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Generation of Thiosulfines by Dithiation of Diarylmethylenetriphenylphosphoranes

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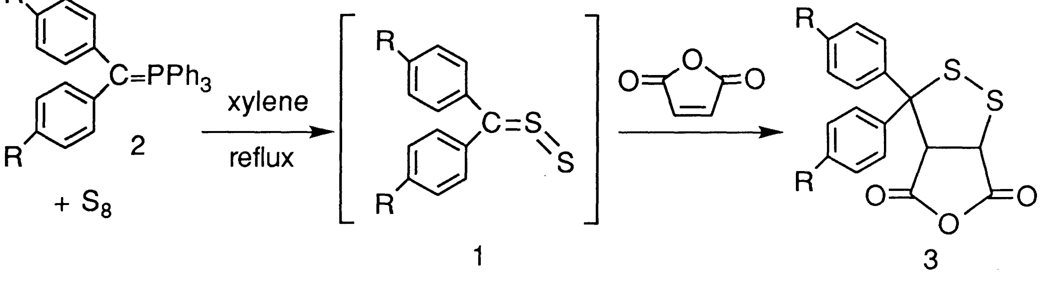
Reaction of phosphonium ylides with excess sulfur afforded the corresponding thiosulfines, which were trapped with maleic anhydride to give the corresponding cycloadducts (1,2-dithiolanes) in good yields. Intermediary thiosulfines were also formed by sulfurization of thiobenzophenones with elemental sulfur to give the 1,2-dithiolanes in moderate yields.

Thiosulfines **1** are reactive heterocumulenes for which some synthetic routes have been developed. The methods include, for example, fragmentation of dithiols or trithiolanes,1) reaction of hydrazones with polysulfur dichloride,2) and thiation of sulfinyl functions by using P_2S_5 or its analogues.3) However, there is no report on the synthesis of thiosulfines from Wittig reagents **2**. Recently, we have reported the synthesis of thio- and selenocarbonyl compounds from **2**.4) These results prompted us to investigate the possibility of the formation of thiosulfines **1** from **2**. In this communication, we report the synthesis of diarylthiosulfines from diarylmethylenetriphenylphosphoranes (**2**).

Treatment of diphenylmethylenetriphenylphosphorane (**2a**) with excess sulfur in the presence of maleic anhydride resulted in the formation of 1,2-dithiolane **3a**, a cycloadduct of diphenylthiosulfine **1a** with maleic anhydride. Reactions with other phosphoranes were carried out in a similar manner to give the corresponding **3** in good yields (Table 1).

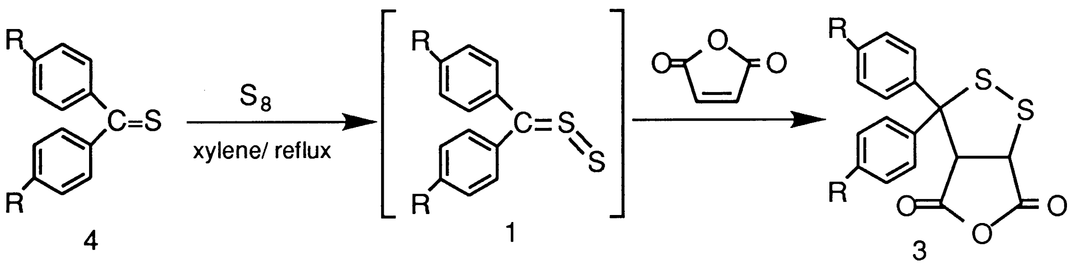


Scheme 1.

Table 1. Reaction of Phosphonium Ylides with Sulfur Followed by the Addition of Maleic Anhydride

Ylide **2**		Conditions				Product (Yield/%)	
	R	Solvent	Temperature	Time/day	Sulfur/equiv.	**3**	
2a	H	Xylene	reflux	1	7	**3a**	74
2b	Me	Xylene	reflux	1	7	**3b**	90
2c	MeO	Xylene	reflux	1	7	**3c**	79
2d	Cl	Xylene	reflux	1	7	**3d**	35
2d	Cl	Xylene	reflux	3	7	**3d**	60

Since thiobenzophenone (**4a**) is generally produced by the reaction of **2a** with elemental sulfur,[5] we then tried the reaction of thiobenzophenones **4** with excess sulfur in the presence of maleic anhydride. The corresponding cycloadducts **3** were obtained in moderate yields (Scheme 2, Table 2).



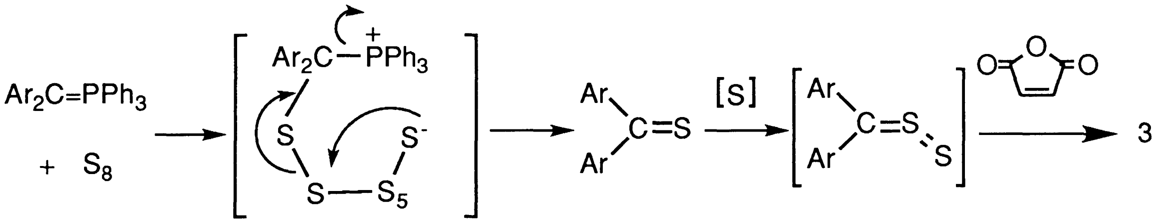
Scheme 2.

Table 2. Reaction of Thiobenzophenones **4** with Sulfur in the Presence of Maleic Anhydride

	R	Solvent	Conditions Temperature	Time/day	Product Yield/%
4a	H	Xylene	reflux	3	**3a** 15
4c	MeO	Xylene	reflux	2	**3c** 30
4c	MeO	Xylene	reflux	5	**3c** 48

The lower yields for **3** is probably due to low concentration of active sulfur. If active sulfur plays an important role in this reaction, addition of triphenylphosphine will improve the yields of cycloadducts **3**.[6] When the reaction of **4c** with excess sulfur was carried out in the presence of triphenylphosphine, the yield of adduct **3c** was increased to 65%, suggesting the generation of **1** from thioketones and active sulfur.[7]

The reaction most likely proceeds as follows; ylides react with sulfur to afford the corresponding betaines, which extrude sulfur to give thiosulfines or thioketones. Since thiosulfines are generally very reactive, they partially decompose to the corresponding thiocarbonyl compounds and active sulfur *via* dithiirane intermediates before trapping by maleic anhydride. At elevated temperatures, thiobenzophenones further react with activated sulfur to give thiosulfines, which are trapped with maleic anhydride to afford 1,2-dithiolanes **3** (Scheme 3).

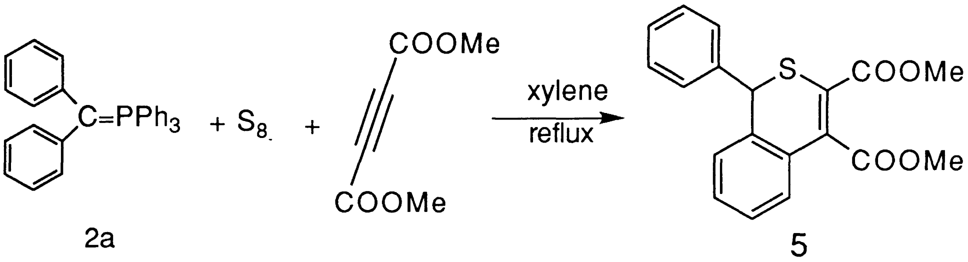


Scheme 3.

Previously, one of the authors found that the reaction of ketone hydrazones with disulfur dichloride afforded the corresponding thioketones *via* thiosulfine intermediates.[8] Recently, Nakayama and his coworkers found that this type of thiosulfines were trapped by intramolecular cyclization.[9] However, there are very few reports on the intermolecular cycloaddition of thiosulfines with dienophiles.[1]

Huisgen, Kutney and Turnbull, and Senning *et al.* reviewed the chemistry of thiosulfines.[10] They state that thioketones do not react with elemental sulfur to give thiosulfines. Only one exception was reported by Motoki and Ohmura.[11] They showed that the reaction of a number of aromatic thioketones with olefins afforded the corresponding dihydrothiopyranes *via* [4+2] cycloaddition reaction. However, compound **3a** was obtained in 18% yield by treatment of **4a** with maleic anhydride, which suggested the formation of **1a** by decomposition of **4a** into benzophenone and active sulfur. Recently, Saito and coworkers reported the reaction of diaryl thioketones having an allyl group with elemental sulfur involving intramolecular [3+2] cycloadditions of thiosulfines.[12]

Huisgen and Rapp reported the formation of diphenylthiosulfine from the corresponding trithiolane, whose formation was confirmed by a cycloaddition reaction with dimethyl acetylenedicarboxylate (DMAD).[1a] We tried the the reaction of **2a** with elemental sulfur in the presence of DMAD in the hope of obtaining the [3+2] cycloaddut of thiosulfine **1a** with DMAD. However, only cyclic sulfide **5**, a [4+2] cycloadduct of **4a** with DMAD was obtained, suggesting that, under these conditions, thiosulfine formation is much slower than the [4+2] cycloaddition (Scheme 4).



Scheme 4.

In summary, we have succeeded in the generation of thiosulfines from diarylmethylene-triphenylphosphorane and elemental sulfur, whose formation was confirmed by the trapping reaction with maleic anhydride. We are currently continuing a study on some applications of these unusual cyclic disulfides.

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13) All new compounds gave satisfactory analytical and spectral data. Selected data; **3b**: Mp 87-90 °C. ^{1}H NMR (400 M Hz, $CDCl_3$) δ= 2.22 (s, 6H, Me), 4.46 (d, J=7.4 Hz, 1H, CH), 4.67 (d, J=7.4 Hz, 1H, CH), 7.00-7.22 (m, 8H, Ar). **3c**: Mp 55-58°C. ^{1}H NMR (400 M Hz, $CDCl_3$) δ=3.77 (s, 3H, MeO), 3.79 (s, 3H, MeO), 4.54 (d, J=7.3 Hz, 1H, CH), 4.62 (d, J=7.3 Hz, CH), 6.82 (br d, 4H, Ar), 7.16 (d, 2H, Ar), 7.24 (d, 2H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$) δ=53.65 (CH), 55.16 (OMe), 55.26 (OMe), 58.03 (CH), 79.89 (Ar_2C), 113.48, 113.57, 128.26, 129.21, 130.64, 134.13, 159.11, 159.24 (Ar), 166.10 (C=O), 167.54 (C=O).

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