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Received December 19, 1997;
in revised form March 27, 1998

Reactions of terminal acylacetylenes with thiocarbohydrazones

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The reactions of terminal acylacetylenes with thiocarbohydrazones give 2-(2-acylvinyl)thiocarbohydrazones or 2,2-bis(2-acylvinyl)thiocarbohydrazones depending on the reagent ratio. Benzoylacetylene reacts with thiocarbohydrazone of *p*-dimethylaminobenzaldehyde to form *S*-[2-(*p*-dimethylaminobenzoyl)vinyl]isothiocarbodihydrazone.

Key words: acylacetylenes, 2-(2-acylvinyl)thiocarbohydrazones, 2,2-bis(2-acylvinyl)thiocarbohydrazones, *S*-(2-benzoylvinyl)isothiocarbodihydrazone, nucleophilic addition.

Previously, we have found that reactions of terminal acylacetylenes with thiosemicarbazones in a medium of acetonitrile, benzene, or methanol at 20 °C afforded 3-acylvinyl-5-amino-Δ^4-1,3,4-thiadiazolines in high yields.[1] The reactions of terminal acylacetylenes with thiocarbohydrazide in aqueous-ethanolic solutions at 60 °C gave 6-acylmethylhexahydro-1,2,4,5-tetrazine-3-thiones.[2]

As part of our continuing studies of the reactions of acylacetylenes with ambident nucleophilic *N*,*S*-containing reagents,[3—5] in this work we studied the reactions of ketones **1a,b** with thiocarbohydrazones **2a,b** and thiocarbodihydrazone **3**.

The reactions of acylacetylenes **1a,b** with thiocarbohydrazones **2a,b** in MeOH or MeCN at 20 °C gave the corresponding 2-(2-acylvinyl)thiocarbohydrazones (**4a—c**) as the only products (Scheme 1). We did not observe the formation of adducts as a result of attack at the triple bond of acetylenes **1a,b** with the participation of the *S*-nucleophilic center of reagents **2a,b**. Evidently, the *S*-nucleophilic center is less nucleophilic than the NH_2 group of hydrazones **2a,b**, whose high nucleophilicity is attributable to the α-effect and to interactions of the lone electron pair of the nitrogen atom of the NH_2 group with the orbitals of the lone electron pair of the adjacent nitrogen atom.[6—8]

The reactions of thiocarbohydrazones **2a,b** with an excess of acetylene-containing ketones **1a,b** gave *N*-diadducts **5a,b** in good yields.

The reaction of ketone **1a** with thiocarbodihydrazone **3**, which does not contain the primary amino group, proceeded differently. In **3**, the S atom serves as the nucleophilic center, which leads to the formation of *S*-monoadduct **6**.

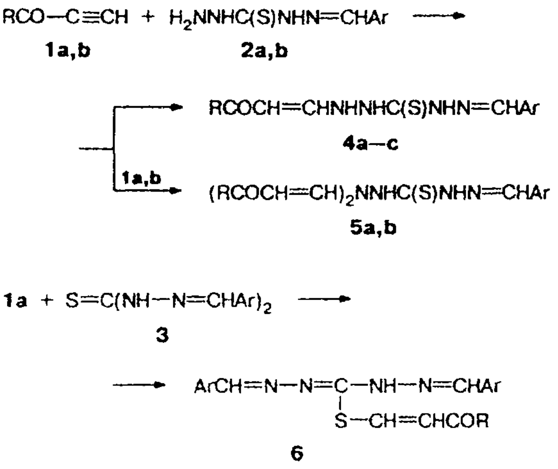
The IR spectra of compounds **4a—c**, **5a,b**, and **6** have absorption bands of the C=O bonds (1615—1640 cm^{-1}), of the C=N and C=C bonds (1515—1605 cm^{-1}), and of the NH stretching vibrations (3120—3230 cm^{-1}). In addition, the spectra of compounds **4a—c** and **5a,b** have absorption bands of the C=S bonds (1200—1210 cm^{-1}) and the spectrum of **6** has an absorption band of the C—S bond (690 cm^{-1}).

Experimental

The ^{1}H NMR spectra (in DMSO-d$_6$) were obtained on a BS-487C spectrometer operating at 80 MHz. The IR spectra were recorded on a Specord IR-75 instrument as KBr pellets.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2083—2085, October, 1998.

Scheme 1



	R	Ar
1a	Ph	
1b	2-thienyl	
2a		Ph
2b		p-$Me_2NC_6H_4$
3		$Me_2NC_6H_4$-p
4a	Ph	Ph
4b	2-thienyl	$Me_2NC_6H_4$-p
4c	Ph	$Me_2NC_6H_4$-p
5a	Ph	Ph
5b	Ph	$Me_2NC_6H_4$-p
6		$Me_2NC_6H_4$-p

Benzaldehyde thiocarbohydrazone (2a) was prepared according to a known procedure.[9] M.p. 185—186 °C. Found (%): C, 49.52; H, 5.30; N, 28.60; S, 16.32. $C_8H_{10}N_4S$. Calculated (%): C, 49.46; H, 5.19; N, 28.84; S, 16.51.

***p*-Dimethylaminobenzaldehyde thiocarbohydrazone (2b)** was prepared analogously to **2a**.[9] M.p. 193—195 °C. Found (%): C, 50.44; H, 6.23; N, 29.20; S, 13.42. $C_{10}H_{15}N_5S$. Calculated (%): C, 50.61; H, 6.37; N, 29.51; S, 13.51.

***p*-Dimethylaminobenzaldehyde thiocarbodihydrazone (3)** was prepared according to a known procedure.[11] M.p. 202—204 °C. Found (%): C, 62.21; H, 6.52; N, 22.92; S, 8.63. $C_{19}H_{24}N_6S$. Calculated (%): C, 61.93; H, 6.56; N, 22.81; S, 8.70.

1,9-Diphenyl-4-thioxo-2,3,5,6-tetraaza-1,7-nonadien-9-one (4a). A solution of benzoylacetylene **1a** (1.3 g, 0.01 mol) in MeOH (35 mL) was added with intense stirring to a suspension of thiocarbohydrazone **2a** (1.94 g, 0.01 mmol) in MeOH (30 mL). The reaction mixture was stirred at 20 °C for 3 h. The precipitate that formed was filtered off, washed with cold ether, and dried *in vacuo*. Compound **4a** was obtained in a yield of 2.3 g (71%) as a bright-yellow powder, m.p. 144—146 °C. When the reaction was carried out in MeCN, compound **4a** was obtained in 72% yield. Found (%): C, 62.98; H, 4.90; N, 17.08; S, 9.92. $C_{17}H_{16}N_4OS$. Calculated (%): C, 62.94; H, 4.97; N, 17.27; S, 9.88. ^1H NMR, δ: 6.45 (d, 1 H, CO—CH=, J = 9.7 Hz); 8.20 (d, 1 H, NH—C$\underline{H}$=, J = 9.7 Hz); 10.95 (s, 1 H, NH); 11.35 (s, 1 H, NH); 12.24 (s, 1 H, NH); 7.58—8.00 (m, 11 H, 2 C_6H_5, N=CH).

1-(*p*-Dimethylaminophenyl)-9-(thien-2-yl)-4-thioxo-2,3,5,6-tetraaza-1,7-nonadien-9-one (4b) was prepared analogously to compound **4a** from 3-(thien-2-yl)-1-propyn-3-one (**1b**) (0.68 g, 0.05 mol) and thiocarbohydrazone **2b** (1.19 g, 0.05 mol). Compound **4b** was obtained in a yield of 1.5 g (80%) as a bright-yellow powder, m.p. 141—143 °C. Found (%): C, 54.61; H, 5.05; N, 19.02; S, 17.11. $C_{17}H_{19}N_5OS_2$. Calculated (%): C, 54.67; H, 5.13; N, 18.75; S, 17.17. ^1H NMR, δ: 2.96 (s, 6 H, 2 CH_3); 6.33 (d, 1 H, CO—CH=, J = 9.8 Hz); 7.90 (s, 1 H, CH=N—); 8.22 (d, 1 H, NH—C$\underline{H}$=, J = 9.8 Hz); 9.52 (s, 1 H, NH); 10.16 (s, 1 H, NH); 11.18 (s, 1 H, NH); 6.74—7.84 (m, 7 H, C_4H_3S, C_6H_4).

1-(*p*-Dimethylaminophenyl)-9-phenyl-4-thioxo-2,3,5,6-tetraaza-1,7-nonadien-9-one (4c) was prepared analogously to compound **4a** from benzoylacetylene **1a** (0.65 g, 0.05 mol) and thiocarbohydrazone **2b** (1.19 g, 0.05 mol). Compound **4c** was obtained in a yield of 1.2 g (65%) as a pale-yellow powder, m.p. 141—143 °C. Found (%): C, 62.10; H, 6.03; N, 18.81; S, 8.60. $C_{19}H_{21}N_5OS$. Calculated (%): C, 62.10; H, 5.76; N, 19.06; S, 8.73. ^1H NMR, δ: 2.97 (s, 6 H, 2 CH_3); 6.42 (d, 1 H, CO—CH=, J = 9.7 Hz); 6.74—7.86 (m, 9 H, C_6H_5, C_6H_4); 8.13 (d, 1 H, =C$\underline{H}$—NH, J = 9.7 Hz); 8.22 (s, 1 H, C_6H_4—C$\underline{H}$=); 10.98 (s, 1 H, NH); 11.26 (s, 1 H, NH); 12.05 (s, 1 H, NH).

1,1-Bis(2-benzoylvinyl)-6-phenyl-3-thioxo-1,2,4,5-tetraaza-5-hexene (5a). Benzaldehyde thiocarbohydrazone **2a** (0.97 g, 0.05 mol) was added with intense stirring to a solution of benzoylacetylene **1a** (1.56 g, 0.12 mol) in MeOH (80 mL). The reaction mixture was stirred at 20 °C for 3 h. The bright-yellow precipitate that formed was washed with cold ether and dried *in vacuo*. The yield of compound **5a** was 1.8 g (79%). When the reaction was carried out in MeCN, the yield was 72%. M.p. 180—181 °C. Found (%): C, 68.42; H, 4.83; N, 12.45; S, 7.30. $C_{26}H_{22}N_4O_2S$. Calculated (%): C, 68.70; H, 4.88; N, 12.33; S, 7.51. ^1H NMR, δ: 6.42 (d, 2 H, 2 CO—CH=, J = 9.7 Hz); 7.52—7.89 (m, 15 H, 3 C_6H_5); 8.18 (s, 1 H, Ph—CH=); 8.20 (d, 2 H, CH—N—CH, J = 9.7 Hz); 11.23 (s, 1 H, NH); 12.35 (s, 1 H, NH).

1,1-Bis(2-benzoylvinyl)-6-(*p*-dimethylaminophenyl)-3-thioxo-1,2,4,5-tetraaza-5-hexene (5b) was prepared analogously to compound **5a** from benzoylacetylene **1a** (1.56 g, 0.12 mol) and thiocarbohydrazone **2b** (1.19 g, 0.05 mol). Compound **5b** was obtained in a yield of 1.8 g (72%) as a bright-yellow powder, m.p. 172—173 °C. Found (%): C, 67.72; H, 5.39; N, 13.83; S, 6.27. $C_{28}H_{27}N_5O_2S$. Calculated (%): C, 67.58; H, 5.47; N, 14.07; S, 6.44. ^1H NMR, δ: 2.98 (s, 6 H, 2 CH_3); 6.41 (d, 2 H, 2 CO—CH=, J = 9.7 Hz); 6.71—7.86 (m, 14 H, C_6H_4, 2 C_6H_5); 8.15 (s, 1 H, C_6H_4—CH=); 8.32 (d, 2 H, HC—N—CH, J = 9.7 Hz); 11.25 (s, 1 H, NH); 12.38 (s, 1 H, NH).

1,7-Bis(*p*-dimethylaminophenyl)-4-(2-benzoylvinylthio)-2,3,5,6-tetraaza-1,3,6-heptatriene (6). *p*-Dimethylaminobenzaldehyde dithiocarbohydrazone **3** (1.84 g, 0.05 mol) was added to a solution of benzoylacetylene **1a** (0.65 g, 0.05 mol) in MeOH (80 mL). The reaction mixture was stirred at 20 °C for 3 h. The dark-yellow precipitate that formed was filtered off, washed with cold ether, and dried *in vacuo*. The yield of compound **6** was 2.32 g (93%). When the reaction was carried out in MeCN, the yield was 78%. M.p. 179—181 °C. Found (%): C, 67.56; H, 6.21; N, 17.02; S, 6.75. $C_{28}H_{30}N_6OS$. Calculated (%): C, 67.44; H, 6.06; N, 16.85; S, 6.43. ^1H NMR, δ: 2.93 (s, 12 H, 4 CH_3); 6.09 (d, 1 H, CO—CH=, J = 10.1 Hz); 6.73—7.73 (m, 13 H, 2 C_6H_4, C_6H_5); 7.29 (d, 1 H, S—CH=, J = 10.1 Hz); 7.89 (s, 2 H, 2 N—CH=); 11.32 (s, 1 H, NH).

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Received December 29, 1997;
in revised form March 28, 1998

High-vacuum pyrolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane. IR spectrum of 1,1,1-trifluoro-2-chloroethyl radical in an argon matrix

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The products of high-vacuum pyrolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane were studied by matrix IR spectroscopy. The decomposition of 1,1,1-trifluoro-2-bromo-2-chloroethane was shown to occur predominantly *via* two directions: to form the 1,1,1-trifluoro-2-chloroethyl radical and trifluoromethylcarbene isomerizing to trifluoroethylene. The CF_3CHCl radical has been detected in the matrix for the first time. The bands observed in the IR spectrum were calculated by the quantum-chemical B3LYP/6-311G(d,p) method and assigned to normal vibrations of the radical.

Key words: 1,1,1-trifluoro-2-chloroethyl radical; pyrolysis; matrix isolation; IR spectroscopy; quantum-chemical calculations.

The interest in products of decomposition of fluorine-containing compounds is associated with their participation in processes in the troposphere favoring the formation of "ozone holes." Many publications devoted to the study of atmospheric chemical reactions, which postulate the participation of free radicals, have appeared in recent years. The mechanisms of similar reactions are mainly elucidated from the data of kinetic studies and analysis of the stable products that formed.[1—5] The direct IR spectroscopic detection makes it possible to study the reaction mechanisms and obtain information about the structure of intermediates. The existence of the 1,1,1-trifluro-2-chloroethyl radical (**1**) was predicted by the theoretical calculations[6] and assumed upon laser irradiation of $CF_3CHBrCl$[7] and on the basis of the UV spectra of the products of the reaction of CF_3CH_2Cl with fluorine atoms;[1] however, IR spectroscopic data on this species were lacking. This work is devoted to the direct IR spectroscopic study of 1,1,1-trifluoro-2-chloroethyl radical formed by the thermolysis of 1,1,1-trifluoro-2-bromo-2-chloroethane (**2**). We have shown previously that the high-vacuum pyrolysis of bromine- or iodine-containing compounds is accompanied by the formation of free radicals.[8—10]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2085—2088, October, 1998.