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SHORT COMMUNICATIONS

Reaction of Dithiomalonamide and Dianilide with α-Acetylene Ketones

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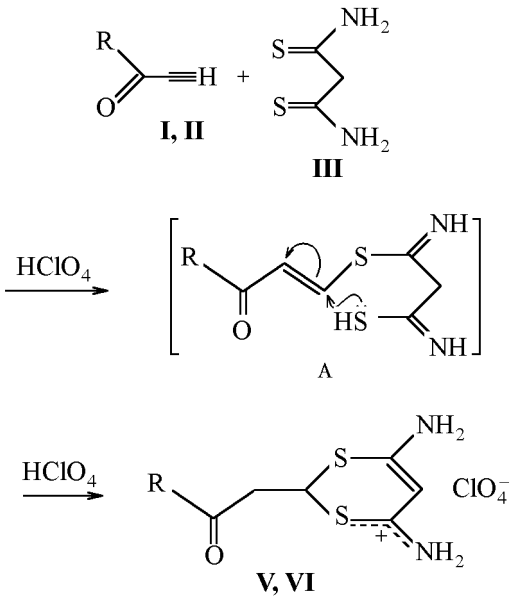
We established formerly that in reaction of thiobenzamide with α-acetylene ketones in AcOH in the presence of $HClO_4$ formed substituted 1,3-thiazinium perchlorates [1], and in alcohol or dioxane bis(ketovinyl) sulfides were obtained in high yield (82–90%) [2]. It is also known that reactions of thioamides with acetylenedicarboxylic acid and its esters in benzene or acetonitrile give rise to substituted 1,3-thiazolin-4-ones [4–6]. However reactions between activated acetylenes with thioamides are still poorly studied.

In extension of our investigations on reactions of α-acetylene ketones with N,S-ambifunctional nucleophiles we report here on the reactions between benzoyl- and thenoyl-2-acetylenes (**I, II**) with dithiomalonamide (**III**) and dithiomalonic acid dianilide (**IV**).

It was established that benzoylacetylene (**I**) and thenoyl-2-acetylene (**II**) reacted with dithiomalonamide (**III**) in the glacial AcOH at 20°C in the presence of equimolar amount of $HClO_4$ affording in good yield 4-amino-2-acylmethyl-1,3-dithiin-6-iminium perchlorates (**V, VI**). The reaction presumably proceeded via intermediate formation of ketovinyl sulfide A originating from addition of the mercapto group to the electron-deficient β-carbon of the initial activated acetylenes **I, II**.



R = Ph (**I, V**), 2-thienyl (**II, VI**).

The attack of the mercapto group on the conjugated C=C bond in the A intermediate results in intramolecular cyclizaton furnishing compounds **V, VI**. In the ^1H NMR spectra of the compounds appear signals of NH_2 groups at 9.03 and 0.27 ppm respectively, and the integral intensity of the signals correspond to four protons attached to nitrogen.

In reaction of benzoylacetylene (**I**) with dithiomalonamide (**III**) performed without $HClO_4$ an unidentified compound was isolated in a very low yield. It is presumably caused by instability of the free substituted 1,3-ditiine. Then the structure of 1,3-dithiin-6-iminium perchlorates (**V, VI**) can be represented as a set of mesomeric structures B–E consisting of cations with a positive charge on N or S atoms and a stabilizing gegenion ClO_4^- (Scheme 1).

Reactions of acylacetylenes **I, II** with an equimolar quantity of dithiomalonic acid dianilide (**IV**) in the glacial acetic acid at 20°C in the presence of $HClO_4$ gave rise to 4-anilino-2-acylmethyl-6-phenylimino-1,3-dithiine salts (**VII, VIII**) (Scheme 2).

In the ^1H NMR spectra of compounds **VII, VIII** are present signals of NH groups in the region 9.27 and 9.02 ppm, and the integral intensities of signals correspond to one hydrogen atom bonded to nitrogen. Thus in contrast to compounds **V** and **VI** protonation of one of nitrogen atoms with formation of ClO_4^- anion did not occur.

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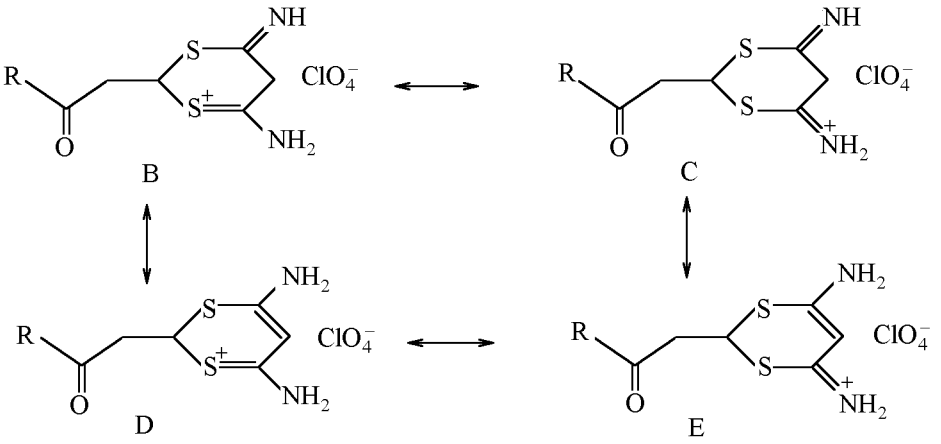
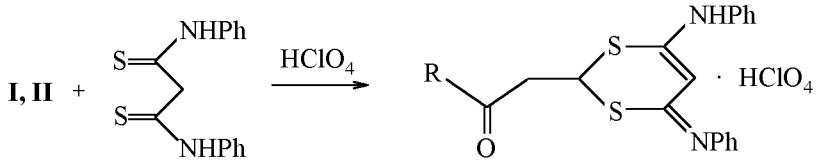
Scheme 1.



Scheme 2.



R = Ph (**I, VII**), 2-thienyl (**II, VIII**).

This fact may be ascribed to shielding of the nitrogen atom with phenyl substituents and to the reduced basicity of the nitrogen caused by conjugation of its unshared electron pair with the π-system of the aromatic ring.

The composition and structure of compounds synthesized **V–VIII** were confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR spectra.

In the IR spectra of compounds **V–VIII** the absorption bands are observed corresponding to C–S bond at 600–635 cm^{-1}, to anion ClO_4^- (in compounds **V, VI**), bonds C=C and C=N at 1540–1620 cm^{-1}, to unconjugated C=O group at 1680–1720 cm^{-1}. The stretching vibrations of NH and NH_2 groups appear as a set of bands in the region 3050–3450 cm^{-1}.

Thus the presented data demonstrate that dithiomalonamide and dithiomalonic acid dianilide reactions with acylacetylenes are promising for the synthesis of difficultly accessible salts of substituted 1,3-dithiine.

4-Amino-2-benzoylmethyl-1,3-dithiine-6-iminium perchlorate (V). To a solution of 0.19 g (1.0 mmol) of dithiomalonamide (**III**) in 20 ml of glacial AcOH was added dropwise a solution of 0.13 g (1.0 mmol) of benzoylacetylene (**I**) and 0.12 ml (1 mmol) of $HClO_4$ in 10 ml of glacial AcOH. The mixture was stirred for 7 h at 20°C. The separated precipitate was filtered off, washed on the filter with ether, and dried in a vacuum. Yield 0.32 g (63%), colorless needles, mp 173–175°C. ^{1}H NMR spectrum, δ, ppm: 3.92 d (2H, CH_2, ^3J 6.8 Hz), 5.40 t (1H, CHS, ^3J 6.8 Hz), 6.06 s (1H, =CH), 7.52–8.00 m (5H, Ph), 9.05 s (2H, NH_2), 9.62 s (2H, NH_2). ^{13}C NMR spectrum, δ, ppm: 39.61 (CHS), 43.50 (CH_2), 89.47 (=CH), 129.32–135.63 (Ph), 168.45 ($C^{4,6}$), 195.33 (C=O). Found, %: C 39.22; H 3.64; Cl 9.12; N 7.72; S 17.88. $C_{12}H_{13}ClN_2O_5S_2$. Calculated, %: C 39.51; H 3.59; Cl 9.72; N 7.68; S 17.58.

4-Amino-2-(2-thienoyl)methyl-1,3-dithiine-6-iminium perchlorate (VI) was obtained similarly to compound **V** from 0.34 g (2.5 mmol) of dithiomalonamide (**III**), 0.34 g (2.5 mmol) of (2-thenoyl)acetylene (**II**), and 0.29 ml (2.5 mmol) of $HClO_4$. Yield 0.64 g (71%), grey-green needles, mp 192– 194°C (from AcOH). ^{1}H NMR spectrum, δ, ppm: 3.83 d (2H, CH_2, ^3J 6.8 Hz), 5.38 t (1H, CHS, ^3J 6.8 Hz), 6.06 s (1H, =CH), 7.25–8.07 m (3H, 2-thienyl), 9.03 s (2H, NH_2), 9.27 s (2H, NH_2). ^{13}C NMR spectrum, δ, ppm: 39.50 (CHS), 43.47 (CH_2), 89.38 (=CH), 129.04–142.54 (4C, 2-thienyl), 142.54, 168.16 ($C^{4,6}$), 188.10 (C=O). Found, %: C 32.12; H 2.82; Cl 9.78; N 7.58; S 26.18. $C_{10}H_{11}ClN_2O_5S_3$.

Calculated, %: C 32.48; H 2.73; Cl 9.59; N 7.57; S 26.01.

4-Anilino-2-benzoylmethyl-6-phenylimino-1,3-dithiine perchlorate (VII) was obtained in the same way as compound **V** from 0.72 g (2.5 mmol) of dithiomalonic acid dianilide (**IV**), 0.33 g (2.5 mmol) of benzoylacetylene (I), and 0.29 ml (2.5 mmol) of $HClO_4$. Yield 0.54 g (42%), yellow powder, mp 198–202°C (from AcOH). ^{1}H NMR spectrum, δ, ppm: 4.02 d (2H, CH_2, ^3J 6.8 Hz), 5.53 t (1H, CHS, ^3J 6.8 Hz), 6.32 s (1H, =CH), 7.31–8.07 m (15H, 3Ph), 9.27 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 39.82 (CHS), 42.34 (CH_2), 89.54 (=CH), 123.24–136.41 (Ph), 166.84, 186.33 ($C^{4,6}$), 194.79 (C=O). Found, %: C 55.65; H 3.84; Cl 6.64; N 5.45; S 12.09. $C_{24}H_{21}ClN_2O_5S_2$. Calculated, %: C 55.75; H 4.09; Cl 6.86; N 5.42; S 12.40.

4-Anilino-2-(2-thienyl)methyl-6-phenylimino-1,3-dithiine perchlorate (VIII) was obtained in the same way as compound **V** from 0.72 g (2.5 mmol) of dithiomalonic acid dianilide (**IV**), 0.34 g (2.5 mmol) of (2-thenoyl)acetylene (**II**), and 0.29 ml (2.5 mmol) of $HClO_4$. Yield 0.82 g (63%), yellow crystals, mp 207–209°C (from AcOH). ^{1}H NMR spectrum, δ, ppm: 3.90 d (2H, CH_2, ^3J 7.2 Hz), 5.51 t (1H, CHS, ^3J 6.8 Hz), 6.38 s (1H, =CH), 7.26–8.06 m (3H, 2-thienyl), 9.02 (1H, NH). ^{13}C NMR spectrum, δ, ppm: 39.85 (CHS), 42.55 (CH_2), 91.70 (=CH), 124.57–136.48 (2-thienyl), 142.42, 166.56 ($C^{4,6}$), 187.47 (C=O). Found, %: C 50.23; H 3.58; Cl 7.01; N 5.49; S 18.1. $C_{22}H_{19}ClN_2O_5S_3$. Calculated, %: C 50.62; H 3.48; Cl 6.79; N 5.37; S 18.43.

IR spectra were recorded on spectrophotometer Specord 75 IR from KBr pellets. ^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 at operating frequencies 400.13 and 100.61 respectively, solvent DMSO-d_6, internal reference HMDS.

REFERENCES

1. Glotova, T.E., Nakhmanovich, A.S., and Mabarakshina, N.S., *Khim. Geterotsikl. Soed.*, 1988, no. 5, pp. 705–708.
2. Basyouni, M.N. and Omar, M.T., *Austral. J. Chem.*, 1974, vol. 27, pp. 1585–1589.
3. Nakhmanovich, A.S., Glotova, T.E., Skvortsova, G.G., Sigalov, M.V., and Komarova, T.N., *Zh. Org. Khim.*, 1984, vol. 20, no. 10, pp. 2145–2148.
4. Mushkalo, L.K., Yangol' G.Ya., *Ukr. Khim. Zh.*, 1955, vol. 21, no. 6, pp. 732–737.
5. Hendrickson, J.B., Rees, R., and Templeton, J.F., *J. Am. Chem. Soc.*, 1964, vol. 86, no. 1, pp. 107–111.
6. Acheson, R.M. and Wallis, J.D., *J. Chem. Soc., Perkin Trans., I*, 1981, no. 2, pp. 415–422.