

### 300. Hydroxide-Promoted Elimination Reactions: Alkyl Halides as Substrates<sup>1)</sup>

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#### Summary

Potassium hydroxide, in presence of tetraethyleneglycol dimethyl ether, easily abstracts hydrogen chloride or hydrogen bromide from secondary and tertiary halides, but primary chlorides lead to roughly equal amounts of elimination and substitution products. Addition of small quantities of trimethylamine, however, starts a catalytic cycle involving ammonium salts and favoring alkene formation. The described method appears to be more efficient and more economic than any other non-pyrolytic process.

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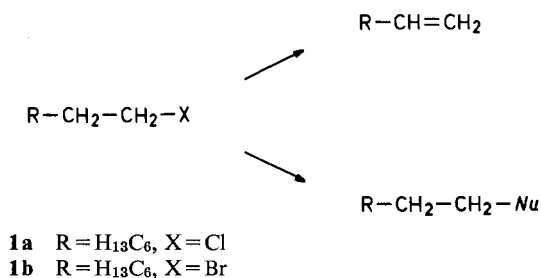
Functional groups represent crossroads in the network of synthetic routes. The carbon-carbon double bond belongs to the most prominent and versatile among such structural turn-tables. Moreover, it can be introduced into any saturated hydrocarbon molecule by a straightforward and apparently economical two-step procedure: chlorination of a CH group followed by base-promoted dehydrochlorination. However, this formal simplicity is overshadowed by practical difficulties. The main obstacle arises from the dualistic character of bases which may act either as proton-acceptors, leading to the desired elimination, or as nucleophiles leading to substitution. Primary alkyl halides clearly prefer substitution when treated with an unbranched alkoxide, and even with a tertiary alkoxide give substantial quantities of the corresponding ether. Actually, only two methods are satisfactory for the direct conversion of a primary halide into the corresponding 1-alkene: heating with sterically hindered diisopropylethylamine ('Hünig's base') or gas-phase pyrolysis. However, both procedures suffer from shortcomings, the first employing an expensive reagent and the second requiring special equipment and, moreover, favoring isomerization and other side-reactions [2].

Solvation is a very important factor influencing the outcome of the competition between substitution and elimination. Anions increase in basicity rather than in nucleophilicity if their interaction with the counter-ion or the solvent is reduced. Tetraalkylammonium fluorides in acetone [3] or potassium-*t*-butoxide in dimethylsulfoxide (see *Table 1*) typically illustrate this change in reactivity. Phase-transfer catalysts are claimed to pick-up hydroxide ions from an alkaline solution and to deliver them 'naked' or at least 'topless' [4] to an organic layer. Intrigued by this perspective, we decided to explore systematically elimination reactions in two-phase

<sup>1)</sup> Part VII of the series 'Base-Induced Elimination Reactions'; preceding paper: [1].

systems<sup>2)</sup>. The technical advantage of a process performing dehydrohalogenation by means of bases as cheap as sodium or potassium hydroxide is obvious. Practical realization first depends on the over-all reactivity. The product turnover should be reasonably fast between 50° and 150°. Next, the reaction has to occur in a 'typo-selective' manner, that is elimination should dominate over competing side reactions, particularly substitution, hopefully by at least one order of magnitude. Finally, the regioselectivity and stereoselectivity of olefin formation should be predictable and, possibly, adjustable.

**Typoselectivity<sup>3)</sup>.** 1-Chlorooctane (**1a**) and 1-bromooctane (**1b**) were chosen as model compounds. All oxygen-bases exhibit a more or less pronounced tendency to undergo substitution with primary halides producing alkyl 1-octyl ethers or 1-octanol (*Table 1*).



Even the sterically hindered potassium *t*-butoxide gives olefin/ether mixtures varying between 35:65 and 78:22. Furthermore, in dimethylsulfoxide (the solvent of choice as far as typoselectivity and reaction rates are concerned) base-catalysed isomerization yielding 2-alkenes competes with the formation of 1-alkenes. Sodium and potassium hydroxide in aqueous medium almost exclusively promote the formation of alcohols and, by consecutive reaction, ethers. The elimination/substitution ratios are raised slightly if hydroxides are employed in a two-phase system in the presence of a transfer catalyst and increase considerably in non-aqueous media with good solvating (complexing) capacity (*Table 2*). Unfortunately the amount of substitution is still too high to render one of these methods practically useful.

Ammonium salts are the only substrates giving nearly exclusively 1-alkenes under the influence of hydroxide ions, no matter what their detailed structure is and

- 2) To avoid misinterpretation, we should state that we do not share the frequently expressed view that complexation of metal halides, metal alkoxides and other metal derivatives with a macrocyclic or polycyclic polyether (*e.g.*, '18-crown-6' or a 'cryptand') generates separated ('loose') ion pairs or even free ions. To our knowledge the alternative structure of a 'peripherally solvated' (or complexed) contact pair [5] has not so far been ruled out in any single case. Differences in rates of reactions in the presence and absence of such a complexing agent can simply be attributed to the existence of more than one contact species. Small aggregates (dimer, trimers or tetramers) of potassium *t*-butoxide were, surprisingly enough, the eliminating reagents in solvents of low polarity [1], while in the presence of a polyether monomeric alkoxides should clearly be favored.
- 3) This term designates the preference of a system for one particular mode out of two or more potentially competing types of reaction. The occasionally employed term 'chemoselectivity' seems to us to be less adequate.

Table 1. Reaction of 1-chlorooctane (in parentheses: 1-bromooctane) with various alkoxides and with aqueous hydroxide<sup>a)</sup>

Base	Solvent	Yield [%]			Ratio of elim. vs. subst. <sup>b)</sup>
		1-octene	2-octene	alkyl octyl ether	
KOC(CH <sub>3</sub> ) <sub>3</sub>	benzene	56 (76)	0 (0)	42 (24)	1.3 (3.2)
	HOC(CH <sub>3</sub> ) <sub>3</sub>	23 (40)	0 (0)	43 (36)	0.53 (1.1)
	DMSO <sup>c)</sup>	1 (2)	76 (75)	23 (21)	3.3 (3.7)
KOCH(CH <sub>3</sub> ) <sub>2</sub>	HOCH(CH <sub>3</sub> ) <sub>2</sub>	9 (16)	0 (0)	91 (84)	0.10 (0.19)
KOC <sub>2</sub> H <sub>5</sub>	HOCH <sub>2</sub> CH <sub>3</sub>	5 (18)	0 (0)	84 (77)	0.060 (0.23)
KOCH <sub>3</sub>	HOCH <sub>3</sub>	2 (4)	0 (0)	98 (94)	0.020 (0.043)
KOH	HOH/dioxane	<1 (4)	0 (0)	15 <sup>d)</sup> (36 <sup>d)</sup>	<0.067 (0.11)

<sup>a)</sup> Reaction conditions: 5 mmol 1-haloctane, 50 mmol base (2.5M), 20 ml solvent, 50 h (1-chlorooctane) or 5 h (1-bromooctane) at 100°.

<sup>b)</sup> The literature reports elimination/substitution ratios for the reaction of primary bromides (other than 1-bromooctane) with sodium methoxide in methanol [6], sodium ethoxide in ethanol [7] and potassium *t*-butoxide in *t*-butyl alcohol [6] or DMSO [8].

<sup>c)</sup> DMSO = dimethylsulfoxide.

<sup>d)</sup> 1-Octanol instead of an ether.

Table 2. Reaction between 1-chlorooctane (in parentheses: 1-bromooctane) and solutions or suspensions of potassium hydroxide<sup>a)</sup>

Solvent	Additive <sup>b)</sup>	Yield [%]				Ratio of elim. vs. subst.
		1-octene	2-octene	1-octanol	diethyl ether	
HOH/dioxane <sup>c)</sup>	–	– (1)	– (0)	– (5)	– (1)	– (0.17)
HOH/dioxane <sup>c)</sup>	[(H <sub>5</sub> C <sub>2</sub> ) <sub>3</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]Cl	– (7)	– (0)	– (26)	– (8)	– (0.21) <sup>d)</sup>
HOH/dioxane <sup>c)</sup>	18-crown-6 <sup>e)</sup>	– (16)	– (0)	– (30)	– (21)	– (0.31)
TGME <sup>f)</sup>	–	58 (59)	0 (0)	0 (0)	39 (41)	1.5 (1.4)
TGME <sup>f)</sup>	(H <sub>5</sub> C <sub>6</sub> ) <sub>3</sub> CH	55 (51)	0 (0)	1 (1)	42 (47)	1.3 (1.1)
PPG-400 <sup>g)</sup> h)	–	24 (24)	0 (0)	2 (1)	1 (1)	8.0 (12.0)
PP-400-B <sup>i)</sup>	–	– (6)	– (0)	– (5)	– (18)	– (0.26)
DMSO	–	33 (36)	18 (11)	12 (1)	36 (50)	1.1 (0.92)

<sup>a)</sup> Reaction conditions: 5.0 mmol 1-haloctane, 50 mmol (2.8 g) KOH pellets, 5 ml solvent, 50 h (1-chlorooctane) or 5 h (1-bromooctane) at 100°.

<sup>b)</sup> 0.5 mmol, except for triphenylmethane (2.5 mmol).

<sup>c)</sup> Liquid/liquid two-phase system.

<sup>d)</sup> For a similar experiment see [9].

<sup>e)</sup> 1, 4, 7, 10, 13, 16-Hexaoxacyclooctadecane.

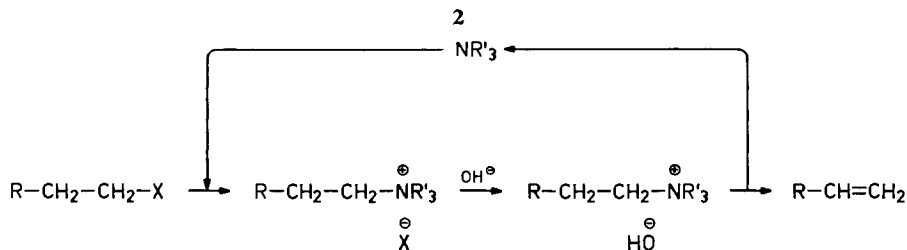
<sup>f)</sup> TGME = Tetraethyleneglycol dimethyl ether (tetraglyme).

<sup>g)</sup> Polypropyleneglycol, average molecular weight about 400.

<sup>h)</sup> At the end of the reaction time no starting material was left; the main course of the reaction must have been the *O*-alkylation of PPG-400.

<sup>i)</sup> (H<sub>3</sub>C)<sub>2</sub>C(OH)–CH<sub>2</sub>–(O–CH(CH<sub>3</sub>)–CH<sub>2</sub>)<sub>n</sub>–O–CH(CH<sub>3</sub>)–C(CH<sub>3</sub>)<sub>2</sub>OH, prepared from PPG-400 by oxidation (H<sub>2</sub>CrO<sub>4</sub>) to an oxo-carboxylic acid and repetitive treatment with methylmagnesium bromide.

the experimental conditions are [10]. We examined whether amines could not be used as catalysts: to convert first a primary halide into the corresponding ammonium salt, which subsequently would act as a phase-transfer reagent and pick up a hydroxide ion with which it could undergo *Hofmann* elimination to afford the olefin and regenerate the amine (2).



The materialization of this idea was hampered by one major obstacle. Tetraalkylammonium hydroxides, prepared with silver oxide or by means of ion exchange, require prolonged heating at *ca.* 200° to be quantitatively decomposed [10]. The hydroxyl ion, a very strong hydrogen bond acceptor ( $\Delta G^\circ_{298}[\text{pentahydrat.}] = -45 \text{ kcal/mol}$  [11]) appears to retain water even under these drastic conditions and thus is deactivated. Consequently, a sufficiently well solvating, but aprotic solvent should permit a notable lowering of the elimination temperature. In fact, trimethyloctylammonium bromide, suspended in tetraethyleneglycol dimethylether (tetraglyme) and heated with an excess of powdered potassium hydroxide 20 h to 100°, afforded 98% 1-octene as the only identified product. (See [12–16] for evidence of the powerful sodium- and potassium-complexing properties of tetraglyme).

As expected, the formation and degradation of the ammonium salt can be carried out simultaneously with less than stoichiometric amounts of trimethylamine (Table 3). The ineffectiveness of other amines or ammonium salts corroborates the postulated reaction mechanism. The highest ratio of elimination vs. substitution thus observed was 8.1. If, for sake of convenience, the solid corresponding hydrochloride instead of the free amine was added, the amount of dioctyl ether increased slightly at the expense of the olefinic products.

**Regioselectivity.** – Branching of the alkyl chain slightly increases the elimination rate and markedly decreases the substitution rate. Thus, almost any anion converts secondary halides such as 2-chlorooctane (3a) and 2-bromooctane (3b) preferentially to a mixture of terminal and non-terminal olefins, although the proportion of substitution products in the reaction mixture is relatively high when methoxide is used.

Hydroxide is practically inefficient when employed in a liquid/liquid phase system (like dioxane/water), no matter whether transfer-catalysts are added or not (Table 4). However, in neat polar solvents such as polypropylene glycol (PPG-400), dimethylsulfoxide or tetraglyme, rapid elimination occurs with potassium hydroxide. Added trimethylamine affects neither the reaction rate nor the product composition. Significantly, 1- and 2-octene are obtained in equal amounts, whereas the potassium hydroxide-promoted decomposition of trimethyl-1-methylheptylammonium bromide furnishes almost exclusively the terminal alkene (Table 3). Obviously the quaternization

Table 3. Reaction between 1-chlorooctane (in parentheses: 1-bromooctane) and potassium hydroxide in the presence of various ammonium salts<sup>a)</sup>

Ammonium salt <sup>b)</sup>	Yield [%]			Ratio of elim. vs. subst.
	1-octene <sup>c)</sup>	1-octanol	dioctyl ether	
–	58 (59)	0 (0)	39 (41)	1.5 (1.4)
[(H <sub>3</sub> C) <sub>3</sub> CCH <sub>2</sub> NH <sub>3</sub> ]Cl	56 (43)	0 (0)	22 (24)	2.5 (1.8) <sup>d)</sup>
[(H <sub>3</sub> C) <sub>2</sub> NH <sub>2</sub> ]Cl	47 (38)	2 (3)	25 (10)	1.7 (2.9) <sup>d)</sup>
[(H <sub>3</sub> C) <sub>3</sub> NH]Cl <sup>e)</sup>	64 (–)	0 (–)	36 (–)	1.8 (–)
[(H <sub>3</sub> C) <sub>3</sub> NH]Cl	85 (57)	0 (4)	15 (34)	5.7 (1.5)
<sup>f)</sup>	89 (–)	0 (–)	11 (–)	8.1 (–)
[(H <sub>3</sub> C) <sub>4</sub> N]Cl	59 (57)	8 (0)	29 (43)	1.6 (1.3)
[(H <sub>3</sub> C) <sub>2</sub> NHC <sub>6</sub> H <sub>5</sub> ]Cl	56 (55)	0 (0)	31 (45)	1.8 (1.2)
[(H <sub>3</sub> C) <sub>2</sub> NHOH]Cl	49 (43)	1 (2)	8 (10)	5.4 (3.6) <sup>d)</sup>
<sup>g)</sup>	98 (–)	0 (–)	0 (–)	>100 (–)

<sup>a)</sup> Same conditions as in footnotes (a) to Tables 1 and 2, the solvent always being TGME.

<sup>b)</sup> 2.5 mmol unless otherwise stated.

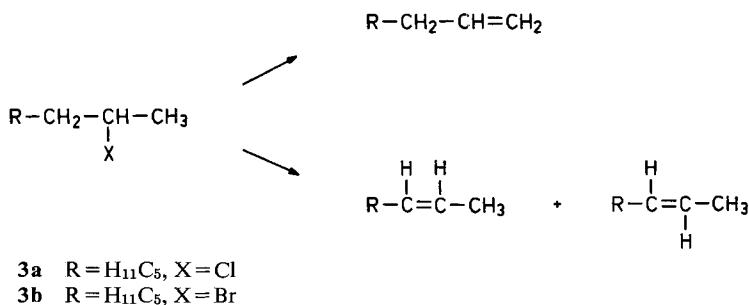
<sup>c)</sup> No traces of 2-octene detected.

<sup>d)</sup> At the end of the reaction time no starting material was left; probably *N*-alkylation accounts for the difference in the product balance.

<sup>e)</sup> Only 1.0 mmol.

<sup>f)</sup> Free trimethylamine (2.5 mmol) instead of the hydrochloride.

<sup>g)</sup> Substrate: trimethyl-1-octylammonium bromide instead of 1-chlorooctane; reaction time 20 h; solvent: TGME or dioxane.



of the amine by a secondary halide is a process too slow to compete successfully with the direct abstraction of hydrogen halide under the influence of tetraglyme-activated hydroxide.

Tertiary halides are generally sufficiently reactive towards bases and substitution occurs only as a negligible side reaction, if at all. A number of base/solvent systems converted 1-chloro-1-methylcyclohexane (**4**) into a mixture of methylenecyclohexane and 1-methylcyclohexene. But once more, the elimination by means of solid potassium hydroxide in tetraglyme deserves special attention, being inexpensive, convenient and affording a virtually quantitative yield. Moreover, the isomer with an endocyclic double-bond is by far the predominant product.

Table 4. Reaction of 2-chlorooctane (in parentheses: 2-bromooctane) with different oxygen bases<sup>a)</sup>

Base	Solvent	Additive <sup>b)</sup>	Yield [%]		2-octene	[Z/E-ratio]	Subst. prod. <sup>i)</sup>	Ratio of elim. vs. subst.
			1-octene	2-octene				
KOC(CH <sub>3</sub> ) <sub>3</sub>	benzene	-	88 (78)	12 (22)	[50:50 (50:50)]	0 (0)	> 100 (>100)	
	HOC(CH <sub>3</sub> ) <sub>3</sub>	-	88 (79)	12 (21)	[43:57 (38:62)]	0 (0)	> 100 (>100)	
KOCH(CH <sub>3</sub> ) <sub>2</sub>	DMSO	-	1 (5)	99 <sup>c)</sup> (95) <sup>c)</sup>	[10:90 (34:66)]	0 (0)	> 100 (>100)	
	HOCH(CH <sub>3</sub> ) <sub>2</sub>	-	56 (50)	36 (48)	[30:70 (28:72)]	2(2)	46 (49)	
KOC <sub>2</sub> H <sub>5</sub>	HOCH <sub>2</sub> CH <sub>3</sub>	-	40 (30)	50 (57)	[25:75 (24:76)]	10 (13)	9.0 (6.7)	
KOCH <sub>3</sub>	HOCH <sub>3</sub>	-	23 (18)	46 (57)	[23:77 (21:79)]	27 (21)	2.6 (3.6)	
KOH	HOH/dioxane	-	2 (2)	2 (2)	[- (-)]	0 (1)	--	
	HOH/dioxane	[(H <sub>5</sub> C <sub>2</sub> ) <sub>3</sub> N-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]Cl	1 (4)	2 (11)	[- (23:77)]	0 (1)	-- (15) <sup>d)</sup>	
PPG-400 <sup>f)</sup>	HOH/dioxane	18-crown-6	2 (6)	4 (15)	[29:71 (23:77)]	0 <sup>e)</sup> (1) <sup>e)</sup>	- (21)	
	PPG-400 <sup>f)</sup>	-	49 (36)	48 (56)	[23:77 (21:79)]	0 (2)	32 (13)	
DMSO	DMSO	-	5 (11)	95 <sup>e)</sup> (86) <sup>e)</sup>	[35:65 (37:63)]	0 (0)	> 100 (48)	
TGME	TGME	<sup>e)</sup> h)	50 (37)	50 (63)	[20:80 (19:81)]	0 (0)	> 100 (>100)	
TGME	TGME	<sup>i)</sup>	95 (-)	5 (-)	[36:84 (-)]	0 (-)	> 100 (-)	

<sup>a)</sup> Same conditions as in footnotes (a) to Tables 1 and 2, except for the reaction times: 20 h with 2-chlorooctane or 2 h with 2-bromooctane.  
<sup>b)</sup> 0.5 mmol.

<sup>c)</sup> The proportion of 2-octene is probably due to base-catalysed isomerization of initially formed 1-octene (cf. [17]; also Table 1).

<sup>d)</sup> For a similar experiment see [9].

<sup>e)</sup> With 3% (6%) of bis(1-methylheptyl) ether.

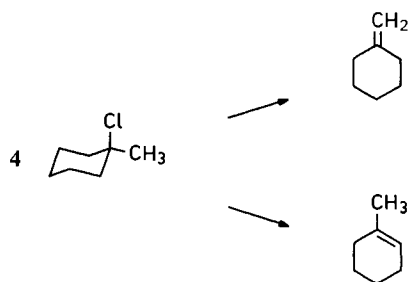
<sup>f)</sup> With NaOH instead of KOH.

<sup>g)</sup> Identical results were obtained in the presence and absence of trimethylamine (0.5 mmol).

<sup>h)</sup> Same results were obtained, when TGME was employed in stoichiometric amounts (1 mol eq.) in 5 ml dioxane rather than as a solvent.

<sup>i)</sup> Substrate: trimethyl-1-methylheptylammonium bromide instead of 1-chlorooctane; reaction time 20 h; solvent: TGME or dioxane.

<sup>j)</sup> According to the base applied, *t*-butyl 1-methylheptyl ether, isopropyl 1-methylheptyl ether, ethyl 1-methylheptyl ether, methyl 1-methylheptyl ether or 2-octanol.

Table 5. Reaction of 1-chloro-1-methylcyclohexane with various oxygen bases<sup>a)</sup>

Base	Solvent	Additive	Olefin yield [%]	Ratio methylenecyclohexane/1-methylcyclohexene
KOC(CH <sub>3</sub> ) <sub>3</sub>	benzene	–	100	0.79
	HOC(CH <sub>3</sub> ) <sub>3</sub>	–	100	0.57
	DMSO	–	100	0.018
KOCH(CH <sub>3</sub> ) <sub>2</sub>	KOC(CH <sub>3</sub> ) <sub>2</sub>	–	100	0.14
KOC <sub>2</sub> H <sub>5</sub>	KOCH <sub>2</sub> CH <sub>3</sub>	–	92	0.063
KOCH <sub>3</sub>	HOCH <sub>3</sub>	–	100	0.051
KOH	HOH/dioxane	–	58 <sup>b)</sup>	0.11
	HOH/dioxane [(H <sub>5</sub> C <sub>2</sub> ) <sub>3</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]Cl	–	5 <sup>b)</sup>	0.11
	HOH/dioxane 18-crown-6	–	40 <sup>b)</sup>	0.11
	PPG-400 <sup>c)</sup>	–	100	0.21
	TGME <sup>d)</sup>	–	100	0.12

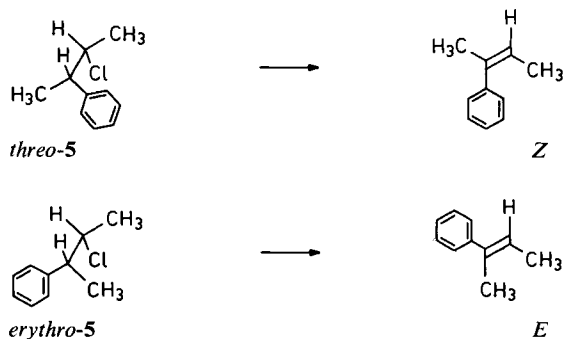
<sup>a)</sup> Same conditions as in footnotes (a) to Tables 1 and 2, except for the reaction time (20 h).

<sup>b)</sup> Besides starting material, some 1-methylcyclohexanol is detected.

<sup>c)</sup> With NaOH instead of KOH.

<sup>d)</sup> Same results were obtained when TGME was employed in stoichiometric amounts (1 mol equivalent) in 5 ml dioxane rather than as a solvent.

**Stereoselectivity.** – As the course of the reaction observed with 2-chloro-3-phenylbutane (**5**) clearly demonstrates, tetraglyme-activated potassium hydroxide effects an *anti*-periplanar elimination of hydrogen halide. The *erythro*-compound produces practically exclusively (*E*)-2-phenyl-2-butene, its *threo*-stereoisomer only (*Z*)-2-phenyl-2-butene.



Potassium hydroxide-promoted elimination reactions of vicinal dihalides will be reported in a subsequent publication. From preliminary studies, the system potassium hydroxide/tetraglyme may also be advantageously applied in reactions such as base-catalysed olefin isomerizations and ester or cyanide condensations with carbonyl compounds.

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### Experimental part

**1. Starting Materials.** – 1.1. Potassium-*t*-butoxide was obtained from *Dynamit-Nobel AG*, D-5210 Troisdorf; other alkoxides were freshly prepared.

1.2. 1-Bromo-, 1-chloro- and 2-bromooctane are commercially available (*Fluka AG*; *Merck KG*). 2-Chlorooctane [18], 1-chloro-1-methylcyclohexane [19] and 2-chloro-3-phenylbutane [20] were prepared according to literature. In the latter case a mixture of diastereoisomers was obtained and separated by preparative GC. (6 m, 30% DEGS, 150°) into the pure *erythro*- and *threo*-components.

1.3. *N,N*-Dimethylhydroxylamine hydrochloride was prepared according to a known method [21]; the other amines or their hydrochlorides are commercial products. Octyl- and trimethyl-1-methylheptylammonium bromides were formed when 0.11 mol trimethylamine and 0.10 mol of the corresponding bromooctane were kept 72 h at 20° in a small steel autoclave; they were recrystallized from acetone, m.p. 215–217° (dec.) and 208–210° (dec.), respectively.

$C_{11}H_{26}BrN$  (252.3) Calc. C 52.38 H 10.39% Found C 52.30 H 10.62%  
Found C 52.16 H 10.68%

Trimethyl-1-methylheptylammonium bromide cannot be stored; it undergoes slow decomposition at 25°.

1.4. The solvents used were anhydrous: benzene was dried by azeotropic distillation, dioxane and tetraglyme with potassium/sodium alloy, dimethylsulfoxide, methanol and the other alcohols by heating 1 h to reflux in the presence of CaH<sub>2</sub>, magnesium and calcium oxide, respectively, followed by distillation.

**2. Elimination Reactions and Product Analysis.** – a) **Halooctanes as substrates:** the conditions are described in the footnotes (a) to *Tables 1* and *2*. When the reaction was over, water (10 ml) and a known quantity of nonane (internal standard for the gas chromatographic determination of yields) were added. The products were extracted with pentane (20 ml) and, after drying the organic layer, identified by comparison of retention times with authentic samples (25 m, glass capillary, SE-30, 30°).

b) *1-Chloro-1-methylcyclohexane* and *2-chloro-3-phenylbutane* as substrates: The conditions are specified in footnote (a) to *Table 5*, the work-up is indicated in the preceding paragraph. Conditions for GC. analysis: 2 m, 15% SE-30 and 2 m, 15% DEGS, temperature program 80 → 220° (internal standard: nonane; materials for comparison: 1-methylcyclohexene (*Fluka AG*), methylenecyclohexane [22], (*Z*)- and (*E*)-2-phenyl-2-butene [23]). Under the usual conditions 2-phenyl-2-butene was obtained as an equilibrium mixture (*Z*:*E*=21:79). When the reaction was carried out at 25° with diastereomerically pure substrates, *erythro*- and *threo*-2-chloro-3-phenylbutane afforded (*Z*)- and (*E*)-2-phenyl-2-butene in the ratios 1:100 and 20:1, respectively (at approximately 10% conversion). Upon treatment with sodium ethoxide in ethanol, the *erythro*-isomer gave exclusively *E*-olefin and the *threo*-isomer only *Z*-olefin.

2-chloro-3-phenylbutanes<sup>4)</sup> *erythro*-isomer: b.p. 30–31°/0.2 Torr. – <sup>1</sup>H-NMR. (CDCl<sub>3</sub>, 80 MHz): 7.2 (fine *m*), 4.10 (*qi*, fine structure, *J*=7), 2.88 (*qi*, fine structure, *J*=7), 1.43 (*d*, *J*=7), 1.34 (*d*, *J*=7).

$C_{10}H_{13}Cl$  (168.7) Calc. C 71.21 H 7.77% Found C 71.39 H 7.89%

*threo*-isomer: b.p. 32–33°/0.2 Torr. – <sup>1</sup>H-NMR. (CDCl<sub>3</sub>, 80 MHz): 7.26 (*s*), 4.23 (*qi*, fine structure, *J*=6.5), 3.05 (*qi*, fine structure, *J*=6.5), 1.40 (*d*, *J*=6.5), 1.38 (*d*, *J*=6.5).

$C_{10}H_{13}Cl$  (168.7) Calc. C 71.21 H 7.77% Found C 71.30 H 7.96%

<sup>4)</sup> Structure assignment in conflict with [24].



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**Erratum**

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lies: *Addition of dinitrogen trioxide to indene and alkylindenes.*