Reaction with Aqueous Alkali of Diammonium Salts with a 1,1-Dimethylbut-2-yne-1,4-diyl Common Group

M. Zh. Ovakimyan, S. K. Barsegyan, and M. G. Indzhikyan

Institute of Organic Chemistry, National Academy of Sciences of Armenia, Erevan, Armenia Research Center of Molecular Structure, Erevan, Armenia

Received February 2, 2001

Abstract—Quaternary ammonium salts with a 1,1-dimethylbut-2-yne-1,4-diyl common group react with aqueous alkali with intermediate formation of 1,2- rather than 1,4-cleavage products. When both nitrogen atoms bear allylic groups, rearrangement–cleavage–substitution occurs to give methyl isopropyl ketones. Salts with two 3-methylbut-2-en-1-yl groups cleave isoprene.

We earlier found that 1,4-diammonium salts with a but-2-yne-1,4-diyl common radical and allylic side groups are cleaved by aqueous alkali to form nitrogenfree allylacetones as major products and lactones derived from 1-allylbut-3-enoic acids as by-products [1].

In the present work we studied transformations under the action of aqueous alkali of 1,4-diammonium salts **I–III** having two methyl substituents in a but-2yne-1,4-diyl common group.

$$(CH_{3})_{2}\overset{+}{N}\overset{R}{\to} CH_{2}-C=C-\overset{CH_{3}}{\to} \overset{R}{\to} \\ X^{-} \overset{-}{\to} \overset{-}{C}H_{3} \overset{-}{\to} \\ CH_{3} \overset{-}{X}^{-} \overset{-}{\to} \\ I-III$$

 $R = CH_3$ (I), CH_2 -CH=CH₂ (II), CH_2 -CH=C(CH₃)₂ (III).

The initial ammonium salts were obtained by reaction of 1,4-bis(dimethylamino)-1,1-dimethylbut-2-yne with alkyl or allyl halides at a 1:2 molar ratio. 1,4-Bis(dimethylamino)-1,1-dimethylbut-2-yne reacts with equimolar amount of methyl bromide to give a monoammonium salt by the nitrogen atom attached to the methylene group, which then transforms into a diammonium salt under the action of the second methyl bromide molecule.

It was found that bis(trimethylammonium) salt **I** fails to react with equimolar amount of aqueous potassium hydroxide at room temperature. The reaction under reflux yields, after 0.5 h, a 1,2-cleavage product, a monoammonium salt with a 3-isopropenyl-prop-2-yn-1-yl group, of the possible 1,2- and 1,4-cleavage products.



Cleavage of the same salt under the action of thrice the molar amount of 25% aqueous sodium hydroxide was accompanied by strong tarring. The only isolable reaction products were acetone (9%) and trimethylamine (76%). Acetone is most likely formed by a scheme involving nucleophilic attack by the δ -carbon atom of the pentatriene system.

$$\overset{+}{\operatorname{Br}^{-}} \overset{+}{\operatorname{Br}^{-}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{Br}^{-}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{Br}^{-}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{Hr}^{-}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{Hr}^{-}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{Hr}^{-}} \overset{+}{\operatorname{CH}_{3}} \overset{+}{\operatorname{CH}_$$

Among the products of alkaline cleavage of salt **II** we found dimethylamine (mole per mole of the initial salt), 32% of isopropyl 3-buten-1-yl ketone, dimethylamine, formic acid, and a high-boiling product. According to GLC and TLC, the latter is a mixture of

several amines.

The substituted methyl isopropyl ketone is most likely formed by a scheme we proposed earlier for cleavage of salts containing no substituents in the butatriene system.

$$\begin{array}{c} Br^{-} \\ (CH_3)_2N \\ \hline CH_2-C \equiv C - C(CH_3)_2 \\ \hline CH_3)_2N \\ \hline CH_2-C \equiv C - C(CH_3)_2 \\ \hline CH_3)_2NH + (CH_3)_2C \equiv C = C - C(CH_3)_2 \\ \hline CH_3)_2CHCOCH_2CH_2CH = CH_2 + HCOO^{-} \\ \hline CH_3)_2CHCOCH_3CHCOCH_2CH_3CH = CH_2 + HCOO^{-} \\ \hline CH_3)_2CHCOCH_3CHCOCH_3CH = CH_3 + HCOO^{-} \\ \hline CH_3)_2CHCOCH_3CHCOCH_3CH = CH_3 + HCOO^{-} \\ \hline CH_3)_2CHCOCH_3CH = CH_3 + HCOO^{-} \\ \hline CH_3)_3CHCOCH = CH_3 + HCOO^{-} \\ \hline CH_3)_3CHCOCH = CH_3 + HCOO^{-} \\ \hline CH_3$$

A substituted methyl isopropyl ketone, while in a much smaller amount (19%), was also obtained by cleavage of salt **III**. Simultaneously, a great amount of a mixture of high-boiling amines was obtained, which we failed to separate by chromatography. From this mixture, 1,1-dimethyl-1,4-(dimethylamino)but-2yne (6%) was isolated. This compound is formed by cleavage of both 3-methylbut-2-en-1-yl groups from the ammonium complex. Among the reaction products we also found isoprene.

$$(CH_3)_2 \overset{+}{N} (CH_3)_2 \overset{+}{N} (CH_3)_2 \overset{+}{N} (CH_3)_2 (CH_3)_2 \overset{+}{N} (CH_3)_2 (CH_3)_2 \xrightarrow{-OH} 2CH_2 = C(CH_3)CH = CH_2 + (CH_3)_2 NCH_2 C \equiv C - C(CH_3)_2 N(CH_3)_2 (CH_3)_2 (CH_3)_2$$

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrometer in thin films. The ¹H NMR spectra were obtained on Perkin–Elmer R-12B (60 MHz, external reference TMS) and Varian Mercury-300 instruments.

1,4-Bis(dimethylamino)-1,1-dimethylbut-2-yne. A mixture of 10.8 g of 1,1-dimethyl-1-(dimethylamino)prop-2-yne [2], 4.7 g of dimethylamine in 50 ml of dioxane, 4 g of Paraform, and 0.15 g of copper acetate was heated for 50 h on a boiling water bath in a germetically sealed steel balloon. The reaction mixture was treated with 15 ml of 36% hydrochloric acid and thoroughly extracted with ether. After reamoval of ca. 20 ml of the solvent in a vacuum, the residue was made alkaline and extracted with ether. Usual workup and vacuum distillation of the ethereal

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 72 No. 12 2002

extracts gave 10.6 g (66%) of 1,4-bis(dimethylamino)-1,1-dimethylbut-2-yne, bp 102°C (36 mm), d_4^{20} 0.8385, n_D^{20} 1.4570. mp 231–232°C (pycrate). ¹H NMR spectrum, δ, ppm: 1.3 s [6H, C(CH₃)₂], 2.1 s [12H, (CH₃)₂N], 3.1 s (2N, CH₂N). Found N, %: 16.72. C₁₀H₂₀N₂. Calculated N, %: 16.66.

Trimethyl[(4,4-dimethyl-4-dimethylamino)but-2-yl]ammonium bromide. Methyl bromide, 2 ml, was barboted through an ice-cooled ethereal solution of 3.4 g of 1,4-bis(dimethylamino)-1,1-dimethylbut-2-yne. A day after, a precipitate formed and washed filtered off, thoroughly was with dry ether, and dried to obtain 5.2 g (99%) of the monoammonium salt. ¹H NMR spectrum, δ , ppm: 1.4 s [6H, C(CH₃)₂], 2.4 s [6H, N(CH₃)₂], 3.3 s [9H, Λ (CH₃)₃], 4.7 s (2H, N– CH₂). Found Br⁻, %: 30.11. C₁₁H₂₃BrN₂. Calculated Br⁻, %: 30.42.

1,4-Bis(trimethylammonio)-1,1-dimethylbut-2-yne dibromide (I). A slight molar excess of methyl bromide was barboted through an ice-cooled methanolic solution of 4 g of trimethyl[4,4-dimethyl-4-(dimethylamino)]but-2-yl]ammonium bromide. A day after, the quaternary ammonium salt was precipitated with dry ether, filtered off, and dried to obtain 5 g (93%) of salt **I.** ¹H NMR spectrum (CDCl₃), δ , ppm: 1.9 s [6H, C(CH₃)₂], 3.2 s [18H, $N(CH_3)_3$], 4.7 s (2H, N–CH₂). Found Br⁻, %: 44.30. C₁₂H₂₆BrN₂. Calculated Br⁻, %: 44.69.

Alkaline cleavage of salt I. A mixture of 17.5 g of salt I and 0.144 mol of 25% aqueous sodium hydroxide was heated on a sand bath in a flask with a Liebig condenser connected to a receiver, a Tishchenko flask filled with a titrated hydrochloric acid solution, and a gasometer. The reaction was performed at $105-115^{\circ}$ C. The aqueous solution distilled off from the combined solutions in the receiver and Tishchenko flask was treated with a solution of 2,4-dinitrophenylhydrazine to obtain 1.04 g (9%) of acetone 2,4-dinitrophenylhydrazone, mp 122°C. The hydrochloric acid solutions were made alkaline and treated with ether to obtain 0.071 mol (74%) of trimethylamine, mp 217°C (pycrate). The reaction flask contained much tar (1.4 g). Found, %: C 54.44; H 7.00; N 5.44.

1,4-Bis(dimethylammonio)-1,1-dimethylbut-2yne dibromide (II). Allyl bromide, 7.4 g, was added dropwise to a methanolic solution of 5.3 g of 1,4-bis-(dimethylamino)-1,1-dimethylbut-2-yne. The mixture was stirred for 5 h, the methanol was distilled off, and the residue was washed with ether and dried in a vacuum to obtain 11 g (90%) of salt **II**. ¹H NMR spectrum (DMSO), δ , ppm: 1.9 s [6H, C(CH₃)₂], 3.1 s and 3.3 s [12H, N(CH₃)₂], 4.2 d and 4.3 d (4H, N– CH₂, J_{HH} 7.3 Hz, 4.85 s (2H, CH₂C≡), 5.6–6.0 m (4H, =CH₂), 6.05–6.3 m (2H, –CH=). Found Br⁻, %: 38.21. C₁₆H₃₀BrN₂. Calculated Br⁻, %: 39.02.

1,4-Bis[dimethyl(3-methylbut-2-en-1-yl)ammonio]-1,1-dimethylbut-2-yne dichloride (III) was obtained in a similar way from 5.3 g of 1,4-bis(dimethylamino)-1,1-dimethylbut-2-yne and 6.3 g of 3-methyl-but-2-en-1-yl chloride. Yield 10.2 g (93%). Found Cl⁻, %: 18.13. $C_{20}H_{38}Cl_2N_2$. Calculated Cl⁻, %: 18.83.

Alkaline cleavage of 1,4-bis(allyldimethylammonio)-1,1-dimethylbut-2-yne bromide was performed similarly to salt I with a difference that the residue in the reaction flask was treated with ether, the ethereal extract was added to the receiver contents, the ethereal layer was separated, dried, and distilled to obtain 2.1 g (32%) of 6-methylhept-1-en-5-one, bp 44°C (9 mm), d_4^{20} 0.8301, n_D^{20} 1.4300. IR spectrum, v, cm⁻¹: 925, 1640, 3080 (vinyl group), 1710 (CO). ¹H NMR spectrum, δ , ppm: 5.1–5.7 m (1H, CH=), 4.6– 4.9 m (2H, =CH₂), 1.5–2.5 m (5H, CH–CO–CH₂CH₂), 0.6 d [6H, CH(CH₃)₂, J_{HH} 6.7 Hz]. Found, %: C 76.31; N 11.70. C₈H₁₄O. Calculated, %: C 76.19; H 11.11.

Back titration of the combined hydrochloric solutions in the receiver and Tishchenko flask gave 0.10 mol of an amine. The reaction mixture was made alkaline, cooled, and, after addition of ether and double the molar amount of acrylonitrile, left to stand for 3 days. (2-Cyanoethyl)dimethylamine, 1.2 g (23%), was added, bp 165–170°C (680 mm), mp 155°C (pycrate). The ethereal distillate was titrated to found 0.05 mol (94%) of allyldimethylamine, mp 100°C (pycrate).

An amine product, 1.6 g, was also obtained, bp 107–108°C (18 mm), containing, according to TLC and GLC, five compound. Found, %: C 73.07; H 10.01; N 8.66.

The residue in the reaction flask was made acidic to isolate 0.0056 mol (11%) of formic acid which gave with a mercuric chloride solution a characteristic white precilitate.

Alkaline cleavage of 1,4-bis[dimethyl(3-methylbut-2-en-1-yl)ammonio)-1,1-dimethylbut-2-yne dichloride was performed like the above with a difference that we first isolated isoprene, and then performed usual workup. From 88 g of the salt we obtained 1,1 g (68%) of isoprene, bp 38–40°C (680 mm), n_D^{20} 1.4170, and 6.8 g (19%) 3,3,6-trimethylhept-1-en-5-one, bp 68–71°C (18 mm), n_D^{20} 1.4348. IR spectrum, v, cm⁻¹: 1640, 3080 (vinyl group), 1710 (CO). Found, %: C 77.63; H 12.22. $C_{10}H_{18}O$. Calculated, %: C 77.92; H 11.68.

The aqueous solution distilled from the combined hydrochloric acid solutions was treated with 2,4-dinitrophenylhydrazine to obtain 0.86 g (1.5%) of acetone 2,4-dinitrophenylhydrazone, mp 122°C. From the hydrochloric acid solutions we isolated 0.0677 mol (29%) of dimethylamine, mp 157°C (pycrate), 10.8 g (44%) of 1-(dimethylamino)-3-methylbut-2-ene, bp 113-115°C (680 mm), mp 102-103°C (pycrate), and 6.4 g (21%) of 1-(dimethylamino)-3-methylbutan-3-ol [3], bp 71°C (30 mm), mp 134–136°C (pycrate). From the fraction with bp 68– 130°C (18 mm) we also isolated 13.5 g of amine compounds which could be separated neither by distillation, nor by chromatography. The only compound isolated from this mixture was 1,4-bis(dimethylamino)-1,1-dimetthylbut-2-yne, 2.4 g (6%), bp 74°C (7 mm), mp 230–231°C (pycrate).

From the residue in the reaction flask we obtained 1.2 g (11%) of formic acid which gave with a mercuric acid solution a characteristic white precipitate.

REFERENCES

- Babayan, A.T., Indzhikyan, M.G., Grigoryan, A.A., Minasyan, R.B., and Ovakimyan, M.Zh., *Izv. Akad. Nauk Arm. SSR, Ser. Khim. Nauk*, 1965, vol. 18, p. 166.
- 2. Hennion, G.F. and Nelson, K.W., J. Am. Chem. Soc., 1957, vol. 79, p. 2142.
- 3. Nazarov, I.N. and Kruglikova, R.I., Zh. Obshch. Khim., 1957, vol. 27, p. 346.