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HYDROGEN FLUORIDE ABSTRACTION FROM VICINAL DIFLUOROALKANES : REACTION CONDITIONS AND *syn/anti*-STEREOSELECTIVITY

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Summary. - *Towards sodium methoxide in methanol, vic-difluoroalkanes are as inert as monofluoroalkanes. Stronger bases, however, can perform dehydrofluorinations relatively smoothly. Potassium tert-butoxide in tetrahydrofuran at 75°C exclusively acts by an anti-periplanar process : meso- and dl-6,7-difluorododecane are converted to (E)- and (Z)-6-fluoro-6-dodecene, respectively. Lithium diisopropylamide was found to be an extremely powerful eliminating reagent when employed in hexane, while its reactivity is considerably diminished in diethyl ether and has almost completely vanished in tetrahydrofuran. This solvent effect together with the loss of stereoselectivity points at an electrophilic assistance as the key event in lithiumamide-induced dehydrofluorinations.*

Unlike cyclic [1, 2] or crowded [3] analogs, simple open-chain *vic*-dichloro- and -dibromoalkanes react with alcoholates such as sodium butoxide in butanol and potassium *tert*-butoxide in benzene or toluene strictly in an *anti*-periplanar mode. Thus, *meso*-4,5-dichlorohexane (*meso*-**1**) leads to (*E*)-4-chloro-4-hexene (*E*-**2**) and the *dl*-diastereoisomer (*dl*-**1**) to (*Z*)-4-chloro-4-hexene (*Z*-**2**) exclusively [1, 2].

Vicinal dihaloalkanes undergo elimination roughly ten times more rapidly than comparable monohaloalkanes provided a primary alcoholate (*e.g.*, sodium methoxide, potassium ethoxide or sodium butoxide) in the corresponding alcohol acts as the base. Replacement of a primary alcoholate by potassium *tert*-butoxide in *tert*-butylalcohol or benzene (or toluene) enhances the rates by one or two orders of magnitudes if a *vic*-dihaloalkane serves as the substrate, but diminishes the rates if a related monohaloalkane is concerned (table 1) [2]. This behavior is in perfect agreement with the model of the "variable transition state" [4] : in the monoalkane case the increased base strength is more than offset by the steric hindrance while with *vic*-dihaloalkanes the acidifying

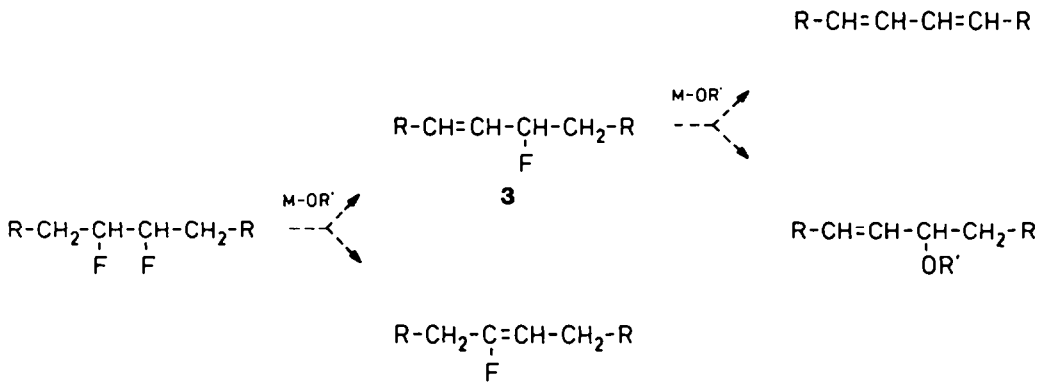
effect of the non-departing halogen atom favors the built-up of more fractional negative charge at this site and thus imparts a greater E1cb-character to the transition state.

Table 1. Reactivity of monohaloalkanes and *vic*-dihaloalkanes (R = alkyl) [a] towards primary alcoholates (R' = H, CH_3, C_3H_7, etc.) in the corresponding alcohols and potassium *tert*-butoxide in *tert*-butylalcohol or benzene [b] : crude relative rates [c] of elimination reactions with chloro (X = Cl) and,in parentheses, bromo (X = Br) compounds at 100°C.

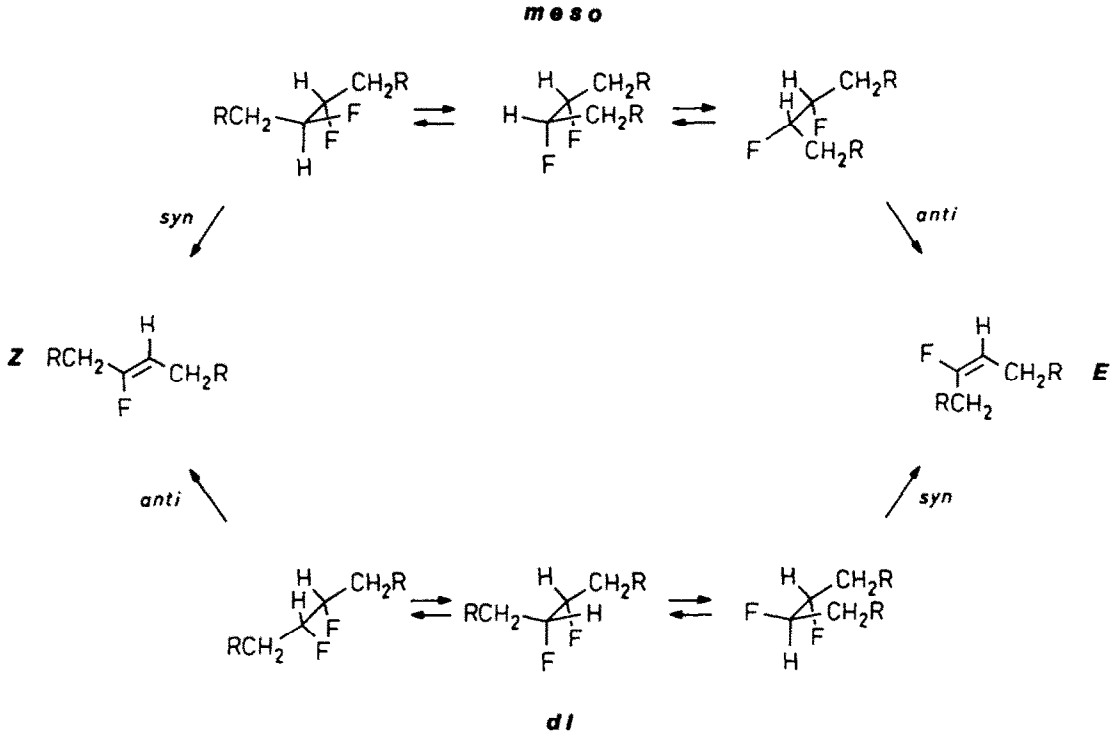
substrate	$NaOCH_2R'$ / $HOCH_2R'$	$KOC(CH_3)_3$ / $HOC(CH_3)_3$	$KOC(CH_3)_3$ / C_6H_6
R-CH_2-CH_2-CH(X)-CH_3	1 (50)	0.5 (20)	- (–)
R-CH_2-CH_2-CH(X)-CH_2-CH_2-R	2 (100)	0.1 (10)	0.5 (50)
R-CH_2-CH_2-CH(X)-CH(X)-CH_2-CH_2-R	10 (5'000)	100 (10'000)	1'000 (50'000)

a) Our estimate refers to *dl*-compounds, the *meso*-diastereoisomers reacting frequently somewhat more slowly.
b) Changing the solvent from benzene (or toluene) to tetrahydrofuran or dimethylsulfoxide increases the *tert*-butoxide reactivity by a factor of 10^2 and, respectively, 10^5 at least.
c) The numbers given imply many extrapolations and simplifications. We compare global rates which may include several elimination processes (for example, the formation of a 1-alkene, a *cis*- and a *trans*-2-alkene). Since rates and product ratios depend on the base concentration in solvents of low or moderate polarity [5], we refer to 1 M conditions.
d) The absolute rate for the dehydrochlorination of 2-hexyl chloride with sodium methoxide in methanol at 100°C is $1.1 \cdot 10^{-4}$ L mol^{-1} s^{-1} [6].

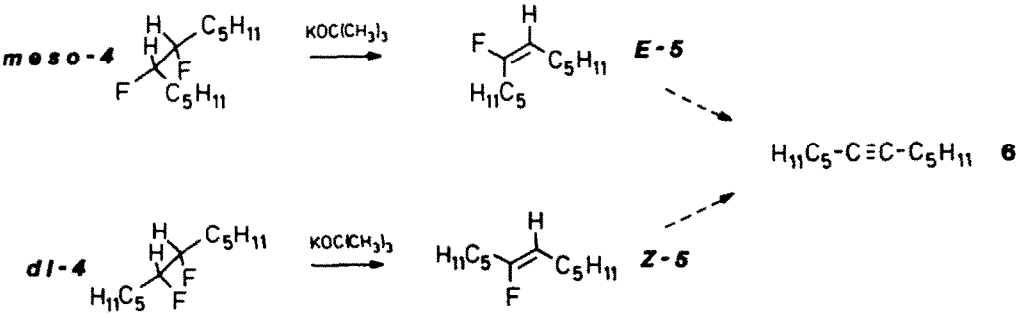
As a first-row element, fluorine has a much weaker acidifying effect than chlorine or bromine. Acidity constants pK_a of about 30, 16 and 14 have been reported for fluoroform, chloroform and bromoform, respectively [7]. Moreover, depending on the nature and structure of the carbanion formed, fluorine substitution may even diminish rather than enhance the kinetic or thermodynamic acidity of a hydrocarbon [8]. If this were the case with *vic*-difluoroalkanes too, proton abstraction from a methylene group would compete with or prevail over proton abstraction from methine positions. The resulting allyl-type fluoride 3 would immediately get attacked by the base (M-OR') to give dienes and allyl ethers, both as mixtures of regio- and stereoisomers.



On the other hand, if 1-fluoroalkenes were obtained as main products, the stereochemistry of hydrogen fluoride elimination from simple aliphatic substrates could be investigated for the first time. A *syn*-periplanar process must be involved, if a vicinal *meso*-difluoride produces the (*Z*)-fluoroalkene, an *anti*-mode operates if the (*E*)-isomer results. For the *dl*-diastereoisomer these correlations are just inversed.



We have chosen *meso*- and *dl*-6,7-difluorododecane [9] (*meso*- and *dl*-**4**) as model compounds. Their reaction with sodium methoxide in methanol proceeded with extreme sluggishness indeed and only trace amounts of elimination products were detected (see table 2). In contrast, potassium *tert*-butoxide in tetrahydrofuran was found to bring about a smooth and perfectly stereoselective dehydrofluorination. After 16 h at 75°C 66% (*E*)- and 56 % (*Z*)-6-fluoro-6-dodecene (*E*- and *Z*-**5**) were obtained from *meso*- and *dl*-**4**, respectively. Some starting material was recovered; but only very little 6-dodecyne (**6**), resulting from a consecutive second elimination, was present (table 2).



Replacement of tetrahydrofuran by dimethylsulfoxide considerably accelerated the reaction between difluorides **4** and potassium *tert*-butoxide. However, extensive decomposition took place and it was not possible to isolate pure compounds from the complex product mixtures (table 2). Lithium diisopropylamide showed similar shortcomings, although to a lesser extent. Due to its superior base strength, eliminations may be carried out already at ice bath temperatures. Nevertheless the typo- and regioselectivity of the reactions is poor, acetylene **6** and mixtures of (*Z*)- and (*E*)-fluoroalkenes being produced (table 2).

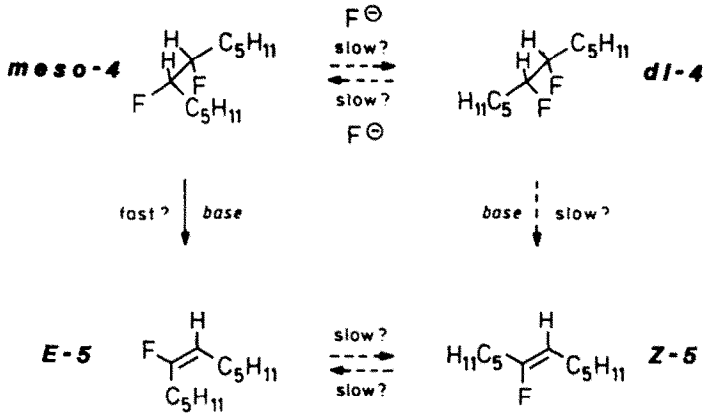
Table 2. Base-promoted elimination of hydrogen fluoride from *meso*- and *dl*-6,7-difluorododecane (**4**) under a variety of conditions : yields of products and stereochemical outcome [a].

base (equivalents)	solvent b,c)	reaction conditions	from *meso*-**4** : **5** (*Z* : *E*)	**6**	from *dl*-**4** : **5** (*E* : *Z*)	**6**
$NaOCH_3$ (10)	$HOCH_3$ [d]	48 h 125°C	6% (2 : 98)	2%	5% (5 : 95)	0%
$KOC(CH_3)_3$ (4)	OC_4H_8	16 h 75°C	66% (0 : 100)	0%	56% (0 : 100)	4%
$KOC(CH_3)_3$ (4)	H_3CSOCH_3	24 h 25°C	e)		68% (11 : 89)	24%
$LiN(^iC_3H_7)_2$ (4)	C_6H_{14}	24 h 0°C	52% (1 : 99)	41%	30% (32 : 68)	2%
$LiN(^iC_3H_7)_2$ (20)	C_6H_{14}	2 h [f] 25°C	75% (1 : 99)	13%	44% (37 : 63)	4%
$LiN(^iC_3H_7)_2$ (20)	$O(C_2H_5)_2$	4 h 25°C	18% (30 : 70)	1%	8% (85 : 15)	2%
$LiN(^iC_3H_7)_2$ (20)	OC_4H_8 [g]	4 h 25°C	0% (-)	0%	0% (-)	0%
$LiN(^iC_3H_7)_2$ (4)	$(H_3COCH_2)_2$	24 h 0°C	10% (1 : 99)	33%	2% (29 : 71)	15%

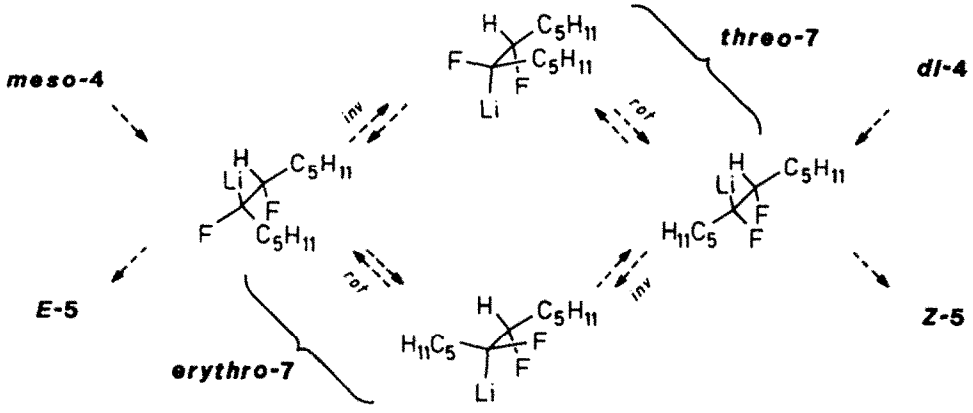
a) With *meso*- and *dl*-**4** as the precursors, *Z*/*E*- and, respectively, *E*/*Z*-ratios correspond to *syn*/*anti*-ratios.
b) OC_4H_8 = tetrahydrofuran, H_3CSOCH_3 = dimethylsulfoxide, C_6H_{14} = hexane, $O(C_2H_5)_2$ = diethyl ether, $(H_3COCH_2)_2$ = monoethylene glycol dimethyl ether.
c) The molarity of the base ranged from 1.5 - 2.5 (see experimental part).
d) In methanol, 1 - 10% of other halogen-free elimination products, presumably dodecadienes and methoxydodecenes, were formed besides 6-dodecyne.
e) The reaction mixture was too "dirty" to allow unambiguous identification of products.
f) With *dl*-6,7-difluorododecane **6** h rather than 2 h of reaction time.
g) From tetrahydrofuran solutions the substrates (*meso*- and *dl*-**4**) were quantitatively recovered.

The loss of stereoselectivity in the reactions between 6,7-difluorododecanes (**4**) and lithium diisopropylamide in hexane or, particularly, diethyl ether is puzzling. The first question is, of course, whether we do not deal with the result of a stereoisomerization of either the starting materials or the reaction products. Such an artefact can be ruled out. If equilibration between fluoroalkenes **5** did occur to some extent, it would have to favor the thermodynamically more stable (*Z*)- rather than the (*E*)-isomer. An epimerization of the difluoroalkanes **4** would imply a fluorine-fluorine substitution. Although such a replacement cannot be performed separately it is well conceivable under the elimination conditions when the fluoride leaving group is expelled in a highly reactive state. Actually, fluorides are potent nucleophiles as long as they escape from deactivation due to oligomerization, complexation with small counterions or hydrogen bonding [10]. The interconversion of *meso*- and *dl*-**4**, however,

would have to occur in both directions with roughly equal rates. Consequently, the "wrong" stereoisomer should sufficiently accumulate in all reaction mixtures to allow detection. But such a contamination has never been observed.



A third and final isomerization mechanism can be rejected too. It assumes the intermediacy of lithium species 7. Such an E1cb process [11] is, however, highly improbable. Although 2-fluoroethyl lithium [12] can be generated by iodine-lithium interconversion and trapped at very low temperatures, lithium diisopropylamide should lack sufficient basicity to produce the α,β-difluorinated organolithium compound 7. If still such an intermediate could could form under the reaction conditions, it would decompose faster by elimination of lithium fluoride than accomplish an epimerization by pyramidal inversion (*"inv"*) and rotation (*"rot"*) around the central carbon bond [13]. And even if this limitation did not exist, the epimerization would have to proceed in both ways. In other words, the sequence of inversion, rotation and *anti*-periplanar elimination (leading to *Z*-5) should also be accessible to the *meso*-precursor (*meso*-4). This is obviously not the case, at least not in hexane.



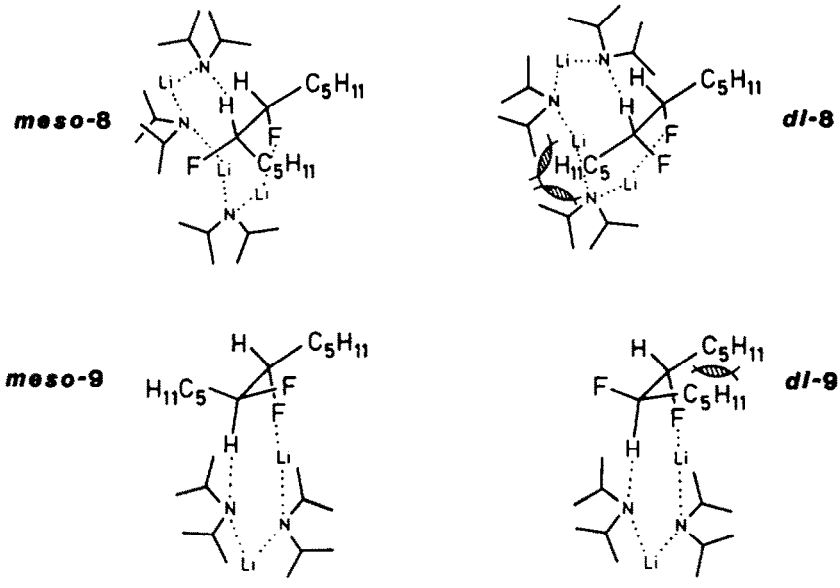
Thus, all evidence points at the same conclusion : for the first time a *syn*-elimination mode was identified with a conformationally unbiased, acyclic *vic*-dihalide. But why ? A convincing answer should not alone rationalize the imperfect stereoselectivity of the studied dehydrofluorinations but also be compatible with the measured relative rates. In aprotic solvents, *meso*-difluorododecane (*meso*-4) was found to react 2.5 to 10 times faster than *dl*-4 and at least 20 times faster than an analogous monofluoride, *i.e.* 5-fluorononane (table 3, next page).

Table 3. Relative rates of base-promoted dehydrofluorination : meso- vs. *dl*-6,7-difluorododecane (k_{meso}/k_{dl}) and *meso*-6,7-difluorododecane vs. 5-nonyl fluoride (k_{meso}/k_{mono}).

base	solvent [a]	conditions [b]	k_{meso}/k_{dl}	k_{meso}/k_{mono}
$NaOCH_3$	$HOCH_3$	48 h 125°C	0.7	~ 1
$KOC(CH_3)_3$	$HOC(CH_3)_3$	24 h 75°C	2	> 20 [c]
$LiN(^iC_3H_7)_2$	C_6H_{12}	24 h 0°C	10	> 20 [c]
$LiN(^iC_3H_7)_2$	$O(C_2H_5)_2$	24 h 0°C	3	> 20 [c]
$LiN(^iC_3H_7)_2$	$(H_3COCH_2)_2$	24 h 0°C	2.5	> 20 [c]

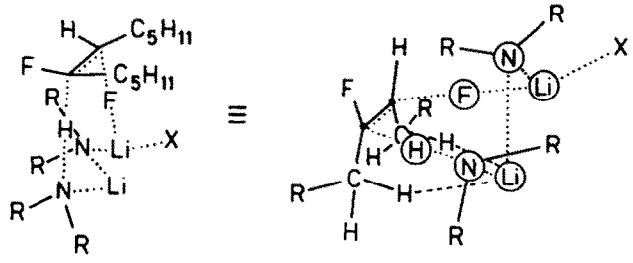
a) C_6H_{12} = hexane, $O(C_2H_5)_2$ = diethyl ether, $(H_3COCH_2)_2$ = monoethylene glycol dimethyl ether.
b) To check on the consistency of the results, samples were also collected and analyzed after 0.25, 1.0, 2.5 and 10 h.
c) Within the limits of detection, no 5-nonyl fluoride was consumed.

The reactivity difference between the two diastereomeric difluoroalkanes **4** can be understood on the basis of a "conveyer belt" mechanism [8] for the *anti*-periplanar modes of elimination (transition states *meso*- and *dl*-**8**). But how to explain that in hexane medium only the *dl*-precursor (transition state *dl*-**9**), not its *meso*-isomer (transition state *meso*-**9**) can opt for *a syn*- at the expense of an *anti*-process ?



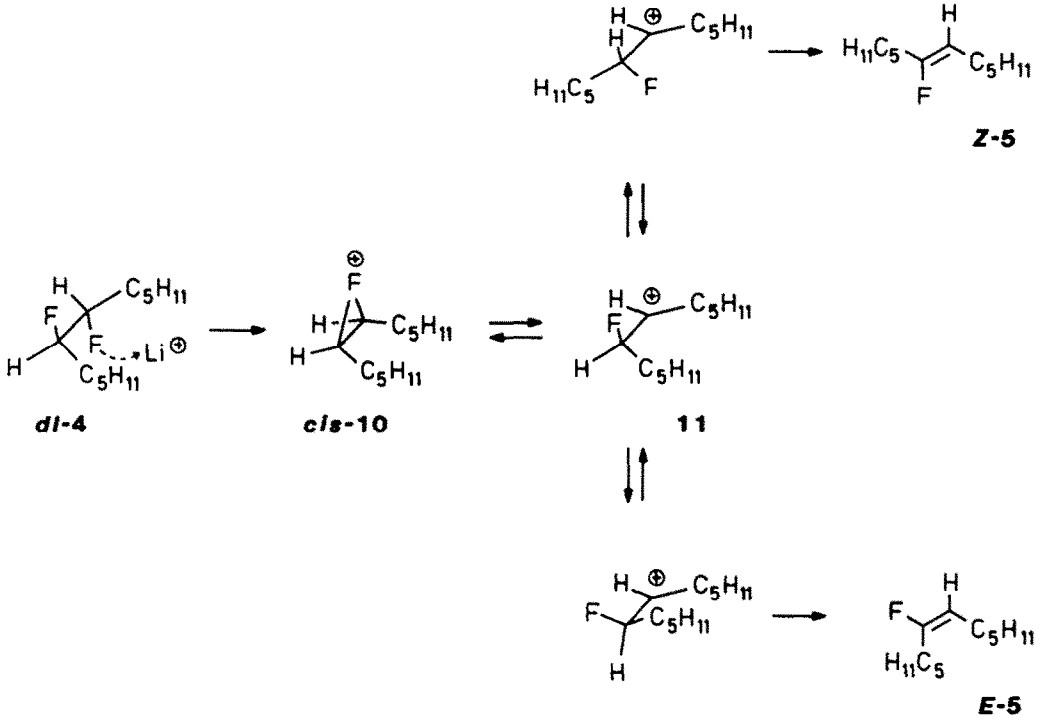
As a matter of fact, *syn*-periplanar eliminations have been frequently identified to produce *trans*-olefins, the structural analogs of (*Z*)-fluoroalkenes. On the other hand, open-chain *cis*-olefins, the structural analogs of (*E*)-fluoroalkenes, almost invariably emerge from *anti*-periplanar processes. The steric repulsion caused by two eclipsing alkyl groups (see transition state *dl*-**8**) is at the origin of this "stereochemical dichotomy" [14]. If now this relationship appears to be inversed, special electronic factors must be responsible. As an inspection of molecular models reveals, the base-dimer "buckle" in the *syn*-arrangements (*meso*- and *dl*-**9**) cannot be straight,

but must be zigzagged. If the two alkyl moieties stay on the same side of the C^{α},C^{β} axis they avoid steric interference with one of the nitrogen-attached isopropyl groups and can at the same time jointly create hydride bonds [15] to "solvate" a coordinatively seminude lithium atom (structure *dl*-**9a**; R = isopropyl, X = nitrogen or, eventually, fluoride of an extraaggregate unit).



***dl*-9a**

Alternatively, one may consider a competition between the "conveyer belt" and a E1-related, cation-triggered mechanism. In this scheme a lithium ion is thought to abstract a fluoride ion. It leaves behind a bridged fluoronium ion **10** which may generate a thermodynamically less stable, open secondary carbenium ion **11**. The latter intermediate would have to twist by 60° around its C^{α},C^{β}-axis to bring the hydrogen in a position suitable for proton transfer and collapse to the (*E*)-fluoroalkene (*E*-**5**). A rotation in the opposite sense, necessitating a 120° walk, and subsequent deprotonation will give rise to the (*Z*)-isomer.



***Z*-5**

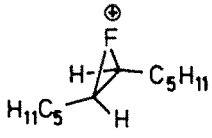
***dl*-4** ***cis*-10** **11**

***E*-5**

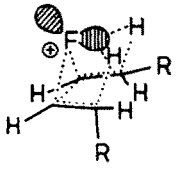
It may appear paradoxal that a strong base should act as an electrophile. However, in many examples organometallic reagents have been recognized to generate transient carbocations [16]. In all these cases the driving force came from the formation of a metal halide or alkoxide. Lithium fluoride is a particularly stable, thermodynamically favorable product as evidenced by its homolytic bond dissociation energy of close to 140 kcal/mol [17]. Moreover, the electrophilic participation of metal ions in the lithium diisopropylamide-promoted dehydro-

fluorination of **4** is well documented indeed by a strong inverse solvent effect, which is even more pronounced than the previously [18] observed one. Lithium diisopropylamide attacks the difluoroalkanes **4** in tetrahydrofuran not at all and in diethyl ether at least 10 times more slowly than in hexane. Moreover, it loses much of its reactivity even in hexane when it gets complexed to lithium fluoride or diisopropylamine produced in the elimination reaction. Thus, the rate decreases as the reaction progresses.

Like in the previous hypothesis the open question is why alone the *dl*-diastereoisomer should have the privilege to choose among two reactions modes while *meso*-**4**, as far as its reaction in hexane is concerned, would continue to depend entirely on the "conveyer belt" mechanism. The only way to reconcile the speculation with the facts is to postulate a higher thermodynamic stability for intermediate *cis*-**10** in comparison with the corresponding fluoronium ion *trans*-**10** which would result from the *meso*-diastereoisomer. If the eclipsing of two alkyl groups should really be more advantageous than their spatial separation we again have to invoke an unprecedented electronic effect. One possiblity could be a hyperconjugation of methylene groups with the electron-difficient three-membered ring and fluorine-hydrogen back-bonding (*cis*-**10a**).



***trans*-10**



***cis*-10a**

EXPERIMENTAL PART

For general remarks see the first article [18] of this series.

Starting materials and samples for comparison : *meso*- and *dl*-6,7-difluorododecane (*meso*- and *dl*-**4**) were prepared as described in the following publication [9]. The physical and spectroscopic properties of 6-dodecyne isolated from our reaction mixtures coincide with those of a product obtained according to a literature procedure [19].

6-Dodecyne (6)

Mp -41 to -40°C; bp 115 - 116°C/30 mmHg (lit. [19] : bp 115°C/30 mmHg); n_D^{20} 1.4407 (lit. [19] : n_D^{25} 1.4374).

IR (film) : 2940 + 2920 + 2850 (s, ν[-$\dot{C}$-H]), 1460 (m, $\delta[CH_2]$), 1380 (w, $\delta[CH_3]$).

^{1}H-NMR : 2.14 (4 H, *tt*, *J* 7.3, 2.0), 1.45 (4 H, symm. *m*), 1.32 (8 H, symm. *m*), 0.90 (6 H, *t*-like *m*, *J* ~ 7).

MS : 166 (2%, M^+), 109 (10%), 95 (54%), 87 (80%), 67 (100%), 54 (67%), 47 (55%).

(*Z*)-6-Fluoro-6-dodecene (*Z*-5)

A solution of *dl*-6,7-difluorododecane (5.2 g, 25 mmol) in tetrahydrofuran (60 mL), was stirred with potassium *tert*-butoxide (11.2 g, 100 mmol) 16 h at 75°C. The reaction mixture was concentrated, absorbed on little silica gel

(about 10 g) which was poured as a dry powder on the top of a column filled with fresh silica gel (50 g). With hexane the fluoroalkene was eluted before 6-dodecyne. After evaporation of the solvent and distillation, the product was collected as a colorless liquid (2.5 g, 53%), mp -43 to -42°C, bp 59 - 60°C/3 mmHg, n_D^{20} 1.4263, and as a pure stereoisomer according to gas chromatography (50 m, OV-1701, 110°C).

IR (film) : 3010 (w, ν[=C-H]), 2950 + 2920 + 2850 (s, ν[-C-H]), 1700 (s, ν[C=C]), 1460 (m, δ[CH_2]).
^{1}H-NMR : 4.45 (1 H, *dt*, *J* 48.5, 7.5), 2.11 (2 H, *dt*, *J* 17.5, 7.5), 2.05 (2 H, *q*, *J* 7.5), 1.45 (2 H, *pent*-like *m*, *J* ~ 7), 1.3 (10 H, *m*), 0.92 (3 H, *t*, *J* 7.5), 0.90 (3 H, *t*, *J* 7.5).
MS : 186 (16%, M^+), 109 (20%), 95 (32%), 81 (28%), 74 (51%), 67 (77%), 59 (100%).
Analysis : calc. for $C_{12}H_{23}F$ (186.3) C 77.36%, H 12.44%; found C 77.52%, H 12.47%

(*E*)-6-Fluoro-6-dodecene (*E*-5)

In the same way as its *dl*-stereoisomer, *meso*-6,7-difluorododecane (25 mmol) was treated with potassium *tert*-butoxide. After chromatographic purification and distillation a 1 : 99 (*Z*/*E*)-mixture (by gas chromatography : 50 m, OV-1701, 110°C) of **6** (2.9 g, 62%) was isolated, mp -52 to -51°C, bp 58 - 59°C/3 mmHg, n_D^{20} 1.4248.

IR (film) : 3010 (w, ν[=C-H]), 2950 + 2920 + 2850 (s, ν[-C-H]), 1695 (m, ν[C=C]), 1460 (m, δ[CH_2]).
^{1}H-NMR : 4.98 (1 H, *dt*, *J* 22.5, 7.0), 2.20 (2 H, *dt*, *J* 23.5, 7.5), 1.91 (2 H, *q*, *J* 7.0), 1.50 (2 H, *pent*-like *m*, *J* ~ 7.2), 1.3 (10 H, *m*), 0.90 (3 H, *t*, *J* 7.0), 0.93 (3 H, *t*, *J* 7.0).
MS : 186 (22%, M^+), 109 (24%), 95 (46%), 81 (36%), 68 (100%).
Analysis : calc. C 77.36%, H 12.44%; found C 77.44%, H 12.60%.

Analytical scale elimination reactions

A mixture of the substrate (1.0 mmol of *meso*- or *dl*-**4**), a small quantity of pentadecane (as an "internal standard") and the base (4.0 mmol) in the appropriate solvent (2.5 mL) was heated in a sealed thick-walled tube. When the reaction was over, hexane and water (2.5 mL each) were added and, after vigorous shaking, the organic layer separated from the aqueous one, the former being analyzed by gas chromatography (2 m 10% OV-17, 125 → 160°C at a rate of 2°C/min; 50 m OV-1701, 100 → 180°C at a rate of 5°C/min). The data are compiled in table 2.

Lithium diisopropylamide was prepared by adding the stoichiometric amount of diisopropylamine to a 1.6 M solution of butyllithium in hexane (instantaneous reaction !). If an ethereal solution was required, the hydrocarbon solvent was stripped off under reduced pressure and under protection against moisture before the precooled (-75°C) diethyl ether, tetrahydrofuran or monoethylene glycol dimethyl ether was added.

Competition kinetics

The two substrates (0.5 mmol each), the "internal standard" (pentadecane for the pair *meso*- and *dl*-**4**; undecane for the pair *meso*-**4** and 5-nonyl fluoride) and the base (4.0 mmol) in the appropriate solvent (2.5 mL) were placed in a small Schlenk tube, which was closed with a ground joint stopper and a same stopcock, and mixed. In intervals of 0, 0.25, 1.0, 2.5, 10 and 24 h samples were withdrawn and analyzed by gas chromatography (on a 2 m 10% OV-17 and a 50 m OV-1701 column (for the temperature program see above). The rate ratios (table 3) were calculated as the ratios of logarithmic concentration differences at zero and finite time [20].

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