223. Competing Fragmentation, Substitution and Elimination in the Solvolysis of Alkylated 3-Chloropropanols and their Ethers

Fragmentation Reactions No. 28

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(26.VI.78)

Summary

The unstrained 3-chloroalcohols **1a**, **2a** and **3a** do not undergo solvolytic fragmentation in neutral and weakly acidic 80% ethanol, only substitution and elimination products being formed by the limiting S_N1-$E1$ mechanisms. This also applies to the corresponding ethers **1b** and **3b**. Addition of sodium hydroxide causes the observed rate constants for the 3-chloroalcohols to rise steeply by factors of at least 10^3 to 10^5. These level off at higher base concentrations due to an opposing ionic strength effect. Whereas **3a** fragments quantitatively in the presence of base, **1a** and **2a** fragment in competition with elimination to the Δ^3-olefins **9a** and **10**, respectively. **2a** also yields 2% of the oxetane **6b**.

These results support a concerted base-induced fragmentation mechanism which competes with intramolecular base-induced elimination (E_i) in the case of the acyclic chloroalcohols **1a** and **2a**. The formation of small amounts of the oxetane **6b** from **2a** is attributed to intramolecular nucleophilic substitution at the tertiary carbon atom.

Several 3-X-substituted propanols I *(Scheme 1)*, where X denotes a nucleofuge such as a chlorine atom, have been reported to undergo base-induced olefin-forming fragmentation (F) [1] [2]. However, cyclization (C) to oxetanes, nucleophilic substitution (S) and elimination (E) often compete with fragmentation [3–5].

Thus, when treated with sodium hydroxide acyclic primary chlorides I tend to undergo substitution and cyclization rather than fragmentation. Only when geminal alkyl groups are present at C(2) does the latter reaction occur to a larger extent [3]. Base-induced fragmentations of acyclic secondary halides I are rare, while tertiary halides do not appear to have been studied, presumably because of their instability [5]. Base-induced fragmentation of a number of rigid secondary and tertiary cyclic 3-X-substituted alcohols has been observed [6] in cases where the sequence of atoms $^-$O–C–C–C–X meets the well-established stereoelectronic requirements

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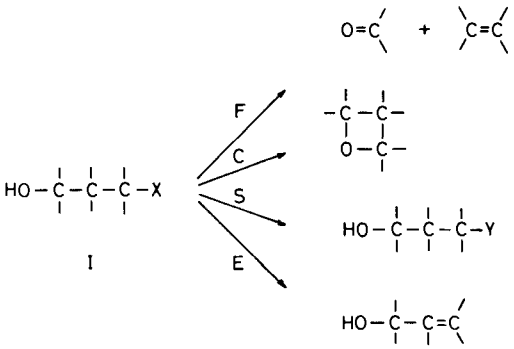
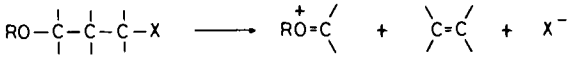
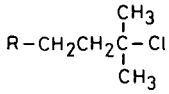
Scheme 1



Scheme 2





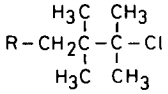
1 R =

a HO

b CH_3O

c CH_3

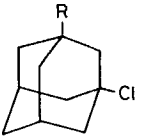
d C_2H_5



2 R =

a HO

b CH_3

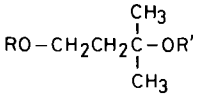


3 R =

a HO

b C_2H_5O

c H

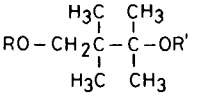


4 **a** R = R' = H

b R = CH_3, R' = H

c R = H, R' = C_2H_5

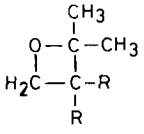
d R = CH_3, R' = C_2H_5



5 **a** R = R' = H

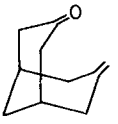
b R = *p*-$CH_3C_6H_4SO_2$, R' = H

c R = H, R' = C_2H_5



6 **a** R = H

b R = CH_3



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for the concerted mechanism, *i.e.* antiperiplanar orientation of an oxygen lone pair and the C–X bond with respect to the C(1)–C(2) bond [7].

Despite these reports reliable data concerning the dependence of the four reactions in *Scheme 1* on base concentration is lacking. In particular, it is still an open question whether alcohols of type I fragment at all under neutral or weakly acidic conditions. Consequently, the products and rates of the solvolysis of some representative 3-chloroalcohols, namely **1a**, **2a** and **3a**, were determined in 80% ethanol as a function of NaOH concentration. Tertiary chlorides were chosen in order to ensure high reactivity and to suppress bimolecular substitution of the chlorine atom by the hydroxide ion in the acylic models.

Included in this study are the corresponding 3-chloroethers **1b** and **3b** as well as the homomorphous tertiary alkyl halides **1c**, **1d**, **2b** and **3c**. The former *(Scheme 2)* were required to establish whether an alkoxy group is a sufficiently effective electron donor to permit fragmentation to alkoxy carbenium ions and olefins. The homomorphs served to gauge the effect of the hydroxy and alkoxy groups on the ionization rates[2]).

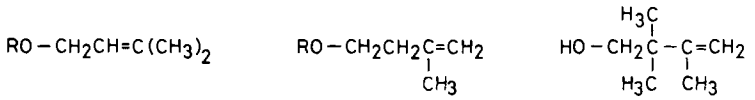
Results. 3-Chloro-3-methyl-1-butanol (**1a**) and its methyl ether **1b** were prepared following known procedures[3]). Treatment of 2,2,3-trimethyl-1,3-butanediol (**5a**) with conc. hydrochloric acid yielded the desired 3-chloro-2,2,3-trimethyl-1-butanol (**2a**). The latter was contaminated with starting material which could not be removed by crystallization. However, pure **2a** resulted when 2,2,3,3-tetramethyloxetane (**6b**) was reacted with dry HCl in ether. **6b** was obtained from the mono-*p*-toluenesulfonate **5b** of the diol **5a** by treatment with potassium *t*-butoxide. 3-Chloroadamantan-1-ol (**3a**) was prepared from 7-methylidenebicyclo[3.3.1]-

Table 1. *Influence of NaOH concentration on the yield* (in %) *of products in 80 vol.-% ethanol*

Chloride	T [°]	Initial concentrations [mol/l]		Yields (in %) of				
		Chloride	NaOH	Alcohols	Ethers	Olefins Δ^2	Δ^3	Fragmentation
1a	70	0.01	0	34	18	13	35	
	0	0.025	0.05				27	73[a])
	0	0.05	0.5				26	74
	0	0.05	1.43				26	74
1b	66	0.01	0	42	19	17	22	
2a	30	0.01	0	20	14		66	
	−27	0.01	0.153				37	61[b])
	−27	0.01	0.94				36	62[b])
3a	100	0.01[c])	0	54	46			
	0	0.10	0.20					100
3b	120	0.01[c])	0	58	42			

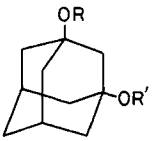
[a]) 77% of fragmentation at −15°, 69% at 50°.
[b]) Beside 2% of oxetane **6b**.
[c]) Buffered with 0.011M glycine.

[2]) For a preliminary report s. [8].
[3]) S. exper. part.



8 **9** **10**

a R = H, **b** R = CH_3



a R = R' = H
b R = C_2H_5, R' = H
c R = R' = C_2H_5

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nonan-3-one (**7**) as described earlier [9]. With HCl in ethanol the latter cyclized to 1-ethoxy-3-chloroadamantane (**3b**).

The chlorides **1a**, **2a** and **3a** were first reacted in 80 vol.-% ethanol in the absence of base, *i.e.* under weakly acidic conditions. However, 1–2 equiv. of glycine were added in the case of the bicyclic chlorides **3a** and **3b** in order to buffer the hydrochloric acid which is generated during the reaction and which would cause recyclization of any methylidene ketone **7** formed by fragmentation[4]). Products were determined quantitatively by GLC. and identified by comparison with authentic samples *(Table 1)*.

Under weakly acidic conditions **1a** yielded 52% of a mixture of diol **4a** and ether **4c** beside 48% of a mixture of the Δ^2- and Δ^3-olefins **8a** and **9a**, respectively, in which the latter predominated *(Table 1)*. The chloroether **1b** yielded a similar mixture of alcohol **4b** and ether **4d** beside the olefins **8b** and **9b**. From the chloroalcohol **2a** 66% of the Δ^3-olefin **10** beside 34% of diol **5a** and ether **5c** were obtained. No oxetanes **6a** or **6b** were formed from **1a**, **1b** and **2a**, nor did fragmentation take place as evidenced by the absence of formaldehyde in the reaction solutions. 3-Chloroadamantan-1-ol (**3a**) and its ethyl ether **3b** reacted to give substitution products only, *i.e.* **11a**, **11b** and **11c**, respectively *(Table 1)*.

Addition of sodium hydroxide to solutions of the chloroalcohols in 80% ethanol drastically changed the course of the reactions *(Table 1)*. Thus, **1a** underwent 74% of fragmentation to isobutene and formaldehyde and 26% of elimination to the Δ^3-olefin **9a**. Likewise, **2a** yielded 62% of tetramethylethylene and formaldehyde and 36% of the Δ^3-olefin **10**. In this case *ca.* 2% of the oxetane **6b** were also formed. 3-Chloroadamantan-1-ol (**3a**) gave a quantitative yield of the fragmentation product 7-methylidene-bicyclo[3.3.1]nonan-3-one (**7**). In all cases the addition of 4–5 equiv. of NaOH sufficed to bring about constant yields of products, the ratio of which was independent of NaOH concentration. Furthermore, the oxetanes **6a** and **6b** were excluded as intermediates in the formation of fragmentation and

[4]) Practically no cyclization of **7** to adamantane-1,3-diol and its monoethyl ether takes place in the presence of glycine, as shown elsewhere [9].

Table 2. *First order rate constants in 80 vol.-% ethanol* [a])

	T [°]	k [s^{-1}]	$\Delta H^{\neq}$ [kcal/mol]	$\Delta S^{\neq}$ [cal/mol · degree]
1a	0	$1.25 \cdot 10^{-7}$ [b])		
	52.05	$1.64 \cdot 10^{-4}$		
	56.00	$2.55 \cdot 10^{-4}$ [b])	23.5	−3.8
	62.00	$4.86 \cdot 10^{-4}$		
	71.90	$1.41 \cdot 10^{-3}$		
1b	0	$5.43 \cdot 10^{-8}$		
	56.00	$1.04 \cdot 10^{-4}$	23.4	−5.7
	66.00	$3.05 \cdot 10^{-4}$		
	76.00	$8.57 \cdot 10^{-4}$		
1c	0	$4.67 \cdot 10^{-7}$ [b])		
	52.05	$3.56 \cdot 10^{-4}$		
	56.00	$5.43 \cdot 10^{-4}$ [b])	21.9	−7.3
	66.00	$1.52 \cdot 10^{-3}$		
	71.90	$2.62 \cdot 10^{-3}$		
1d	56.00	$5.14 \cdot 10^{-4}$ [c])		
2a	0	$1.11 \cdot 10^{-6}$ [b])		
	20.00	$2.41 \cdot 10^{-5}$		
	25.00	$4.80 \cdot 10^{-5}$ [b])		
	30.00	$9.23 \cdot 10^{-5}$		
	40.00	$3.50 \cdot 10^{-4}$		
	56.00	$2.32 \cdot 10^{-3}$ [b])	23.7	1.4
2b	56.00	$1.98 \cdot 10^{-3}$ [d])	21.4	−6.2
3a	0	$2.43 \cdot 10^{-10}$ [b])		
	56.00	$3.47 \cdot 10^{-7}$ [b])	22.8	−19.0
	100.00	$2.54 \cdot 10^{-5}$		
	110.00	$5.84 \cdot 10^{-5}$		
	120.00	$1.27 \cdot 10^{-4}$		
3b	120.00	$6.88 \cdot 10^{-5}$ [e])		
3c	120.00	$2.92 \cdot 10^{-4}$ [e])		

[a])Average of three measurements; maximum deviation from mean values 1.5%. [b])Extrapolated. [c])S. [18]. [d])S. [19]. [e])S. [20].

Table 3. *Relative rate constants and* k/k_h [a]) *values*

	k_{rel} (56°)	k_{rel} (120°)	k/k_h [a])
HO–$CH_2CH_2C(CH_3)_2Cl$ (**1a**)	2.45		0.47
$CH_3CH_2CH_2C(CH_3)_2Cl$ (**1c**)	5.43		
$CH_3OCH_2CH_2C(CH_3)_2Cl$ (**1b**)	1		0.20
$CH_3CH_2CH_2CH_2C(CH_3)_2Cl$ (**1d**)	4.94		
HO–$CH_2C(CH_3)_2C(CH_3)_2Cl$ (**2a**)	22.3		1.17
$CH_3CH_2C(CH_3)_2C(CH_3)_2Cl$ (**2b**)	19		
3-Chloroadamantan-1-ol (**3a**)	$3.34 \cdot 10^{-3}$	1.85	0.43
1-Ethoxy-3-chloroadamantane (**3b**)		1	0.24
1-Chloroadamantane (**3c**)		4.24	1

[a])k_h = rate constant for the homomorphs **1c**, **1d**, **2b**, and **3c**. For the values of k and k_h, s. *Table 2.*

Table 4. *Dependence of the observed first order rate constants for chloroalcohols* **1a**, **2a** *and* **3a** *(0.005M) upon base concentration*

Compound	T [°]	NaOH [mol/l][a])	k_{obs}	k_{rel}
$HO-CH_2CH_2C(CH_3)_2Cl$ (**1a**)	0.00	0	$1.25 \cdot 10^{-7}$[b])	1
		0.1007	$2.64 \cdot 10^{-5}$[c])	
		0.248	$6.61 \cdot 10^{-5}$[c])	
		0.445	$1.04 \cdot 10^{-4}$[d])	
		0.723	$1.24 \cdot 10^{-4}$[d])	
		0.958	$1.24 \cdot 10^{-4}$[d])	10^3
		1.410	$1.19 \cdot 10^{-4}$[d])	
$HO-CH_2C(CH_3)_2C(CH_3)_2Cl$ (**2a**)	−27.00	0	$7.99 \cdot 10^{-9}$[b])	1
		0.100	$3.89 \cdot 10^{-4}$[c])	
		0.149	$4.63 \cdot 10^{-4}$[c])	
		0.201	$5.35 \cdot 10^{-4}$[c])	
		0.351	$5.39 \cdot 10^{-4}$[c])	
		0.403	$5.40 \cdot 10^{-4}$[c])	$6.8 \cdot 10^4$
3-Chloroadamantan-1-ol (**3a**)	0.00	0.00	$2.43 \cdot 10^{-10}$[b])	1
		0.0497	$1.57 \cdot 10^{-5}$[c])	
		0.0920	$2.30 \cdot 10^{-5}$[c])	
		0.309	$6.20 \cdot 10^{-5}$[c])	
		0.584	$9.43 \cdot 10^{-5}$[d])	
		1.004	$1.13 \cdot 10^{-4}$[d])	
		1.347	$1.18 \cdot 10^{-4}$[d])	$4.86 \cdot 10^5$

[a]) Initial concentrations. [b]) Extrapolated. [c]) Conductometric determination. [d]) Titrimetric determination.

elimination products since they proved to be stable under the reaction conditions. The fragmentation/elimination ratio in the case of **1a** was distinctly temperature dependent and varied from 3.3 at −15° to 2.2 at 50°.

The first order rate constants k for the solvolysis of the chloroalcohols, ethers and homomorphs in 80 vol.-% ethanol are listed in *Table 2*, relative rate constants k_{rel} in *Table 3*. Addition of NaOH to solutions of the chloroalcohols caused a striking rate increase *(Table 4)*. This is further illustrated by plotting the logarithms of the observed first order rate constants k_{obs} for **1a** and **3a** against NaOH concentration *(Figure)*. The curves rise steeply, level off at *ca.* 0.5M NaOH and reach a maximum beyond which an increase in base concentration has little further effect[5]). In fact k_{obs} for **1a** even decreases slightly due to a negative ionic strength effect since addition of 0.3M sodium nitrate to 0.85M NaOH caused k_{obs} at 0° to decrease from $1.24 \cdot 10^{-4}$ to $0.922 \cdot 10^{-4}$, *i.e.* by 26%.

Discussion. – These results clearly show that the chloroalcohols **1a**, **2a** and **3a** undergo different reactions in the absence and in the presence of base. In the former case the typical products of the unimolecular substitution *(S_N1)* and elimination *(E1)* mechanisms are formed, namely alcohols, ethyl ethers and olefins *(Table 1)*. This also applies to the chloro ethers **1b** and **3b** and implicates carbocations of the

[5]) Above *ca.* 0.05M NaOH, *i.e.* 10 equiv., the reactions follow a pseudo first order rate law.

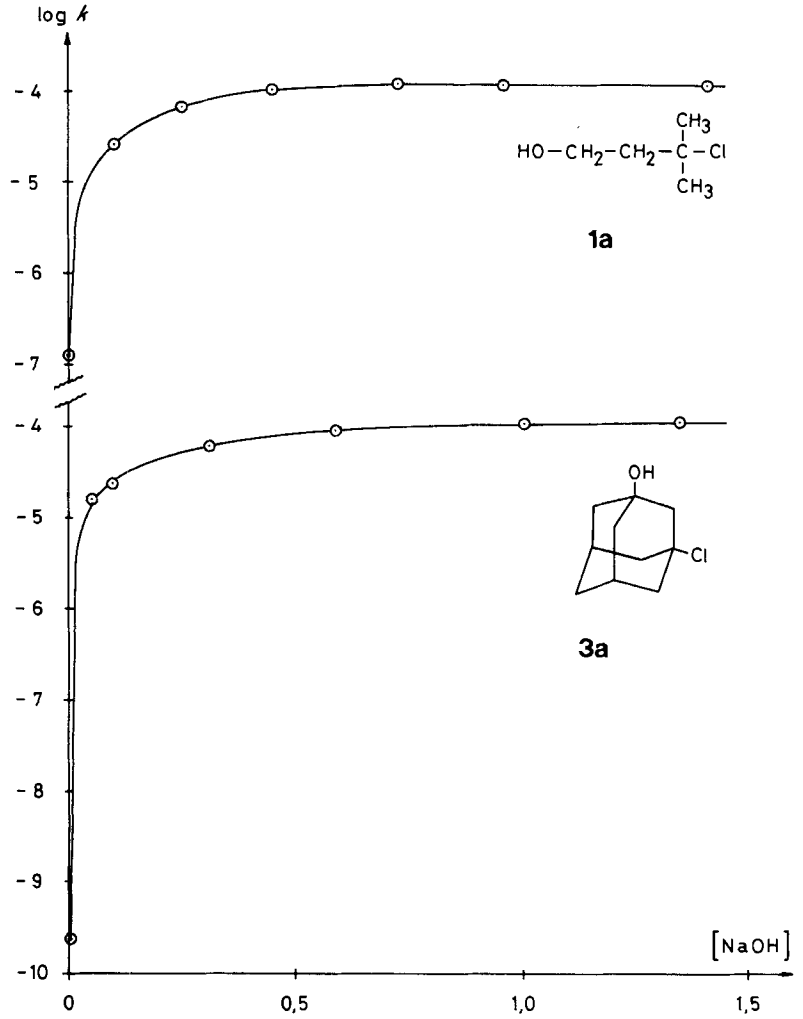
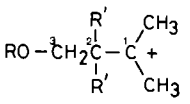


Figure. *Plot of the observed rate constants for* **1a** *and* **3a** *against NaOH concentration in 80 vol.-% ethanol at 0°*

type **12** as intermediates. In the case of the chloroadamantanes **3a** and **3b** elimination is of course excluded due to the operation of *Bredt's* rule. The predominant formation of the Δ^3-olefins **9a** and **10** from **1a** and **2a** suggests that the oxygen atoms are involved in proton abstraction from the cation, as illustrated in **13**. The high elimination/substitution ratio of 1.94 in the case of **2a** is in agreement with this view. Conspicuously, fragmentation is not observed under these kinetically controlled conditions. In contrast hexamethyl-1,3-propanediol (**14**) *(Scheme 3)* fragments completely to acetone and tetramethylethylene when heated with aqueous acid [10]. Obviously, the cation **15** is repeatedly formed under these conditions allowing the slower but thermodynamically favored fragmentation reaction to intervene.



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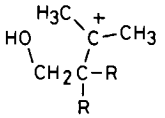

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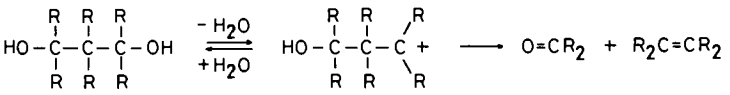
a R = H

b R = CH_3

Scheme 3

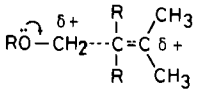


14 **15**

R = CH_3

A comparison of the rate constants for the chloroalcohols and ethers (k) with those for the sterically equivalent homomorphs (k_h) supports the above conclusions *(Table 3)*. The ratios k/k_h which vary from 0.20 to 0.47 for **1a**, **1b**, **3a** and **3b** indicate a small rate retarding inductive effect of the oxygen atom in the chloroalcohols and ethers. The chloroalcohol **2a** is a notable exception since it reacts slightly faster than its homomorph **2b**, ($k/k_h = 1.17$). As pointed out elsewhere [9] there are good reasons to assume that the electron-withdrawing inductive effect of the oxygen atom in carbocations of the type **12** is more or less compensated by C,C-hyperconjugation (σ-conjugation) of the C(2)–C(3) bond, as illustrated in **16**. Hydroxy and alkoxy groups will tend to augment the delocalisation of the σ bond by donating electrons to C(3), but not sufficiently to cause fragmentation. On this basis the k/k_h values in *Table 3* reflect the result of opposing inductive and C,C-hyperconjugative effects [9] [11].

A different situation prevails when the chloroalcohols I *(Scheme 4)* are partially converted into their conjugate bases II by NaOH. As more of the latter is added the acid-base equilibrium is shifted in favor of the anions II, the negatively charged oxygen atoms of which are simultaneously strong electron donors and strong bases. This is reflected in greatly enhanced rates *(Table 4)* and in the appearance of fragmentation products *(Table 1)*. While the k observed in 80% ethanol *(Table 2)* equals the rate constant for the chloroalcohols I themselves the maximum value of k_{obs} under basic conditions *(Table 4)* only approximates the true rate constant k_2 for the reaction of the anion II. This is due to the negative ionic strength effect which lowers k_2 and to the fact that k_{obs} also



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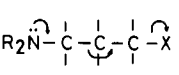

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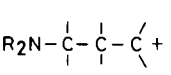

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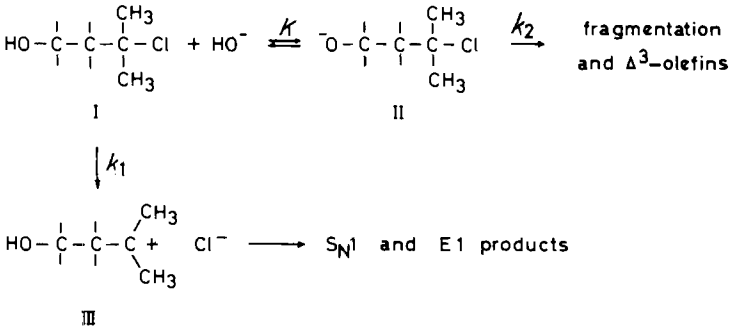
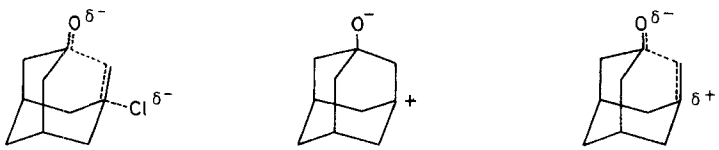
Scheme 4



includes the equilibrium constant K. Assuming, however, that at NaOH concentrations above 0.5 M substancial portions of the chloroalcohols I are converted to their conjugate bases II k_{obs} provides a useful, albeit rough measure for the reaction rates of II. On this basis the anions II of **1a**, **2a** and **3a** react at least 10^3, $6.8 \cdot 10^4$ and $4.8 \cdot 10^5$ times faster than the chloroalcohols I themselves *(Table 4)*.

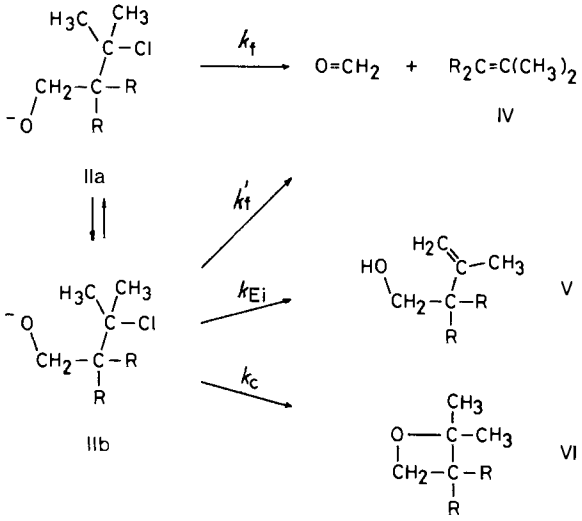
For **3a** the entire rate increase of *ca.* $4.8 \cdot 10^5$ is due to fragmentation of the corresponding anion II, the sole reaction in basic solution *(Table 1)*. Large accelerations are a characteristic feature of concerted fragmentation reactions, it being well established that the latter are faster than those proceeding by the alternative two-step process. Thus, 3-X-substituted amines **17** fragment up to 10^4 times faster by the concerted mechanism than by way of an intermediate carbocation **18** [7], the rate ratio of the two processes serving as a measure for the frangomeric effect. Since a negatively charged oxygen atom is a better electron donor than a neutral nitrogen atom [9], the observed acceleration of more than 10^5 for the anion from **3a** is a strong indication that it fragments by the concerted mechanism. In the transition state **19** of this process the negative charge, originally located on the oxygen atom, is dispersed. A medium of high ionic strength would therefore be expected to retard the reaction, as is actually observed[6]). This negative salt effect militates against a two-step fragmentation mechanism involving an intermediate zwitter-ion **20**, for in this case the negative charge on the oxygen atom is not reduced in the transition state. Also, substitution products derived from **20**, *i.e.* diol and ether, are not obtained. Furthermore, a zwitter-ionic intermediate is unlikely on theoretical grounds. As shown elsewhere [9] [11] hyperconjugation of a strong electron donor and a strong acceptor, as in **20**, should lead to extensive σ-delocalisa-



19 **20** **21**

[6]) For a further example of a negative salt effect in a concerted fragmentation reaction see [12] and a subsequent paper.

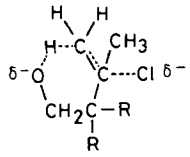
Scheme 5



tion, as illustrated in **21**. Since the latter also represents the transition state for fragmentation it is unlikely that the zwitter-ion **20** would require further activation in order to fragment to **7**.

The rate increase of *ca.* 10^3 observed for the chloroalcohol **1a** is accompanied by 74% of fragmentation and 26% of elimination to the Δ^3-olefin **9a** *(Table 1)*. These two processes therefore account for 74% and 26% of the acceleration, respectively. The rate increase of $6.8 \cdot 10^4$ observed for the chloroalcohol **2a** is due to three reactions, *i.e.* fragmentation (62%), elimination to the Δ^3-olefin **10** (36%) and cyclization to the oxetane **6b** (2%), which contribute to k_{obs} by factors of $4.2 \cdot 10^4$, $2.5 \cdot 10^4$ and $1.3 \cdot 10^3$, respectively. Since the ratio of the products is independent of the NaOH concentration they must be derived from common intermediates, *i.e.* the conjugate bases from **1a** and **2a**.

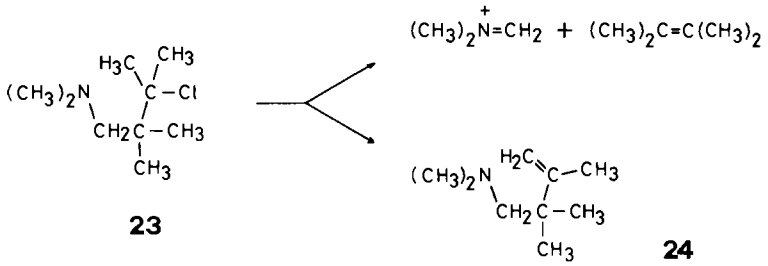
The latter can adopt conformations such as IIa and IIb *(Scheme 5)* in which a lone electron pair on the oxygen atom and the C(3)–Cl bond are both antiperiplanar with respect to the C(1)–C(2) bond. Fragmentation to formaldehyde and olefin IV should therefore occur by the concerted mechanism[7]) [7]. However, in conformation IIb (R = H or CH_3) the negatively charged oxygen atom is also suitably located to remove a proton from a methyl group at C(3) with simul-



22

[7]) All rotamers derived from IIa by rotation around the C(1)–C(2)-bond should fragment concertedly, as pointed out in [13], footnote 2).

Scheme 6



taneous expulsion of chloride ion. The geometry of the transition state **22** for this intramolecular base-induced elimination favors the formation of the Δ^3-olefin V (s. *Scheme 5*). A similar mechanism was postulated earlier to explain the accelerated formation of the Δ^3-olefin **24** which accompanies the fragmentation of the 3-chloroamine **23** *(Scheme 6)* [14]. This type of anchimerically assisted elimination has also been observed in sulfur analogues of **1** and **2** [12][8]) and can be called the E_i mechanism to indicate that an internal base such as N, O^- or S^- induces 1,2-elimination in the manner of external bases[9]).

The negatively charged oxygen atom in conformation IIb *(Scheme 5)* is also suitably located to attack the carbon atom C(3) with displacement of chloride ion to form an oxetane VI. Involvement of the negatively charged oxygen atom in a concerted process is evidenced for **2a** by the rate increase of *ca.* 10^3 which is due to the formation of the oxetane **6b**, albeit in low yield. Nucleophilic displacement at a tertiary carbon atom is usually not observed, not even in cyclization reactions [15][10]). It is therefore noteworthy that cyclization only occurs in the anion IIb when R equals CH_3 *(Scheme 5)*, undoubtedly the result of the geminal alkyl effect [17].

In conclusion, the unstrained 3-chloroalcohols **1a**, **2a** and **3a** and the corresponding ethers **1b** and **3b** do not undergo solvolytic fragmentation in neutral or weakly acidic 80% ethanol[11]). In the presence of NaOH accelerated fragmentation, E_i-elimination and cyclization occur. In these cases the observed rate constant is composed of the rate constants k_f, k_f', k_{E_i} and k_c *(Scheme 5)* for the transformation of the reactive conformers and the mol fractions of the latter. However, a quantitative treatment appears impracticable at the present time due to the number of unknown factors involved.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*, grant No. 2.617.72.

Experimental Part

Melting points (m.p.) were determined on a *Kofler*-Block and are corrected to ± 1°. IR. spectra in cm^{-1}. NMR. spectra in ppm relative to TMS (= 0 ppm), coupling constants J in Hz.

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[8]) S. the subsequent paper in this series.

[9]) The E_i mechanism is thus the intramolecular version of the bimolecular $E2$ mechanism.

[10]) For an exception s. [16].

[11]) This does not hold for strained analogues as shown in a forthcoming paper.

Syntheses. – *3-Chloro-3-methyl-1-butanol* (**1a**). A solution of 26.1 g (0.25 mol) of 3-methyl-1,3-butanediol (**4a**) [21] in 75 ml (*ca.* 0.9 mol) of conc. hydrochloric acid was extracted with 100 ml of methylene chloride after standing at 25° for 4, 12, 30, 60 and 150 min, respectively. The combined extracts were shaken with anhydrous Na_2CO_3 and dried over Na_2SO_4. Evaporation of the solvent and distillation of the residue yielded 18.8 g (62%) of **1a**, b.p. 27.5–29°/0.08 Torr ([22]: 32%, b.p. 50–65°/15 Torr) with slight evolution of HCl. After three crystallizations from pentane at −70°, m.p. −8 to −7°. – IR. (CCl_4): 3640 (prim. OH). – NMR. (CCl_4): 1.61 (*s*, 6 H, $(CH_3)_2C$); 2.01 (*t*, *J* = 6.75, 2 H, 2 H–C(2)); 3.29 (*s*, 1 H, OH); 3.83 (*t*, *J* = 6.75, 2 H, 2 H–C(1).

$C_5H_{11}ClO$ (122.595) Calc. C 48.99 H 9.04% Found C 49.21 H 8.88%

3-Chloro-1-methoxy-3-methylbutane (**1b**) was prepared by a known procedure [23]. Distillation through a spinning-band column yielded 62% of **1b**, b.p. 33.8–34°/16 Torr ([23]: 60%, b.p. 81°/120 Torr). – NMR. (CCl_4): 1.58 (*s*, 6 H, $(CH_3)_2C$); 1.97 (*t*, *J* = 6.25, 2 H, 2 H–C(2)); 3.27 (*s*, 3 H, CH_3O); 3.52 (*t*, *J* = 6.25, 2 H, 2 H–C(1)).

$C_8H_{18}O_2$ (136.622) Calc. C 52.74 H 9.59% Found C 52.93 H 9.65%

2-Chloro-2-methylpentane (**1c**) was prepared according to [24]. Yield 79%, b.p. 43.5–44°/70 Torr ([24]: 36–37°/15 Torr). – NMR. (CCl_4): 0.96 (*t*, *J* = 6.5, 3 H, 3 H–C(5)); 1.4–1.9 (br. *m*, 2 H, CH_2); 1.57 (*s*, 6 H, $(CH_3)_2C$); 1.68 (*t*, *J* = 3, 2 H, CH_2).

3-Chloro-2,2,3-trimethyl-1-butanol (**2a**). 0.5 g (4.38 mmol) of 2,2,3,3-tetramethyloxetane (**6b**) dissolved in 20 ml of a *ca.* 0.6M solution of HCl in ether (12 mmol) were reacted at 0° for 1 h. After evaporation *in vacuo* the resulting chloride **2a** was crystallized from pentane at −15°. Yield 0.47 g (71%), m.p. 120–122° (decomp.). **2a** is stable at −15° but evolves HCl at room temp. – IR. (CCl_4): 3642 (prim. OH). – NMR. (CCl_4): 1.05 (*s*, 6 H, $(CH_3)_2C$); 1.61 (*s*, 6 H, $(CH_3)_2C$); 2.21 (*s*, 1 H, OH); 3.59 (*s*, 2 H, 2 H–C(1)).

$C_7H_{15}ClO$ (150.649) Calc. C 55.80 H 10.04% Found C 56.35 H 10.14%

2,2,3-Trimethyl-1,3-butanediol (**5a**) was prepared from ethyl 3-hydroxy-2,2,3-trimethylbutyrate [25] by reduction with $LiAlH_4$. From petroleum ether yield 52%, m.p. 144–146° ([25]: 34%, m.p. 127–129°. – IR. (CCl_4): 3640 (prim. OH), 3620 (tert. OH). – NMR. ($(CD_3)_2SO$): 0.81 (*s*, 6 H, $(CH_3)_2C$); 1.07 (*s*, 6 H $(CH_3)_2C$); 3.34 (*d*, *J* = 5, 2 H, 2 H–C(1)); 4.23 (*s*, 1 H, HO–C(3)); 4.67 (*t*, *J* = 5, 1 H, HO–C(1)).

$C_7H_{16}O_2$ (132.204) Calc. C 63.59 H 12.20% Found C 63.82 H 12.32%

3-Hydroxy-2,2,3-trimethyl-1-butyl-p-toluenesulfonate (**5b**). 2.6 g (20 mmol) of diol **5a** and 3.8 g (20 mmol) of *p*-toluenesulfonyl chloride in 15 ml of pyridine were reacted at −4° for 48 h. The mixture was acidified with aqueous HCl solution and extracted 3 times with ether; the extracts were washed with water and dried over Na_2SO_4. Evaporation *in vacuo* yielded 4.4 g (78%) of **5b** after drying at 0.01 Torr. The viscous oil solidified at *ca.* −20° and was used in the subsequent step. – IR. (CCl_4): 3620 (tert. OH).

2,2,3,3-Tetramethyloxetane (**6b**). 7.0 g (23.4 mmol) of the oily *p*-toluenesulfonate **5b** were added to a suspension of 4.5 g (40 mmol) of potassium *t*-butylate in 100 ml of ether under vigourous stirring at 22°. After heating under reflux for 48 h water was added to dissolve the precipitate, the water layer was separated and washed twice with ether. The dried ether extracts were concentrated by distillation through a 10 cm *Vigreux* column and the residue was purified by prep. GLC. on a 20% SE-30 column: 1.75 g (66%) of **6b**, b.p. 115° ([26]: b.p. 113°). – NMR. (CCl_4): 1.14 (*s*, 6 H, $(CH_3)_2C$); 1.24 (*s*, 6 H, $(CH_3)_2C$); 4.03 (*s*, 2 H, 2 H–C(4)).

$C_7H_{14}O$ (114.188) Calc. C 73.63 H 12.36% Found C 73.87 H 12.36%

3-Methyl-1,3-butanediol (**4a**) was prepared from ethyl 3-hydroxy-3-methylbutyrate by reduction with $LiAlH_4$ [21]. Yield 92%, b.p. 100–103°/11 Torr ([21]: 67%, b.p. 104°/14 Torr). – NMR. (CCl_4): 1.12 (*s*, 6 H, $(CH_3)_2C$); 1.56 (*t*, *J* = 6.5, 2 H, 2 H–C(2)); 3.56 (*t*, *J* = 6.5, 2 H, 2 H–C(1)); 3.60, 3.73 and 4.04 (unresolved band, 2 H, H-bridged OH).

$C_5H_{12}O_2$ (104.150) Calc. C 57.66 H 11.61% Found C 57.86 H 11.47%

2-Methyl-4-methoxy-2-butanol (**4b**) was prepared by hydrolysis of **1b** with aqueous Na_2CO_3 solution according to [23]. Yield 73%, b.p. 88–89.5°/90 Torr ([23]: 75%, b.p. 144°/764 Torr). – IR. (CCl_4): 3620 (tert. OH). – NMR. (CCl_4): 1.14 (*s*, 6 H, $(CH_3)_2C$); 1.64 (*t*, *J* = 7, 2 H, 2 H–C(3)); 2.90 (*s*, 1 H, OH); 3.23 (*s*, 3 H, CH_3O); 3.46 (*t*, *J* = 7, 2 H, 2 H–C(4)).

$C_6H_{14}O_2$ (118.187) Calc. C 60.98 H 11.94% Found C 60.86 H 11.89%

3-Ethoxy-3-methyl-1-butanol (**4c**) was prepared from 2,2-dimethyloxetane (**6a**) [27] and abs. ethanol with a trace of conc. sulfuric acid as described for **5c**. Yield 65%, b.p. 62–64°/10 Torr. – NMR. (CCl_4): 1.15 (*t*, *J* = 7, 3 H, CH_3CH_2O); 1.20 (*s*, 6 H, $(CH_3)_2C$); 1.70 (*t*, *J* = 6, 2 H, 2 H–C(2)); 2.96 (*s*, 1 H, OH); 3.44 (*qa*, *J* = 7, 2 H, CH_3CH_2O); 3.70 (*t*, *J* = 6, 2 H, 2 H–C(1)).

$C_7H_{16}O_2$ (132.204) Calc. C 63.59 H 12.20% Found C 63.73 H 12.19%

3-Ethoxy-1-methoxy-3-methylbutane (**4d**). A solution of 15 g (0.109 mol) of **1b** and 16.2 g (0.160 mol) of triethylamine in 55 ml of abs. ethanol was heated under reflux for 48 h. The solution was acidified with aqueous 2N HCl, diluted with 100 ml of water and extracted 3 times with 100 ml of ether. After washing with water and drying over Na_2SO_4 the combined extracts were evaporated at 0° *in vacuo*. The residue was separated by prep. GLC. and yielded 9.3 g (58%) of **4d**, b.p. 147–148°/740 Torr, beside the olefins **8b** and **9b**. – NMR. (CCl_4): 1.11 (*t*, *J* = 7, 3 H, CH_3CH_2O); 1.13 (*s*, 6 H, $(CH_3)_2C$); 1.70 (*t*, *J* = 7, 2 H, 2 H–C(2)); 3.28 (*s*, 3 H, CH_3O); 3.36 (*qa*, *J* = 7, 2 H, CH_3CH_2O); 3.41 (*t*, *J* = 7, 2 H, 2 H–C(1)).

$C_8H_{18}O_2$ (146.231) Calc. C 65.71 H 12.41% Found C 65.80 H 12.41%

3-Ethoxy-2,2,3-trimethyl-1-butanol (**5c**). To a solution of 0.57 g (5 mmol) of oxetane **6b** in 9 ml of abs. ethanol were added 50 mg of conc. sulfuric acid. After 3 days at 22° the solution was shaken with anhydrous Na_2CO_3, filtered and evaporated *in vacuo*. The residue was distilled in a bulb-tube and yielded 0.66 g (82%) of **5c**, b.p. 99–101°/10 Torr. – NMR. (CCl_4): 0.89 (*s*, 6 H, $(CH_3)_2C$); 1.17 (*s*, 6 H, $(CH_3)_2C$); 1.18 (*t*, *J* = 7, 3 H, CH_3CH_2O); 3.39 (*s*, 1 H, OH); 3.40 (*s*, 2 H, 2 H–C(1)); 3.47 (*qa*, *J* = 7, 2 H, CH_3CH_2O).

$C_9H_{20}O_2$ (160.258) Calc. C 67.45 H 12.58% Found C 67.65 H 12.56%

3-Methyl-2-buten-1-ol (**8a**) was prepared by dehydration of ethyl 3-hydroxy-3-methylbutyrate with P_2O_5 [28] and reduction with $LiAlH_4$. Distillation through a 75 cm spinning band column yielded 69% of pure **8a**, b.p. 137–137.5°/740 Torr ([28]: 62%, b.p. 141°/760 Torr). – IR. (CCl_4): 3630 (prim. OH), 1672 (C=C). – NMR. (CCl_4): 1.60 (*s*, 3 H, H_3C–C(3)); 1.67 (*s*, 3 H, H_3C–C(3)); 3.51 (*s*, 1 H, OH); 3.90 (*d*, *J* = 7, 2 H, 2 H–C(1)); 5.20 (*t*, *J* = 7, 1 H, H–C(2)).

$C_5H_{10}O$ (86.134) Calc. C 69.72 H 11.70% Found C 69.55 H 11.62%

3-Methyl-3-buten-1-ol (**9a**). 10.5 g (100 mmol) of **4a** and 0.58 g (5 mmol) of 84% phosphoric acid were heated to 162° (bath temp.). The water/olefin mixture which distilled over was taken up in CH_2Cl_2; the latter was washed with aqueous $NaHCO_3$-solution and water, dried and evaporated *in vacuo* through a *Vigreux* column. Analysis by GLC. revealed the presence of *ca.* 30% of isoprene, 10% of **8a** and 60% of **9a**. Fractional distillation gave 2.8 g (33%) of pure **9a**, b.p. 129.5–130°/740 Torr ([22]: 129–133°). – IR. (CCl_4): 3640 (prim. OH); 3095, 1650 and 895 ($C=CH_2$). – NMR. (CCl_4): 1.75 (*s*, 3 H, H_3C–C(3)); 2.25 (*t*, *J* = 7, 2 H, 2 H–C(2)); 3.05 (*s*, 1 H, OH); 3.67 (*t*, *J* = 7, 2 H, 2 H–C(1)); 4.81 (*m*, 2 H, 2 H–C(4)).

$C_5H_{10}O$ (86.134) Calc. C 69.72 H 11.70% Found C 70.00 H 11.71%

1-Methoxy-3-methyl-2-butene (**8b**) *and 4-methoxy-2-methyl-1-butene* (**9b**). 20 g (169 mmol) of **4b** and 0.93 g (8 mmol) of 84% phosphoric acid were heated to *ca.* 150° (bath temp.). The water/olefin mixture which distilled over was worked-up as described for **9a**, except that 20% aqueous NaCl-solution was used. Prep. GLC. on a 20% SE-30 column yielded 62% of **9b**, b.p. 93–94°/740 Torr, and 15% of **8b**, b.p. 101–103°/740 Torr ([29]: 104.5–105°/764 Torr). *Olefin* **8b**. – IR. (CCl_4): 1675 (CH=C), 1095 (C–O). – NMR. (CCl_4): 1.65 (*s*, 3 H, H_3C–C(3)); 1.74 (*s*, 3 H, H_3C–C(3)); 3.20 (*s*, 3 H, CH_3O); 3.80 (*d*, *J* = 7, 2 H, 2 H–C(1)); 5.28 (*t*, *J* = 7, 1 H, H–C(2)).

$C_6H_{12}O$ (100.161) Calc. C 71.95 H 12.08% Found C 71.78 H 12.30%

Olefin **9b**. – IR. (CCl_4): 3080, 1650 and 993 ($C{=}CH_2$). – NMR. (CCl_4): 1.72 (*s*, 3 H, $H_3C{-}C(2)$); 2.21 (*t*, $J{=}7$, 2 H, 2 H–C(3)); 3.24 (*s*, 3 H, CH_3O); 3.40 (*t*, $J{=}7$, 2 H, 2 H–C(4)); 4.67 (*m*, 2 H, 2 H–C(1)).

$C_6H_{12}O$ (100.161) Calc. C 71.95 H 12.08% Found C 72.14 H 12.18%

2,2,3-Trimethyl-3-buten-1-ol (**10**) was prepared according to [30], b.p. 152°, yield 75% ([30]: b.p. 152°). – IR. (CCl_4): 3642 (prim. OH); 3097, 1636 and 897 ($C{=}CH_2$). – NMR. (CCl_4): 1.01 (*s*, 6 H, $(CH_3)_2C$); 1.73 (*s*, 3 H, $H_3C{-}C(3)$); 1.73 (*s*, 1 H, OH); 3.28 (*s*, 2 H, 2 H–C(1)); 4.78 (*m*, 2 H, 2 H–C(4)).

$C_7H_{14}O$ (114.188) Calc. C 73.63 H 12.36% Found C 73.89 H 12.47%

3-Chloro-1-ethoxyadamantane (**3b**) [20]. A solution of 3 g (19.7 mmol) of 7-methylidenebicyclo[3.3.1]nonan-3-one (**7**) [31] in 10 ml of abs. ethanol containing a small amount of dry HCl was heated under reflux for 2 h. The solvent was removed *in vacuo* and the residue eluated under reflux with 13 ml of ether and 21.5 g (0.181 mol) of thionyl chloride for 3 h. The mixture was evaporated to dryness *in vacuo*, the oily residue taken up in pentane, and insoluble impurities were filtered off. The solution was evaporated to dryness and the residue chromatographed on silica gel with $CCl_4/CHCl_3$. Evaporation of the solvent and sublimation yielded 2.12 g (50%) of **3b**, m.p. 45.5°. – IR. (CCl_4): 1120 (C–O). – NMR. (CCl_4): 1.08 (*t*, $J{=}7$, 3 H, CH_3CH_2O); 1.4–1.7 (*m*, 6 H, CH and CH_2); 1.9–2.4 (*m*, 8 H, CH and CH_2); 3.27 (*qa*, $J{=}7$, 2 H, CH_3CH_2O).

$C_{12}H_{19}ClO$ (214.74) Calc. C 67.12 H 8.92 Cl 16.51% Found C 66.96 H 9.00 Cl 16.23%

3-Ethoxy-1-adamantanol (**11b**) and *1,3-diethoxyadamantane* (**11c**). A solution of 1.0 g of ketone **7** in 20 ml of abs. ethanol containing one drop of conc. sulfuric acid was heated under reflux for 3 days, then shaken with dry Na_2CO_3, filtered and evaporated to dryness *in vacuo*. The crude product was separated by prep. GLC. on a 20% SE-30 column at 170° yielding 0.21 g (16%) of **11b**, m.p. 74–74.5° ([32]: 77.5°) and 0.4 g (30%) of **11c**, which was distilled in a bulb tube at 272°/740 Torr. – NMR. (CCl_4): 1.08 (*t*, $J{=}7$, 6 H, $2\,CH_3CH_2O$); 1.3–1.7 (*m*, 12 H, 6 CH_2); 2.22 (br. *s*, 2 H, 2 CH); 3.33 (*qa*, $J{=}7$, 4 H, 2 CH_3CH_2O).

$C_{14}H_{24}O_2$ (224.345) Calc. C 74.95 H 10.78% Found C 75.20 H 10.94%

11b: NMR. (CCl_4): 1.11 (*t*, $J{=}7$, 3 H, CH_3CH_2O); 1.4–1.7 (*m*, 12 H, 6 CH_2); 1.95 (*s*, 1 H, OH); 2.28 (br. *s*, 2 H, 2 CH); 3.42 (*qa*, $J{=}7$, 2 H, CH_3CH_2O).

$C_{12}H_{20}O_2$ (196.291) Calc. C 73.43 H 10.27% Found C 73.33 H 10.18%

Adamantane-1,3-diol (**11a**) was prepared according to [32]. From $CHCl_3$ m.p. 310–315° ([32]: 315°). – NMR. ($(CD_3)_2SO$): 1.2–1.6 (*m*, 12 H, 6 CH_2); 2.08 (br. *s*, 2 H, 2 CH); 4.34 (*s*, 2 H, 2 OH).

$C_{10}H_{16}O_2$ (168.237) Calc. C 71.39 H 9.59% Found C 71.38 H 9.56%

Solvolyses. – 80 vol.-% ethanol was prepared from 1000 g of 'superdry' ethanol and 317.5 g of bidistilled water. Products were determined quantitatively by analyzing the reaction solutions after ten half-lives by GLC. and by comparison of retention times with those of authentic samples. Peak areas were calibrated with known quantities of the compounds. The yields *(Table 1)* are the average of three determinations; they varied by ±2%. Compounds **1a**, **1b** and **2a** were solvolyzed in 0.1–0.4M solution, **3a** and **3b** in 0.01M solution. In the latter case 2 equiv. of glycine were added.

The test for formaldehyde, a potential fragmentation product from **1a**, **1b** and **2a**, was carried out by adding 60 ml of aqueous 1N CH_3COONa, 30 ml of 1N HCl and 2 equiv. of dimedone. The mixture was held at 60° for 1 h and then cooled to 0°. The bis-dimedone adduct was filtered off quantitatively on a sintered glass funnel, washed with ice water and dried to constant weight, m.p. 189–191°. As little as 3 mg of formaldehyde can be detected by this method.

The solvolyses of the chloroalcohols **1a** and **2a** in the presence of NaOH (*Tables 1* and *4*) were carried out under nitrogen. The solutions were prepared by dissolving NaOH in 80 vol.-% ethanol, filtration and titration against 0.100N H_2SO_4. After ten half lives the solutions were neutralized with 2N HCl and then tested for formaldehyde as described. Solvolysis of **3a** produced the unsaturated ketone **7** only, as determined by GLC.

Rate measurements were carried out in water thermostats for temp. between 20 and 80°; above 80° polyethylene glycol, below 20° ethanol was used; temp. fluctuation was less than 0.05°. Rate constants for the chlorides in the absence of NaOH *(Table 2)* were determined by the conductometric method [33] in 0.005M solution. Rate constants in the presence of less than 0.3M NaOH were also followed conductometrically, at higher NaOH concentrations by potentiometric titration of chloride ion with 0.005M $AgNO_3$. In the latter case 5 ml aliquots were withdrawn from the well-stoppered reaction flask with an automatic pipette and acidified with *ca.* 2 equiv. of aqueous HNO_3 solution. Each measurement was repeated at least once.

Combustion analyses were carried out by Mr. *E. Thommen;* NMR. spectra were measured by Mr. *K. Aegerter* and Mr. *P. Jucker.*

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