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Syntheses of 1,2-Dithiole Derivatives[1]

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Sulfurization of 1,3-diarylpropanetrione (**1**) with hydrogen sulfide and hydrogen chloride afforded a mixture of 4-hydroxy-3,5-diaryl-1,2-dithiolium chlorides (**3**) and 3,5-diaryl-1,2-dithiolium chlorides (**4**). Treatment of a mixture of **3a** and **4a** with triethylamine in alcohol gave anhydro-4-hydroxy-3,5-diphenyl-1,2-dithiolium hydroxide (**5a**) and the 4-substituted product (**6**). Sulfurization of dibenzoyldibromomethane yielded 3,5-diphenyl-1,2-dithiolium bromide. Reactions of **5a** with picric acid and acetic anhydride in the presence of perchloric acid were carried out.

Sulfurization of 1,3-diphenylpropanetrione (**1a**) with hydrogen sulfide and hydrogen chloride in a mixture of chloroform and ethanol afforded a crude product, from which a mesoionic compound **5a** (anhydro-4-hydroxy-3,5-diphenyl-1,2-dithiolium hydroxide) was obtained by treatment with triethylamine.[2] Schönberg[3] reported recently that the reaction of potassium ethyl xanthogenate with 1,1,3,3-tetrabromo-1,3-diphenylacetone gave the same compound as **5a** which is regarded as a valence isomer of 1,3-diphenylpropane-1,3-dithione-2-one (**2**). In this report, we wish to describe our results on the sulfurization products in detail. Further examination of the crude sulfurization product of **1a** revealed that the product was composed of two components, **3a** and **4a**. Since the mixture was not separable by recrystallization and detection by tlc was unsuccessful, the mixture was subjected to further reaction without separation. Structures of **3a** and **4a** were confirmed as stable perchlorates **7** and **8** by treating the mixture with perchloric acid or silver perchlorate. They were identical with those reported by Schönberg[3] and Leaver.[4] Dehydrohalogenation of the mixture with triethylamine in ethanol afforded a mixture of a mesoionic compound **5a** and 3-ethoxy-3,5-diphenyl-1,2-dithiole (**6a**). The latter was prepared by the reaction of 3,5-diphenyl-1,2-dithiolium perchlorate with sodium ethoxide.[5] 3-Methoxy derivative (**6b**) was obtained when the mixture was treated with triethylamine in methanol. When the mixture was treated with pyridine in methanol, **5a** and unreacted **4a** were obtained. This result shows that **4a** is convertible to **6** only in the presence of a strong

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[1] Studies of mesoionic compounds. XXXVI. Part XXXV: Y. Huseya, A. Chinone, and M. Ohta, This Bulletin, **44**, 1667 (1971).

[2] K. Inouye, S. Sato, and M. Ohta, *ibid.*, **43**, 1911 (1970).

[3] A. Schönberg and E. Frese, *Chem. Ber.*, **103**, 3885 (1970).

[4] D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, **1960**, 252.

[5] D. Leaver, D. M. McKinnon, and W. A. H. Robertson, *J. Chem. Soc.*, **1965**, 32.

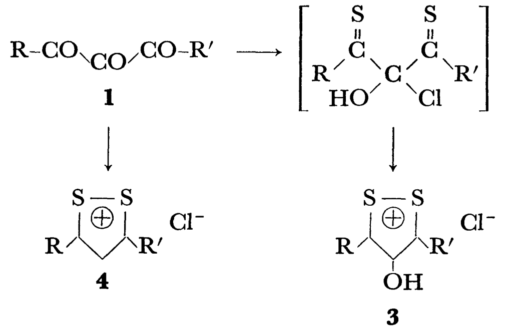
base. In a similar way, sulfurization of 1-(*p*-methoxyphenyl)-3-phenylpropanetrione (**1b**) gave two products, **3b** and **4b**. As in the case of sulfurization of **1a**, **3b**, and **4b** could not be separated by recrystallization. Treatment of the mixture of **3b** and **4b** with triethylamine in methanol gave a mesoionic compound **5b**, but the methoxy-substituted product corresponding to **6** was not isolated. The IR spectrum of **5b** was similar to that of **5a** in the region 1500—1400 cm^{-1} due to the CO group and dithiole ring. In UV spectra of **5b**, a hypsochromic shift was observed as in the case of **5a**,[3] as shown below.

UV SPECTRA OF **5b**

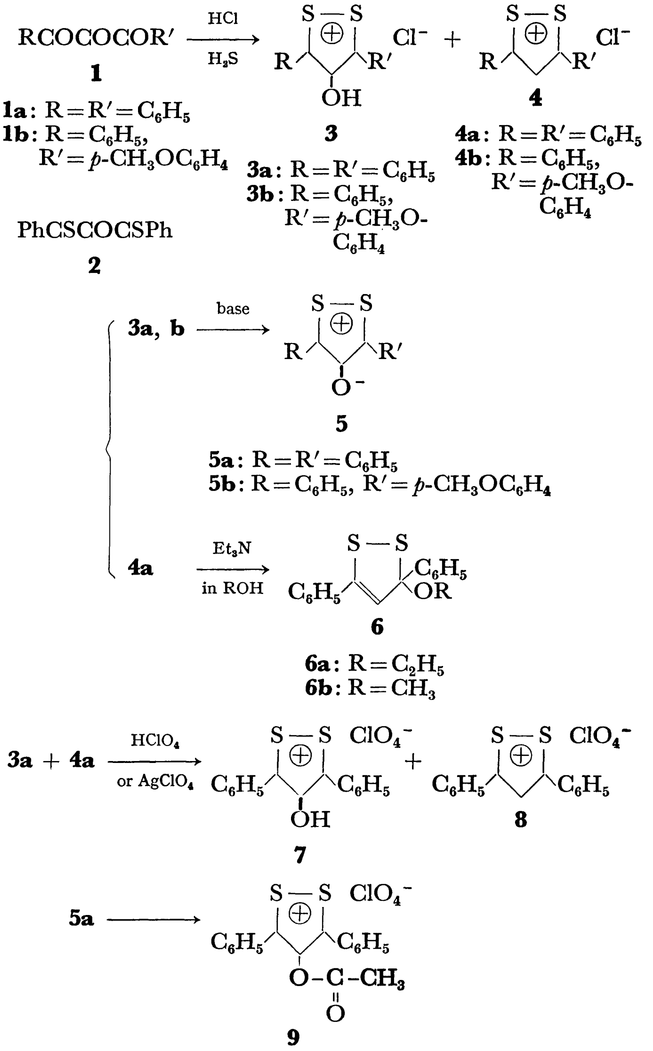
Solvent	λ_{max}(mμ)	log ε
Benzene	586	4.12
Pyridine	574	4.38
DMF	574	4.36
Acetonitrile	558	4.11

Sulfurization of 1-methyl-3-phenylpropanetrione did not afford the aimed product. Under the same conditions, dibenzoyldibromomethane was subjected to sulfurization to give 3,5-diphenyl-1,2-dithiolium bromide, which was converted into perchlorate **8** by treating with silver perchlorate.

The mechanism for the formation of **3** and **4** from **1** could be explained *via* a chlorohydrin intermediate and the reduction with hydrogen sulfide during the course of the reaction.



The reaction of 1,2-dithiolium salts without hydroxyl group at its 4-position has been extensively studied.[4-6] It is known that the 3- and 5-positions of 1,2-dithiole show high reactivity toward nucleophilic reagents.[5,6] Treatment of **5a** with acetic anhydride and perchloric acid yielded the *O*-acetyl derivative **9**, which showed an absorption peak at 1790cm^{-1} due to the C=O group in its IR spectrum. This is consistent with the fact that the CO bond of **5a** is highly polarized as shown in its IR spectrum, in which the CO group showed absorption peak at 1495 cm^{-1}. Methylation of **5a** with methyl iodide was not successful and resulted in the recovery of the starting material. The picrate of **5a** was obtained by treatment with picric acid. Reaction of **5a** with aniline gave a product which was recrystallized from ethanol to give dark blue needles with a mp of 168—170° C. The results of elementary analysis and molecular weight measurement (304 in DMF) indicate that the molecular formula is $C_{21}H_{15}SN$. It was assumed to be 3,4,5-triphenylisothiazole from its IR spectrum and NMR spectrum. Reaction of **5a** with dry ammonia in refluxing methanol afforded a product which was recrystallized from benzene or ligroin to give colorless needles with a mp of 102—105°C, $C_{15}H_{11}NSO$, which is most likely to be 4-hydroxy-3,5-diphenylisothiazole from its elementary analysis and spectral data. Reaction of **5a** with a dipolarophile such as dimethyl acetylenedicarboxylate, tolane or phenyl isocyanate did not give the adduct and resulted in the recovery of the starting material.



1a: $R=R'=C_6H_5$
1b: $R=C_6H_5$, $R'=p\text{-}CH_3OC_6H_4$

3a: $R=R'=C_6H_5$
3b: $R=C_6H_5$, $R'=p\text{-}CH_3O\text{-}C_6H_4$

4a: $R=R'=C_6H_5$
4b: $R=C_6H_5$, $R'=p\text{-}CH_3O\text{-}C_6H_4$

5a: $R=R'=C_6H_5$
5b: $R=C_6H_5$, $R'=p\text{-}CH_3OC_6H_4$

6a: $R=C_2H_5$
6b: $R=CH_3$

Experimental

Sulfurization of 1,3-Diphenylpropanetrione. To a solution of 100 g of 1,3-diphenylpropanetrione in 200 m*l* of chloroform, 1400 m*l* of ethanol was added. Into the solution, dry hydrogen chloride and hydrogen sulfide were bubbled for 1.5 hr under ice cooling, and then hydrogen sulfide was bubbled at room temperature for further 5.5 hr. During the course of bubbling, the color of the solution turned from yellow to reddish brown. After the solution was kept to stand for 2 days at room temperature, precipitates contaminated with sulfur were filtered off and the filtrate was concentrated *in vacuo* at 40—50°C. Ether was added to the residue to give a crude mixture of **3a** and **4a**. When the mixture was re-

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6) G. Duguay and H. Quiniou, *Bull. Soc. Chim. Fr.*, **1970**, 1918.

crystallized from acetonitrile, two forms of crystal separated out, silky crystals melting at about 200°C (dec.) and needles melting at about 110°C (dec.). We could not find a suitable solvent for fractional crystallization.

*Sulfurization of 1-(*p*-Methoxyphenyl)-3-phenylpropanetrione.* Dry hydrogen chloride was bubbled into 90 m*l* of methanol under ice cooling until the volume of the methanol solution became 110 m*l*, to which a solution of 1-(*p*-methoxyphenyl)-3-phenylpropanetrione (5g) in 20 m*l* of chloroform was added. Dry hydrogen sulfide was bubbled into the solution for 3.5 hr with stirring under ice cooling. After the solution was kept to stand for 2 days at room temperature, precipitates were filtered off and the filtrate was concentrated *in vacuo* at 40—45°C. Ether was added to the residue to give a mixture of **3b** and **4b**, which partially melted at about 120°C (dec.) and 190°C (dec.), but the mixture could not be separated analytically pure by recrystallization.

Sulfurization of Dibenzoyldibromomethane. Dibenzoyldibromomethane was dissolved in 50 m*l* of chloroform, to which 300 m*l* of ethanol was added. Dry hydrogen chloride and hydrogen sulfide were bubbled into the solution for 2 hr at room temperature with stirring. After the solution was kept to stand for 2 days at room temperature, percipitates containing sulfur were filtered off and filtrate was concentrated *in vacuo* at 40—50°C. Recrystallization from ethanol afforded reddish yellow needles with a mp of 190—200°C, yield 5 g (54%). Although the value of elementary analysis was not satisfactory, the structure of this product was assigned to be 3,5-diphenyl-1,2-dithiolium bromide by treatment with silver perchlorate to give the perchlorate **8**.

Reaction of Sulfurization Products with Base. i) To a solution of a mixture (57 g) of **3a** and **4a** in 500 m*l* of ethanol, 19 g of triethylamine was added dropwise. After being stirred for 1 hr, precipitates were collected (filtrate was treated as described in ii)), washed with ether repeatedly, and recrystallized from acetic acid, DMF, or pyridine to give dark brown needles with a mp of 240—241°C (dec.), yield 21 g (41%).

Found: C, 66.48; H, 3.89; S, 23.40%. Calcd for $C_{15}H_{10}OS_2$: C, 66.67; H, 3.73; S, 23.68%.

ii) The filtrate obtained as described in i) was concentrated in a vacuum. The residue was washed with water and recrystallized from acetonitrile to give 3-ethoxy-3,5-diphenyl-1,2-dithiole, yield 15 g (29%), as pale yellow needles with a mp of 68—69°C.

iii) To a solution of a mixture (22 g) of **3a** and **4a** in methanol was added 7 g of triethylamine, and precipitates were filtered off and washed with ether, and the ether and filtrate were combined and concentrated *in vacuo.* The residue was washed with ether and recrystallized from methanol to give **6b** as yellow needles with a mp of 83—84°C, yield 9 g (42%).

Found: C, 63.52; H, 4.64; S, 21.90%. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.52; H, 4.64; S, 21.20%. VU: λ_{max}^{MeOH} mμ(log ε) 227 (4.18), 345 (2.55). NMR: τ($CDCl_3$) 2.40—2.82 (m, 10H), 4.10 (s, 1H), 6.49 (s, 3H).

Reaction of ***5a*** *with Acetic anhydride in the Presence of Perchloric Acid.* To a solution of 0.27 g of **5a** in acetic anhydride, 0.3 g of 70% perchloric acid was added dropwise with stirring under ice cooling. Ether was added to the reaction mixture to give orange crystals, which were recrystallized from methanol yielding **9** as orange needles with a mp of 174—176°C; yield 0.38 g (92%).

Found: C, 49.41; H, 3.41; S, 15.50%. Calcd for $C_{17}H_{13}O_6S_2Cl$: C, 49.45; H, 3.15; S, 15.52%.

Picrate of ***5a.*** A mixture of picric acid and **5a** (0.13 g) in benzene was stirred at room temperature for 30 min. Precipitates were collected and recrystallized from methanol to give the picrate of **5a** as orange plate with a mp of 245—246°C.

Found: C, 50.73; H, 2.71; N, 8.45; S, 12.76%. Calcd for $C_{21}H_{13}N_3O_8S_2$: C, 50.50; H, 2.61; N, 8.42; S, 12.83%. IR: 3500—3200, 1560, 1440—1400, 1350 cm^{-1}.

Reaction of ***5a*** *with Aniline.* After treating 0.35 g of **5a** in 30 m*l* of refluxing aniline for 3 hr, excess aniline was removed by filtration and methanol was added to the residue. Precipitates were collected and recrystallized from ethanol to give dark blue needles with a mp of 168—170°C, yield 0.36 g (88%).

Found: C, 80.78; H, 4.01; N, 4.41; S, 9.99%. Calcd for $C_{21}H_{15}SN$: C, 80.51; H, 4.79; N, 4.47; S, 10.22%.

Reaction of ***5a*** *with Ammonia.* Ammonia was bubbled into a refluxing solution of **5a** (1.0 g) in 60 m*l* of methanol for 1.5 hr. After cooling, precipitates were filtered off and the filtrate was concentrated to give a crude product. Recrystallization from benzene or ligroin afforded colorless needles with a mp of 102—105°C.

Fould: C, 71.29; H, 4.57; N, 5.75; S, 12.40%. Calcd for $C_{15}H_{11}NSO$: C, 71.15; H, 4.35; N, 5.53; S, 12.65%.