, and $PhCH(CF_3)CF_2OEt$ with 56,40,and 15 % yields, respectively [5,7] . Intermediate carbanions involved in the above series follow another order of leaving group ability for a fluoride ion:

$$Ph\bar{C}F\underset{CF_3}{C}FOEt > Ph\bar{C}\underset{CF_3}{C}F_2OEt \gg Ph\bar{C}ClCF_2OEt > Ph\bar{C}FCF_2OEt$$

The latter order is not clear. It seems to be a result of the sum of following factors: strength of the carbon-fluorine bond for the atom adjacent to the lone pair, carbanion stability, and steric factors of competing protonation reaction.

EXPERIMENTAL

Melting and boiling points are uncorrected. NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer. Mass spectra were obtained with an Analytical GCMS System LKB-2091 and IR spectra were recorded with a Beckmann IR 4240 spectrometer. GLC separations were performed with a Chromatron GCHF.18.3.4 instrument (G.D.R.) using a 3.5 m x 4 mm column for analytical work and 4.0 m x 10 mm column for preparative work, both columns packed with Chromosorb G coated with 3 % silicon oil SE-52.

Reactions of 1-phenylpentafluoropropenes 1 with sodium ethoxide

A solution of sodium ethoxide prepared from sodium metal (3.5 g, 0.15 mole) and absolute ethanol (60 ml) was warmed up under a reflux condenser to 80° and than an alkene 1 (0.05 mole) was added in one portion and the reaction mixture was stirred

at 80° for the required time. The course of the reaction was monitored by taking small samples (ca.0.5 ml) diluting them with water and analysing the organic layer by GLC. Finally, the reaction mixture was diluted with water, adjusted with hydrochloric acid to pH = 7.5 and the organic material was extracted with ether. The extract was dried over $MgSO_4$, the solvent was removed and the residue was subjected to GLC, MS, and ^{19}F and ^{1}H NMR analyses. The amounts of crude samples were as follows: 14.0 g from 1a, 12.3 g from 1b, 11.0 g from 1c, 13.5 g from 1d, and 15.5 g from 1e .

At first, the crude samples were investigated by spectral methods, then they were subjected to vacuum distillation and two fractions were collected: a lower boiling fraction containing compounds 2,3,and 4, and a higher boiling fraction containing compound 5. The latter fraction was further purified by preparative GLC. Also the lower fraction obtained from alkene 1e was subjected directly to preparative GLC separation. The lower fractions obtained from alkenes 1a - 1d were hydrolysed as below.

Hydrolysis of compounds 2, 3, and 4

Fractions containing compounds 2, 3, and 4 were mixed with five volumes of concentrated hydrochloric acid and stirred together at 20° for 18 hours, then neutralised with Na_2CO_3 and extracted with ether. The solvent was distilled off and the residue was subjected to GLC and spectral investigations. Preparative GLC separation gave pure compounds 3 (E and Z mixtures), 4 and ketones 7. Compounds 2 were absent.

ACKNOWLEDGMENTS

Comments and discussion on elimination - addition competition by Professor H.F.Koch of Ithaca College, Ithaca N.Y., are greatfully acknowledged.

This work has been supported by the Polish Academy of Sciences within the project MR-I-12.

REFERENCES

1 W.Dmowski, J.Fluorine Chem., 15 (1980) 299
2 W.Dmowski, J.Fluorine Chem., 18 (1981) 25
3 T.Nguyen, M.Rubinstein, C.Wakselman, J.Fluorine Chem., 11 (1978) 573
4 K.Schwetlick, Kinetische Methoden zur Untersuchung von Reaktions-mechanismen, VEB Deutscher Verlag der Wissenschaften, Berlin (1971) p.83
5 H.F.Koch, A.J.Kielbania,Jr., J.Am.Chem.Soc., 92 (1970) 573
6 R.J.Koshar, T.C.Simmons, F.W.Hoffmann, J.Am.Chem.Soc., 79 (1957) 1741
7 H.F.Koch, J.G.Koch, D.B.Donovan, A.G.Toczko,A.J.Kielbania,Jr., J.Am.Chem.Soc., 103 (1981) 5417
8 C.J.M.Stirling, Acc.Chem.Res., 12 (1979) 198
9 C.Hensch, A.Leo, S.H.Unger, Ki Hwan Kim, D.Nikaitani, E.J. Lien, J.Med.Chem., 16 (1973) 1207; J.March, Advanced Organic Chemistry, McGraw-Hill (1977) p.253