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## LETTERS TO THE EDITOR

# Reaction of *N,N'*-Dibenzyldithiooxamide with Benzoylacetylene

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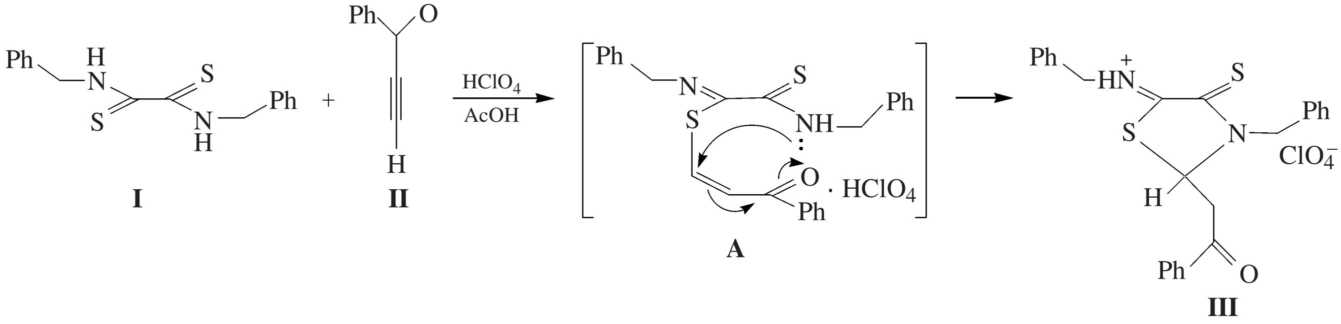
Reactions of thioamides with activated acetylenes normally involve the sulfur and nitrogen atoms and give rise to substituted 1,3-thiazolines [1,2] and 1,3-thiazines [3,4]. It is also known that reactions of thioamides with acetylenedicarboxylic acid and its esters in benzene and acetonitrile form substituted 1,3-thiazolin-4-ones [3, 4]. However, reactions of activated acetylenes with dithioamides still remain poorly studied.

We earlier described the synthesis of 4-amino(anilino)-2-benzoylmethyl-1,3-dithiin-6-iminium perchlorates by the reaction of diamide and dianilide of dithiomalonic acid with acetylenic ketones in glacial AcOH in the presence of perchloric acid [5–7]. The only products of the reaction of dithiooxamide with benzoylacetylene in MeOH, MeCN, or benzene at 20°C, were the *E,Z* and *Z,Z* isomers of bis(benzoylvinyl) sulfide [8].

In continuation of our research on reactions of α-acetylenic ketones with N,S-ambifunctional nucleophiles we have studied the reaction of *N,N'*-dibenzyldithiooxamide with benzoylacetylene. We anticipated that, like in [8], *N,N'*-dibenzyldithiooxamide in MeOH and MeCN would act as a thiylating agent to afford the isomeric *E,Z*- and *Z,Z*-bis(benzoylvinyl) sulfides. However, *N,N'*-dibenzyldithiooxamide failed to react with benzoylacetylene under these conditions. At the same time, under electrophilic conditions, that is, in acetic acid in the presence of an equimolar amount of 58% perchloric acid at 20°C, substituted 1,3-thiazolidiniminum perchlorate **III** was obtained in a good yield (74%).



Apparently, the reaction proceeds via intermediate formation of ketovinyl sulfide perchlorate **A** via addition of the SH group of dithiooxamide to the activated triple bond of benzoylacetylene, followed by intramolecular cyclization to form product **III**.

**[2-(Benzoylmethyl)-3-benzyl-4-thioxo-5-1,3-thiazolidin-5-yl]benzyliminium perchlorate (III).** To a solution of 0.37 g (1.2 mmol) of *N,N'*-dibenzyldithiooxamide in 20 ml of acetic acid, 0.14 ml (1.2 mmol, recalculated to 100% acid) of 58% perchloric acid was added, and a solution of 0.16 g (1.2 mmol) of benzoylacetylene in 15 ml of acetic acid was then slowly added under stirring. The reaction mixture was stirred for 7 h at 20°C. Reaction progress was monitored by TLC (eluent benzene–ether, 3 : 1) until the spot of benzoylacetylene disappeared. The reaction mixture was cooled to 0°C, the precipitate that formed was filtered off, washed with cold water and ether, and dried in a vacuum to obtain 0.48 g (74%) of compound **III**, mp 93–95°C. IR spectrum, ν, cm$^{-1}$: 3173 (NH), 1707 (C=O), 1520 (C=N), 1230 (C=S), 1075 ($ClO_4^-$), 685 (C–S). $^1$H NMR spectrum, δ, ppm: 4.11 s (2H, $CH_2Ph$), 4.16–4.40 d.d (2H, $CH_2NH$), 5.26 d (1H, CH), 7.15–8.02 m (15H, 3Ph), 11.01 s (1H, NH). $^{13}$C NMR spectrum, δ, ppm: 187.56 (C=O), 172.19 (C=S), 160.02 (C=N), 119.14–138.64 (Ph), 42.52; 43.47 ($CH_2Ph$), 21.13 (CH). Found %: C 56.12; H 4.40; Cl 6.78; N 5.21; S 11.95. $C_{25}H_{23}ClN_2S_2O_5$. Calculated %: C 56.55; H 4.34; Cl 6.69; N 5.28; S 12.08.

The IR spectra were recorded on a Specord IR-75 instrument in KBr pellets. The $^1$H and $^{13}$C NMR spectra were taken at 55°C on a Bruker DPX 400 spectrometer (400.13 and 100.62 MHz, respectively) in DMSO-$d_6$, internal reference HMDS.

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