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Synthesis of 1,4-Bis(dimethylamino)-2,3-dibromo-2-butene and Its Quaternary Derivatives

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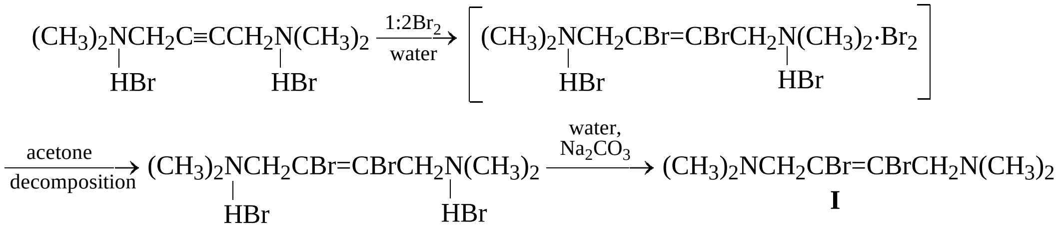
Abstract—Alkylation of 1,4-bis(dimethylamino)-2,3-dibromo-2-butene yielded its previously inaccessible quaternary analogs.

We have shown previously that the reaction of bromine with 1,4-bis(trimethylammonio)-2-butyne dibromide does not result in addition of bromine across the triple bond but yields a complex in which the Br_3^- anion coordinates with the unchanged triple bond, whereas the reaction of bromine with the related tertiary compound, 1,4-bis(dimethylamino)-2-butyne dihydrobromide, occurs along the common pathway, with the addition of one bromine molecule across the triple bond. Such a dramatic difference in the behavior of closely related compounds was attributed to steric hindrance caused by the methyl groups at the quaternary ammonium nitrogen atoms [1].

In this study, with the aim to prepare 1,4-bis(quaternary) ammonium salts with the common 2,3-dibromo-2-butenyl group, we attempted alkylation of 1,4-bis(dimethylamino)-2,3-dibromo-2-butene **I**.

Free amine **I** was obtained as flaky crystals (mp 45–46°C) by neutralization of dihydrobromide of **I** with a sodium carbonate solution, followed by extraction with ether.

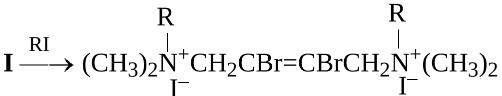


$$(CH_3)_2\underset{\displaystyle HBr}{\underset{|}{N}}CH_2C\equiv CCH_2\underset{\displaystyle HBr}{\underset{|}{N}}(CH_3)_2 \xrightarrow[\text{water}]{1:2Br_2} \left[(CH_3)_2\underset{\displaystyle HBr}{\underset{|}{N}}CH_2CBr{=}CBrCH_2\underset{\displaystyle HBr}{\underset{|}{N}}(CH_3)_2\cdot Br_2\right]$$

$$\xrightarrow[\text{decomposition}]{\text{acetone}} (CH_3)_2\underset{\displaystyle HBr}{\underset{|}{N}}CH_2CBr{=}CBrCH_2\underset{\displaystyle HBr}{\underset{|}{N}}(CH_3)_2 \xrightarrow{\text{water, } Na_2CO_3} \underset{\textbf{I}}{(CH_3)_2NCH_2CBr{=}CBrCH_2N(CH_3)_2}$$

In [1], we ascribed to hydrobromide of **I** the *cis* structure, which, however, is improbable from the energy viewpoint. A single crystal X-ray diffraction study of **I**, in combination with the ^1H and ^{13}C NMR data, unambiguously proved its *trans* configuration (see figure; Tables 1–3).

Treatment of **I** with alkyl iodides yielded the corresponding alkyl derivatives **II**–**V** (Table 1):

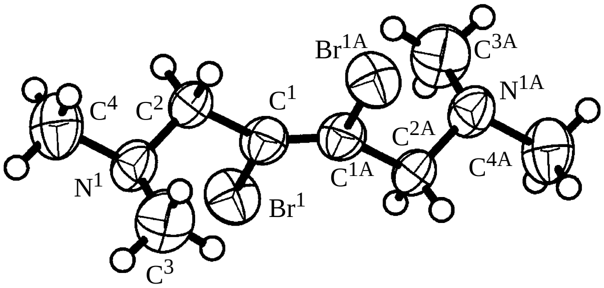


$$\textbf{I} \xrightarrow{RI} (CH_3)_2\overset{\displaystyle R}{\overset{|}{\underset{I^-}{N^+}}}CH_2CBr{=}CBrCH_2\overset{\displaystyle R}{\overset{|}{\underset{I^-}{N^+}}}(CH_3)_2$$

II–**V**

R = CH_3 (**I**), C_2H_5 (**III**), C_3H_7 (**IV**), C_4H_9 (**V**).

Thus, we unambiguously proved that the inertness to bromination of the triple bond in 1,4-bis(trimethylammonio)-2-butyne dibromide is due to steric factors.



Molecular structure of **I**, with the numbering of non-hydrogen atoms.

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Table 1. Ammonium salts **II–V**

Comp. no.	Yield, %	mp, °C	R_f	^{1}H NMR spectrum, δ, ppm (*J*, Hz)	Found, %		Formula	Calculated, %		M^a	
					I	N		I	N	found	calculated
II	100	184–185	0.56	3.38 s (18H, $\mathrm{NCH_3}$), 4.80 s (4H, $\mathrm{NCH_2}$)	44.16	4.96	$\mathrm{C_{10}H_{22}Br_2I_2N_2}$	43.49	4.79	582	584
III	78	161–162	0.79	1.38 t (6H, $\mathrm{NCH_2C}H_3$, *J* 8.0), 3.18 s (12H, $\mathrm{NCH_3}$), 3.62 q (4H, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.75 s (4H, $\mathrm{CH_2CBr{=}}$)	41.43	4.70	$\mathrm{C_{12}H_{26}Br_2I_2N_2}$	41.50	4.58	612.4	612
IV	82	148–149	0.69	0.98 t (6H, $\mathrm{NCH_2CH_2C}H_3$, *J* 8.0), 1.8 m (4H, $\mathrm{NCH_2C}H_2$), 3.43 m (4H, $\mathrm{NC}H_2\mathrm{C_2H_5}$), 3.18 s (12H, $\mathrm{NCH_3}$), 4.75 s (4H, $\mathrm{CH_2CBr{=}}$)	9.58	4.20	$\mathrm{C_{14}H_{30}Br_2I_2N_2}$	39.68	4.37	641.8	640
V	81	123–124	0.51	0.95 t (6H, $\mathrm{CH_2C}H_3$, *J* 8.0), 1.31 m (4H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.75 m (4H, $\mathrm{C}H_2\mathrm{C_2H_5}$), 3.0–3.48 m (4H, $\mathrm{C}H_2\mathrm{C_3H_7}$), 3.20 s (12H, $\mathrm{NCH_3}$), 4.65 s (4H, $\mathrm{CH_2CBr{=}}$)	38.22	3.89	$\mathrm{C_{16}H_{34}Br_2I_2N_2}$	38.02	4.19	672.7	668

[a] Determined titrimetrically.

Table 2. Coordinates of nonhydrogen atoms in the symmetrically independent part of the molecule of **I** (Å × 10^4) and their isotropic equivalent temperature factors (Å^2 × 10^3)

Atom	*x*	*y*	*z*	B_{iso}
Br	1611(2)	2311(2)	3711(1)	71(1)
N^1	5649(16)	8352(12)	1973(8)	62(2)
C^1	4481(19)	9857(13)	4437(10)	58(2)
C^2	5030(20)	7860(13)	3609(9)	58(2)
C^3	7930(20)	8890(30)	1552(14)	93(4)
C^4	5810(30)	6420(20)	1171(13)	87(3)

Table 3. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of **I**

Bond	*d*	Angle	ω
$\mathrm{Br{-}C^1}$	1.926(9)	$\mathrm{C^2N^1C^3}$	114.8(9)
$\mathrm{N^1{-}C^3}$	1.44(1)	$\mathrm{C^3N^1C^4}$	109.3(8)
$\mathrm{C^1{-}C^{1A}}$	1.30(2)	$\mathrm{BrC^1C^{1A}}$	116.9(8)
$\mathrm{N^1{-}C^2}$	1.43(1)	$\mathrm{N^1C^2C^1}$	112.2(7)
$\mathrm{N^1{-}C^4}$	1.51(1)	$\mathrm{C^2N^1C^4}$	110.0(7)
$\mathrm{C^1{-}C^2}$	1.50(1)	$\mathrm{C^2C^1C^{1A}}$	131.4(10)
		$\mathrm{BrC^1C^2}$	111.5(7)

EXPERIMENTAL

The NMR spectra were recorded on a Varian Mercury-300 spectrometer [working frequencies 300.077 and 75.453 MHz for ^{1}H and ^{13}C, respectively; solvent $\mathrm{(CD_3)_2SO}$]. The chemical shifts are given relative to internal TMS. The UV spectra were measured with a Specord U-40 spectrometer from solutions in water (salt) or acetonitrile (complex). The TLC analysis was performed on Silufol UV-254 plates in the solvent system *n*-butanol–ethanol–water–acetic acid, 10 : 7 : 6 : 4, development with iodine vapor. The melting points were measured on a Boetius microheating stage equipped with a PHMK-0.5 observation device.

The crystals for the X-ray diffraction study were of poor quality but nevertheless suitable for the measurements. The low accuracy of the results is caused by the fact that the measurements were performed at room temperature, and the compound was low-melting (mp 45–46°C).

The unit cell parameters and the intensities of 1086 reflections were measured on an Enraf-Nonius CAD-4 four-circle diffractometer (MoK_α radiation, graphite monochromator, $\omega/2\theta$ scanning, θ_{max} 28°). The crystals are triclinic: *a* 5.700(1), *b* 6.420(1), *c* 8.768 (2) Å; α 79.30(3)°, β 80.91 (3)°, γ 69.45(3)°; *V* 293.7(1) Å^3, *Z* 1 ($C_8H_{16}Br_2N_2$), space group *P*1. The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for the nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and included in the calculation of F_{calc} with the fixed isotropic parameters B_{iso} 8 Å^2, using the riding group method. The correction for the absorption was not made. The final divergence factors were R 0.085 and R_W 0.204 for 979 unique reflections with $I > 2\sigma(I)$.

The structure of the molecule with the numbering of nonhydrogen atoms is shown in the figure. The molecule occupies the [0.5, 1, 0.5] special position and has apparently the *trans* configuration. The coordinates of the independent nonhydrogen atoms are given in Table 2, and the bond lengths and angles, in Table 3. There is no sense in detailed discussion of the data obtained because of their low accuracy; on the whole, the geometric parameters have expected values [2] and unambiguously confirm the structure of the molecule.

1,4-Bis(dimethylamino)-2,3-dibromo-2-butene I. To 7.3 g of 1,4-bis(dimethylamino)-2-butyne prepared according to [3], we added dropwise 21 ml of 40% aqueous HBr. Then, without isolation of the hydrobromide formed, we added dropwise 16 g of bromine with vigorous stirring at room temperature. The complex of bromine with 1,4-bis(dimethylamino)-2,3-dibromo-2-butene dihydrobromide was filtered off. Yield 22.3 g (69%), mp 182–183°C. The UV spectrum of the complex contained absorption bands at 220 and 270 nm (at 205 nm in the spectrum of the starting compound), typical of such complexes [4]. After decomposition of the complex with acetone (chemically pure grade), we obtained 16.5 g (100%) of 1,4-bis(dimethylamino)-2,3-dibromo-2-butene dihydrobromide, mp 245–246°C. ^{1}H NMR spectrum, δ, ppm: 2.88 s (12H, NCH_3), 4.50 s (4H, NCH_2), 9.95 br.s (2H, NH). ^{13}C NMR spectrum, δ_C, ppm: 42.85 (CH_3), 62.64 (CH_2), 119.44 (=CH_2). Found, %: Br 34.57; N 6.36. $C_8H_{18}Br_4N_2$. Calculated, %: Br 34.63; N 6.06. By treatment of 8 g of this dihydrobromide with an aqueous solution of sodium or potassium carbonate, followed by extraction with diethyl ether and solvent removal under reduced pressure (40–50 mm Hg), we obtained 4.6 g (88%) of 1,4-bis(dimethylamino)-2,3-dibromo-2-butene **I** in the form of platelike crystals, mp 45–46°C. ^{1}H NMR spectrum, δ, ppm: 2.20 s (12H, NCH_3), 3.20 s (4H, NCH_2). ^{13}C NMR spectrum, δ_C, ppm: 44.14 (CH_3), 65.42 (CH_2), 121.53 (=CH_2). Found N, %: 9.27. $C_8H_{18}Br_2N_2$. Calculated N, %: 9.30. *M* found 301.4, calculated 300. Melting point of the picrate (alcohol) 185–186°C and of the dihydroiodide 189–190°C.

Bis(alkyl iodide) derivatives of 1,4-bis(dimethylamino)-2,3-dibromo-2-butene II–V. A double (in moles) amount of appropriate alkyl iodide was added to an alcoholic solution of 0.02 mol of **I**. The mixture was left for 2 days, after which the solvent was distilled off at reduced pressure (40–50 mm Hg), and the residue was washed with absolute ether and dried.

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