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RING TRANSFORMATION OF 1,4-DITHIIN TO 1,3-DITHIOLE

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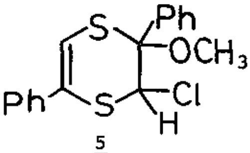
2,5-Diphenyl-1,4-dithiin-1-oxide (1) when heated in acetonitrile around 70°C afforded 2-formyl-2,4-diphenyl-1,3-dithiole (2) along with 2,4-diphenylthiophene. The yield of 2 was increased when the thermolysis was carried out in carbon tetrachloride, whereas in methanol or dimethyl sulfoxide 1 gave only the thiophene due to the extrusion of sulfur oxide. The thermal rearrangement was assumed to proceed through 1,2,5-oxadithiepin (3) as an intermediate in connection with the mass spectral behaviour of 1.

In contrast to the thermal reaction, photolysis of 1 in methanol under a nitrogen atmosphere gave rise to another rearranged product, 2-benzoyl-4-phenyl-1,3-dithiole (4) as well as 2.

Treatment of 1 with hydrochloric acid-dioxane (1:2 V/V) caused again a skeletal rearrangement to give 4. However, when gaseous HCl was introduced to a methanol solution of 1, the additive Pummerer product 5 was obtained, which was further converted into 4 by heating in 95% ethanol. The transformation of 1 to 4 initiated by the additive Pummerer reaction was explained by means of the carbonium ion rearrangement.



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