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Reactions of 1-bromo-2-benzoylacetylene with 2,4-dithiobiuretes

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2-Benzoylmethylene-1,3,5-dithiazinium hydrobromides were prepared in high yield by the reaction of 1-bromo-2-benzoylacetylene with 2,4-dithiobiurete and its mono- and disubstituted derivatives in glacial AcOH. The ability of the compounds synthesized to undergo further chemical transformations has been studied.

Keywords: 1-Bromo-2-benzoylacetylene; 2,4-Dithiobiurete; Nucleophilic substitution; Heterocyclization; 1,3,5-Dithiazines

1. Introduction

2,4-Dithiobiuretes are interesting research subjects as polyfunctional systems in which the nucleophilic centers are in mesomeric interaction with each other. The use of reagents of this kind in heterocyclization reactions makes it possible to introduce into the structure of cyclic compounds some fragments with predetermined arrangement of heteroatoms and, depending on the reaction conditions and the structure of the initial compounds, allows diverse "electrophile-nucleophile" combinations.

2,4-Dithiobiuretes and their mono-, di- and trisubstituted derivatives are known for their reactions with various electrophilic reagents (aldehydes, ketones, phenylisocyanodichloride) leading to 1,3,5-dithiazine- [1–3], 1,3,5-thiadiazine- [3], 1,3,5-triazine [3–5] derivatives, and spiroconjugated N,S-heterocycles [6].

Continuing our previous research on the reactions of α-acetylenic ketones with polydentate functionally-substituted thioamides [7, 8], we have been concerned with the reaction of 1-bromo-2-benzoylacetylene with 2,4-dithiobiurete and its mono- and disubstituted derivatives with a goal to prepare new N,S-containing heterocycles and to examine their ability further chemical transformations.

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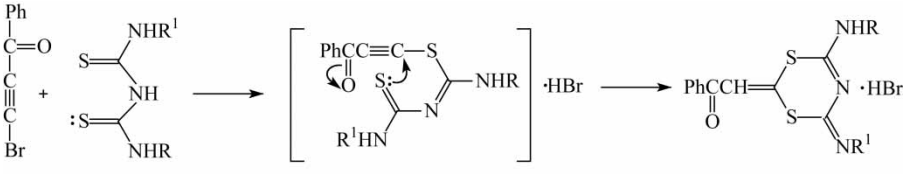
2. Results and discussion

It has been established that 1-bromo-2-benzoylacetylene **1** reacts with 2,4-dithiobiurete **2a**, 1-methyl-2,4-dithiobiurete **2b**, 1-phenyl-2,4-dithiobiurete **2c** and 1,5-diphenyl-2,4-dithiobiurete **2d** in glacial AcOH at 20°C, to give 2-benzoylmethylene-1,3,5-dithiazinium substituted hydrobromides **3a–d** in good yield (scheme 1). The reaction is likely to occur initially *via* direct nucleophilic substitution of the bromine atom at the triple bond to intermediately form ethynylsulfide **A**. The formation of intermediate **A** can, alternatively, involve an addition-elimination mechanism with intermediate formation of enolate ion followed by elimination of the bromine atom [9].

In the next stage of the reaction, a nucleophilic addition of the second sulfur atom to the β-carbon atom of the activated triple bond with closure of the 1,3,5-dithiazine takes place.



1 **2 a–d** **A** **3 a–d**

R = R^1= H (**a**); R = H, R^1 = Me (**b**); R = H, R^1 = Ph (**c**); R = R^1= Ph (**d**)

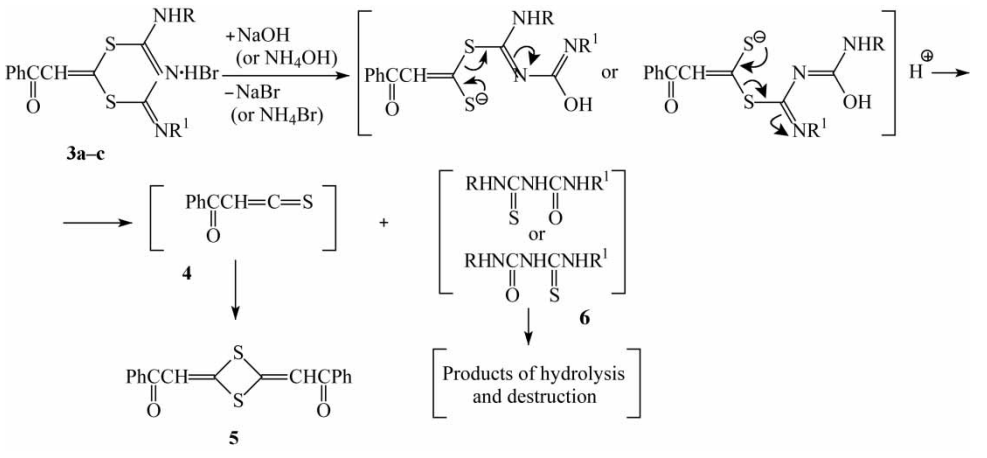
SCHEME 1

An attack of the second sulfur atom on the conjugated triple bond in intermediate **A** occurs as trans-addition to form only one isomer of 1,3,5-dithiazines **3**. The conformation of this isomer with respect to substituents R and R^1 will depend on which of the sulfur atoms is involved in the nucleophilic substitution reaction and which one enters the nucleophilic addition reaction. Such information is not known at this point of the investigation.

The composition and structure of compounds **3a–d** was established by examination of data from elemental analysis and ^{1}H, ^{13}C NMR and IR spectroscopies. The IR spectra of compounds **3a–d** show an absorption band of the conjugated carbonyl group in the 1620–1625 cm^{-1} region and the NH and HN^+ group stretching vibrations are observed as a set of bands in the 3120–3320 and 2840–3100 cm^{-1} region, respectively, depending on the nature of substituents R and R^1. In the ^{1}H NMR spectra of **3a–d** the methylene group protons give rise to a resonance signal in the 7.63–8.03 ppm region, the chemical shifts of NH and HN^+ manifests themselves as broadened singlets in the 10.11–11.01 ppm region. Unambiguous interpretation of the NH and HN^+ group proton signals in the ^{1}H NMR spectrum is hindered by prototropic tautomerism 1,3,5- between exocyclic and ring nitrogen atoms.

It has been found that 1,2,3-dithiazinium hydrobromides **3a–c** are readily hydrolyzed with water in the presence of bases (NaOH, method **A** or ammonia, Method **B**) to form 2,4-bis(benzoylmethylene)-1,3-dithietane (**5**) (scheme 2). Compound **5** is likely to be formed as a result of attack of hydroxyl anion on the dithiazine ring C-6 or C-4 atom with intermediate formation of thioketene **4** followed by dimerization to 1,3-dithiethane **5** [10].

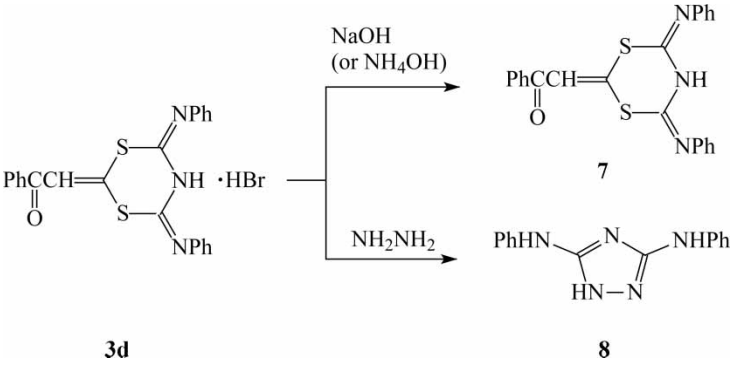
Thiobiurete derivatives **6** are proposed co-products of this reaction; however, none of them had been found in the reaction mixture probably owing to hydrolysis accompanied by decomposition.



SCHEME 2

When treated with aqueous alkali solutions (methods A or B), 2-benzoylmethylene-4,6-diphenylimino-*5-H*-1,3,5-dithiazinium hydrobromide (**3d**) affords in good yield a free base, 2-benzoylmethylene-4,6-diphenylimino-*5-H*-1,3,5-dithiazine (**7**) (scheme 3). In the IR spectrum of compound **7** there is an absorption band of conjugated C=O group and a band of free amino group at 1615 and 3270 cm^{-1}, respectively. In the ^1H NMR spectrum the protons of methylene and amino groups bring about resonance signals at δ 7.55 and 10.76 ppm, respectively. The structural symmetry of 1,3,5-dithiazine **7** is supported by equivalence of the C^4 and C^6 signals in the ^{13}C NMR spectrum (171.16 ppm).

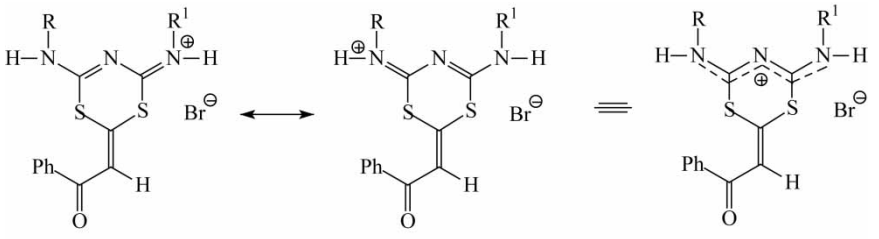
On heating with hydrazine hydrate in an alcohol solution compound **3d** forms 3,5-diphenylamino-1,2,4-triazole (**8**) in good yield (scheme 3). The reaction occurs *via* nucleophilic substitution of the sulfur atoms in the dithiazine cycle C^4 and C^6 position by hydrazine nitrogen atoms. The structure of triazole **8** is confirmed by the presence in its ^1H NMR spectrum of three different signals of amino groups with chemical shifts at δ 8.94, 9.26 and 11.77 ppm and two signals from C^3 and C^5 atoms at 151.47 and 158.17 ppm in the ^{13}C NMR spectrum.



SCHEME 3

X-Ray diffraction has shown [11] 6-amino-4-imino-1,3,5-dithiazine hydroiodide to have a structure of cation with the charge delocalized between the cyclic and exocyclic nitrogen

atoms. In our opinion, we can apply this conclusion to the results of the present study and describe the structure of **3a–d** as a cation with delocalized charge stabilized by counter-ion Br^-.



3a–d

In this case, upon the treatment of base, the anion attack will take place at the most electron-deficient C-4 and/or C-6 atoms of the dithiazine ring and this will prompt breakdown. The introduction in exocyclic nitrogen atoms of substituents displaying mesomeric effect will promote stabilization of the 1,3,5-dithiazine ring, and make compound **3d** prone to form the free base **7**.

3. Experimental

IR spectra were recorded on an IFS-25 Fourier spectrometer (KBr pellets). ^{1}H and ^{13}C NMR spectra were run on a Bruker-DPX 400 instrument (400.13 MHz ^{1}H; 100.61 MHz ^{13}C) using DMSO-d_6 as the solvent. Mono- and disubstituted 2,4-dithiobiuretes **2b–d** were synthesized using techniques described earlier [12, 13].

3.1 *2-Benzoylmethylene-4-amino-6-imino-1,3,5-dithiazinium hydrobromide (3a)*

1-Bromo-2-benzoylacetylene **1** (1.05 g, 5 mmol) was dissolved in 20 mL of glacial AcOH and then 2,4-dithiobiurete **2a** (0.68 g, 5 mmol) was added in batches upon stirring. The reaction mixture was stirred at 20°C 5 h, the precipitate was filtered off, washed with AcOH, then with dry ether, dried in vacuum, recrystallized from AcOH to obtain 1.48 g (86%) of compound **3a**. Mp 240–242°C. IR (ν, cm^{-1}): 3270, 3320 (NH_2); 2900–3100 (H_2N^+=); 1620 (C=O); 1490–1590 (C=C, C=N). ^{1}H NMR (δ, ppm): 7.63 (s, 1H, CH=), 7.80–8.20 (m, 5H, Ph), 10.11 (br.s., 2H, NH_2), 10.35 (br. s, 2H, H_2N^+=). ^{13}C NMR (δ, ppm): 121.08 (CH=); 128.63, 129.02, 133.96, 136.17 (Ph); 140.01 (C^2); 165.57, 167.78 (C^4, C^6); 187.03 (C=O). Anal. Calcd. for $C_{11}H_{10}BrN_3OS_2$: C, 38.37; H, 2.91; Br, 23.26; N, 12.21; S, 18.16. Found: C, 38.42; H, 3.00; Br, 23.08; N, 12.29; S, 18.42%.

3.2 *2-Benzoylmethylene-4-amino-6-methylimino-1,3,5-dithiazinium hydrobromide (3b)*

2-Benzoylmethylene-4-amino-6-methylimino-1,3,5-dithiazinium hydrobromide (**3b**) was prepared, analogously to **3a**, from 1-bromo-2-benzoylacetylene **1** (1.05 g, 5 mmol) and 1-methyl-2,4-dithiobiurete **2b** (0.75 g, 5 mmol) in 1.5 g (84%) yield. Mp 196–198°C. IR (ν, cm^{-1}): 3260, 3304 (NH_2), 2861–2942 (HN^+=); 1620 (C=O); 1485–1595 (C=C, C=N).

^{1}H NMR (δ, ppm): 3.14 (s, 3H, CH_3), 8.03 (s, 1H, CH=), 7.54–8.15 (m, 5H, Ph), 10.54 (br. s, 2H, NH_2), 11.01 (br. s, 1H, HN^+=). ^{13}C NMR (δ, ppm): 30.42 (CH_3); 120.97 (CH=); 128.61, 129.09, 133.97, 136.15 (Ph); 139.90 (C^2); 164.74, 165.29 (C^4, C^6); 187.07 (C=O). Anal. Calcd. for $C_{12}H_{12}BrN_3OS_2$: C, 40.22; H, 3.35; Br, 22.35; N, 11.73; S, 17.88. Found: C, 40.08; H, 3.66; Br, 22.18; N, 11.77; S, 17.96%.

3.3 *2-Benzoylmethylene-4-amino-6-phenylimino-1,3,5-dithiazinium hydrobromide (3c)*

2-Benzoylmethylene-4-amino-6-phenylimino-1,3,5-dithiazinium hydrobromide (**3c**) was prepared in an analogous manner to **3a** from 1-bromo-2-benzoylacetylene (1.05 g, 5 mmol) and 1-phenyl-2,4-dithiobiurete **2c** (1.05 g, 5 mmol) in 1.72 g (82%) yield. Mp 173–174°C. IR (ν, cm^{-1}): 3264, 3318 (NH_2), 2841–2900 (HN^+=), 1625 (C=O), 1440–1590 (C=C, C=N). ^{1}H NMR (δ, ppm): 7.75 (s, 1H, CH=), 7.30–8.08 (m, 10H, 2Ph), 10.82 (br. s, 3H, NH_2, HN^+). ^{13}C NMR (δ, ppm): 121.53 (CH=); 123.52, 127.14, 128.63, 129.05, 129.15, 133.94, 136.11, 136.76 (2Ph); 139.74 (C^2); 162.63, 165.92 (C^4, C^6); 186.99 (C=O). Anal. Calcd. for $C_{17}H_{14}BrN_3OS_2$: C, 48.57; H, 3.33; Br, 19.05; N, 10.00; S, 15.24. Found: C, 48.40; H 3.51; Br, 19.34; N, 9.93; S, 15.02%.

3.4 *2-Benzoylmethylene-4,6-diphenylimino-5H-1,3,5-dithiazinium hydrobromide (3d)*

2-Benzoylmethylene-4,6-diphenylimino-5H-1,3,5-dithiazinium hydrobromide (**3d**) was prepared, analogously to compound **3a**, from 1-bromo-2-benzoylacetylene **1** (1.05 g, 5 mmol) and 1,5-diphenyl-2,4-dithiobiurete **2d** (1.43 g, 5 mmol) in 2.08 g (84%) yield. Mp 168–170°C. IR (ν, cm^{-1}): 3120, 3182 ($^+NH_2$), 1620 (C=O), 1440–1597 (C=C, C=N). ^{13}C NMR (δ, ppm): 119.06 (CH=); 123.27, 123.38, 128.13, 128.24, 128.43, 128.63, 133.17, 137.53 (3Ph); 140.03 (C^2); 161.50, 163.70 (C^4, C^6); 187.04 (C=O). Anal. Calcd. for $C_{23}H_{18}BrN_3OS_2$: C, 55.64; H, 3.63; Br, 16.13; N, 8.47; S, 12.90. Found: C, 55.36; H, 3.33; Br, 15.99; N, 8.80; S, 12.70%.

3.5 *Reaction of compounds 3a–c with bases*

3.5.1 Method A. 0.89 g (2.6 mmol) of **3a** was dissolved in 15 mL of DMSO, cooled to 8°C and slowly added upon stirring 25 mL of 0.1 N NaOH. The reaction mixture temperature was raised to 20°C, then 50 mL of water was added and the mixture was stirred for 1 h. The precipitate was filtered off, washed with water, dried in vacuum over $CaCl_2$, recrystallized from dioxane and 0.35 g (83%) of 2,4-bis(benzoylmethylene)-1,3-dithiethane (**5**) was prepared. Mp 235–238°C (Literature data [10] Mp 237–238°C). IR (ν, cm^{-1}): 1615 (C=O); 1490–1510 (C=C); 690 (C−S). ^{1}H NMR (δ, ppm): 7.82 (s, 2H, 2CH=); 7.54–8.01 (m, 10 H, 2Ph). ^{13}C NMR (δ, ppm): 111.62 (2CH=); 127.70, 128.63, 133.11, 136.56 (2Ph); 157.17 (C^2, C^4); 187.73 (2C=O). Anal. Calcd. for $C_{18}H_{12}O_2S_2$: C, 66.66; H, 3.70; S, 19.75. Found: C, 66.38; H, 3.45; S, 19.82%.

3.5.2 Method B. 0.69 g (2 mmol) of **3a** was added in small portions upon stirring to 30 mL of 20% NH_4OH, stirred for 1 h. The precipitate was filtered off, washed with water, dried in vacuum over $CaCl_2$, recrystallized from dioxane and prepared 0.24 g (74%) of compound **5**.

Analogously, from 0.72 g (2 mmol) of **3b** and 0.84 g (2 mmol) of **3c** 0.27 g (83%) and 0.22 g (68%), respectively, of compound **5** was prepared.

3.6 *2-Benzoylmethylene-4,6-diphenylimino-5H-1,3,5-dithiazine (7)*

3.6.1 Method A. 0.5 g (1 mmol) of **3d** was dissolved in 5 mL of DMSO, cooled to 8°C and then 10 mL of 0.1 N NaOH was slowly added upon stirring. The reaction mixture temperature was raised to 20°C, then 20 mL of water was added and the mixture was stirred for 1 h. The precipitate was filtered off, washed with water, dried in vacuum over $CaCl_2$. Compound **7** was obtained in 0.38 g (92%) yield. Mp 99–101°C (from EtOH). IR (ν, cm^{-1}): 3270 (NH); 1615 (C=O); 1450–1590 (C=C, C=N). ^{1}H NMR (δ, ppm): 7.55 (s, 1H, CH=); 7.08–8.18 (m, 15H, 3Ph); 10.76 (br.s., 1H, NH). ^{13}C NMR (δ, ppm): 117.14 (CH=); 121.55, 124.12, 124.22, 128.24, 128.60, 128.90, 133.22, 136.97 (3Ph); 143.12 (C^2); 171.16 (C^4, C^6); 186.57 (C=O). Anal. Calcd. for $C_{23}H_{17}N_3OS_2$: C, 66.50; H, 4.12; N, 10.11; S, 15.43. Found: C, 66.24; H, 4.31; N, 9.96; S, 15.21%.

3.6.2 Method B. 1.0 g (2 mmol) of **3d** was added in small portions upon stirring to 30 mL of 20% NH_4OH, stirred for 1 h. The precipitate was filtered off, washed with water, dried in vacuum over $CaCl_2$; 0.8 g (96%) of compound **7** was prepared.

3.7 *3,5-Diphenylamino-1,2,4-triazole (8)*

To a suspension of 0.5 g (1 mmol) of **3d** in 30 mL of EtOH 3 mL of hydrazine hydrate was added; the reaction mixture was stirred at 78°C 3 h and filtered. The filtrate was boiled down in half, cooled and poured into a three-fold volume of water. The precipitate was filtered off, washed with water, dried in vacuum and recrystallized from EtOH. Compound **8** was obtained in 0.8 g (80%) yield. Mp 210–212°C. IR (ν, cm^{-1}): 3100, 3290, 3380 (NH); 1490–1590 (C=C, C=N). ^{1}H NMR (δ, ppm): 6.80–7.74 (m, 10H, 2Ph); 8.94 (s, 1H, NH); 9.26 (s, 1H, NH); 11.77 (s, 1H, NH). ^{13}C NMR (δ, ppm): 115.81, 116.71, 118.80, 120.58, 128.70, 128.92, 141.05, 142.55 (2Ph); 151.47, 158.17 (C^3, C^5). Anal. Calcd. for $C_{14}H_{13}N_5$: C, 66.93; H, 5.18; N, 27.88. Found: C, 66.87; H, 5.35; N, 27.84%.

References

[1] P.P. Pathe, M.G. Paranjpe. *J. Indian Chem. Soc.*, **61**, 149 (1984).
[2] T.E. Glotova, N.I. Protsuk, A.I. Albanov, A.S. Nakhmanovich, V.A. Lopyrev. *J. Gen. Chem. (Russia)*, **73**, 834 (2003).
[3] T.E. Glotova, A.S. Nakhmanovich, A.I. Albanov, N.I. Protsuk, T.V. Nizovtseva, V.A. Lopyrev. *Chem. Heterocyclic Compounds (Latvia)*, 81 (2002).
[4] M.S. Chande, N.P. Shetgiri. *J. Indian Chem. Soc.*, **67**, 849 (1990).
[5] P.P. Pathe, M.G. Paranjpe. *Indian J. Chem. (B)*, **20**, 824 (1981).
[6] M.S. Chande, J.D. Bhandari, A.S. Karyekar. *Indian J. Chem. (B)*, **34**, 990 (1995).
[7] A.S. Nakhmanovich, T.E. Glotova, T.N. Komarova, V.A. Lopyrev. *Chem. Heterocyclic Compounds (Latvia)*, 417 (1998).
[8] T.E. Glotova, N.I. Protsuk, A.I. Albanov, V.A. Lopyrev, G.V. Dolgushin. *Central European Journal of Chemistry*, **3**, 222 (2003).
[9] M.I. Rybinskaya. *Journal of the D.I. Mendeleev All-Union Chemical Society (Russ.)*, **12**(N1), 11 (1967).
[10] P. Yates, D.R. Moore, T.R. Lynch. *Can. J. Chem.*, **49**, 1456 (1971).
[11] D.E. Lynch, I. McClenaghan. *Acta Cryst.*, **E57**, 670 (2001).
[12] C.P. Joshua, V.P. Rajan. *Aust. J. Chem.*, **29**, 415 (1976).
[13] C.P. Joshua, E. Prasannan, S.K. Thomas. *Aust. J. Chem.*, **34**, 917 (1981).