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A NEW REARRANGEMENT–CLEAVAGE REACTION OF QUATERNARY AMMONIUM SALTS UNDER THE INFLUENCE OF AQUEOUS ALKALIS*

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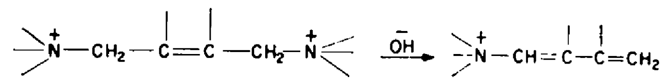
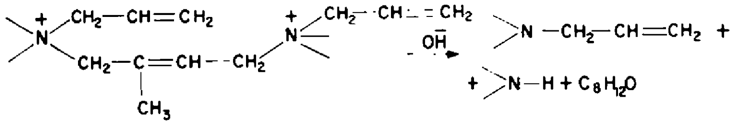
Abstract—It has been established that quaternary ammonium salts which are capable, on interaction with aqueous alkalis, of turning into ammonium compounds containing α,β- and β,γ-unsaturated groups, undergo a rearrangement–cleavage reaction with the elimination of a secondary amine and formation of carbonyl compounds at the expense of both groups mentioned.

It has been shown[1] that aqueous-alkaline cleavage of 1,4-diquaternary ammonium salts containing a common β,γ-unsaturated group proceeds through the diene ammonium salt A:†


(A)

It was found that, when allyl-type groups are present in such salts, interaction with aqueous alkalis leads to the formation of carbonyl compounds with the number of carbon atoms in the molecule equal to the sum of carbon atoms in the common and allyl-type groups of the initial salt.[2] For example:



The formation of a carbon–carbon bond between the unsaturated groups appears to proceed through a six-membered cyclic mechanism as a result of a nucleophilic attack by the hydroxide ion on the α-carbon atom of the α,β-unsaturated group in the intermediate enammonium salt A.

According to this scheme, 1,2-diquaternary ammonium salts containing allyl-type groups on the nitrogen atom should behave similarly and these expectations were justified experimentally.[3] All the 1,2-diammonium salts synthesized with the general formula I, were cleaved by aqueous alkali forming secondary and tertiary amines,

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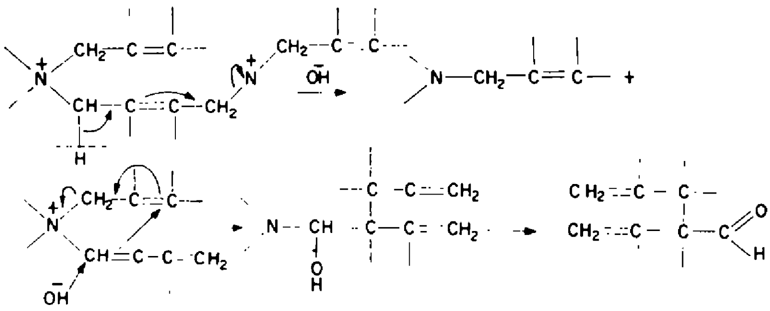
* Presented at the *19th International Congress of Pure and Applied Chemistry* London, July (1963).

† In all formulae methyl or ethyl groups are attached to the nitrogen atoms, while hydrogen and alkyl groups are attached to the carbon atoms.

[1] A. T. Babayan, M. H. Indjikyan and H. B. Bagdassaryan, *Dokl Akad. Nauk SSSR* **133**, N6, 1334 (1960).

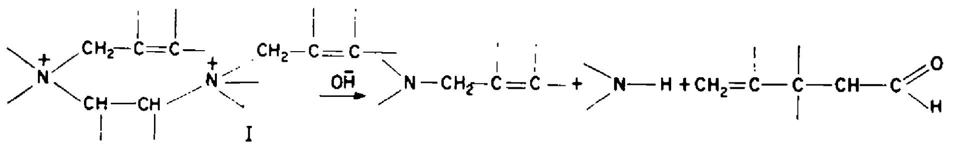
[2] A. T. Babayan, M. H. Indjikyan and H. B. Bagdassaryan, *Dokl. Akad. Nauk Armyan. SSR* **34**, N2, 75 (1962).

[3] A. T. Babayan, M. H. Indjikyan and N. M. Davtyan, *Dokl. Akad. Nauk Armyan. SSR* **35**, N4, 173 (1962).



A

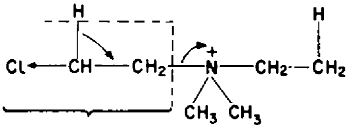
and carbonyl compounds with the number of carbon atoms in the molecule equal to the sum of atoms of the common and allyl-type groups present in the initial salt:



I

Similarly, it was concluded that a rearrangement–cleavage reaction would take place with all quaternary ammonium salts in which together with the allyl-type group there is also a group which under the action of aqueous alkali becomes α,β-unsaturated.

It has been established that quaternary ammonium salts containing chlorine atoms at the β- or γ-position with regards to nitrogen, readily undergo dehydrochlorination reactions.[4] The cleavage reaction of dimethylethyl-β-chloroethylammonium, under



the influence of a nucleophilic reagent, required re-investigation since this reaction is presented in handbooks of Theoretical Organic Chemistry as an example of the electron-compelling action of a substituent on the elimination reaction of amines,[5] and is based on the work of Ingold and Hanhart,[6] devoted to the mechanism of exhausting methylation in which among other quaternary ammonium salts, dimethylethyl-β-chloroethylammonium iodine was investigated.

The only nitrogenous product was proved to be dimethylethylamine and no non-amine was isolated. According to the results reported,[4] the elimination of hydrogen chloride should precede that of the amine leading to the formation of a vinylammonium compound. In fact, dimethylethyl-β-chloroethylammonium chloride

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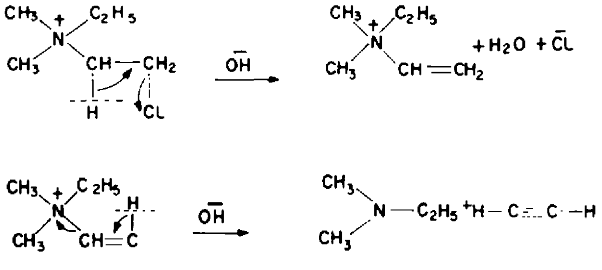
[4] A. T. Babayan, I. J. Zurabov, *Zh. Obsch. Khim.* **25**, 2445 (1955); A. T. Babayan and A. A. Grigoryan *Ibid.* **26**, 1945 (1956); *Ibid.* **27**, 1827 (1957).

[5] C. K. Ingold, *Structure and Mechanism in Organic Chemistry;* H. Becker, *Einfuhrung in die Elektronentheorie organischchemischer Reaktionen* p. 183, Berlin (1961).

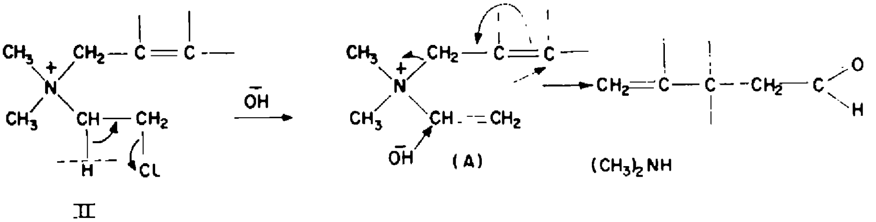
[6] W. Hanhart and C. K. Ingold, *J. Chem. Soc.* 997 (1927).

is readily dehydrochlorinated at room temperature with aqueous alkali and only after heating does cleavage take place with formation of dimethylethylamine and acetylene.[7] Consequently, the reaction with aqueous alkalis proceeds in two stages according to the following scheme:



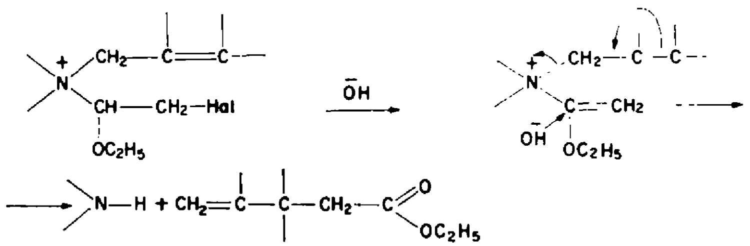
The elimination of acetylene rather than ethylene is governed by the second stage of the reaction. The dehydrochlorination reaction finds extensive application in the synthesis of ammonium salts containing α,β- and β,γ-unsaturated groups.

A series of salts having the general formula II were synthesized and submitted to aqueous-alkaline cleavage and in all cases investigated secondary amines and carbonyl compounds were obtained in accordance with the following scheme:



II

The dehydrohalogenation reaction takes place at room temperature, and the second stage of the reaction, namely, the rearrangement–cleavage reaction, also proceeds readily without heating in these salts. This reaction may be used not only for the synthesis of unsaturated aldehydes, but also for esters having a similar structure:



In the alkylation reaction of carbonyl compounds via the intermediate stage of enamines, known in the literature as Stork's reaction, it has been suggested,[8–10] that in the carbon-alkylation of the enamines with allyl-type haloalkyls, nitrogen-alkylation

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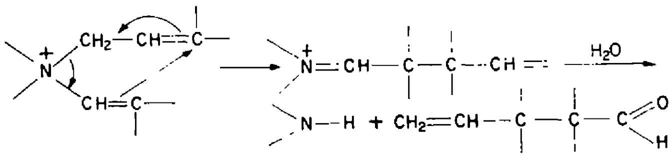
[7] A. T. Babayan, L. Kh. Gamburyan, E. O. Chukhadjyan and E. S. Ananyan, *Dokl. Akad. Nauk Armyan. SSR* **35**, N5. 209 (1962).

[8] E. Elkik, *Bull. Soc. Chim. Fr.* **186**, 4167 (1960).

[9] K. C. Brannock and R. D. Burpitt, *J. Org. Chem.* **26**, 3576 (1961).

[10] G. Opitz, *Liebigs Ann.* **650**, 122 (1961).

is followed by migration of the allyl-type group to the carbon atom and that the reaction is analogous to that of a Claisen rearrangement of vinylallylethers:

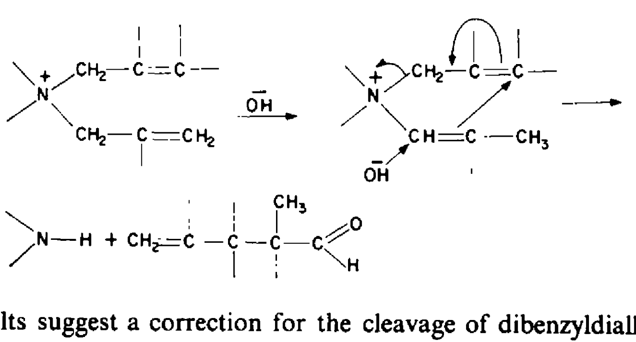


Although a purely intermolecular reaction is comprehensible in vinyl allyl ether molecules, it is less probable in ammonium ions and, more particularly in an aqueous-alkaline medium. Consequently, we maintain that the rearrangement–cleavage reaction does not proceed without external influence.

The well-known Stevens, Sommelet and Wittig rearrangement reactions of quaternary ammonium salts proceed through the stage of a bipolar ion formation, called by Wittig an ylid. The new rearrangement–cleavage reaction no doubt, also proceeds through the stage of a bipolar ion formation, but in this case the anion center is formed not at the α- but at the β-carbon atom, and not at the expense of a proton elimination but due to addition of the nucleophilic agent to the α-carbon atom of the α,β-unsaturated group.

In connection with reactions, capable of forming intermediate enammonium salts, the shifting reaction of multiple bonds in unsaturated groups catalysed by bases was considered. There are references in the literature concerning the isomerization of double bonds in ammonium compounds from β,γ- to α,β-position with regard to nitrogen atom.[11,12]

Consequently, quaternary ammonium salts containing two allyl-type groups one of which was deprived of an alkyl substituent at the γ-position with regards to nitrogen were synthesized. These salts on interaction with aqueous-alkali are split into a secondary amine with the formation of a carbonyl compound[13] at the expense of both unsaturated groups:



These results suggest a correction for the cleavage of dibenzyldiallylammonium hydroxide described by Ingold and Hey,[14] in which they claim the formation of

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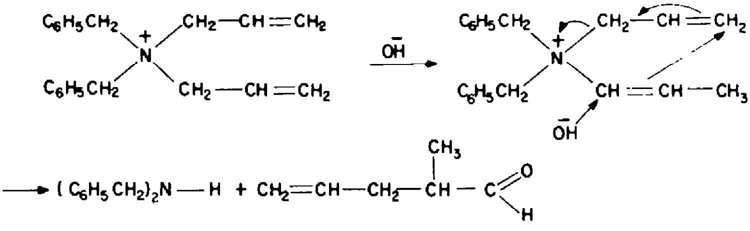
[11] D. R. Howton, *J. Org. Chem.* **14**, 1 (1949).

[12] R. Lukes and J. Trojanek, *Collect.* **14**, 688 (1949).

[13] A. T. Babayan. M. H. Indjikyan and L. R. Tumanyan, *Dokl. Akad. Nauk Armayan SSR* **36**, N2, 95 (1963).

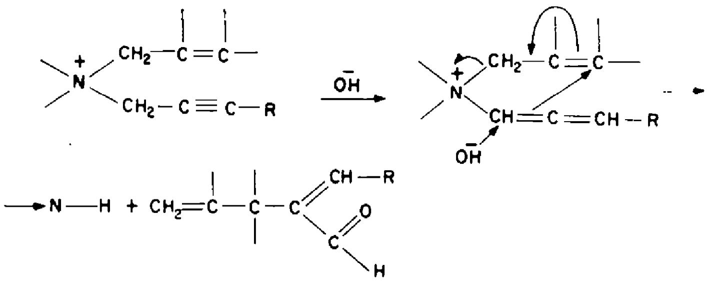
[14] C. K. Ingold and L. Hey, *J. Chem. Soc.* 66 (1933).

dibenzylamine and acrolein. No doubt the 2-methylpenten-4-al, which should be formed was erroneously taken for acrolein:

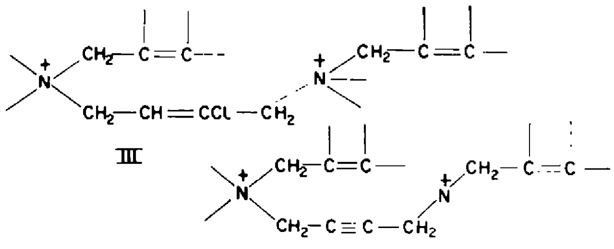


In repeating the reaction, it was found that besides dibenzylamine, 2-methylpenten-4-al was also produced and not even traces of acrolein could be detected among the reaction products.[13]

Further proof of the isomerization of β,γ-acetylenic to α-allenic groups are provided, in the reaction products of alkaline cleavage of quaternary ammonium salts containing in addition to allyl-type groups, propargyl or butyn-2-yl groups. It was found that secondary amines and carbonyl compounds are formed at the expense of both unsaturated groups according to the following scheme:



Interesting results also were obtained by alkaline cleavage of 1,4-diquaternary ammonium salts having the general formulas III and IV.

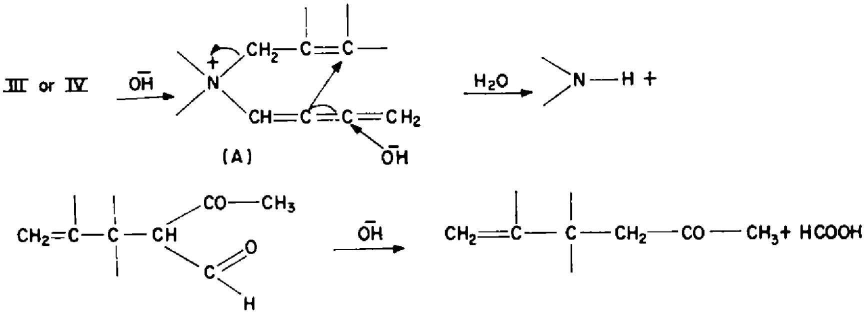


III

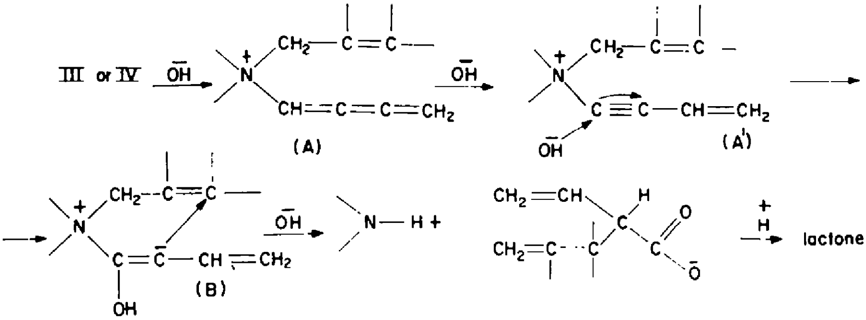
IV

Among the reaction products were found dialkylallylamine, dialkylamine, formic acid, an unsaturated acid with the number of carbon atoms equal to the sum of carbon atoms of the common and allyl-type groups, and a ketone containing one carbon atom less than the acid mentioned.

Apparently the ketone and formic acid are related, although the yield of the latter is much lower than that of the former. Apparently, as a result of the rearrangement-cleavage reaction of the intermediate monoammonium salt, a β-dicarbonyl compound is formed which in alkaline medium splits further into the ketone and formic acid:



The formation of the acid, isolated in the form of a lactone, could take place only through the intermediate α-ethynyl grouping (A′) the reaction proceeding according to the following scheme.[15]



A purely intermolecular six-membered cyclic mechanism renders the possibility of the α-ethynylallyl system participating in the rearrangement less likely. Consequently, it is believed that the formation of an acid provides very definite support for the proposed rearrangement scheme including the attack by a nucleophilic reagent on the α-carbon atom of the α,β-unsaturated group with opening of one of the multiple bonds. As a result of this the carbon atom of the ethynyl group from Sp hybridization state in the ammonium ion passes into that of Sp^2 hybridization in the bipolar ion B.

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[15] A. T. Babayan, M. H. Indjikyan, A. A. Grigoryan and R. B. Minasyan, *Izv. Akad. Nauk Armyan SSR Khim. Nauk*. XY,N6, 567 (1962).