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Abstract

Full Text

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Formation of Conjugated Dienamines in the Reaction of Mono- and Diquaternary Salts of 1,4-Diamines with Aqueous Alkali

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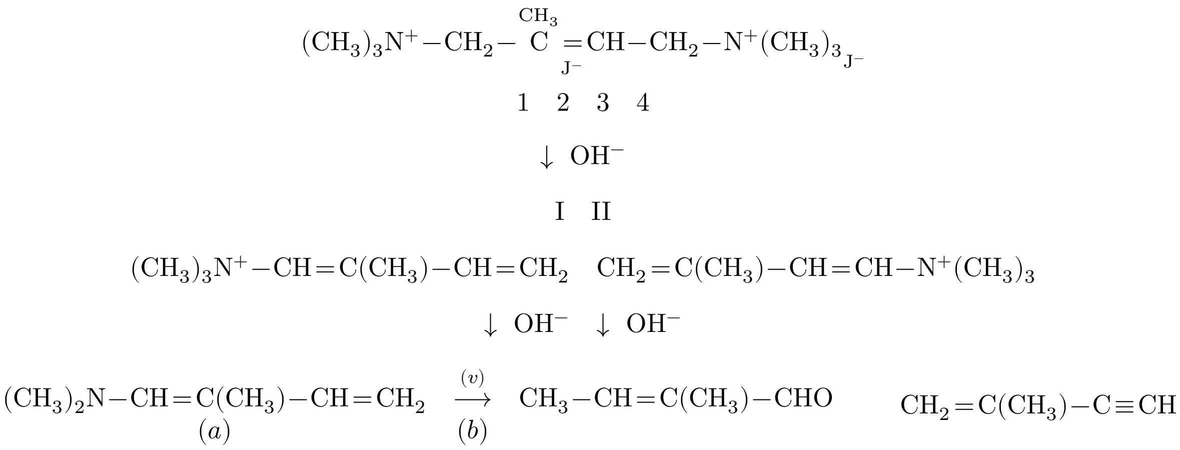
Quaternary ammonium salts containing a β,γ-unsaturated radical are readily cleaved by aqueous alkali at the site of the 1,4 bonds, with formation of compounds with conjugated multiple bonds (1-3). Diammonium salts of similar structure, under analogous reaction conditions, undergo double 1,4 cleavage (4).

The present article is devoted to the reaction of aqueous alkali with mono- and diquaternary salts of 1,4-di-(dimethylamino)-2-methylbutene-2.

For the double cleavage reaction of a diammonium salt, both the simultaneous occurrence of both reactions and a stepwise course are theoretically possible. The asymmetry of the common radical in the diquaternary ammonium salts studied by us makes a stepwise course of the reaction according to one of the schemes given below more probable:



$$(CH_3)_3N^+-CH_2-\overset{CH_3}{C}\underset{J^-}{=}CH-CH_2-N^+(CH_3)_{3\,J^-}$$

$$1\quad 2\quad 3\quad 4$$

$$\downarrow OH^-$$

$$\text{I}\quad \text{II}$$

$$(CH_3)_3N^+-CH=C(CH_3)-CH=CH_2 \qquad CH_2=C(CH_3)-CH=CH-N^+(CH_3)_3$$

$$\downarrow OH^- \quad \downarrow OH^-$$

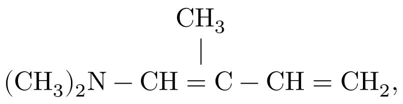
$$\underset{(a)}{(CH_3)_2N-CH=C(CH_3)-CH=CH_2} \xrightarrow[(b)]{(v)} CH_3-CH=C(CH_3)-CHO \qquad CH_2=C(CH_3)-C\equiv CH$$

It may be considered that the inductive effect of the methyl group will not cause any particular difference in the ease of protonation of the hydrogen atoms at C_1

and C_4 (vinylogy). The conjugation effect of this same methyl group, however, should suppress protonation of the hydrogen atoms at C_4 and thereby determine the sequence of cleavage reactions according to scheme 1. The question of how decisive the conjugation effect of the methyl group is in this reaction had to be resolved experimentally.

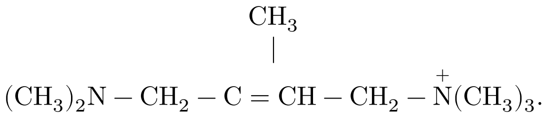
From the complex mixture of products of the reaction of the iodide salt of 1,4-di-(trimethylammonium)-2-methylbutene-2 with aqueous alkali, we succeeded in isolating an aldehyde—corresponding, according to the analysis of its semicarbazone and molecular refraction, to the dimer of methylcrotonaldehyde—and a high-boiling amine product, which is apparently the product of condensation of methylcrotonaldehyde with 1-dimethylamino-(methyl)-butadiene. The picture was completely repeated on passing from the mixture of the quaternary ammonium salt and alkali to the ammonium base. In the reaction products, contrary to the assertion of Slobodin (5), we were unable to detect any traces of 2-methylvinylacetylene, which argues in favor of scheme 1.

A clearer picture might have been expected upon cleavage of the monoiodomethyl derivative of 1,4-di(dimethylamino)-2-methylbutene-2. For this purpose, by partial iodomethylation of 1,4-di(dimethylamino)-2-methylbutene-2, the monoiodomethylate was obtained. The position of the methyl group in the monoiodomethylate was established in the course of studying the cleavage reaction of the latter. The interaction of the monoiodomethyl salt with aqueous alkali proceeded at a lower temperature (120°), but nevertheless led to the formation of the very same products as in the cleavage of the diquaternary salt, differing only in better yields of these products and in a marked decrease in the amounts of resinification products. The hydroxide obtained by treating the monoiodomethylate of 1,4-di(dimethylamino)-2-methylbutene-2 with an aqueous suspension of silver oxide was then subjected to cleavage in vacuo. Cleavage occurred mainly at a reaction-mixture temperature of 105–107°. In this way we succeeded in isolating 1-dimethylamino-2-methylbutadiene-1,3 in a yield of about 40% of theory. This compound is stable: it can be distilled at atmospheric pressure and does not change on standing. It undergoes most reactions of carbonyl compounds: it reacts with solutions of semicarbazide, 2,4-dinitrophenylhydrazine, and hydroxylamine, with formation of dimethylamine and the corresponding derivative of α-methylcrotonaldehyde. With ammoniacal silver oxide solution it gives a silver mirror; with maleic anhydride it forms a crystalline adduct. The formation of derivatives of α-methylcrotonaldehyde indicates the β-position of the methyl group with respect to the amino group in the dienamine:



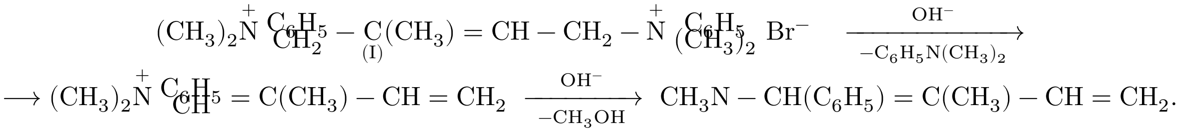
$$(\mathrm{CH_3})_2\mathrm{N} - \mathrm{CH} = \overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{C}} - \mathrm{CH} = \mathrm{CH_2},$$

and consequently also in the starting monoiodomethylate:



$$(CH_3)_2N - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 - \overset{+}{N}(CH_3)_3.$$

The data obtained gave grounds to suppose that it is precisely the second stage of cleavage of the diiodomethylate (stage (a) in scheme 1) that requires the higher temperature (140–145°). In this connection it was of interest to investigate the behavior toward aqueous alkali of two more diquaternary ammonium salts: the bromide of 1,4-di(methylphenylammonium)-2-methylbutene-2 (I) and the bromide of 1,4-di(methylbutyn-2-ylammonium)-2-methylbutene-2 (II). For the compounds indicated, stage (a) should be facilitated by the presence in the ammonium complex: in the first case, of a phenyl radical, which facilitates the cleavage reaction; in the second, of such an easily eliminated radical as butyn-2-yl. Alkaline cleavage of salt I takes place under considerably milder conditions (the temperature of a boiling water bath) and leads to the formation of a molar amount of dimethylaniline and of 1-methylphenylamino-2-methylbutadiene-1,3 (80%)

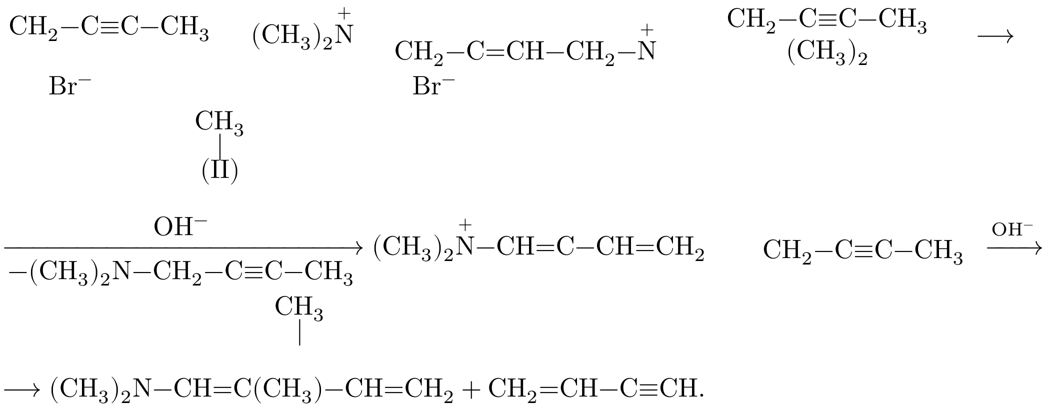


$$(CH_3)_2\overset{+}{N}\genfrac{}{}{0pt}{}{C_6H_5}{CH_2} - \underset{(I)}{C}(CH_3) = CH - CH_2 - \overset{+}{N}\genfrac{}{}{0pt}{}{C_6H_5}{(CH_3)_2}\ Br^- \xrightarrow[-C_6H_5N(CH_3)_2]{OH^-}$$

$$\longrightarrow (CH_3)_2\overset{+}{N}\genfrac{}{}{0pt}{}{C_6H_5}{CH} = C(CH_3) - CH = CH_2 \xrightarrow[-CH_3OH]{OH^-} CH_3N - CH(C_6H_5) = C(CH_3) - CH = CH_2.$$

The structure of the latter was proved by conversion, under the action of a semicarbazide solution, into methylaniline and the semicarbazone of α-methylcrotonaldehyde. In contrast to 1-dimethylamino-2-methylbutadiene-1,3, 1-methylphenylamino-2-methylbutadiene-1,3 begins to change immediately after distillation—turning red—and undergoes resinification already on brief standing.

The cleavage of salt II proceeds analogously. The products of cleavage of this salt in vacuum are molar amounts of 1-dimethylaminobutyne-2, vinylacetylene, 1-dimethylamino-2-methylbutadiene-1,3, and products of transformation of the latter. The reaction proceeds according to the scheme:



$$\underset{Br^-}{CH_2-C\equiv C-CH_3} \quad \overset{+}{(CH_3)_2N} \quad \underset{Br^-}{CH_2-C=CH-CH_2-\overset{+}{N}} \quad \underset{(CH_3)_2}{CH_2-C\equiv C-CH_3} \longrightarrow$$

$$\underset{(II)}{\overset{CH_3}{|}}$$

$$\xrightarrow[-(CH_3)_2N-CH_2-C\equiv C-CH_3]{OH^-} (CH_3)_2\overset{+}{N}-CH=\underset{|}{\overset{}{C}}-CH=CH_2 \quad CH_2-C\equiv C-CH_3 \xrightarrow{OH^-}$$

$$\overset{CH_3}{|}$$

$$\longrightarrow (CH_3)_2N-CH=C(CH_3)-CH=CH_2 + CH_2=CH-C\equiv CH.$$

Thus, the alkaline cleavage of diquaternary ammonium salts I and II proceeds stepwise according to scheme 1 through stage (a); stages (b) and (c) do not occur.

1,4-Di-(dimethylamino)-2-methylbutene-2 was obtained by the interaction of 1,4-dibromo-2-methylbutene-2 with a 60% aqueous solution of dimethylamine. Yield 41%, b.p. 71-72°/10 mm, d_4^{20} 0.8095; n_D^{20} 1.4453; found % N 18.23; calculated % N 17.95; m.p. of picrate 172°.

The monoiodomethylate of 1,4-di-(dimethylamino)-2-methylbutene-2 was obtained by reaction of the amine with a molar amount of methyl iodide in ether medium. It dissolves well in water and alcohol. Found % J 42.48; calculated 42.6. Yield of salt 95%. The diiodomethylate was obtained by reaction with a double molar amount of methyl iodide in alcohol medium. Yield 97%; this salt is poorly soluble in water and alcohol. Found % J 57.3; calculated 57.7.

Salts I and II were obtained by reaction of 1,4-dibromo-2-methylbutene-2 with a double molar amount of dimethylaniline and dimethylaminobutyne-2, respectively, in alcohol medium, followed by distillation of the alcohol at room temperature.

Cleavage of the salts with aqueous alkali was carried out as usual (^{1,4}). Below we give the physical constants and elemental-analysis data of those cleavage products which are described for the first time:

1-Dimethylamino-2-methylbutadiene-1,3: b.p. 111-113°/680 mm, d_4^{20} 0.7902; n_D^{20} 1.4539; found % N 13.42; calculated 12.70; m.p. of semicarbazone 225°, m.p. of oxime 43°, m.p. of 2,4-dinitrophenylhydrazone 220°.

Dimer of α-methylcrotonaldehyde: b.p. 71-72°/8 mm, d_4^{20} 1.0762; n_D^{20} 1.5305; m.p. of semicarbazone 194-195°; found % N in semicarbazone 18.45; calculated % 18.70.

1-Methylphenylamino-2-methylbutadiene-1,3: b.p. 160°/10 mm, d_4^{20} 0.9832; n_D^{20} 1.5900; found % N 8.23; calculated % N 8.09; gives the same derivatives as 1-dimethylamino-2-methylbutadiene-1,3.

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Note: Figure translations are in progress. See original paper for figures.