

SHORT
COMMUNICATIONS

Synthesis and Reactions of 2-Benzoylmethyl-2-phenyl-4,6-di(phenylimino)-5H-1,3,5-dithiazinium Perchlorate

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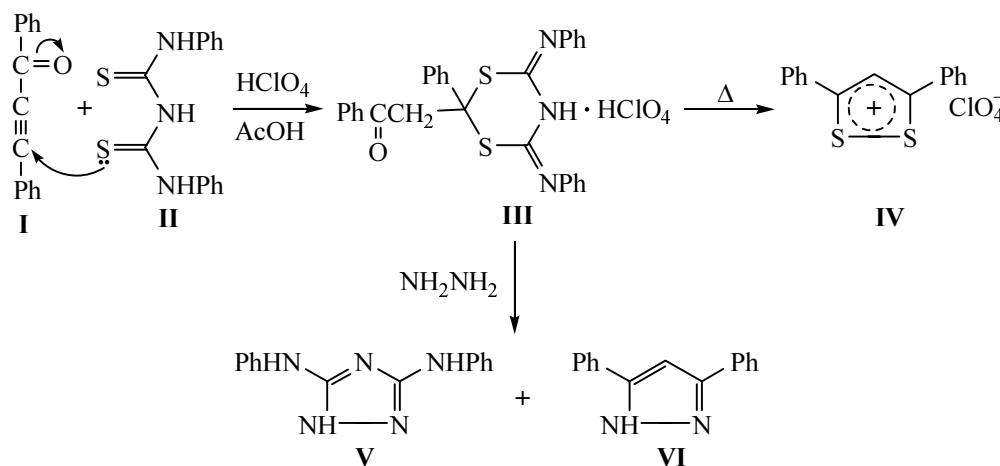
It is known that in reactions of 2,4-dithiobiurets with aldehydes and ketones [1, 2], phenylisocyanide dichloride [3, 4, 44-dibromo-1,3-disubstituted pyrazolin-2-ones [5] various derivatives of 1,3,5-dithiazine and 1,3,5-triazine were obtained that might be of interest as possible biologically active compounds. We formerly by reactions of benzoylacetylene with 2,4-dithiobiuret and its 1-mono and 1,5-disubstituted analogs prepared new derivatives of 1,3,5-dithiazine, 1,3,5-thiadiazine, and 1,3,5-triazine (depending on reaction conditions and solvent used) [6].

In this work we established that 1-benzoyl-2-phenylacetylene (**I**) readily reacted with 1,5-diphenyl-2,4-dithiobiuret (**II**) in glacial acetic acid in the presence of equimolar amount of HClO_4 at 20°C affording 2-benzoylmethyl-2-phenyl-4,6-di(phenylimino)-5H-1,3,5-dithiazinium perchlorate (**III**) in 77% yield.

Compound **III** is thermally unstable: At heating in solutions in EtOH or AcOH or in a vacuum at 135°C it

decomposes rearranging into 3,5-diphenyl-1,2-dithiolium perchlorate (**IV**). With hydrazine hydrate in ethanol at 20°C compound **III** afforded products of nucleophilic substitution at C⁴ and C⁶ atoms of dithiazine ring, and also at C² atom of this ring and carbonyl group: 3,5-diphenylamino-1,2,4-triazole (**V**) and 3,5-diphenylpyrazole (**VI**) respectively.

2-Benzoylmethyl-2-phenyl-4,6-di(phenylimino)-5H-1,3,5-dithiazinium perchlorate (III). To a dispersion of 1.43 g (5 mmol) of 1,5-diphenyl-2,4-dithiobiuret in 20 ml of glacial acetic acid at stirring was slowly added a solution of 1.03 g (5 mmol) of 1-benzoyl-2-phenylacetylene and 0.58 ml of 58% HClO_4 in 10 ml of glacial acetic acid. The reaction mixture was stirred for 3 h at 20°C, the precipitate was filtered off, washed with AcOH and ether, and dried in a vacuum. Yield 2.28 g (77%), light-yellow crystals, mp. 120–122°C. IR spectrum, cm^{-1} : 3235 (NH), 1680 (C=O), 1440–1590



(C=C, C=N), 1040–1120 (ClO₄⁻). ¹H NMR spectrum, δ , ppm: 4.86 s (2H, CH₂), 7.40–8.13 m (20H, 4C₆H₅), 12.50 br.s (1H, NH). ¹³C NMR spectrum, δ , ppm: 48.67 (CH₂), 58.80 (C²), 123.38, 124.19, 126.27, 127.07, 127.59, 128.48, 128.80, 129.02, 129.99, 134.10, 135.76, 136.21, 138.38 (4C₆H₅), 165.83 (C⁴, C⁶), 194.49 (C=O). Found, %: C 58.89; H 3.83; Cl 5.93; N 7.33; S 10.47. C₂₉H₂₄ClN₃O₅S₂. Calculated, %: C 58.63; H 4.07; Cl 5.97; N 7.07; S 10.79.

3,5-Diphenyl-1,2-dithiolium perchlorate (IV). In 20 ml of boiling AcOH was heated 0.594 g (1 mmol) of dithiazine **III**. The separated precipitate was filtered off, washed with ether, and dried in a vacuum. Yield 0.27 g (76%), dark-yellow crystals, mp 222–224°C. IR spectrum, cm⁻¹: 1590 (C=C in ring), 1420–1490 (C=C, Ph). ¹H NMR spectrum, δ , ppm: 7.66–8.25 m (10H, 2Ph), 9.38 s (1H, CH in ring). ¹³C NMR spectrum, δ , ppm: 129.29, 130.20, 130.68, 134.95 (2Ph), 133.52 (C⁴), 188.16 (C³ and C⁵). Found, %: C 51.04; H 3.37; Cl 9.60; S 17.89. C₁₅H₁₁ClO₄S₂. Calculated, %: C 50.77; H 3.12; Cl 9.99; S 18.07.

Reaction of compound **III** with hydrazine hydrate.

To a dispersion of 0.594 g (1 mmol) of compound **III** in 20 ml of EtOH was added at stirring a solution of 3 ml of hydrazine hydrate in 10 ml of EtOH, and the mixture was stirred for 3 h at 20°C. The yellow solution was filtered from a light suspension and maintained at 5°C for 3 days. The separated precipitate was filtered off, and dried to obtain 0.14 g (56%) of 3,5-diphenylamino-1,2,4-triazole (**V**), colorless crystals, mp 211–212°C. IR spectrum, cm⁻¹: 3290, 3380 (NH), 1490–1610 (C=C, C=N). ¹H NMR spectrum, δ , ppm: 6.80–7.74 m (10H, 2Ph), 8.93 s (1H, NHPH), 9.26 s (1H, NHPH), 11.76 s (1H, NH in ring). ¹³C NMR spectrum, δ , ppm: 115.81,

116.70, 118.80, 120.57, 128.70, 128.92, 141.05, 142.54 (2Ph), 151.46, 158.18 (C³ and C⁵). Found, %: C 66.87; H 5.08; N 27.53. C₁₄H₁₃N₅. Calculated, %: C 66.91; H 5.21; N 27.87.

The mother liquor after isolation of compound **V** was evaporated to 1/3 of initial volume, cooled, and poured in a 5-fold volume of water. The separated precipitate was filtered off and dried to obtain 0.19 g (86%) of 3,5-diphenylpyrazole (**VI**), mp 198–199°C (publ.: mp 199–200°C [7]). ¹³C NMR spectrum, δ , ppm: 99.62 (C⁴), 115.61, 116.54, 125.13, 127.45, 128.12, 128.63, 129.00, 133.69 (2Ph), 143.38 (C⁵), 151.34 (C³). Found, %: C 81.57; H 5.28; N 12.53. C₁₅H₁₂N₂. Calculated, %: C 81.79; H 5.49; N 12.71.

IR spectra were recorded on Specord 75IR instrument from pellets with KBr. ¹H and ¹³C NMR spectra were registered on spectrometer Bruker-DPX 400 [400.13 MHz (¹H) and 100.61 MHz (¹³C)] in DMSO-*d*₆.

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