Phenylthioacetylene

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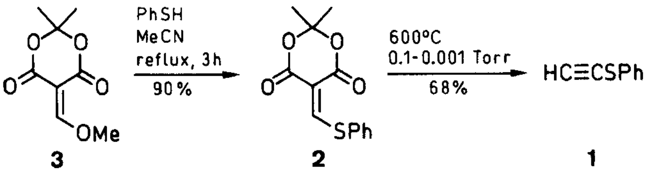
A two-step synthesis of phenylthioacetylene from thiophenol and methoxymethylene Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) is described.

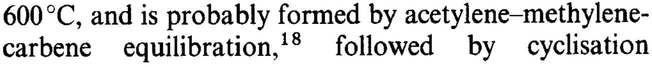
Although it was first reported in 1956,[1] the potential use of phenylthioacetylene (**1**) in synthesis has been recognised only in the last 10 years.[2-13] Some recent authors have found that previous methods of preparation may be unreliable,[9,12-14] and three new routes have been advocated.[12,13,15] However, some require expensive starting materials, or employ basic conditions, though the product is thought to be unstable to base.[8] We report here a short thermal synthesis of phenylthioacetylene which employs cheap starting materials and avoids the use of base in the reaction or workup.

As an extension of our work on the flash vacuum pyrolysis (FVP) reactions of alkylthiomethylene Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives,[16] we made the phenylthio analogue **2** (90%) by reaction of thiophenol with methoxymethylene Meldrum's acid[17] **3** in refluxing acetonitrile. Pyrolysis of **2** at 600 °C (10^{-1}–10^{-3} Torr) gave crude phenylthioacetylene (**1**) (86%) which was purified by distillation to give the pure product (68%) (Scheme 1). Because of the stability of **2** at its distillation temperature (200 °C at 10^{-1} Torr) (involatile residue just 2% on a 20 mmol scale) the reaction is amenable to large scale pyrolyses, and phenylthioacetylene can be accumulated without attention at the rate of ca. 1 g h^{-1}.

Although **1** is the major product from **2** over a range of furnace temperatures, these conditions were optimised for best results. Thus, at temperatures below 600 °C in our apparatus, a significant amount of dark polymeric material condensed at the exit point of the furnace, whereas at higher temperatures (> 800 °C), benzothiophene **4** was the major product. This is already present (ca. 6%) at 600 °C, and is probably formed by acetylene–methylenecarbene equilibration,[18] followed by cyclisation (Scheme 2).



Scheme 1



Scheme 2

2,2-Dimethyl-5-(phenylthiomethylene)-1,3-dioxane-4,6-dione (2): Thiophenol (4.40 g, 40 mmol) was added to a solution of 2,2-dimethyl-5-methoxymethylene-1,3-dioxane-4,6-dione[17] (**3**) (methoxymethylene Meldrum's acid) (7.96 g, 40 mmol) in CH_3CN (40 mL), and the mixture was heated under reflux for 3 h. The solvent was evaporated under vacuum, and the solid product which remained was filtered and was washed thoroughly with hexane. The yield of crude material, which was sufficiently pure for the next stage, was 9.49 g (90%); mp 134–135 °C (from ethanol).

$C_{13}H_{12}O_4S$	calc.	C 59.1	H 4.58
(264.3)	found	58.9	4.38

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.04$ (s, 1 H), 7.41–7.55 (m, 5 H), 1.73 (s, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.26$ (CH), 160.89 and 160.22 (carbonyls), 133.51 (phenyl quaternary), 130.87 (ortho), 129.77 (meta and para), 108.49 (quaternary; 5-position), 105.13 (quaternary, 2-position), 27.44 (methyls).

MS: m/z (%) = 264 (M^+, 80), 206 (92), 161 (28), 134 (100), 105 (27).

Phenylthioacetylene (1):

2,2-Dimethyl-5-(phenylthiomethylene)-1,3-dioxane-4,6-dione **(2)** (5.28 g, 20 mmol) was distilled at 200 °C and 10^{-3} Torr into a horizontal silica tube (35 × 2.5 cm) which was maintained at 600 °C by an electrical furnace. The distillation rate was ca. 1.5 g h^{-1}. The products were collected in a liquid nitrogen trap at the exit point of the furnace. The pressure rose to 10^{-1} Torr during the pyrolysis due to the evolution of carbon monoxide. When the distillation was complete, the products were rinsed from the trap with acetone; a small amount of black oil which formed at the furnace joint was discarded. The acetone solution was filtered to remove a trace of polymeric material and was concentrated in vacuo to give the crude phenylthioacetylene (2.46 g) as a red–yellow liquid which was purified by distillation (Kugelrohr) at 48–50 °C (0.1 Torr) [Lit.[1] bp 78–79 °C (7 Torr)]. The pure acetylene was almost colourless and crystallised on storing at − 20 °C; yield: 1.82 g (68 %).

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.26$–7.52 (m, 5 H), 3.29 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 131.38$ (phenyl quaternary), 129.20 (meta), 126.72 (para), 126.48 (ortho), 86.89 (acetylene CH), 70.94 (acetylene quaternary).

MS: m/z (%) = 134 (M^+, 100), 90 (12), 77 (13), 51 (17).

Pyrolysis of 2 at 800 °C:

The Meldrum's acid derivative **2** (0.062 g, 0.23 mmol) was distilled at 160 °C (3–20×10^{-3} Torr) during 30 min into a horizontal silica tube (as above), and the products were collected in a U-tube cooled by liquid nitrogen. The entire pyrolysate was dissolved in $CDCl_3$ and analysed by ^{1}H and ^{13}C NMR spectroscopy. It consisted of a 1 : 10 mixture of phenylthioacetylene and benzothiophene [^{13}C NMR: $\delta = 139.58$ and 139.46 (quaternaries), 126.15, 124.04 (2 C's), 123.70, 123.48, 122.35] whose spectra were identical with those of an authentic sample.

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