

Sulfurization of 1,3-Diphenylpropanetrione

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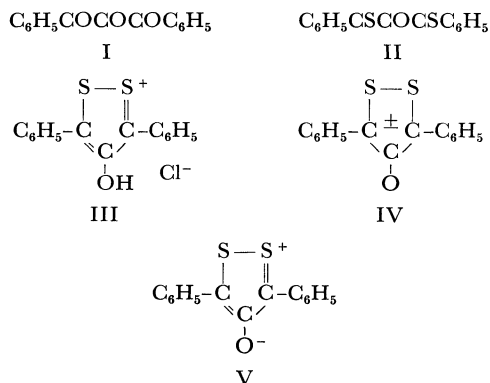
During the course of synthesis of mesoionic 1,2-dithiole compounds, we attempted the sulfurization of 1,3-diphenylpropanetrione(I), expecting the formation of 1,3-dithion-2-one(II) which might be stabilized by the S-S bond formation to give mesoionic compound(V).

Treatment of a solution of I in chloroform-ethanol mixture (1 : 7) with hydrogen sulfide and hydrogen chloride afforded yellow crystalline salt (A) of mp 197—204°C (dec.) in 40% yield. The chloride is unstable and can not be purified by recrystallization. When the chloride was treated with a base such as triethylamine, pyridine, or sodium bicarbonate, chlorine-free brown crystals (B) ($C_{15}H_{10}OS_2$, mp 236—241°C, dec.) were obtained. IR (KBr): 1495 cm^{-1} (highly polarized carbonyl), 1490, 1480, 1435 cm^{-1} (aromatic 1,2-dithiolium ring).¹⁾ UV: λ_{max}^{DMF} (log ϵ): 317 (3.78), 366 (3.62), 562 $m\mu$ (4.20). Mass spectrum: M^+ , m/e 270. Compound B gave perchlorate (mp 232—233°C), picrate (mp 192—195°C) and acetylated perchlorate (mp 171—174°C) by acetyl perchlorate. Compound B was also obtained in poor yield when I was refluxed in toluene with phosphorus pentasulfide.

Recently, Schönberg²⁾ reported that the reaction

of 1,1,3,3-tetrabromo-1,3-diphenylpropan-2-one with potassium xanthate yielded 1,3-diphenylpropane-1,3-dithion-2-one (II). The physical and chemical properties of compound B are almost the same as those of II. However, considering the reaction sequence of the formation of B from I, and its spectroscopic and chemical properties, B should be more appropriately expressed by mesoionic structure (or anhydro-3,5-diphenyl-4-hydroxy-1,2-dithiolium hydroxide (IV or V) rather than 1,3-dithion-2-one structure (II) as proposed by Schönberg.²⁾

On the basis of the above observation, it may safely be concluded that the product A is 3,5-diphenyl-4-hydroxy-1,2-dithiolium chloride (III) and the deprotonated product B is mesoionic 1,2-dithiole compound (V).



1) K. A. Jensen, H. R. Baccaro and O. Buchardt, *Acta Chem. Scand.*, **17**, 163 (1963).

2) A. Schönberg and E. Frese, *Tetrahedron Lett.*, **1969**, 4063.