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CONCERTED FRAGMENTATION AND ANCHIMERICALLY ASSISTED ELIMINATION IN THE SOLVOLYSIS OF 3-CHLOROPROPANOLS

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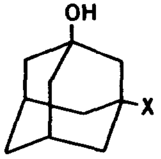
The 3-chloropropanols 1a, 2a and 3a undergo concerted olefin-forming fragmentation with sodium hydroxide in 80 vol. % ethanol. In addition, the acyclic compounds 2a and 3a undergo anchimerically assisted elimination. In the absence of base only substitution and elimination by the unimolecular mechanisms S_N1-E1 occur [1].



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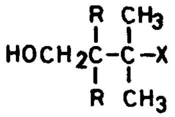
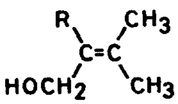
a) Cl
X = b) OH
c) OEt

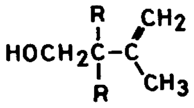


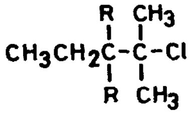
$HOCH_2CR_2-C(CH_3)_2-X$

2 R = H

3 R = CH_3







$CH_3CH_2CR_2-C(CH_3)_2-Cl$

6 R = H

7 R = CH_3

4

a) R = H

b) R = CH_3

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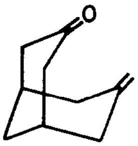
Thus, 3-chloroadamantanol (1a), 3-chloro-3-methyl-1-butanol (2a) and 3-chloro-2,2,3-trimethyl-1-butanol (3a) yield the corresponding diols 1b, 2b and 3b and their monoethers 1c, 2c and 3c, respectively [2]. From 2a the olefins 4a and 5a are obtained, from 3a only the olefin 5b. Due to the -I effect of the oxygen atom compounds 1a, 2a and 3a react only approximately 0.25 times as fast as the "homomorphous" tertiary chlorides, i.e. adamantyl chloride, 6 and 7, respectively.



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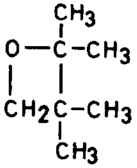

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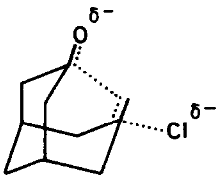
In 80 % ethanol, 0.2 m in NaOH, 3-chloroadamantanol (1a) (0.05 m) fragments quantitatively to the unsaturated ketone 8. Under these conditions 2a yields 73 % of fragmentation products, i.e. formaldehyde and isobutene, beside 27 % of the $\Delta^{3,4}$ alcohol 5a. 3a yields 61 % of formaldehyde and tetramethylethylene by fragmentation, 37 % 5b by elimination and 2 % of the oxetane 9 by cyclization [3]. Since the ratio of the products is independent of the NaOH concentration, they must be derived from common intermediates, i.e. the conjugate bases of 1a, 2a and 3a, respectively.

The first order rate constants (k_{obs}) for 1a, 2a and 3a increase by several orders of magnitude when NaOH is added (Table). They level off at higher NaOH concentration and then decrease. Since the rate depression is also bought about by neutral sodium salts, it must be due to a negative salt effect. Thus, increasing the ionic strength of 0.85 m NaOH to 1.145 by the addition of $NaNO_3$ causes the observed rate constant to fall from 1.24×10^{-4} to 0.922×10^{-4}, i.e. by 26 %. Extrapolation of k_{obs} to zero ionic strength according to the equation [4]:

$$\log k_o = \log k_{obs} + 0.345\sqrt{[NaOH]}$$

leads to corrected rate constants k_o (Table). The ratios of k_o for the reactions with and without base (k_{rel} in the Table) measure the assistance to ionization due to oxygen in the conjugate bases of 1a, 2a and 3a.



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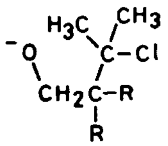

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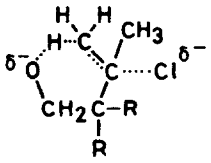

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Table. Observed and corrected first order rate constants for <u>1a</u>, <u>2a</u> and <u>3a</u> (0.005 m) in 80 vol. % ethanol [a].

compound	temp. °C	$[NaOH]^{b)}$ mole/l	k_{obs} (s^{-1})	k_o	k_{rel}
<u>1a</u>	0.00	--	2.43×10^{-10} [c]	2.43×10^{-10}	1
		0.306	6.20×10^{-5}	9.64×10^{-5}	
		0.581	9.43×10^{-5}	1.73×10^{-4}	
		1.001	1.13×10^{-4}	2.49×10^{-4}	
		1.343	1.18×10^{-4}	2.96×10^{-4}	1.2×10^{6}
<u>2a</u>	0.00	--	1.25×10^{-7} [c]	1.25×10^{-7}	1
		0.442	1.04×10^{-4}	1.79×10^{-4}	
		0.720	1.24×10^{-4}	2.46×10^{-4}	
		0.955	1.24×10^{-4}	2.72×10^{-4}	
		1.407	1.19×10^{-4}	3.09×10^{-4}	2.5×10^{3}
<u>3a</u>	-27.00	--	7.99×10^{-9} [c]	7.99×10^{-9}	1
		0.148	5.56×10^{-3}	7.85×10^{-3}	
		0.310	5.26×10^{-3}	8.63×10^{-3}	
		0.933	5.08×10^{-3}	1.19×10^{-2}	1.5×10^{6}

a) maximum deviation from mean value 1.5 %. b) mean concentration during the reaction
c) extrapolated from rate measurements at higher temperature.

The large k_{rel} values for <u>1a</u>, <u>2a</u> and <u>3a</u> and the negative salt effects indicate a concerted fragmentation mechanism involving a dispersal of negative charge in the transition state, as in <u>10</u>. In the acyclic cases <u>2a</u> and <u>3a</u>, however, fragmentation is accompanied by the accelerated formation of the $\Delta^{3,4}$ alcohols <u>5a</u> and <u>5b</u>, respectively. This suggests an anchimerically assisted elimination of HCl by the oxygen atom in conformation <u>11</u>, the transition state <u>12</u> of which also involves a dispersal of negative charge. This type of intramolecular base-induced elimination was originally proposed to explain the accelerated fragmentation-elimination of certain 3-chloroamines [5].

Conformation 11 and those derived from it by rotation around the C(1)-C(2) bond meet the stereoelectronic requirements for concerted fragmentation [6]. Conformation 11 also accounts for the oxetane 9 formed from 3a. Although unusual, nucleophilic displacements at tertiary carbon were recently observed in the cyclization of certain 4-chloroamines [7].

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1) For previous studies on the fragmentation of 3-chloropropanol derivatives see: G. Forsberg, Acta chem. scand. 8, 135 (1954); S. Searles, R.G. Nickerson & W.K. Witsiepe, J. org. chem. 24, 1839 (1959); M. Bartok et al., Acta chim. Acad. Sci. Hung. 66, 115 (1970), 70, 133 (1971), 72, 297 (1972); W.H. Richardson, C.M. Golino, R.H. Wachs & M.B. Yelvington, J. org. chem. 36, 943 (1971).

2) The structure of all new compounds are supported by elemental and spectroscopic analyses.

3) This compound is stable under the reaction conditions and therefore cannot be an intermediate.

4) The coefficient 0.345 was derived from corresponding measurements with 3-chlorothiols, see the following article.

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