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LETTERS TO THE EDITOR

4-PHENYL-2-[(*Z*)-PHENYLMETHYLIDENE]-1,3-DITHIOLE FROM ELEMENTAL SULFUR AND PHENYLACETYLENE

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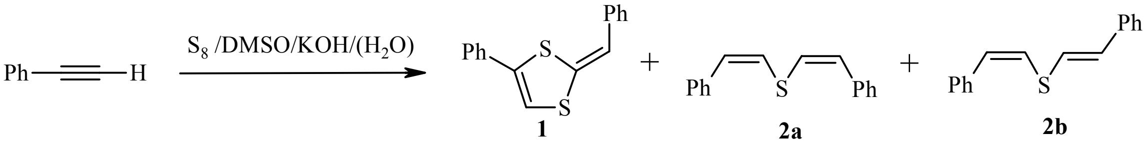
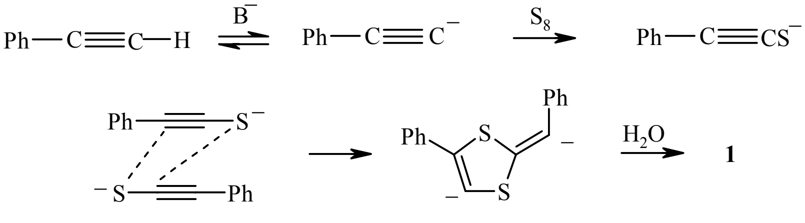
Keywords: distyryl sulfide, phenylacetylene, 4-phenyl-2[(*Z*)-phenylmethylidene]-1,3-dithiole, elemental sulfur, superbase.

In previous work [1], we briefly reported that heating elemental sulfur and phenylacetylene at 90-97°C in the KOH–DMSO–$SnCl_2$–H_2O system leads to *Z,E*-distyryl sulfide in 20% yield. No experimental details were given.

We have now found that phenylacetylene reacts with the S_8–KOH–DMSO triad stereoselectively in the presence of a small amount of water at 49-52°C to give 4-phenyl-2-[(*Z*)-phenylmethylidene]-1,3-dithiole (**1**) in 10% yield as well as the *Z,Z*-distyryl sulfide (**2a**) in 9% yield and *Z,E*-distyryl sulfide (**2b**) in 11% yield. These yields were not optimized.



The formation of 1,3-dithiole **1** should probably be ascribed to the cyclodimerization of phenylethynyl sulfide anions generated from elemental sulfur and phenylacetylene in the superbase system.



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A similar scheme was discussed by Mayer et al. [2], who obtained dithiole **1** by a more complicated method involving a synthesis of the corresponding phenylacetylenide from phenylacetylene and metallic sodium in dry ether, treatment of phenylacetylenide with elemental sulfur, and passing dry HCl through the suspension of sodium phenylethynyl sulfide in ether.

The preparative scope and reaction mechanism are under study.

Thus, a new, convenient method has been discovered for obtaining 1,3-dithiole **1** from elemental sulfur and phenylacetylene in a single step under mild conditions. 1,3-Dithiole **1** is a promising synthetic intermediate used for the manufacture of semiconductors [3], efficient radioprotectors [4], and active cathode materials for lithium power sources [5].

4-Phenyl-2-[(*Z*)-phenylmethylidene]-1,3-dithiole (1). A mixture of phenylacetylene (4 g, 40 mmol), elemental sulfur (1.6 g, 50 mmol), water (1 ml, 50 mmol), and KOH (5.6 g, 100 mmol) in DMSO (40 ml) was stirred at 49-52°C for 4 h. The reaction mixture was diluted with water (150 ml) and extracted with benzene. The extract was washed with water and dried over potassium carbonate. Benzene was distilled off in vacuum. The residue was dissolved in ether. The yellow crystalline precipitate formed was filtered off, washed with ether, and dried in vacuum to give 0.51 g (10%) of 1,3-dithiole **1**; mp 198-200°C ($CHCl_3$). Mass spectrum, *m/z* (I_{rel}, %): 268 $[M]^+$ (100), 134 $[M - PhCH{=}CS]^+$ (45), 121 (18), 102 (8), 89 (15), 77 $[Ph]^+$ (4). ^1H NMR spectrum (400 MHz, $CDCl_3$, with HMDS as the internal standard), δ, ppm (*J*, Hz): 6.44 (1H, d, $^5J_{HH}$ = 1.2, =CH); 6.59 (1H, d, $^5J_{HH}$ = 1.2, =CH); 7.10-7.40 (10H, m, Ph). Found, %: C 71.94; H 5.14; S 23.37. $C_{16}H_{12}S_2$. Calculated, %: C 71.60; H 4.51; S 23.89. The ethereal solution was passed through a layer of alumina and ether was evaporated. The residue was dried in vacuum to obtain 0.95 g (20%) of a 1:1.1 mixture of **2a** and **2b**. ^1H NMR spectrum ($CDCl_3$, 400 MHz, with HMDS as the internal standard), δ, ppm (*J*, Hz): for **2a**: 6.45 (2H, d, *J* = 10.5, =CH); 6.57 (2H, d, *J* = 10.5, =CH); 7.26-7.53 (10H, m, Ph); for **2b**: 6.34 (1H, d, *J* = 10.8, =CH); 6.51 (1H, d, *J* = 10.8, =CH); 6.65 (1H, d, *J* = 15.5, =CH); 6.80 (1H, d, *J* = 15.5, =CH); 7.26-7.53 (10H, m, Ph).

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