2,6-DIPHENYL-1,4-DITHIINE AND ITS DISULFONE

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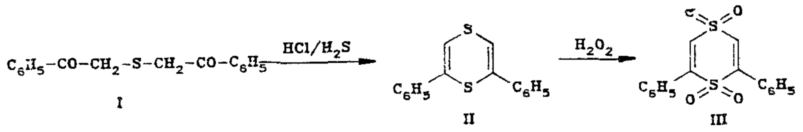
The compound 1,4-dithiine and its derivatives have been little studied [1]; only the synthesis of 1,4-dithiine from the acetals of mercaptoacetaldehyde [2] and the synthesis of 2,5-diaryl-1,4-dithiines from α-mercapto-substituted methyl aryl ketones [3] were described.

We developed a method for the isolation of 2,6-diphenyl-1,4-dithiine (II) in 93% yield; it is based on the hydrothiolysis of a methanolic solution of diphenacyl sulfide in the presence of hydrogen chloride at −20°C. The product has the mp 79°C, and consists of bright yellow crystals. Its PMR spectrum ($CDCl_3$) is as follows: 7.38 (H—Ph) and 6.54 ppm (=C—H). One two-electron cathode wave is observed on the polarogram of the compound (II) in acetonitrile in the presence of 0.1 M Bu_4NClO_4. The value of the half-wave potential ($E_{1/2}$) is −2.05 V. The comparison of this with the $E_{1/2}$ of the reduction of styrene (−2.35 V in 70% dioxane in the presence of −0.175 M Bu_4NI [4]) shows that the observed wave corresponds with the reduction of the activated double bond to C—C.



The dithiine is readily oxidized by hydrogen peroxide in acetic acid to 2,6-diphenyl-1,4-dithiine-1,1,4,4-tetraoxide (III) in 78% yield; the product comprises colorless crystals with the mp 155°C. The PMR spectrum is as follows (CDCl): 7.55 (H-Ph) and 6.95 ppm (C—H).

The attempt to obtain 2,6-dimethyl-1,4-dithiine under analogous conditions from diacetonyl sulfide led to macrocyclic oligosulfides.

The data of the elemental analysis of the compounds (II) and (III) for C, H, and S correspond to the calculated values.

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