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SHORT COMMUNICATIONS

Reaction of Dithiomalonamide with Benzoylacetylene

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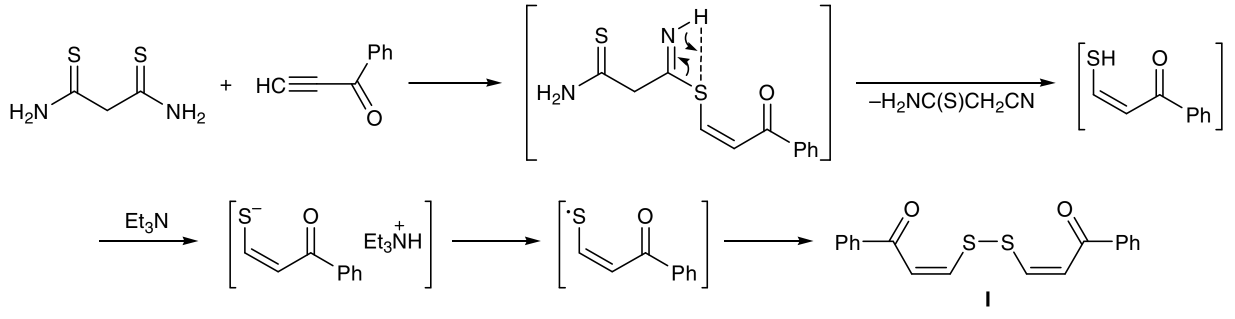
Reactions of thioamides with activated acetylenic compounds usually involve the sulfur and nitrogen atoms in the former and lead to the formation of substituted dihydro-1,3-thiazoles and 1,3-thiazines [1–3]. Reactions of bis-thioamides with acetylenic ketones have been poorly studied. We previously described the synthesis of 4-amino(arylamino)-2-benzoylmethyl-1,3-dithiin-6-iminium perchlorates by reactions of dithiomalonamide and dithiomalonic acid dianilide with acylacetylenes and 1-acyl-2-bromoacetylenes in glacial acetic acid in the presence of perchloric acid [4, 5].

We have found that dithiomalonamide reacts with benzoylacetylene in ethyl acetate at 20°C in the presence of triethylamine to give 39% of bis(2-benzoylvinyl) disulfide (**I**) as the only product. No cyclic compounds have been detected in the reaction mixture. A probable reaction scheme is shown below. We failed to isolate cyanothioacetamide, presumably due to its easy polymerization. Intermediate thiolate ion (formed by the action of triethylamine) is likely to be converted into sulfanyl radical via oxidation with atmospheric oxygen, and its dimerization gives disulfide **I** [6].

3,3'-Dithiobis(1-phenylprop-2-en-1-one) (I). Triethylamine, 0.35 ml (2.5 mmol), was added to a solution of 0.34 g (2.5 mmol) of dithiomalonamide in 10 ml of ethyl acetate, the mixture was stirred for 15 min at 20°C, and a solution of 0.35 g (2.5 mmol) of benzoylacetylene in 15 ml of ethyl acetate was slowly added under vigorous stirring. The mixture was stirred for 2 h at 20°C, the resulting black oily material was dissolved in 100 ml of ethanol on heating to 50–55°C, 100 ml of cold water was added, and the mustard-colored precipitate was filtered off, washed on a filter with aqueous ethanol (1 : 1), and dried under reduced pressure. Yield 0.31 g (39%), *Z*,*Z* isomer, yellow crystals, mp 120–122°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1580 (C=C), 705 (C–S), 685 (CH=CH, *cis*). ^{1}H NMR spectrum, δ, ppm: 8.07–8.09 d (4H, CH=CH, $J = 7.0$ Hz), 7.81–8.16 m (10H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 112.96 (=CHCO), 127.68–140.06 (C_6H_5), 162.32 (=CHS), 187.99 (C=O). Found, %: C 65.99; H 4.18; S 19.84. $C_{18}H_{14}O_2S_2$. Calculated, %: C 66.26; H 4.29; S 19.63.

The IR spectrum was recorded in KBr on a Specord IR-75 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400.13 and 100.61 MHz, respectively, using DMSO-d_6 as solvent and HMDS as internal reference.



REFERENCES

1. Morzherin, Yu.Yu., Kosterina, M.F., Berseneva, V.S., Dehaen, W., and Bakulev, V.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, p. 1194.
2. Belen'kii, L.I., Shirinyan, V.V., Gromova, G.P., Kolotaev, A.V., Strelenko, Yu.A., Tandura, S.N., Shumskii, A.N., and Krayushkin, M.M., *Khim. Geterotsikl. Soedin.*, 2003, p. 1785.
3. Belen'kii, L.I., Kolotaev, A.V., Shirinyan, V.V., Krayushkin, M.M., Strokach, Yu.P., Valova, T.M., Golotyuk, Z.O., and Barachevskaya, V.A., *Khim. Geterotsikl. Soedin.*, 2005, p. 100.
4. Nizovtseva, T.V., Komarova, T.N., Nakhmanovich, A.S., and Lopyrev, V.A., *Khim. Geterotsikl. Soedin.*, 2002, p. 1293.
5. Nizovtseva, T.V., Komarova, T.N., Nakhmanovich, A.S., Larina, L.I., Lopyrev, V.A., and Kalistratova, E.F., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1205.
6. Oae, S., *Khimiya organicheskikh soedinenii sery* (Chemistry of Organic Sulfur Compounds), Moscow: Khimiya, 1975, p. 98.