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BASE-PROMOTED ELIMINATION OF HYDROGEN FLUORIDE FROM ALKYL FLUORIDES : REACTIVITY AND STEREOCHEMISTRY

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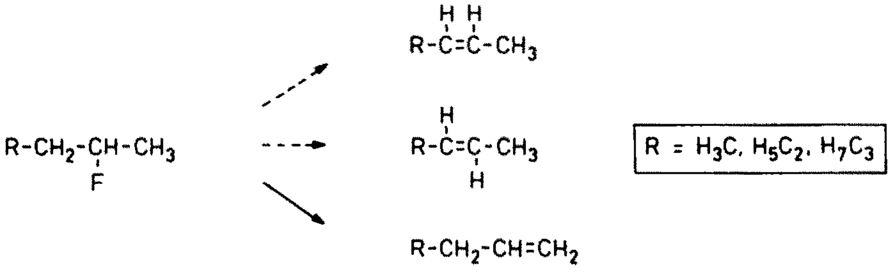
Summary. - *The alcoholate-promoted dehydrohalogenation of 5-nonyl fluoride and cyclododecyl fluoride, typical straight-chain and, respectively, medium-size cyclic substrates, leads to cis- and trans-alkenes in an approximate ratio of 1 : 3. With bulky bases such as lithium diisopropylamide the trans isomer may be obtained almost exclusively. In general, the elimination of hydrogen fluoride proceeds very slowly. Increase of the base strength has only a moderate effect on the rates. Electrophilic assistance as provided by lithium cations in media of low polarity can, however, considerably accelerate the reaction. - Cyclododecyl fluoride cannot be prepared from cyclododecanol. It is, however, readily accessible by bromofluorination of cyclodecene and subsequent reduction of the adduct with stannane.*

It lended strong support to the concept [1] of the "variable transition state" of elimination reactions [2, 3], when 2-butyl [4], 2-pentyl [5] and 2-hexyl [6,7] fluoride were recognized to favor Hofmann rather than Saytzeff orientation. Upon treatment with sodium methoxide in methanol or sodium ethoxide in ethanol the corresponding 1- and 2-alkenes were formed with ratios ranging from 70 : 30 to 82 : 18.



At the same time alkyl fluorides proved to be much less prone to dehydrofluorination than chlorides or bromides. Actually we estimate bromides to be 10^5 times more reactive than fluorides when alkenes having an internal double bond are produced (table 1). If the resulting olefin is an aliphatic terminal alkene [6] or a styrene [8] the leaving group effect is somewhat attenuated (table 1). This may be attributed to an enhanced E1cb character of the transition state.

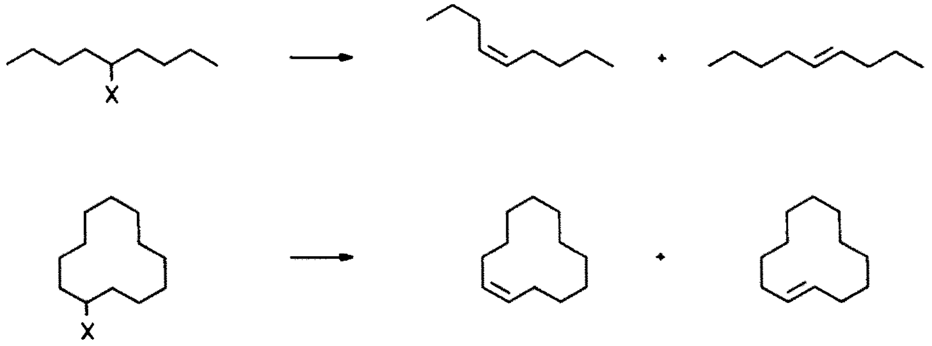
Table 1. Base-promoted dehydrohalogenation of 2-hexyl [6] and 2-phenylethyl [8] halides : rates of chlorides, bromides and iodides relative to fluorides.

substrate	base/solvent [a), b)]	product	X = F	X = Cl	X = Br	X = I
$H_7C_3\text{-}CH_2\text{-}CHX\text{-}CH_3$	$NaOCH_3/HOCH_3$	$H_7C_3\text{-}\overset{H}{C}=\underset{H}{C}\text{-}CH_3$	1	$2 \cdot 10^3$	$1 \cdot 10^5$	-
$H_7C_3\text{-}CH_2\text{-}CHX\text{-}CH_3$	$NaOCH_3/HOCH_3$	$H_7C_3\text{-}\underset{H}{C}=C\text{-}CH_3$	1	$2 \cdot 10^3$	$1 \cdot 10^5$	-
$H_7C_3\text{-}CH_2\text{-}CHX\text{-}CH_3$	$NaOCH_3/HOCH_3$	$H_7C_3\text{-}CH_2\text{-}CH=CH_2$	1	$5 \cdot 10^2$	$2 \cdot 10^4$	-
$H_5C_6\text{-}CH_2\text{-}CH_2\text{-}X$	$NaOC_2H_5/HOC_2H_5$	$H_5C_6\text{-}CH=CH_2$	1	$7 \cdot 10^1$	$4 \cdot 10^3$	$3 \cdot 10^4$

a) Reaction between 2-hexyl halides and sodium methoxide in methanol : graphical extrapolation (lg *k* : 1/T[K] plot) of the chloride and bromide rates to 130°C, the average rate enhancement per 10°C temperature raise being 2.3, 2.7 and 3.0 times for fluorides, chlorides and bromides, respectively.

b) Reaction between 2-phenylethyl halides and sodium ethoxide : at 30°C.

Up till now, the literature provides no information about the reactivity and selectivity pattern of aliphatic fluorides carrying the heteroatom at a position near the center of an alkane chain or being attached to a cycloalkane ring. Therefore, we wanted to study the behavior of both 5-nonyl and cyclododecyl fluoride (**1a** and **2a**) and to compare it with that of the corresponding bromides (**1b** and **2b**) as well as ammonium salts (**1c** and **2c**).

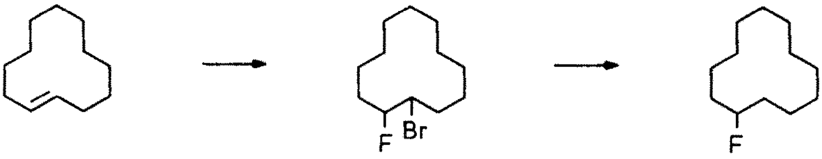


1

2

a : X = F **b** : X = Br **c** : X = $\overset{\oplus}{N}(CH_3)_3$

The 5-nonyl fluoride (**1a**) was readily prepared by reacting 5-nonanol with diethylaminosulfur trifluoride in the presence of pyridine. The same approach failed with cyclododecanol completely; elimination rather than substitution took place. The same happened when cyclododecyl *p*-toluenesulfonate was heated with potassium fluoride or tetrabutylammonium fluoride. The addition of hydrogen fluoride to cyclododecene gave only a very poor yield (8%) when carried out on a small scale, as described [9], and even much less when larger quantities were employed. Finally, we found a very satisfactory, indirect access to cyclododecyl fluoride (**2a**) : simultaneous treatment [10] of cyclododecene with *N*-bromosuccinimide and hydrogen fluoride in the presence of triethylamine afforded the vicinal bromofluoro adduct (82%) from which the heavier halogen could be selectively removed by reduction with tributyltin hydride (65%). This two-step sequence should be considered as an attractive alternative in all cases where a direct hydroxy/fluorine substitution is difficult to perform.



2a

Both, the open-chain and the cyclic fluoride were quite slowly attacked by sodium methoxide in methanol, even at 125°C. Thus, they turned out to be much less reactive than the corresponding ammonium salts which for their part fell behind the bromides by a factor of about 250 [11]. Clean dehydrofluorination could only be achieved with lithium diisopropylamide as the base, in the absence or presence [12] of potassium *tert*-butoxide (table 2).

Table 2. Base promoted elimination of hydrogen bromide, hydrogen fluoride and trimethylamine from 5-nonyl and cyclododecyl substrates : *cis/trans*-ratios of 5-nonene or cyclododecene and, in parentheses, yields.

X	base/solvent [a)]	time, temp.		$(H_9C_4)_2$CH-X		$(H_2C)_{11}$CH-X	
	$NaOCH_3/HOCH_3$ [b)]	10 h	110°C	23 : 77	(-)	48 : 52	(-)
	$KOC(CH_3)_3$/DMSO [c)]	10 h	50°C	14 : 86	(-)	35 : 65	(-)
Br	$KOC(CH_3)_3/C_6H_6$ [13]	10 h	100°C	56 : 44	(-)	10 : 90	(-)
	LIDA/THF	24 h	25°C	42 : 58	(65%)	10 : 90	(85%)
	LIDAKOR/THF [d)]	24 h	25°C	27 : 63	(72%)	44 : 56	(97%)
	$NaOCH_3/HOCH_3$	48 h	125°C	29 : 71	(8%)	31 : 69	(21%)
	$KOC(CH_3)_3$/DMSO	24 h	50°C	19 : 81	(29%)	–	
F	$KOC(CH_3)_3/C_6H_6$	24 h	100°C	9 : 91	(10%)	–	
	LIDA/DEE [e)]	48 h	40°C	6 : 94	(74%)	2 : 98	(82%)
	LIDAKOR/THF	24 h	25°C	–		29 : 71	(86%)
	$KOCH_3/HOCH_3$ [14]	40 h	135°C	80 : 20	(28%)	54 : 46	(31%)
	$KOC(CH_3)_3$/DMSO [14]	0.5 h	25°C	23 : 77	(99%)	3 : 97	(99%)
$\overset{\oplus}{N}(CH_3)_3$	$KOC(CH_3)_3/C_6H_6$ [14]	4 h	100°C	5 : 95	(-)	1 : 99	(99%)
	LIDA/THF	24 h	25°C	11 : 89	(88%)	4 : 96	(68%)
	LIDAKOR/THF	24 h	25°C	–		1 : 99	(58%)

a) DMSO = dimethylsulfoxide; THF = tetrahydrofuran; DEE = diethyl ether; LIDA(KOR) = lithium diisopropylamide (in the presence of potassium *tert*-butoxide). **

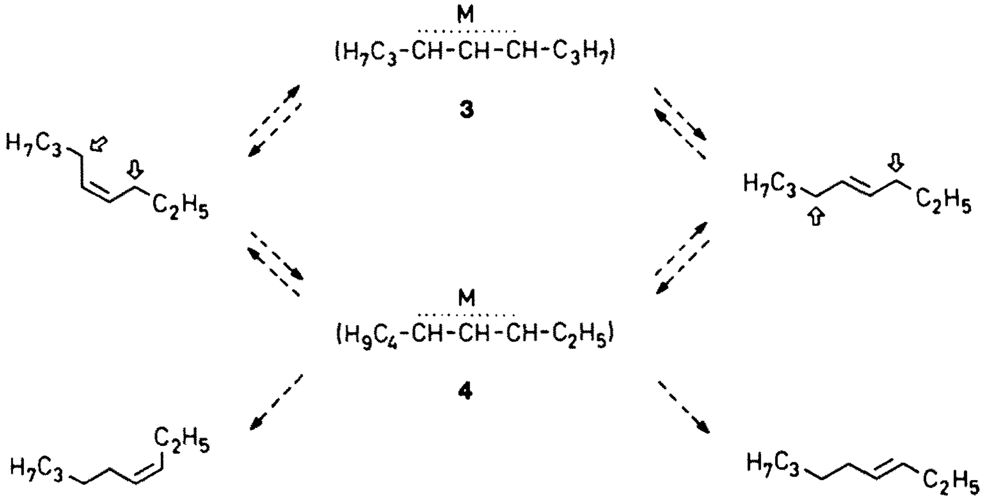
b) Using potassium ethoxide in ethanol at 58.5°C, cyclododecyl bromide gave a *cis/trans*-ratio of 48 : 52 under otherwise identical conditions [13].

c) Using lithium *tert*-butoxide in dimethylformamide at 40°C, cyclododecyl bromide gave a *cis/trans*-ratio of 40 : 60 under the same conditions [13].

d) With lithium 2,2,6,6-tetramethylpiperidide rather than LIDA, the reaction with the cyclic substrate is complete after 15 min and gives 89% of *cis*- and *trans*-cyclododecene with a 90 : 10 ratio. **

e) With LIDA/THF (24 h at 25°C) only 2% of 5-nonene and 61% of cyclododecene (*Z/E* = 2 : 98) were found. **

With alcoholate bases the fluorides invariably gave rise to *cis/trans*-mixtures of alkenes not far from their equilibrium composition. Thus, one may wonder whether the observed stereoisomeric ratios really reflect kinetically controlled differences in elimination processes or whether they are not just the result of subsequent isomerization, a large excess of base being always employed and long reaction times being required. The suspected *cis/trans*-equilibration, however, can be ruled out. Lithium diisopropylamide produced almost pure trans-5-nonene and trans-cyclododecene while isomerization would have led to substantial proportions of cis-isomers. Moreover, no trace of regioisomeric olefins were detected in the reaction mixtures. Since base-catalyzed isomerizations [15] of olefins involve allyl-type carbanions (or related organometallic compounds), the deprotonation of a 4-nonene would have to occur with roughly equal probability at position 6, generating a 1,3-dipropylallyl species 3, and at position 3, generating a 1-butyl-3-ethylallyl species 4. The latter would be a precursor to both 4-nonene and 3-nonene.



The most striking finding of this investigation was the discovery of an inverse relationship between solvent polarity and lithium diisopropylamide reactivity towards fluorides **1a** and **2a**. While 5-nonyl fluoride did not undergo elimination to any reasonable extent (≤ 10% after 24 h) when exposed to this base in tetrahydrofuran at 60°C the reaction proceeded slowly but smoothly in diethyl ether or in 1:1 diethyl ether/hexane mixture at 40°C. In neat hexane, however, elimination again occurred only in trace amounts. Apparently the departure of the poor leaving group fluoride is facilitated by the electrophilic assistance which a lithium cation can provide most efficiently as long as it is only weakly solvated.

EXPERIMENTAL PART

General remarks

Starting materials have been purchased from Fluka AG, Buchs, Aldrich-Chemie, Steinheim, or Merck-Schuchardt, Darmstadt, unless literature sources or details for the preparation are given. *Butyllithium* and *potassium tert-butoxide* were supplied by CheMetall, Frankfurt, and Dynamit-Nobel, Troisdorf. All commercial reagents were used without further purification.

Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995% pure nitrogen.

Anhydrous diethyl ether and *tetrahydrofuran* were obtained by distillation as soon as the characteristic blue color of in situ generated sodium diphenylketyl [16] was found to persist. *Hexane* and *benzene* were dried by careful azeotropic distillation, *dimethylsulfoxide* by vigorous stirring with finely powdered calcium hydride and distillation from it under reduced pressure.

Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice-methanol baths is consistently indicated as -75°C, "room temperature" (22 - 26°C) as 25°C. If no reduced pressure is specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg). *Melting ranges* (mp) are reproducible after resolidification, unless otherwise stated ("dec."), and are corrected using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attempts to crystallize the liquid product have failed even at temperatures as low as -75°C.

Whenever reaction products were not isolated, their yields were determined by *gas chromatography* comparing their peak areas with that of an internal standard and correcting the ratios by calibration factors. The purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 - 100 and, respectively, 60 - 80 mesh particle size were chosen as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). All packed columns were made of glass, while quartz was chosen as the material for coated, GROB-type capillary columns (≥ 10 m long). The type of the stationary phase used is abbreviated as SE-30 (silicone rubber), OV-17 (silicone rubber), Ap-L (Apiezon L hydrocarbon), DEGS (diethylene glycol succinate polyester) and C-20M (polyethylene glycol of average molecular weight 20'000).

Infrared spectra were recorded of films if the sample was liquid at room temperature, while solid substances were embedded in potassium bromide pellets. The intensities of absorption bands are abbreviated : s (strong), m (moderate), w (weak) and b (broad).

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded in the 360 MHz field, of carbon-13 nuclei in the 90.6 MHz field (either under broad band or gated decoupling) and of fluorine-19 nuclei in the 188 MHz field. Unless otherwise stated, deuterochloroform was used as the solvent. Chemical shifts refer to the signal of tetramethylsilane (δ = 0 ppm), which served as an internal standard in the case of ^{1}H and ^{13}C spectra, and of α,α,α-trifluorotoluene for ^{19}F spectra. Coupling constants (J) are measured in Hz. Coupling patterns are described by abbreviations : *s* (singulet), *d* (dublet), *t* (triplet), *q* (quadruplet), *pent* (pentuplet), *td* (triplet of a dublet) and *m* (multiplet).

In general, *mass spectra* were obtained at a 70 eV ionisation potential. Whenever no molecular peak was observed under standard conditions, chemical ionization ("c.i.") in an ammonia atmosphere was applied.

1. Substrates

5-Nonyl bromide [17] as well as cyclododecyltrimethylammonium chloride (or iodide) [18] were prepared according to literature procedures. Also (1-butylpentyl)trimethylammonium chloride and iodide had previously been described [17]. Nevertheless the corresponding bromide was made accessible by a different route.

5-Nonyl fluoride (1a)

At 0°C a solution of diethylaminosulfur trifluoride (47 g, 0.29 mol) in dichloromethane (100 mL) was added dropwise, in the course of 30 min, to 5-nonanol (36 g, 0.25 mol) in dichloromethane (400 mL). At -50°C pyridine (35 mL, 34 g, 0.43 mol) was added dropwise in the course of 15 min. The reaction mixture was kept 4 h at 25°C, before being poured into ice-water and extracted with diethyl ether (3 x 150 mL). The combined organic layers were washed with 5% hydrochloric acid (3 x 100 mL), saturated aqueous solution of sodium hydrogencarbonate (3 x 100 mL) and brine (3 x 100 mL), After drying and evaporation of the solvent, the residue was distilled under reduced pressure. A colorless liquid was obtained (16.5 g, 45%); bp 55 - 56°C/15 mmHg; n_D^{20} 1.4005.

IR (film) : 2945 + 2920 + 2860 (s, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1460 (m, $\delta[\mathrm{CH_2}]$), 1375 (m, $\delta[\mathrm{CH_3}]$).
^{1}H-NMR : 4.45 (1 H, *dtt*, *J* 50.0, 7.5, 4.0), 1.5 (12 H, *m*), 0.93 (6 H, *t*, *J* 7.5).
Analysis : calc. for $C_9H_{19}F$ (146.2) C 73.91%, H 13.10%; found C 73.58%, H 13.29%.

Cyclododecyl fluoride

N-Bromosuccinimide (17.8 g, 100 mmol) and the 3:1 complex (24.1 g, 150 mmol) of hydrogen fluoride with triethylamine were added to a solution of cyclododecene (16.6 g, 100 mmol) in dichloromethane (250 mL). After stirring for 3 h at 25°C, the reaction mixture was poured into ice-water and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with a saturated solution of sodium hydrogencarbonate (3 x 50 mL) and brine (3 x 50 mL). After drying and evaporation of the solvent, the residue was purified by column chromatography on silica gel (approx. 50 g) using hexane as the eluent to afford 1-bromo-2-fluorocyclododecane [10] as a *cis/trans*-mixture(21.7 g, 82%).

IR (film) : 2910 + 2850 (s, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1460 (m, $\delta[\mathrm{CH_2}]$).
^{1}H-NMR : 4.78 (0.6 H, *dtd*, *J* 47.0, 6.5, 2.0), 4.70 (0.4 H, *ddt*, *J* 46.5, 7.5, 5.0), 4.3 (1 H, *m*), 1.9 (4 H, *m*), 1.4 (16 H, *m*).

This colorless liquid (19.9 g, 75 mmol) together with tributyltin hydride (26.2 g, 90 mmol) was heated 2 h at 50°C. The material was poured into ice-water and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with 5% hydrochloric acid, a saturated solution of sodium hydrogencarbonate and brine (3 x 50 mL of each). After drying and evaporation of the solvent, the residue was recrystallized from hexane at -30°C. Colorless crystals (9.1 g, 65%) were obtained; mp 49 - 50°C (lit. [9] : 50 - 52°C).

IR (film) : 2930 + 2860 (s, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1470 (m, $\delta[\mathrm{CH_2}]$).
^{1}H-NMR : 4.73 (1 H, *dtt*, *J* 47.5, 7.5, 4.5), 1.8 (2 H, *m*) 1.6 (2 H, *m*), 1.4 (18 H, *s*-like *m*).
Analysis : calc. for $C_{12}H_{23}F$ (186.3) C 77.36%, H 12.44%; found C 77.44%, H 12.64%.

Cyclododecyl bromide (2b)

In the course of 30 min phosphorus tribromide (20.3 g, 75 mmol) was added dropwise to cyclododecanol (27.6 g, 150 mmol). After 3 h at 100°C, the reaction mixture was poured into ice-water and extracted with diethyl ether (3 x 150 mL). The combined organic layers were washed with a saturated solution of sodium hydrogencarbonate (3 x 150 mL) and brine (3 x 150 mL). After drying and evaporation of the solvent, a 1:2 mixture of bromocyclododecane and cyclododecene was left which was separated by column chromatography on silica gel (approx. 80 g). With hexane, bromocyclododecane (12.6 g, 34%) was eluted after cyclododecene; bp 111 - 112°C/3 mmHg; n_D^{20} 1.5097.

IR (film) : 2920 + 2850 (s, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1465 (m, $\delta[\mathrm{CH_2}]$).
^{1}H-NMR : 4.27 (1 H, *tt*, *J* 5.0, 4.0), 2.1 (2 H, *m*), 1.9 (2 H, *m*), 1.4 (18 H, *m*).

(1-Butylpentyl)trimethylammonium bromide (1c)

Potassium hydroxide pellets (4.0 g, 71 mmol) were dissolved in a solution of dimethylamine hydrochloride (21.4 g, 250 mmol) in methanol (75 mL) before 5-nonanone (28.4 g, 200 mmol) and sodium cyanoborohydride (4.7 g, 76 mmol) in methanol (25 mL) were added [19]. After 1 h, again potassium hydroxide (15.0 g, 267 mmol) was added and stirring was continued for 3 days until they had completely dissolved. The reaction mixture was concentrated to approximately 50 mL at a rotary evaporator. The remainder being poured into brine (100 mL) was extracted with diethyl ether (3 x 100 mL) and, from the solvent with 5 M hydrochloric acid (3 x 20 mL). The combined aqueous phases were saturated with sodium chloride and washed with diethyl ether (3 x 20 mL), before being cooled to 0°C, treated with 2 N potassium hydroxide (until pH ~ 12) and once more extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with brine (3 x 50 mL), dried and evaporated. Upon distillation *N,N*-dimethyl-1-butylpentylamine was collected as a colorless liquid (13.0 g, 38%); bp 58 - 59°C/ 3 mmHg (lit. [20] : 85 - 87°C/10 mmHg); n_D^{20} 1.4303 (lit. [20] : n_D^{20} 1.4297).

IR (film) : 2950 + 2920 + 2850 (s, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 2810 + 2760 + 1450 (m, $\delta[\mathrm{CH_2}]$), 1020 (m, $\nu[\mathrm{C\text{-}N}]$).
^{1}H-NMR : 2.3 (1 H, *m*), 2.23 (6 H, *s*), 1.5 (2 H, *m*), 1.3 (10 H, *m*), 0.93 (6 H, *t*, *J* 7.5).

This amine (12.1 g, 71 mmol) was cooled to -20°C and bromomethane (7.7 mL, 13.3 g, 140 mmol) was added in one portion. When the temperature was allowed to raise slowly to 10°C, colorless crystals progressively deposited. After solidification of the mixture the product was throughly washed with diethyl ether and filtered. White crystals were collected (17.5 g, 93%); mp 238 - 239°C (dec.).

IR (KBr) : 3000 + 2950 + 2910 (s, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1475 (s, $\delta[\mathrm{CH_2}]$).
^{1}H-NMR : 3.5 (1 H, *m*), 3.42 (9 H, *s*), 2.0 (2 H, *m*), 1.5 (10 H, *m*), 0.93 (6 H, *t*, *J* 7.5).

2. Olefins

For comparison with the elimination products a number of authentic olefins were required. A *cis/trans*-mixture of 3-nonene [21], *cis*-4-nonene [22] and *cis*-cyclododecene [23] were prepared according to literature procedures. On the other hand, *trans*-4-nonene and *trans*-cyclododecene were isolated from preparative scale reactions.

trans-4-Nonene

Potassium *tert*-butoxide (8.9 g, 80 mmol) and (1-butylpentyl)trimethylammonium bromide (5.4 g, 20 mmol) were heated in benzene (50 mL) 24 h to 100°C. A colorless liquid (70%, 1.8 g), distilled at bp 62 - 63°C/40 mmHg; n_D^{20} 1.4198; showing a *cis/trans*-ratio of 4 : 96 by gas chromatography : 50 m OV-1701, 50°C).

IR (film) : 3020 (m, $\nu[=\overset{|}{C}\text{-H}]$), 2950 + 2920 + 2860 (s, $\nu[\text{-}\overset{|}{\underset{|}{C}}\text{-H}]$), 1650 (vw, $\nu[C=C]$), 1460 (m, $\delta[CH_2]$), 1380 (w, $\delta[CH_3]$), 960 (m, $\delta[=C\text{-H}]$).

^{1}H-NMR : 5.39 (2 H, symm. *m*), 2.0 (4 H, *m*), 1.4 (6 H, *m*), 0.89 (3 H, *t*, *J* 7.3), 0.88 (3 H, *t*, *J* 7.3).

cis-Cyclododecene [23]

Mp -5 to -6°C; bp 64 - 65°C/1 mmHg; n_D^{20} 1.4860.

IR (film) : 3000 (m, $\nu[=\overset{|}{C}\text{-H}]$), 2910 + 2840 (s, $\nu[\text{-}\overset{|}{\underset{|}{C}}\text{-H}]$), 1650 (vw, $\nu[C=C]$), 1460 (m, $\delta[CH_2]$).

^{1}H-NMR : 5.33 (2 H, *tt*-like *m*, *J* 5.1), 2.13 (4 H, *q*-like *m*, *J* ~ 6.5), 1.4 (16 H, *m*).

trans-Cyclododecene

To diisopropylamine (9.0 mL, 6.5 g, 64 mmol) in tetrahydrofuran (50 mL) consecutively butyllithium (24 mL of a 1.47 M solution in hexane, 35 mmol) and cyclododecyl fluoride (3.0 g, 16 mmol) were added under cooling. After 24 h at 25°C, the reaction mixture was poured into cold 5% hydrochloric acid (25 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with a saturated aqueous solution of sodium hydrogencarbonate (3 x 5 mL), dried and concentrated. Column chromatography on silica gel (50 g) with hexane as the eluent gave pure *trans*-cyclododecane [24] (55%, 1.5 g) having a *cis/trans*-ratio of 2 : 98 (according to gas chromatography : 50 m OV-1701, 140°C); mp -36 to -35°C; n_D^{20} 1.4840 (lit. [24] : n_D^{20} 1.4850).

IR (film) : 3010 (w, $\nu[=\overset{|}{C}\text{-H}]$), 2910 + 2840 (s, $\nu[\text{-}\overset{|}{\underset{|}{C}}\text{-H}]$), 1650 (vw, $\nu[C=C]$), 1460 (m, $\delta[CH_2]$), 970 (s, $\delta[=\overset{|}{C}\text{-H}]$).

^{1}H-NMR : 5.38 (2 H, *tt*, *J* 4.0, 1.8), 2.05 (4 H, *q*-like *m*, *J* ~ 6), 1.4 (4 H, *m*), 1.3 (12 H, *s*-like *m*).

3. Elimination reactions

A thick-walled test tube was filled with the substrate (1.0 mmol), a known amount of undecane as an internal reference compound and the base (4.0 mmol) dissolved in the appropriate solvent (2.5 mL). The sealed tube was immersed into an oil bath and kept at constant temperature for the required time (see table 2). After opening of the tube, the reaction mixture was vigorously shaken with water (2.5 mL). After freezing the aqueous phase in a dry ice-bath, the organic layer was decanted and analyzed by gas chromatography (for nonenes : 2 m 10% OV-17, 70 → 160°C at a rate of 4°C/min; 50 m OV-1701, 50°C; for cyclododecenes : 1 m 10% SE-30, 70 → 180°C at a rate of 8°C/min; 50 m OV-1701, 120 → 180°C at a rate of 10°C/min).

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[**] Unlike in Europe, in Anglo-Saxon countries lithium diisopropylamide is contracted to either "LDA" or "LIDA". We prefer the latter acronym since it is consistent with related abbreviations such as "LICA" (lithium dicyclohexylamide) or "BULI" (butyllithium).