Organic Chemistry

Synthesis of 1-[1-bromo-2-benzoyl(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromides from 1-bromo-2-benzoyl(2-thenoyl)acetylenes and 1,1-dimethylhydrazine

V. N. Elokhina,[a] A. S. Nakhmanovich,[a] L. I. Larina,[a]*
O. V. Shishkin,[b] V. N. Baumer,[b] and V. A. Lopyrev[a]

[a]Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 35 6046
[b]Institute of Single Crystals of the National Academy of Sciences of Ukraine, 60 prosp. Lenina, 310001 Khar'kov, Ukraine. Fax: +7 (057 2) 32 0273

1-[1-Bromo-2-benzoyl(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromides were synthesized by the reactions of 1-aroyl-2-bromoacetylenes with *N,N*-dimethylhydrazine in acetonitrile at 20 °C. The structure of 1-(2-benzoyl-1-bromovinyl)-1,1-dimethylhydrazinium bromide was established by X-ray diffraction analysis.

Key words: 1-aroyl-2-bromoacetylenes, *N,N*-dimethylhydrazine, 1-[1-bromo-2-benzoyl(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromides, X-ray diffraction analysis.

The reactions of ketones and aldehydes of the acetylene series with *N,N*-dimethylhydrazine remain poorly studied. It is known that aroylphenylacetylenes react with *N,N*-dimethylhydrazine on heating to form 1,1-dimethyl-2-[β-(α-aroyl)styryl]hydrazines in high yields (78—96%).[1] The reaction of 1-acetyl-2-dialkylamino(morpholino)acetylene with *N,N*-dimethylhydrazine in THF on heating afforded *N,N*-dimethyl-3-oxobutanamide hydrazones.[2] The reaction of propiolaldehyde with *N,N*-dimethylhydrazine in an aqueous solution in the presence of NaH_2PO_4 gave propiolaldehyde *N,N*-dimethylhydrazone in 18% yield.[3]

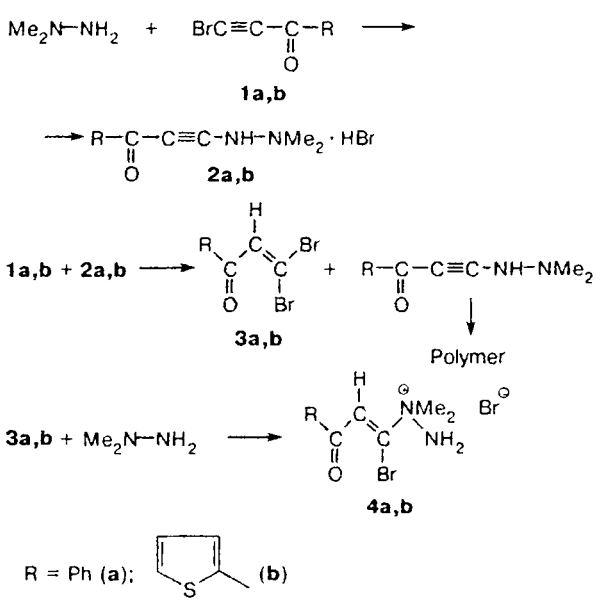
We studied for the first time the reaction of 1-acyl-2-bromoacetylenes (**1a,b**) with *N,N*-dimethylhydrazine in MeCN at 20 °C (Scheme 1).

Apparently, 1-acyl-2-(2,2-dimethylhydrazino)acetylene hydrobromides (**2a,b**) were formed in the first stage of the reaction of 1,1-dimethylhydrazine with an equimolar amount of 1-acyl-2-bromoacetylene as a result of elimination of HBr. Compounds **2a,b** reacted with another molecule of acetylene ketones (**1a,b**) (the second stage) to form 1-acyl-2,2-dibromoethylenes (**3a,b**) and 1-acyl-2-(2,2-dimethylhydrazino)acetylenes, which extremely readily polymerized under the reaction conditions. Attempts to isolate these compounds failed. In this stage, hydrobromides **2a,b** served as a source of HBr. Finally, the third stage (the reaction of 1-acyl-2,2-dibromoethylenes (**3a,b**) with 1,1-dimethylhydrazine) involved alkylation of the tertiary nitrogen atom of 1,1-dimethylhydrazine (quaternization) to form 1-[1-bro-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1536—1538, August, 1999.

1066-5285/99/4808-1516 $22.00 © 1999 Kluwer Academic/Plenum Publishers

Scheme 1



mo-2-benzoyl(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromide (**4a,b**).

The prerequisite for Scheme 1 to be realized is a higher rate of the second stage compared to that of the first stage.

Analysis of the IR and ^{1}H NMR spectra did not provide data sufficient to confirm structures **4a,b**. The IR spectra of compounds **4a,b** have absorption bands of the C=C bond and of the C=O and NH_2 groups at 1605—1608, 1640—1670, and 3400—3440 cm^{-1}, respectively. X-ray diffraction study demonstrated that the product of the reaction of *N,N*-dimethylhydrazine with ketone **1a** has structure **4a** (Fig. 1).

The carbonyl group and the phenyl ring in compound **4a** are coplanar (the O(1)—C(7)—C(1)—C(6) torsion angle is −1.6°). The steric strain in the conjugated system of the molecule, which occurs due to repulsion between the O(1) and Br(2) atoms (the distance is 3.10 Å; the sum of the van der Waals radii[4] is 3.26 Å), between the H(2C) and C(8) atoms (2.56 Å and 2.87 Å, respectively), and between the H(2C) and H(8A) atoms (2.27 Å and 2.32 Å, respectively), is partially relieved as a result of distortion of the enone fragment (that has the cisoid conformation) from planarity (the O(1)—C(7)—C(8)—C(9) torsion angle is −45.6°). The amino group adopts a pyramidal configuration (the sum of the bond angles at the N(2) atom is 347°) and is virtually perpendicular to the C(8)=C(9) double bond (the C(8)—C(9)—N(1)—N(2) torsion angle is −113.3°). Apparently, this orientation of the substituent is due to the balance of repulsion between the Br(2) and H(10A) atoms (the distance is 2.62 Å; the sum of the van der Waals radii is 3.13 Å) and attraction between the oppositely charged

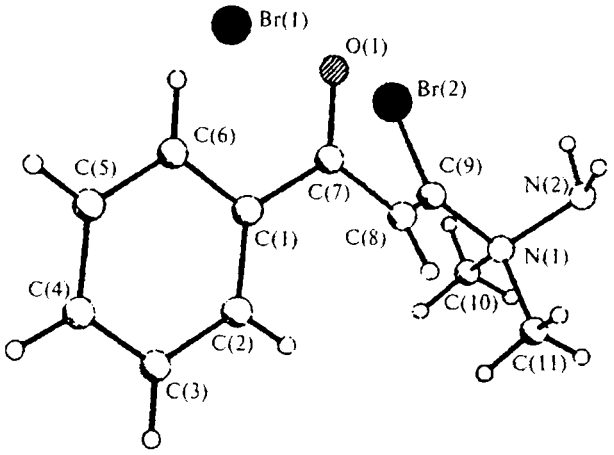


Fig. 1. Molecular structure of **4a**.

Br(2) and H(2B) atoms (2.77 Å). The Br atom in the cation is also located in close proximity to the halogen atom of the anion (the Br(1)...Br(2) distance is 3.23 Å; the sum of the van der Waals radii is 3.94 Å).

In the crystal, molecules **4a** are linked in a three-dimensional framework through intermolecular hydrogen bonds H(2A)...Br(1)′ (1 + *x*, *y*, *z*) (H...Br, 2.50 Å; N—H...Br, 157°) and H(2B)...Br(1)′ (0.5 + *x*, *y*, 0.5 − *z*) (H...Br, 2.66 Å; N—H...Br, 139°) and the shortened contacts Br(1)...N(2)′ (−1 + *x*, *y*, *z*) (3.40 Å; 3.47 Å), Br(1)...N(2)′ (−0.5 + *x*, *y*, 0.5 − *z*) (3.44 Å), Br(1)...H(10B)′ (*x*, −1 + *y*, *z*) (2.96 Å), and Br(1)...H(11C)′ (0.5 − *x*, −0.5 + *y*, *z*) (2.98 Å).

Bromides **4a,b** obtained are stable compounds and do not undergo subsequent conversions under the conditions of the synthesis.

Experimental

The ^{1}H NMR spectra of compounds **4a** (CD_3OD) and **4b** (DMSO-d_6) were measured on a Bruker DPX-250 spectrometer (250 MHz, HMDS). The IR spectra were recorded on a Specord IR-75 instrument in KBr pellets.

1-(2-Benzoyl-1-bromovinyl)-1,1-dimethylhydrazinium bromide (4a). *N,N*-Dimethylhydrazine (0.6 g, 0.01 mol) was slowly added with stirring to a solution of 1-benzoyl-2-bromoacetylene (**1a**) (2.09 g, 0.01 mol) in anhydrous MeCN (20 mL) at 20 °C (exothermic reaction). Then the mixture was stirred for 4 h and left for ~10 h. The precipitate that formed was filtered off and recrystallized from EtOH.

The filtrate was concentrated, the precipitate was dissolved in $CHCl_3$ (15 mL), and petroleum ether was added. Compound **2a** could not be isolated from the resinous precipitate that formed.

Compound **4a** was obtained in a yield of 1.2 g (68.6%) as yellow crystals, m.p. 123—124 °C. Found (%): C, 37.48; H, 3.95; Br, 45.56; N, 7.88. $C_{11}H_{14}Br_2N_2O$. Calculated (%): C, 37.74; H, 4.03; Br, 45.65; N, 8.00. ^{1}H NMR (CD_3OD), δ: 3.79 (s, 6 H, $N(CH_3)_2$); 7.64—8.04 (m, 5 H, H arom.); 8.23 (s, 1 H, =CH).

Table 1. Bond lengths (d) in molecule **4a**

Bond	d/Å	Bond	d/Å
Br(2)—C(9)	1.91(1)	C(1)—C(7)	1.46(2)
O(1)—C(7)	1.24(1)	C(2)—C(3)	1.42(2)
N(1)—N(2)	1.46(1)	C(3)—C(4)	1.35(2)
N(1)—C(9)	1.49(1)	C(4)—C(5)	1.35(2)
N(1)—C(10)	1.50(1)	C(5)—C(6)	1.39(2)
N(1)—C(11)	1.50(1)	C(7)—C(8)	1.51(2)
C(1)—C(2)	1.35(2)	C(8)—C(9)	1.31(2)
C(1)—C(6)	1.40(2)		

Table 2. Bond angles (ω) in molecule **4a**

Angle	ω/deg	Angle	ω/deg
N(2)—N(1)—C(9)	111.0(8)	C(3)—C(4)—C(5)	120(1)
N(2)—N(1)—C(10)	107.5(8)	C(4)—C(5)—C(6)	122(1)
C(9)—N(1)—C(10)	110.2(8)	C(5)—C(6)—C(1)	118(1)
N(2)—N(1)—C(11)	105.0(8)	O(1)—C(7)—C(1)	122(1)
C(9)—N(1)—C(11)	113.4(9)	O(1)—C(7)—C(8)	119(1)
C(10)—N(1)—C(11)	109.5(9)	C(1)—C(7)—C(8)	119(1)
C(2)—C(1)—C(6)	119(1)	C(9)—C(8)—C(7)	126(1)
C(2)—C(1)—C(7)	123(1)	C(8)—C(9)—N(1)	124(1)
C(6)—C(1)—C(7)	118(1)	C(8)—C(9)—Br(2)	122.7(9)
C(1)—C(2)—C(3)	122(1)	N(1)—C(9)—Br(2)	113.5(7)
C(4)—C(3)—C(2)	119(2)		

1-[1-Bromo-2-(2-thenoyl)vinyl]-1,1-dimethylhydrazinium bromide (4b) was prepared analogously from ketone **1b** (1.08 g, 5 mmol) and *N,N*-dimethylhydrazine (0.3 g, 5 mmol) in a yield of 0.4 g (44.9%) as yellow crystals, m.p. 130—132 °C. Found (%): C, 30.14; H, 3.50; Br, 44.72; N, 7.59; S, 9.10. $C_9H_{12}Br_2N_2OS$. Calculated (%): C, 30.36; H, 3.40; Br, 44.88; N, 7.87; S, 8.99. ^{1}H NMR (DMSO-d_6), δ: 3.74 (s, 6 H, $N(CH_3)_2$); 7.36—8.24 (m, 3 H, C_4H_3S); 8.29 (s, 1 H, =CH).

X-ray diffraction study of compound 4a. Crystals of compound **4a** are orthorhombic. At 20 °C, a = 7.726(1) Å, b = 11.994(1) Å, c = 27.999(3) Å, V = 2594.7(5) Å^3, d_{calc} = 1.792 g cm^{-3}, space group *Pbca*, Z = 8. The unit cell parameters and intensities of 1137 independent reflections (R_{int} = 0.021) were measured on an automated Siemens P3/PC diffractometer (λ-Cu-Kα, β filter, $\theta/2\theta$ scanning technique, $2\theta_{max}$ = 110°). The absorption correction was applied using direct integration over the crystal volume (T_{min} = 0.5789, T_{max} = 0.7196).

The structure was solved by the direct method using the SHELXTL PLUS program package.[5] The positions of the H atoms were located from the difference electron density synthesis and refined using the riding model with fixed temperature factors $U_{iso} = nU_{eq}$ of the nonhydrogen atoms to which the H atoms are attached (n = 1.5 for the methyl groups and 1.2 for the remaining H atoms). The refinement based on F^2 by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using 1046 reflections converged to wR_2 = 0.014 (R_1 = 0.056 using 1000 reflections with $F > 4\sigma(F)$, S = 1.09). The bond lengths and bond angles are given in Tables 1 and 2, respectively. The coordinates of the nonhydrogen atoms of molecule **4a** are listed in Table 3. The structure of molecule **4a** and the atomic numbering scheme are shown in Fig. 1.

Table 3. Coordinates of nonhydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters (U_{eq}) in the structure of **4a**

Atom	x	y	z	$U_{eq} \cdot 10^3$/Å^2
Br(1)	−3319(2)	5217(1)	1935(1)	45(1)
Br(2)	380(2)	6248(1)	1627(1)	42(1)
O(1)	2166(14)	4855(7)	836(3)	66(3)
N(1)	3269(11)	7633(8)	1831(3)	39(2)
N(2)	3587(13)	7060(7)	2283(3)	41(2)
C(1)	3038(16)	6029(9)	202(4)	42(3)
C(2)	3697(19)	7009(14)	51(4)	65(4)
C(3)	3917(21)	7249(15)	−443(5)	83(5)
C(4)	3416(19)	6477(14)	−767(5)	69(4)
C(5)	2770(21)	5487(13)	−618(5)	70(4)
C(6)	2534(22)	5236(12)	−136(4)	66(4)
C(7)	2818(16)	5754(11)	707(4)	44(3)
C(8)	3436(16)	6565(10)	1082(4)	48(3)
C(9)	2588(16)	6853(9)	1467(4)	35(3)
C(10)	1981(14)	8543(10)	1925(4)	43(3)
C(11)	4980(16)	8140(11)	1696(4)	50(3)

This work was financially supported by the International Science and Engineering Center (Grant 427-96).

References

1. F. H. Al-Hajjar, M. S. El-Ezaby, and N. R. El-Rayyes, *Chem. Pharm. Bull.*, 1977, **25**, 548.
2. I. G. Ostroumov, A. E. Tsil'ko, I. A. Maretina, and A. A. Petrov, *Zh. Org. Khim.*, 1987, **23**, 1635 [*J. Org. Chem. USSR*, 1987, **23** (Engl. Transl.)].
3. B. V. Ioffe and D. D. Tsitovich, *Izv. Vuzov, Ser. Khim. i Khimich. Tekhnol.* [*Proceedings of Institutes: Chemistry and Chemical Technology*], 1967, **10**, 301 (in Russian).
4. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1989, **58**, 713 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
5. G. M. Sheldrick, *SHELXTL PLUS. PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data*, Rev. 5.02.1994.

Received November 20, 1998;
in revised form January 25, 1999