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LETTERS TO THE EDITOR

Reaction of Dithiooxamide with Benzoylacetylene

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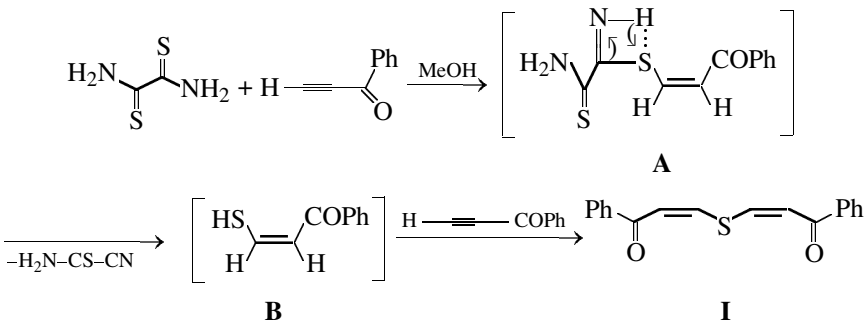
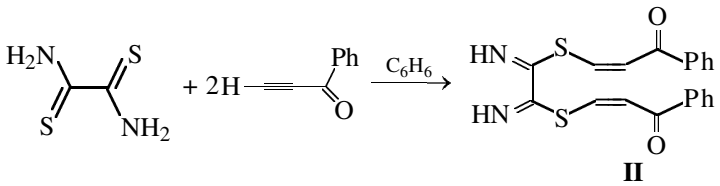
Previously we described the synthesis of 4-amino-(anilino)-2-(benzoylmethyl)-1,3-dithiin-6-iminium perchlorate by the reaction of dithiomalonamide and dithiomalonanilide with c acylacetylenes and 1-bromo-2-acylacetylenes in glacial AcOH in the presence of perchloric acid [1, 2].

We found that dithiooxamide reacts with benzoylacetylene in methanol, benzene, and acetonitrile at 20°C to form the *E,Z* and *Z,Z* isomers of bis(benzoylvinyl) sulfide (**I**). The reaction of dithiooxamide with benzoylacetylene was also performed under microwave activation in DMF for 1–2 min. In this case, bis(benzoylvinyl) sulfide (**I**) was isolated in 64% yield, along with unidentified reaction products.



The reactions of dithiooxamide with benzoylacetylene in benzene, acetonitrile, or glacial AcOH at 65–70°C provide 1,2-bis(benzoylvinylsulfanyl)ethanediimine (**II**) in 17–30% yields.



Bis(benzoylvinyl) sulfide (I). A solution of 2.6 g of benzoylacetylene in 20 ml of methanol was added to a solution of 1.2 g of dithiooxamide in 30 ml of methanol. The mixture was stirred for 8 h at 20°C and cooled to 0°C. The precipitate that formed was filtered off, dried in a vacuum, and recrystallized from methanol–benzene, 1 : 1, to obtain 1.17 g of sulfide **I**, yield 38%, mp 143–145°C (*E,Z* isomer). IR spectrum,

ν, cm^{-1}: 1640 (C=O), 1523 (C=C), 957 (*trans*-CH=CH), 733 (CS), 695 (*cis*-CH=CH). Found, %: C 73.34; H 4.71; S 10.54. $C_{18}H_{14}O_2S$. Calculated, %: C 73.47; H 4.76; S 10.88.

The reaction in benzene gave 0.71 g of sulfide **I**, yield 23%, mp 194–195°C (*Z,Z* isomer). IR spectrum, ν, cm^{-1}: 1638 (C=O), 1545 (C=C), 730 (CS), 696 (*cis*-CH=CH). Found, %: C 73.52; H 4.81; S 10.95. $C_{18}H_{14}O_2S$. Calculated, %: C 73.47; H 4.76; S 10.88.

The reaction in acetonitrile in the presence of Et_3N gave 0.65 g of compound **I**, yield 21%, mp 194–195°C (*Z,Z* isomer).

The reaction of dithiooxamide with benzoylacetylene in DMF under microwave activation (360 W, 1–2 min) gave 1.97 g of sulfide **I**, yield 64%, mp 143–145°C (*E,Z* isomer).

1,2-Bis(benzoylvinylsulfanyl)ethanediimine (II). A solution of 2.6 g of benzoylacetylene in 30 ml of benzene was added to a solution of 1.2 g of dithiooxamide in 20 ml of benzene. The mixture was heated at 65–70°C with stirring for 3 h and then kept for 4 days at 20°C with intermittent stirring. Reaction progress was followed by TLC, eluent benzene–ether, 3 : 1. Benzene was partially evaporated, the residue was poured to a stirred cold ether. The precipitate that formed was filtered off and dried in a vacuum to obtain 0.84 g of compound **II**, yield 22%, mp 148–150°C (*E,Z* isomer). IR spectrum, ν, cm^{-1}: 3385 (=NH), 1640 (C=O), 1535 (C=C), 950 (*trans*-CH=CH), 740 (CS), 690 (*cis*-CH=CH). ^1H NMR spectrum, ν, ppm: 7.52–8.00 m (5H, C_6H_5), 8.07–8.09 d (2H, CH=CH, $J_{\alpha,\beta}$ 9.3 Hz), 8.81–8.83 d (2H, CH=CH, $J_{\alpha,\beta}$ 9.3 Hz), 9.02 (2H, 2NH). Found, %: C 63.28; H 4.15; N 7.44; S 16.68. $C_{20}H_{16}N_2O_2S_2$. Calculated, %: C 63.16; H 4.21; N 7.37; S 16.84.

The reaction under the same conditions in glacial acetic acid gave 1.37 g of compound **II**, yield 36%, mp 172–174°C (*Z,Z* isomer). IR spectrum, ν, cm^{-1}: 3380 (=NH), 1680 (C=O), 1580 (C=C), 760 (CS), 690 (*cis*-CH=CH).

The IR spectra were obtained on a Specord IR-75 instrument in KBr. The ^1H NMR spectrum is recorded on a Bruker-400 spectrometer in DMSO-d_6, internal reference HMDS.

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