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A CONVENIENT SYNTHESIS OF 2-ALKYL- and 2-ARYL-1,3-BENZODITHIOLES

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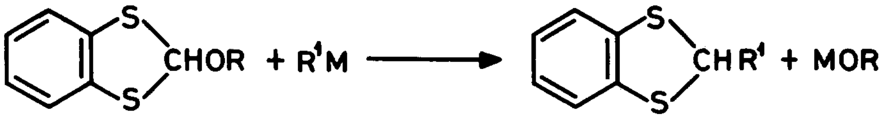
2-Alkyl- and 2-aryl-1,3-benzodithioles are obtained in high yield by the reaction of Grignard reagents or lithium alkyls with 2-alkoxy-1,3-benzodithioles, themselves available in one step from anthranilic acid.

In connection with our studies of the reactions of acyl carbanion equivalents with organoboranes[1], we had need of anions derived from 2-alkyl or 2-aryl-1,3-benzodithioles (2). We were surprised at the paucity of information available about such anions, indeed in the latest review of acyl carbanion equivalents[2] they are not even mentioned. It was soon apparent that the reason for the small utilisation of these attractive anions is that the compounds (2) are normally derived by reaction of aldehydes with benzene-1,2-dithiol, and the latter compound is available only by extremely tedious methods.[3]

Recently, however, 2-alkoxy-1,3-benzodithioles (1) have become readily available by the action of benzyne (conveniently generated from anthranilic acid) on carbon disulphide in the presence of alcohols.[4a] Compounds (1) have been shown to be susceptible to nucleophilic attack at carbon[4b] and it seemed reasonable that they should undergo reaction with Grignard reagents or organolithium compounds to give (2).



(1) (2)

Due to the ready availability of isoamyl nitrite for the production of benzyne from anthranilic acid, we used 2-(3-methylbutoxy)-1,3-benzodithiole (1, R = 3-methylbutyl) as our general precursor and found that indeed it reacted in the desired fashion. The Grignard reactions were carried out in refluxing diethyl ether for 4h and reactions with organolithium reagents in diglyme at low temperature ($-70^{\circ} \rightarrow 20^{\circ}$). The isolated yields of purified products (2) were excellent (Table) making these compounds available in a simple two step procedure from anthranilic acid.

The process not only provides a route to anion precursors that is amenable to large scale working, but is a direct and general high yield synthesis of protected aldehydes. The precursor (1) (R = 3-methylbutyl) is a stable, easily handled material that may be kept for long periods. Very recently, after completion of this work, a similar route was reported which utilises the reaction of 1,3-benzodithiolium perchlorate with Grignard reagents.[5] This process involves an extra step and the handling of an unstable solid without any corresponding advantage in yield. The present reaction is considerably simpler in practice. The reactions of anions derived from compounds (2) will be reported separately.

TABLE

Organometallic Reagent	m.p. (°C)/b.p. (°C)/mm Hg	Yield of (2) (%)[a]
Pr^{n}MgBr	m. 39-40°C	89
Pr^{i}MgBr	b. 76-80°C/0.1mm Hg	80
Cyclohexyl MgBr	m. 69.5 - 70°C	77
PhMgBr	m. 69.5 - 70°C	68 (83)[b]
BuLi	b. 92-96°C/0.1-0.2mm Hg	64[c]

[a] Yield of distilled or recrystallised product.

[b] Figure in parenthesis is the yield from column chromatography.

[c] Some decomposition occurred during distillation.

The following procedure is typical. To the Grignard reagent prepared from 2-bromopropane (2.46g, 20 mmol) and magnesium turnings (0.5g, 20 mmol) in diethyl ether (7 cm^3) was added, by syringe, 2-(3-methylbutoxy)-1,3-benzodithiole (2.40g, 10 mmol). The mixture was stirred under nitrogen whilst the reaction was heated under reflux for 4h. The mixture was cooled and excess Grignard reagent destroyed by the addition of crushed ice (20g) and dilute hydrochloric acid (5 cm^3). The organic products were then taken into diethyl ether (100 cm^3), washed with water (2 x 200 cm^3), dried ($MgSO_4$), and the ether removed. The product was distilled *in vacuo* to give 2-(2-propyl)-1,3-benzodithiole (1.57g, 80%), b. 76-80°C at 0.1mm Hg.

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