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ANCHIMERICALLY ASSISTED ELIMINATION AND NUCLEOPHILIC DISPLACEMENT AT A TERTIARY CARBON ATOM

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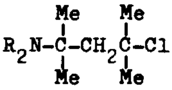
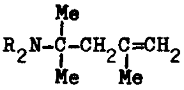
The formation of the aminoolefines 2, 6 and 10 from the γ- and δ-aminoalkylchlorides 1, 5 and 9 by a first-order reaction in "80 % ethanol*" cannot be explained by the unimolecular elimination (E 1) mechanism typical of tertiary alkyl halides. It is, however, in accord with a novel elimination mechanism which involves participation of the amino group in an intramolecular variant of the E 2 reaction.


$R_2N-\underset{Me}{\overset{Me}{C}}-CH_2\underset{Me}{\overset{Me}{C}}-Cl$

1


$R_2N-\underset{Me}{\overset{Me}{C}}-CH_2\underset{Me}{C}=CH_2$

2

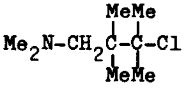
$R_2\overset{+}{N}=CMe_2$

3

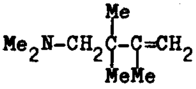
$CH_2=CMe_2$

4

a) R = H b) R = CH_3


$Me_2N-CH_2\underset{Me}{\overset{Me}{C}}-\underset{Me}{\overset{Me}{C}}-Cl$

5


$Me_2N-CH_2\underset{Me}{\overset{Me}{C}}-\underset{Me}{C}=CH_2$

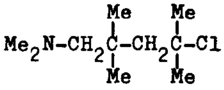
6

$Me_2\overset{+}{N}=CH_2$

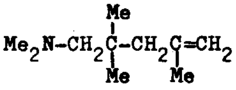
7

$Me_2C=CMe_2$

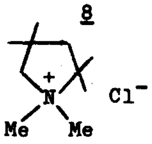
8


$Me_2N-CH_2\underset{Me}{\overset{Me}{C}}-CH_2\underset{Me}{\overset{Me}{C}}-Cl$

9


$Me_2N-CH_2\underset{Me}{\overset{Me}{C}}-CH_2\underset{Me}{C}=CH_2$

10



11

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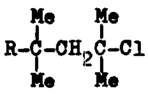
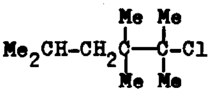
* 1 - 2 mole equivalents of triethylamine were added to neutralize the HCl formed during the reaction.

α,α,γ,γ-Tetramethyl-γ-aminopropylchloride (1a) and the corresponding N-dimethyl derivative 1b react 3 and 27 times, respectively, as fast as the homomorphous alkyl chlorides 12a and 12b yielding 70 % and 20 %, respectively, of the aminoolefines 2a and 2b, besides the fragmentation products 3a, 3b and 4, respectively. γ-Dimethylamino-α,α,β,β-tetramethylpropylchloride (5) reacts 125 times as fast as the homomorph 13 yielding 30 % aminoolefine 6 besides 70 % of the fragmentation products 7 and 8.



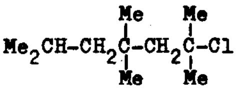
$R\text{-}\overset{Me}{\underset{Me}{C}}\text{-}CH_2\overset{Me}{\underset{Me}{C}}\text{-}Cl$

12



$Me_2CH\text{-}CH_2\overset{Me}{\underset{Me}{C}}\text{—}\overset{Me}{\underset{Me}{C}}\text{-}Cl$

13

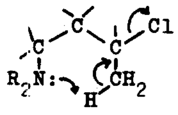


$Me_2CH\text{-}CH_2\overset{Me}{\underset{Me}{C}}\text{-}CH_2\overset{Me}{\underset{Me}{C}}\text{-}Cl$

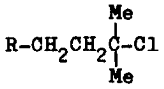
14

a) R = Me b) R = Me_2CH

The relationship between rates and product composition reveals that a substantial part of the rate enhancement must be due to accelerated elimination reactions. It is, therefore, concluded that in these cases a synchronous fragmentation reaction [1] is accompanied by the anchimerically assisted 1.2-elimination 15. This conclusion is supported by the exclusive isolation of the terminal olefines 2a and 2b from 1a and 1b, whereas, under the same reaction conditions, the homomorphous dimethylneopentylcarbinylchloride (12a) is reported to yield ca. 20 % of the non-terminal 2-olefine in addition to the 1-olefine [2].



15



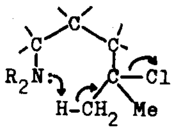
$R\text{-}CH_2CH_2\overset{Me}{\underset{Me}{C}}\text{-}Cl$

16

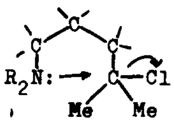
a) R = Me_2N
b) R = Me_2CH

It is noteworthy that the β- and γ-unbranched γ-aminochloride 16a reacts without N-participation by way of a carbonium ion since a rate decrease compared to the homomorph 16b is observed [3]. Geminal methyl substitution at the β- and γ-positions therefore favours conformation 15 which leads to anchimerically assisted elimination.

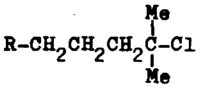
δ-Dimethylamino-$\alpha,\alpha,\gamma,\gamma$-tetramethyl-butylchloride (9) which for structural reasons cannot undergo fragmentation reacts 7.2 times as fast as its homomorph 14 yielding 77 % of the pyrrolidinium salt 11 and 12 % of the terminal olefine 10 besides minor amounts of alcohol and the corresponding ethyl ether. The latter substitution products are undoubtably formed via the carbonium ion in a S_N1 process.



17



18



$R-CH_2CH_2CH_2\overset{Me}{\underset{Me}{C}}-Cl$

19

a) R = Me_2N
b) R = Me_2CH

The relative rate of the δ-aminochloride 9 indicates participation of the amino group in the rate determining steps involving concurrent anchimerically assisted elimination and ring closure, as in 17 and 18. The latter reaction is of particular interest since it constitutes a distinct case of nucleophilic displacement at a tertiary carbon atom, i.e. an intramolecular variant of the S_N2 reaction.

These unusual anchimeric effects must also be due to the presence of additional geminal methyl groups in compound 9, for the solvolysis rate of the γ-unsubstituted δ-aminochloride 19a is practically indistinguishable from that of its homomorph 19b.

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