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NUCLEOPHILIC REACTIONS OF FLUOROOLEFINS.
IV.* REGIOSELECTIVITY IN THE REACTIONS OF 1-PHENYLPENTA-
FLUOROPROPENES WITH ALKYL LITHIUM REAGENTS**

Wojciech DMOWSKI

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

SUMMARY

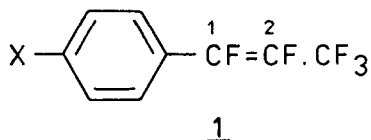
Reactions of 1-phenylpentafluoropropenes 1a-c with a number of alkyl lithium reagents were investigated in detail. In all cases mixtures of 1-alkyl-1-phenyltetrafluoropropenes 2 and 2-alkyl-1-phenyltetrafluoropropenes 3 were obtained. The ratio of products 2 and 3 is strongly influenced by both the electronegativity of the benzene ring substituents and the bulk of the alkyl group of the alkyl lithium reagents. The increase of both of these factors favours formation of 2-alkyl-substituted alkenes 3 with a reduced yield of 1-alkyl-substituted alkenes 2. The influence of the benzene ring substituents in alkenes 1 obeys the Hammett type correlation, while the influence of the bulk of the alkyl lithium reagents exhibits good relationships with the Fellous and Luft scale of steric substituent constants E_s^x ; no linear correlation with other scales of steric constants was found. Overall regioselectivity in the reaction of 1-phenylpentafluoropropenes 1 with alkyl lithium reagents, considering both the influence of the benzene ring substituents and steric factors, is expressed by the Pavelich-Taft type equation. Observed direction of the influence of the bulk of the alkyl lithium reagents on the ratio of products 2 and 3 is interpreted in terms of steric strains influencing the geometry and free energy of the supposed intermediates involved in these reactions.

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INTRODUCTION

1-Phenylpentafluoropropenes 1 are unique fluoroalkenes which have proved to be susceptible to nucleophilic attack at both vinylic carbon atoms C-1 and C-2 .



a: X = CH₃

c: X = Cl

b: X = H

d: X = CF₃

It has been demonstrated [1] that in reactions of alkene 1 with ethanolic sodium ethoxide overall regioselectivity of the attack of the ethoxide ion gives a Hammett plot with σ_p values of the benzene ring substituents X. Electron withdrawing substituents effectively direct the attack of the ethoxide ion to vinylic carbon C-2 bearing the trifluoromethyl group, while electron donating substituents favour the attack on the C-1 carbon atom. The Hammett plot has a slope of ca. 2 ($\rho_2 - \rho_1$ value) indicating relative sensitivity of the reactive centres C-1 and C-2 to the influence of the ring substituents X. In alkenes 1a and 1b the inductive influence of the CF₃ group affecting the double bond is nearly counterbalanced by resonance and inductive effects of the phenyl substituent, so in the reactions of these compounds with sodium ethoxide comparable amounts of attack on both vinylic positions C-1 and C-2 are observed.

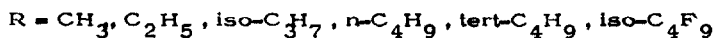
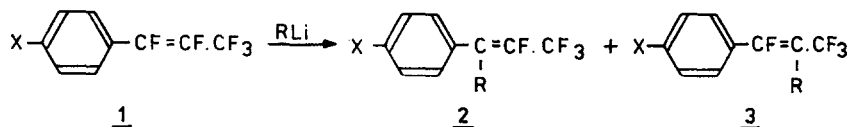
These results contrast with those obtained by Nguyen *et al.* [2] for the reaction of alkene 1b with lithium diethylamide, in which a 92% regioselectivity in favour of the attack on the C-1 carbon atom was reported. It seems reasonable that in the latter reaction high regioselectivity could be attributed to lower steric hindrance for the attack of bulky diethylamino moiety on the C-1 carbon atom than on the C-2 carbon bearing the trifluoromethyl group.

In view of above results it was interesting to study the influence of the bulk of the attacking nucleophiles on the regioselectivity of their reactions with 1-phenylpentafluoropropenes 1. The most convenient nucleophiles for such studies are alkyl lithium reagents. They allow for gradual change within a wide range of the bulk of nucleophilic species, while going from primary to tertiary alkyl groups, without changing the character of the nucleophilic centre. Moreover, a number of sets of steric effect values have been obtained for alkyl substituents [3,4,5,6]. The present paper reports results obtained on the reactions of 1-phenylpentafluoropropenes 1a-d with commercially available

methyl-, *n*-butyl-, and *tert*-butyl-lithium reagents, and of alkene 1b also with ethyl-, *iso*-propyl-, *iso*-butyl-, and phenyl-lithium reagents prepared from the appropriate alkyl halides and lithium metal.

RESULTS

1-Phenylpentafluoropropenes 1 reacted with alkyl lithium reagents to give mixtures of the *E* and *Z* isomers of 1-alkyl-1-phenyltetrafluoropropenes 2 and 2-alkyl-1-phenyltetrafluoropropenes 3.



Diethyl ether was used as a solvent for the reactions with methyl lithium (commercial solution) and *n*-hexane or *n*-pentane for the reactions with other alkyl lithium reagents. The reactions were carried out, in general, in the temperature range from 0 to 20°, but ethyl- and *iso*-butyllithium reagents required refluxing to complete the reaction. The reactions were monitored by GLC and when conversion of the reactant alkene reached 92 - 96 % they were quenched by addition of methanol and water. This procedure allowed the formation of di-alkyl-substituted products to be limited to trace amounts.

However, further substitution could not be avoided in the reaction with phenyllithium in which, even at early stages of the reaction, a considerable amount (ca.30%) of the disubstitution was observed. Thus, 1-phenylpentafluoropropene 1b reacted with phenyllithium in ethereal solution to give 1,1-diphenyltetrafluoropropene 4, the *E* and *Z* isomers of 1-fluoro-2-(trifluoromethyl)-stilbene 5, and 1,1,2-triphenyltrifluoropropene 6 in the ratio of 1 to 3.3 to 2.1. This latter result is of little value in the studies on regioselectivity.

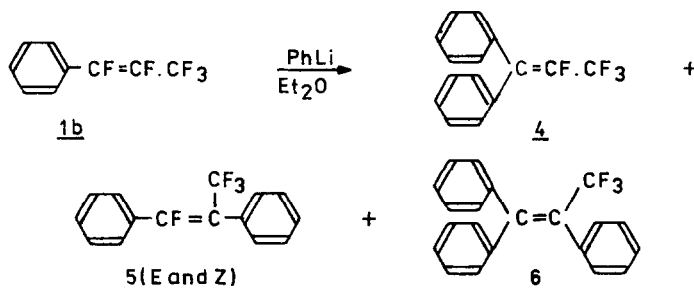


TABLE 1

Reactions of 1-phenylpentafluoropropenes 1 with alkyl lithium reagents

Substrates			Products distribution ^a				Ratio of products <u>3/2</u>
XPhCF=CFCF ₃ ^b		RLi	<u>2</u>		<u>3</u>		
no.	X	R	%	E/Z	%	E/Z	
<u>1a</u>	CH ₃	CH ₃	33.1	0.72	66.9	10.92	2.02
<u>1b</u>	H	CH ₃	27.9	0.67	72.1	7.80	2.58
<u>1c</u>	Cl	CH ₃	21.2	0.54	78.8	7.38	3.90
<u>1d</u>	CF ₃	CH ₃	15.8	0.20	84.2	4.80	5.33
<u>1b</u>	H	C ₂ H ₅	27.3	1.24	72.7	8.32	2.66
<u>1b</u>	H	iso-C ₃ H ₇	23.6	0.82	76.4	2.78	3.24
<u>1a</u>	CH ₃	n-C ₄ H ₉	21.5	0.41	78.5	5.04	3.65
<u>1b</u>	H	n-C ₄ H ₉	18.8	0.48	81.2	4.45	4.32
<u>1c</u>	Cl	n-C ₄ H ₉	15.9	0.64	84.1	6.25	5.29
<u>1d</u>	CF ₃	n-C ₄ H ₉	12.0	0.64	88.0	3.63	7.33
<u>1b</u>	H	iso-C ₄ H ₉	22.0	0.34	78.0	3.94	3.55
<u>1a</u>	CH ₃	tert-C ₄ H ₉	11.6	0.73	88.4	5.18	7.62
<u>1b</u>	H	tert-C ₄ H ₉	9.0	1.09	91.0	4.87	10.11
<u>1c</u>	Cl	tert-C ₄ H ₉	6.6	0.94	93.4	5.67	14.15
<u>1d</u>	CF ₃	tert-C ₄ H ₉	9.8	1.33	90.2	3.44	9.20
<u>1b</u>	H	C ₆ H ₅ ^c	15.7(<u>4</u>)		51.6(<u>5</u>)	4.33	3.28

^a GLC estimate in the row reaction mixtures .^b Z/E = 1/9 for compounds 1b and approx. 1/6 for compounds 1a,1c,1d^c Integrated ¹⁹F estimate. The reaction mixture also contained 32.7 % of 1,1,2-triphenyltrifluoropropene 6 .

TABLE 2

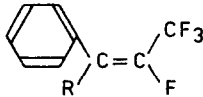
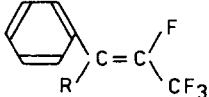
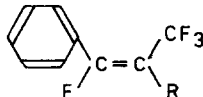
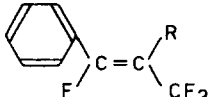
Physical properties and analyses of E-2-alkyl-1-phenyltetrafluoropropenes 3

Compound		B.p. (M.P.)	$\nu(\text{C}=\text{C})$	Found (calculated) %		
R	X	$^{\circ}\text{C}$	cm^{-1}	C	H	F
CH_3	CH_3	201-202	1685 1695	60.5(60.6)	4.5(4.6)	34.7(34.8)
	H	182.5	1688 1793	58.7(58.8)	4.0(4.0)	37.2(37.2)
	Cl^{a}	215.5	1685 1695	50.4(50.3)	2.9(3.0)	31.9(31.8)
	CF_3	193-194	1695 1698	48.8(48.5)	2.7(2.6)	48.8(48.9)
C_2H_5	H	193-194	1685 1695	60.4(60.6)	4.6(4.6)	34.7(34.8)
iso- C_3H_7	H	203-204	1672	62.0(62.1)	5.1(5.2)	33.0(32.7)
n- C_4H_9	CH_3	243-244	1680 1690	64.5(64.6)	6.0(6.2)	29.1(29.2)
	H	228-229	1685 1695	63.5(63.4)	5.6(5.7)	30.8(30.8)
	Cl^{b}	249-250	1680 1690	55.5(55.6)	4.6(4.7)	26.9(27.1)
	CF_3	224-225	1683	53.5(53.5)	4.1(4.2)	42.4(42.3)
iso- C_4H_9	H		1688	63.3(63.4)	5.5(5.7)	31.0(30.8)
tert- C_4H_9	CH_3	(37-39)	1665	64.2(64.6)	6.2(6.2)	28.9(29.1)
	H	223-224	1662	63.4(63.4)	5.7(5.7)	30.9(30.8)
	Cl^{c}	(38-40)	1665	55.3(55.6)	4.6(4.7)	27.2(27.1)
	CF_3	220-221	1665	53.6(53.5)	4.1(4.2)	42.3(42.3)
$\text{C}_6\text{H}_5^{\text{d}}$	H	(37-39)	1660 1670	67.8(67.7)	3.9(3.8)	28.3(28.5)

^a Found 14.9% Cl, calc. 14.9% Cl. ^b Found 12.8% Cl, calc. 12.6% Cl^c Found 12.7% Cl, calc. 12.6% Cl.^d Compound 5(E)

TABLE 3

¹⁹F NMR data of compounds 2, 3, 4, 5, and 6^a

Compound		$\phi(\text{CF}_3)$	$\phi(\text{F})$	$J(\text{F-CF}_3)$	$\phi(\text{CF}_3)$	$\phi(\text{F})$	$J(\text{F-CF}_3)$	
no.	R	p.p.m.	p.p.m.	Hz	p.p.m.	p.p.m.	Hz	
		 Z			 E			
<u>2</u>	CH ₃	65.2dq	130.2qq	10.0	65.2dq	130.2qq	8.0	
<u>2</u>	C ₂ H ₅	65.0	132.4qt	10.5	65.1	130.5	9.7	
<u>2</u>	iso-C ₃ H ₇	65.0	132.1	9.7	64.5	125.8	8.0	
<u>2</u>	n-C ₄ H ₉	65.2dt	131.7qm	10.0	64.8dt	130.1qm	8.5	
<u>2</u>	iso-C ₄ H ₉	64.8	130.2	10.0	64.0	128.8	8.6	
<u>2</u>	tert-C ₄ H ₉	64.4	123.9	8.1	62.5	113.2	8.1	
<u>4</u>	C ₆ H ₅	64.2	128.7	10.3				
		 Z			 E			
<u>3</u>	CH ₃	60.5	81.8qq	11.3	61.5	90.5qq	23.0	
<u>3</u>	C ₂ H ₅	58.2	83.3qt	11.5	59.6	87.9	20.4	
<u>3</u>	iso-C ₃ H ₇	56.9	80.0	10.1	56.3	84.8	21.5	
<u>3</u>	n-C ₄ H ₉	58.3	82.7qt	11.0	60.0	87.2	20.5	
<u>3</u>	iso-C ₄ H ₉	57.0	79.5	11.5	59.3	83.3	19.4	
<u>3</u>	tert-C ₄ H ₉	52.9	68.4	11.0	54.9	64.5	28.2	
<u>5</u>	C ₆ H ₅	56.1	76.3	12.7	58.3	92.6	24.2	
<u>6</u>	C ₆ H ₅	55.7s						

^a Chemical shifts are related to internal CCl₃F, positive upfield. If not indicated, the CF₃ group signals appeared as doublets and signals the vinylic fluorines as quartets. The data for compounds 2b and 3b, where X = H, are given. The data for other compounds in the series 2a-d and 3a-d were different from the reported ones ± 0.3 ppm for $\phi(\text{CF}_3)$, ± 3.0 ppm for $\phi(\text{F})$, and ± 0.3 Hz for $J(\text{F-CF}_3)$.

Distribution of the reaction products 2 and 3 (and also 4,5, and 6), their ratios, and the ratios of the E and Z isomers of these products are summarised in Table 1. The contents of individual compounds, inclusive of the geometric isomers, in the crude reaction mixture were determined by the GLC analysis. The most abundant compounds 3(E) were isolated by preparative GLC and identified by elemental analysis and ^{19}F and ^1H NMR spectrometry. Characteristic data and analyses of E-2-alkyl-1-phenyltetrafluoropropenes 3 are given in Table 2. Other compounds were identified as their mixtures after GLC purification by subjecting them to NMR investigations and elemental analysis; the latter were identical with those obtained for pure compounds 3(E).

Chemical shifts of the CF_3 groups and especially of vinylic fluorines of compounds 2 and 3 were characteristically different from each other (Table 3) allowing these compounds to be easily identified in their mixtures by ^{19}F NMR spectrometry. Also, the ^{19}F NMR investigations allowed the E and Z isomers of compounds 3 to be easily distinguished from the characteristic vinylic fluorine to the CF_3 group coupling constants. Assignment of the E and Z isomers of compounds 2 is somewhat ambiguous. It was based on the relative magnitude of coupling constants or chemical shifts in the ^{19}F NMR spectra of these compounds as compared with the data previously reported for 1-ethoxy-1-phenyltetrafluoropropenes [1].

DISCUSSION

Quantitative approach to the regioselectivity problem

The ratios of 2-alkylsubstituted products 3 to 1-alkylsubstituted products 2 (Table 1) considerably increased both with the increasing electronegativity of the ring substituents X and with the bulk of the alkyl groups R. These ratios were approximately two and a half times higher for the reactions of alkene 1d than of alkene 1a and four times higher for the reactions with tert-butyllithium than for the reactions of these same alkenes with methylolithium. As it is shown on Figure 1, the effect of alkyl groups R in alkyllithium reagents was practically the same for the reactions with all alkenes 1 i.e. independent of the nature of the ring substituents X and *vice versa*. A plot of the relative rates of the reactions at carbons C-2 and C-1 ($\log k_2/k_1$)* *versus* σ_p values [7]

* Relative rates k_2/k_1 were assumed to be equal to the ratios of the concentration of the corresponding products 3 and 2 [8].

of substituents X gave parallel lines for the reactions with methyl, n-butyl, and tert-butyl lithium reagents. The only exception was the reaction of tert-butyl lithium with alkene 1d for which the $\log k_2/k_1$ value deviated dramatically from the linearity obtained with alkenes 1a-c.

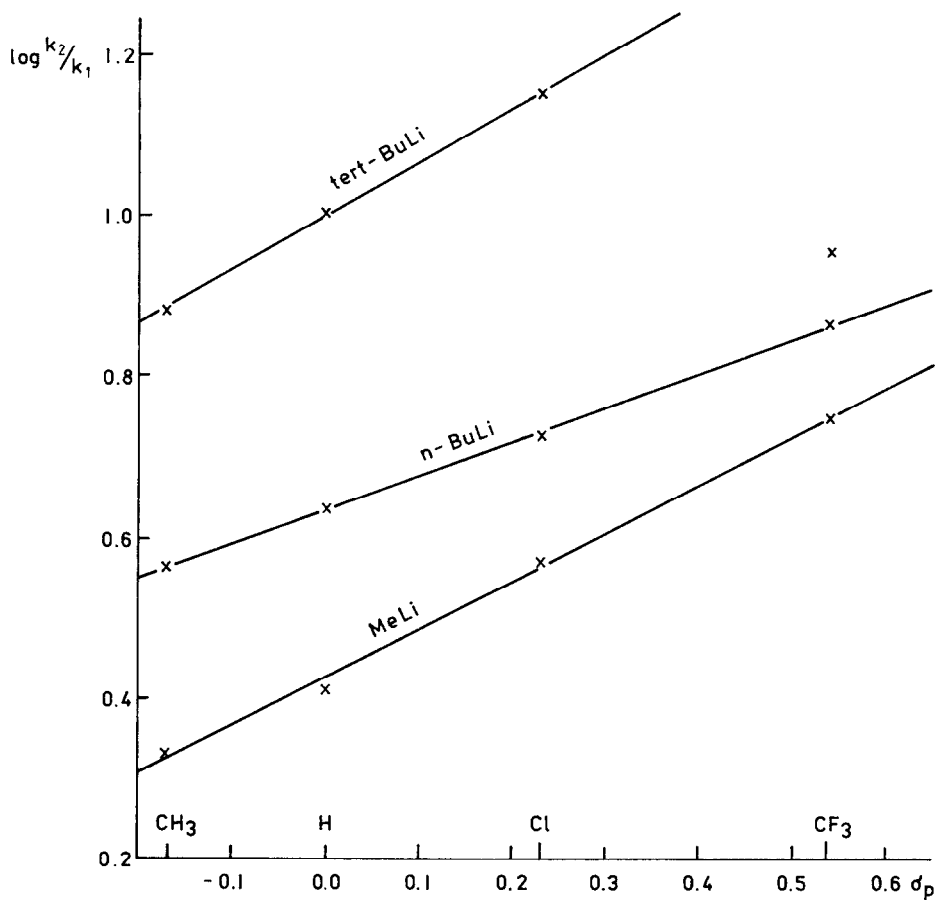


Fig. 1. Correlation of the relative rates of the reactions of 1-phenyl-pentafluoropropenes 1ad at carbons C-2 and C-1 with alkyl-lithium reagents .

By analogy to the reactions of alkenes 1 with sodium ethoxide [1], each line on Figure 1 is described by the equation :

$$\log k_2/k_1 = (\rho_2 - \rho_1) \sigma_p + \log k_2^0/k_1^0 \quad (1)$$

where: k_1 and k_2 are rate constants for the reactions of a given alkyl-lithium reagent with any alkene 1 at carbons C-1 and C-2.

k_1^0 and k_2^0 are the corresponding rate constants for the reactions with alkene 1b, where X = H .

ρ_1 and ρ_2 are reaction constants for the reactions at carbons C-1 and C-2, respectively .

In the above equation, the expression $\log k_2^0/k_1^0$ includes also steric interactions between the reagents, and for the reactions with alkene 1b (arbitrarily assumed as the reference compound) steric influence of alkyl lithium reagents on the ratios of 2-alkyl- to 1-alkyl-substituted products can be expressed by the-Taft type relationship :

$$\log k_2^0/k_1^0 = \Delta\delta E + \text{constant} \quad (2)$$

where E is a steric factor of alkyl group R and $\Delta\delta = \delta_2 - \delta_1$ is a proportionality factor, analogous to $\rho_2 - \rho_1$. The $\delta_2 - \delta_1$ value (a difference of the steric reaction constants) is a measure of the relative sensitivity of both reactive centres C-2 and C-1 to the bulk of the attacking nucleophile.

Consequently, an equation taking into account both the influence of the ring substituents X (mesomeric and field effects) in alkenes 1 and steric factors of alkyl groups R, is the Pavelich-Taft type equation :

$$\log k_2/k_1 = (\rho_2 - \rho_1) \sigma_p + (\delta_2 - \delta_1) E + \text{constant} \quad (3)$$

In order to determine the $\delta_2 - \delta_1$ value, attempts were made to correlate $\log k_2^0/k_1^0$ values, obtained for the reactions of 1-phenylpentafluoropropene 1b with six alkyl lithium reagents, with different sets of steric substituent constants available in the literature for alkyl groups. Although, $\log k_2^0/k_1^0$ values, in general, increased with the increasing steric constants of all sets, no straight-line correlation has been found with the Taft constants E_s [3] and Charton constants v_x and v'_x [5,6], even when ignoring the most deviant points obtained with n-butyllithium (Figure 2) . On the contrary, using the Fellous and Luft

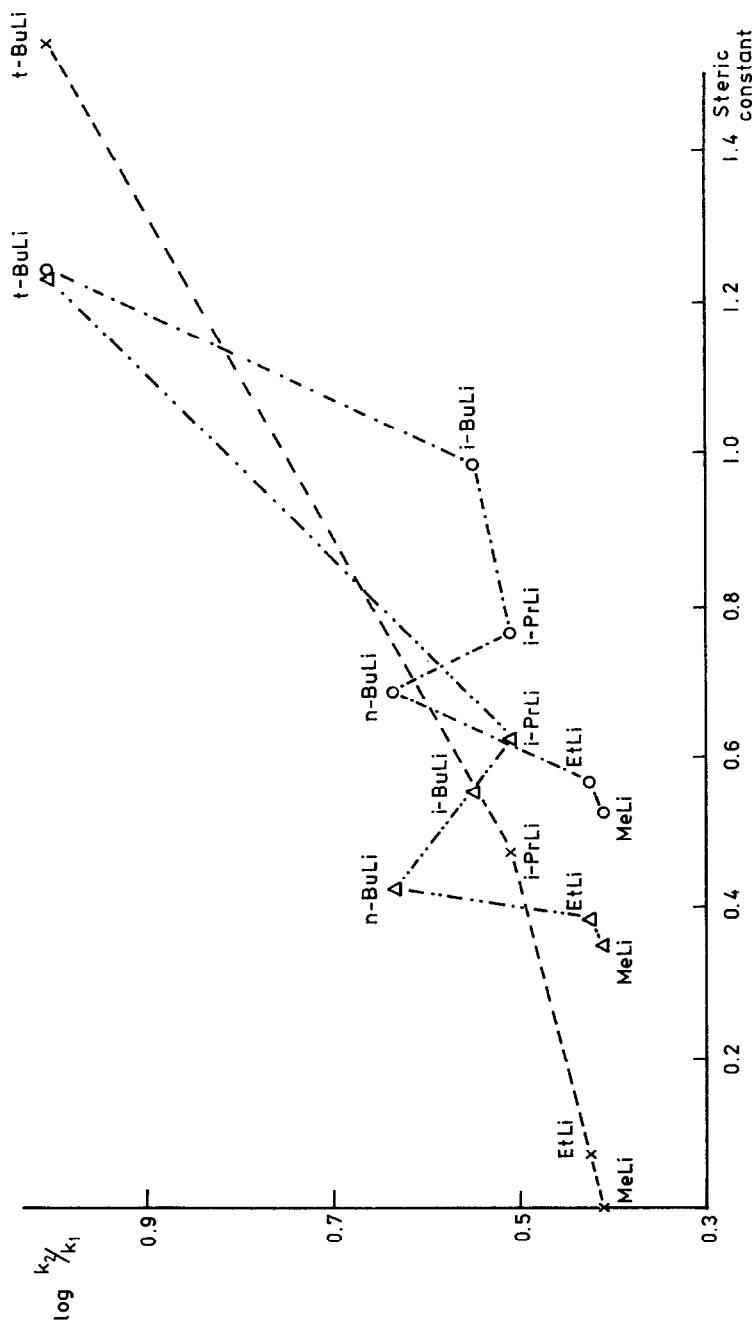


Fig. 2. Attempted correlation of the relative rates of the reactions of $\text{PhCF}=\text{CFCF}_3$ at carbons C-2 and C-1 with alkyl lithium reagents with different sets of steric substituent constants. Steric constants: x - E_s (Taft), o - v_x (Charton), Δ - v'_x (Charton)

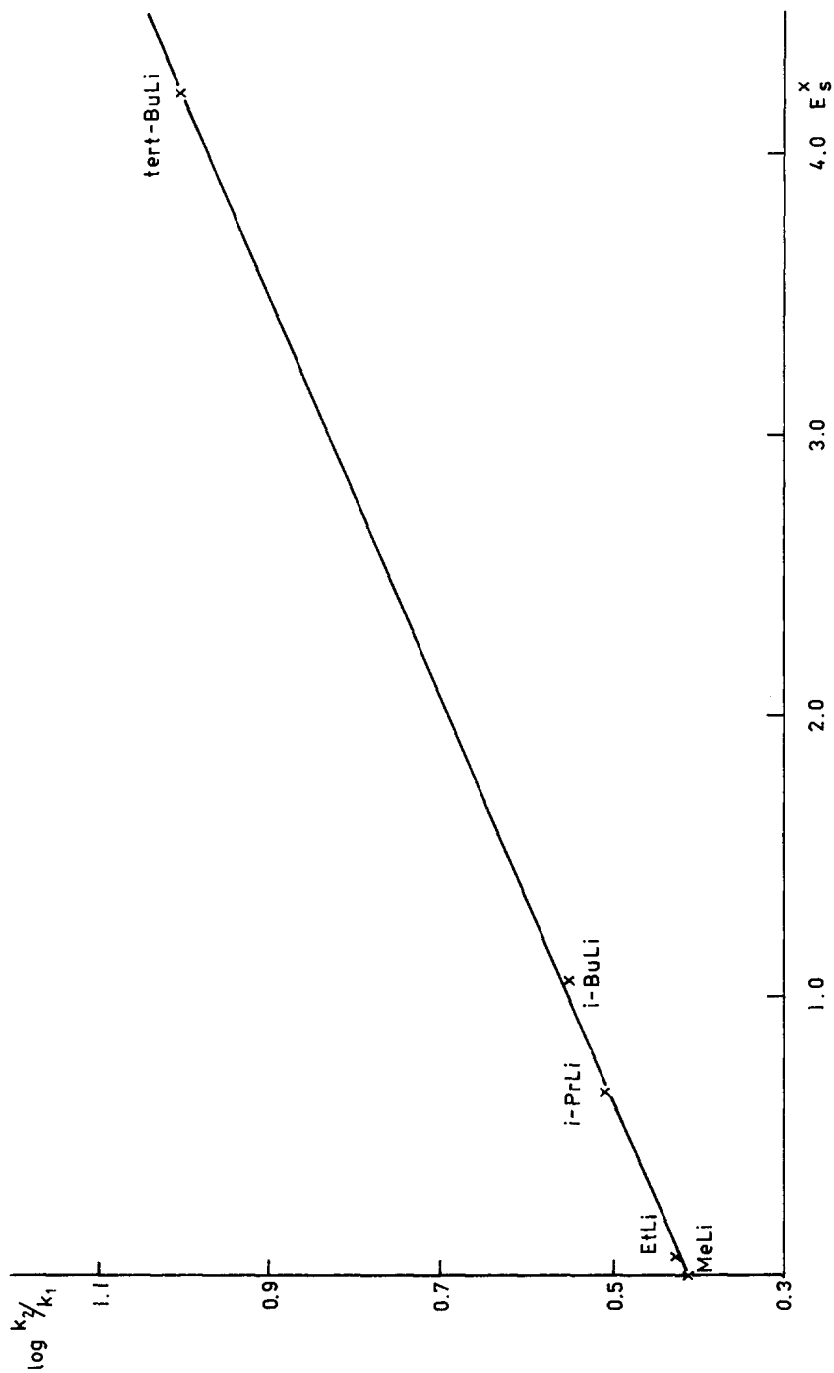


Fig. 3. Correlation of the relative rates of the reactions of $\text{PhCF}=\text{CFCF}_3$ at carbons C-2 and C-1 with alkyl lithium reagents with steric substituent constants E_s^x (Fellous and Luft).

scale of steric substituent constants E_s^x [4] good correlation for all alkyllithium reagents has been obtained (Figure 3). This correlation gives the $\delta_2 - \delta_1$ value of 0.140 .

Plots of $\log k_2/k_1$ versus σ_p values for the reactions of alkenes 1a-d with methyl-, n-butyl-, and t-butyl-lithium reagents (Fig. 1) give the $\rho_2 - \rho_1$ values equal to 0.60, 0.42, and 0.67, respectively (average 0.56).

Assuming the reaction of alkene 1b with methyllithium as the reference reaction ($\sigma_p = 0$, $E_s^x = 0$) a constant in the equation (3) has a value of 0.412. Thus, the ratio of 2-substituted to 1-substituted products 3 and 2 of the reaction of any alkene 1 with any alkyllithium reagent RLi can be calculated as follows :

$$\log k_2/k_1 = 0.56\sigma_p - 0.14E_s^x + 0.412 \quad (4)^*$$

On the other hand, equation (4) can be applied for a determination of new steric constants. For example, the ratio of products obtained in the reaction of n-butyllithium with alkene 1b and 1c (Table 1) gave for n-butyl group the E_s^x value of 1.60 and 1.53 (not quoted by Fel-lous and Luft).

Interpretation of an unusual steric effect on the regioselectivity

The trifluoromethyl group is quite bulky. The maximum van der Waals radius (perpendicular to the group axis) of the CF_3 group (2.743 Å) is somewhat closer to that of the tert-butyl group (3.150 Å) than to that of the methyl group (2.230 Å) [9]. The trifluoromethyl group, as shown by conformational studies of monosubstituted cyclohexanes, creates more steric strain than even the iodine atom, methyl group, or phenyl group [10,11,12]. Recently, Oberhammer [13] observed a considerable increase in the oxygen, nitrogen, and carbon bond angles in $O(CF_3)_2$, $N(CF_3)_3$, and $CH(CF_3)_3$ as compared with that in OF_2 , OCl_2 , $O(CH_3)_2$, NF_3 , NCl_3 , $N(CH_3)_3$, and CHF_3 , $CHCl_3$, $CH(CH_3)_3$, and concluded that steric requirements of CF_3 groups are greater than those of fluorine, chlorine, and methyl groups. By the magnitude of the Taft E_s [3] or Charton v_x [5,6] steric substituent constants one

* Since E_s^x constants are negative the sign 'minus' should be put before them in equation (4).

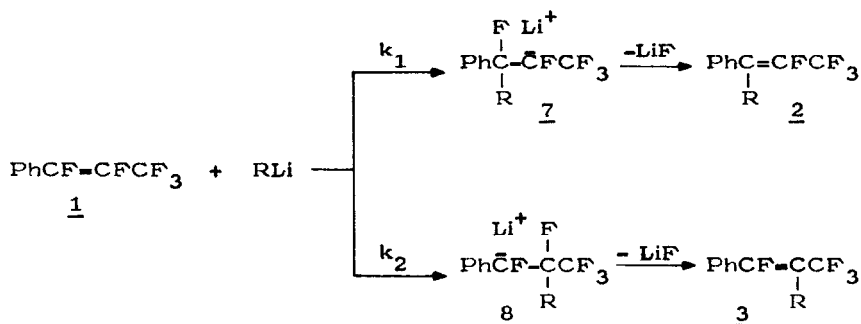
can consider the steric effect of the trifluoromethyl group ($E_s = -1.16$, $v_x = 0.91$) as similar to that of the sec-butyl group ($E_s = -1.13$, $v_x = -1.02$) or cyclohexyl group ($E_s = -0.99$, $v_x = 0.87$).

The magnitude of the steric effect of the phenyl group is not precise (two v_x values, 0.57 and 1.66 have been quoted [5]) but it is generally accepted that the phenyl substituent has only a moderate steric effect. This should be particularly true for substrates in which, due to conjugation, the phenyl substituent is co-planar with the multiple bond and the nucleophilic attack occurs perpendicular to the plane.

In the light of the above data it is quite obvious that the trifluoromethyl group creates more steric hindrance than does the phenyl ring so, it would be expected that the increasing bulk of alkyllithium reagents favours the reaction at the less-hindered carbon atom C-1. However, in contrast to this expectation, results of the present work have unambiguously shown that the increasing bulk of alkyllithium reagents effectively directs the substitution of an alkyl group for fluorine to the more hindered carbon atom C-2 bearing the trifluoromethyl group. This is rather a puzzling phenomenon.

It seems reasonable that, similar to the reactions of 2-phenyl-substituted fluoroalkenes reported by Koch and co-workers [14] and also to the reactions of alkenes 1 with the ethoxide ion reported in our earlier work [1], the reactions of alkenes 1 with alkyllithiums follow a two-step pathway in which formation of carbanion-like* intermediates 7 and 8 is the rate-limiting step.

* In contrast to alkyllithium reagents which apparently have a polar covalent carbon-lithium bond [15], by considering delocalisation of the negative charge due to mesomeric and inductive effects and also by considering the presence of large substituents hindering a close approach of cation and anion, intermediates 7 and 8 may be expected to have an essentially ionic carbon-lithium bond and therefore may be regarded as carbanions [15,16,17]. Resonance-stabilised organolithiums such as triphenylmethyl lithium and allylic organolithiums and also sterically crowded organometallic compounds have pronounced ionic character [15,16]. However, it is rather unlikely that in nonpolar solvents such as hydrocarbons, intermediates 7 and 8 exist in the form of free ions; contact or solvent-separated ion pairs are more likely.



All steps in these reactions are fully irreversible so, the reactions are kinetically controlled and the ratio of 1-substituted and 2-substituted products 2 and 3 is governed by the relative rates of the formation of both intermediates 7 and 8. These rates are, in turn, inversely proportional to the corresponding free-energies of activation ΔG_1^\ddagger and ΔG_2^\ddagger for the formation of these intermediates (Figure 4).

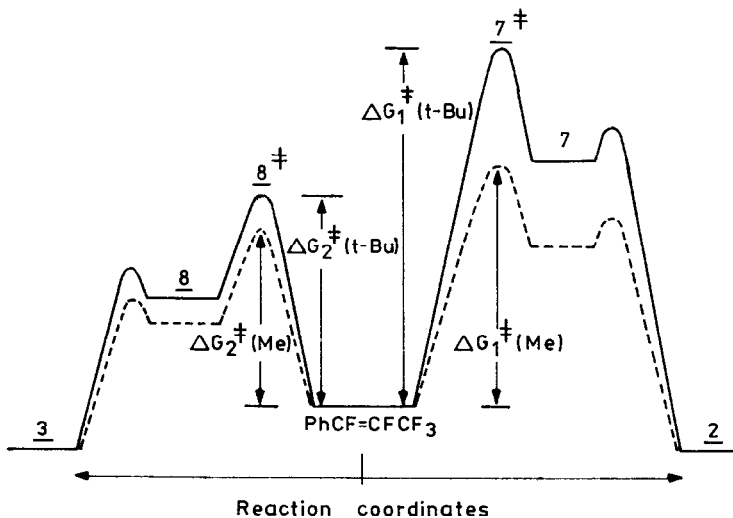


Fig. 4. Possible free-energy profiles for the reactions of 1-phenyl-pentafluoro 1b with methyl-lithium (dashed line) and tert-butyllithium (continuous line).

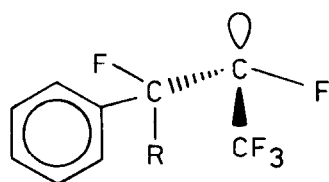
Thus, the increasing bulk of a nucleophile from methylolithium to tert-butyllithium results in an increase of the activation energy, more for the formation of carbanions 7 than for the formation of carbanions 8 $[\Delta G_1^\ddagger(\text{tert-Bu}) - \Delta G_1^\ddagger(\text{Me}) > \Delta G_2^\ddagger(\text{tert-Bu}) - \Delta G_2^\ddagger(\text{Me})]$. This phenomenon is opposite to that which could be expected on the basis of the structure of the substrates and implies that a solution of the problem of the steric factors - regioselectivity relationship is in the structure of transition states 7[‡] and 8[‡] leading to carbanions 7 and 8, rather than in steric hindrance in the reactant alkene to attack by alkylolithium reagents.

According to the Hammond postulate [18] structures of transition states 7[‡] and 8[‡] should resemble structures of the corresponding carbanions so that the effect of the bulk of alkyl substituents on the geometry and free-energy of these carbanions should be considered.

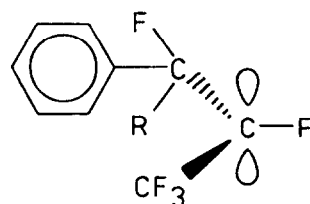
All evidence accumulated so far points out that, beside other factors, steric strains have a substantial influence on the geometry of carbanions [19,20]. In general, carbanions prefer pyramidal sp^3 hybridised geometry in which the lone pair of electrons has maximum s-character and thus, is closer to the nucleus [19,21]. However, on the basis of kinetic acidity studies of a series of halogenated carbon acids, Klabunde and Burton [22] concluded that carbanions $(CF_3)_2\bar{C}I$ and $(CF_3)_3\bar{C}$ are planar, largely as a result of steric repulsions between bulky substituents adjacent to the carbanionic centre*. Pyramidal geometry has also been derived for benzylic carbanions $Ph\bar{C}(CF_3)_2$ [23] and $Ph\bar{C}F_2$ [24] which were found to exhibit poor conjugation with the phenyl system; this is in contrast to the benzyl anion $Ph\bar{C}H_2$ which is obviously planar [19,20].

By analogy to the fluorocarbanions discussed above, both carbanions 7 and 8 should also be expected to have pyramidal geometry 7a and 8a. However, it seems reasonable that the increasing bulk of alkyl group R, and therefore of the carbanion substituents $PhC(R)F-$ and $CF_3C(R)F-$, forces a shift in geometry

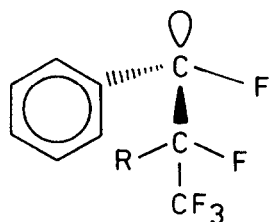
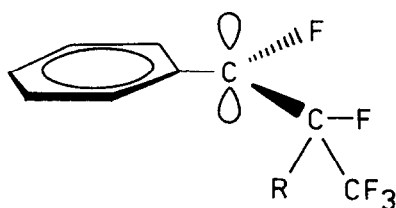
* In those studies high acidity of $(CF_3)_3CH$ and therefore high stability of its conjugated base $(CF_3)_3\bar{C}$ has been accounted for by the lack of a p-orbital electron feedback from α -fluorines and by the inductive effect of the CF_3 group, which are much larger than destabilisation of the carbanion from deviation from sp^3 hybridisation.

7a

pyramidal

7b

planar

8a8b

of these carbanions to planar 7b and 8b. Planar geometry is, however, energetically more tolerable for carbanions 8 than for carbanions 7. This is because, in contrast to carbanions 7, planar geometry of carbanions 8 is stabilized by a conjugation of the sp^2 hybridised lone-pair of electrons with the π -electron system of the aromatic ring, and this effect opposes the destabilisation due to the reduced s-character effect.

The above reasoning applies also to the carbanion-like transition states 7[‡] and 8[‡] and seems to be a logical explanation why the increasing bulk of alkyl substituents R has a less pronounced effect on the increase of the free-energy of activation ($\Delta G^\ddagger(\text{tert-Bu}) - \Delta G^\ddagger(\text{Me})$) for the formation of carbanions 8 than for the formation of carbanions 7.

In conclusion, unusual effects of the bulk of alkyllithium reagents on the regioselectivity of their reactions with 1-phenylpentafluoropropenes 1 is interpreted in terms of steric strains forcing planar geometry on intermediate carbanions 7 and 8 and the corresponding transition states 7[‡] and 8[‡]. Planar geometry is energetically more tolerable for benzylic transition state 8[‡] than for 7[‡] and this results in a lower free energy of activation and thus, higher rate of the formation of carbanions

8 and then 2-substituted products 3 , as compared with carbanions 7 and 1-substituted products 2. These effects are proportional to the bulk of alkyl groups R .

The effect of the phenyl ring substituents

The increasing electronegativity of the phenyl ring substituents X acts in accord with the bulk of the alkyl groups R in shifting the regioselectivity in the reactions of 1-phenylpentafluoropropenes 1 with alkyl-lithium reagents towards a substitution at the C-2 carbon atom. This is due both to the increasing susceptibility of this reactive centre, as related to the C-1 carbon atom, to the attack by a nucleophile, and to the enhanced conjugational and inductive delocalisation of the negative charge of planar species 8 and 8[‡] and thus, further decrease in the free-energy of activation for their formation. No reasonable explanation was found for the lower effect of the CF₃ group in alkene 1d than the effect of chlorine atom in alkene 1c in the reactions with tert-butyllithium

The reactions of alkenes 1 with alkylolithiums, as evidenced by a slope of the plots of $\log k_2/k_1$ versus σ_p (Figure 1), are less sensitive to the influence of the phenyl ring substituents than the corresponding reactions with sodium ethoxide reported earlier [1] ($\rho_2 - \rho_1 = 0.56$ and 2.0 , respectively). This may be simply because the absolute rates of the reaction with alkylolithiums are much higher (at least one order of magnitude) than with the ethoxide ion, and the difference between the rates of the reactions at carbon atoms C-2 and C-1 becomes less pronounced.

EXPERIMENTAL

Boiling and melting points are uncorrected. NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer, and IR spectra with a Beckmann IR AccuLab-TM-1 spectrometer. GLC separations were performed with a Chromatron GCHF.18.3.4 instrument (GDR) using a 3.5m x 4mm column for analytical work and 4.0m x 10mm column for preparative work, both columns packed with Chromosorb G coated with 3 % Silicon Oil SE-52 .

1-Phenylpentafluoropropenes 1a-d were prepared according to the procedure described previously [25]. Methylolithium, n-butyolithium, and tert-butyolithium were commercial reagents. Ethylolithium, iso-propylolithium, and iso-butyolithium were prepared in n-pentane from lithium metal and the corresponding alkyl chlorides. Phenylolithium was prepared in ethereal solution from lithium metal and bromobenzene.

Reactions of 1-phenylpentafluoropropenes 1a-d with alkylolithium reagents

A solution of 0.03 mole of alkene 1 in 20 ml of dry n-pentane or n-hexane (diethyl ether was used for the reactions with methylolithium and phenylolithium) was cooled down to 0° and then, while stirring, 0.035 mole of an alkylolithium reagent was added dropwise during a period of ca. 30 minutes. The reaction mixture was allowed to warm up slowly to ambient temperature and stirring was continued until at least a 90 % conversion of the starting alkene was achieved (usually 1 to 2 hours). The course of the reaction was monitored by taking small samples, quenching them with water and analysing the organic layer by GLC. Finally, the reaction mixtures were quenched by addition of a small amount of methanol followed by water and acidified with hydrochloric acid to dissolve a suspension of lithium salts. The organic layer was separated, dried over magnesium sulphate, and solvents were removed under vacuum. The residue was at first analysed by GLC then subjected to GLPC separation. Pure compounds 3E and fractions of a mixture of 2E, 2Z, and 3Z were isolated and subjected to elemental analysis and spectroscopic investigations.

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REFERENCES

- 1 W.Dmowski, J.Fluorine Chem., 21 (1982) 201
- 2 T.Nguyen, M.Rubinstein, C.Wakselman, J.Fluorine Chem., 11(1978) 573
- 3 R.W.Taft Jr., in M.S.Newman, Steric Effects in Organic Chemistry, Wiley and Sons, New York (1956) p.642 - 648

- 4 R.Fellous, R.Luft, J.Am.Chem.Soc., 95 (1973) 5593
- 5 M.Charton, J.Am.Chem.Soc., 97 (1975) 1552
- 6 M.Charton, J.Am.Chem.Soc., 97 (1975) 3694
- 7 C.Hensh, A.Leo, S.H.Unger, Ki Hwan Kim, D.Nikaitani, R.J.Lien, J.Med.Chem., 16 (1973) 1207; J.March, *Advanced Organic Chemistry*, McGraw-Hill (1977) p.253
- 8 K.Schwetlick, *Kinetische Methoden zur Untersuchung von Reac-tionmechanismen*, VEB Deutscher Verlag der Wissenschaften, Berlin (1971) p.83
- 9 M.Charton, J.Am.Chem.Soc., 91 (1969) 615
- 10 A.J.Berlin, F.R.Jensen, Chem.Ind.(London), (1960) 998
- 11 E.W.Della, Tetrahedron Lett., (1966) 3347
- 12 J.A.Hirsch, Top.Stereochem., 1 (1967) 199
- 13 H.Oberhammer, J.Fluorine Chem., 23 (1983) 147
- 14 H.F.Koch, J.G.Koch, D.B.Donovan, A.G.Toczko, A.J.Kielbania Jr., J.Am.Chem.Soc., 103 (1981) 5417
- 15 L.D.McKeever, in M.Szwarc, *Ions and Ion Pairs in Organic Reac-tions*, Wiley-Interscience (1972) Vol.1, Chapter 6, p.263 - 287
- 16 J.Smid, reference [15], Chapter 3.4, p.110 -114
- 17 E.Buncel, *Carbanions: Mechanistic and Isotopic Aspects*, Elsevier Scientific Publishing Company (1975) Chapter 1.2, p.10 - 15
- 18 G.S.Hammond, J.Am.Chem.Soc., 77 (1955) 334
- 19 Reference [17], Chapter 1 and 2
- 20 C.Bugg, R.Desiderato, R.L.Sass, J.Am.Chem.Soc., 86 (1964) 3157
- 21 D.J.Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York-London (1965) Chapter 2
- 22 K.J.Klabunde, D.J.Burton, J.Am.Chem.Soc., 94 (1972) 5985
- 23 K.J.Klabunde, D.J.Burton, J.Am.Chem.Soc., 94 (1972) 820
- 24 D.Holtz, Prog.Phys.Org.Chem., 8 (1971) 1
- 25 W.Dmowski, J.Fluorine Chem., 18 (1981) 25