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A NOVEL AND CONVENIENT SYNTHESIS OF BIS[ARYLTHIO]METHANES

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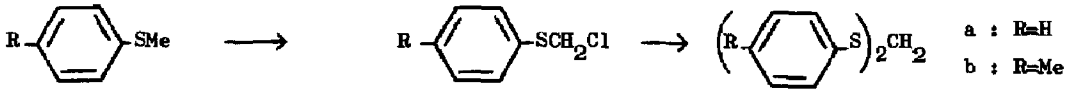
Summary - Bis[arylthio]methanes are produced in high yield on treatment of aryl chloromethyl sulphides with neutral alumina.

The use of metal derivatives of dithioacetals as nucleophilic alkylating and acylating agents in the umpolung of carbonyl reactivity is now a well-established technique in organic synthesis[1]. A compound of considerable use in this connection[2] is bis[phenylthio]methane (1a); one might particularly note the ability of metal derivatives of acyclic dithioacetals such as (1a) to undergo conjugate addition to α,β-unsaturated carbonyl compounds[3]. We wish to report a novel, high yielding and preparatively convenient synthesis of dithioacetals (1a-c); unlike previous syntheses[4], in the case of the parent system (1a), our route does not require the use of unpleasant thiophenol.

Treatment of thioanisole (2a) with an equimolar amount of chlorine in benzene, or, preferably, with sulphuryl chloride[5] in dichloromethane gave chloromethyl phenyl sulphide (3a) essentially quantitatively. On brief warming to 50-55° with neutral alumina, (3a) was transformed into bis[phenylthio]methane[4] (1a) in 98% yield.

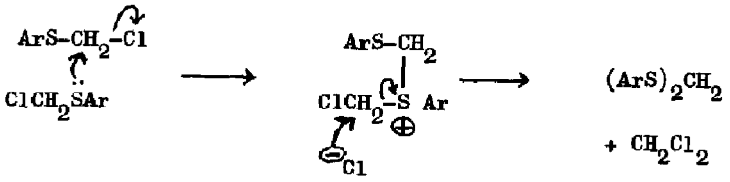


(2) (3) (1)

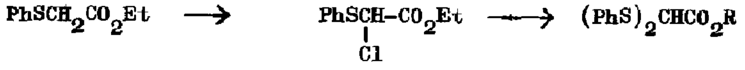
a : R=H
b : R=Me
c : R=Br

Equally, thioacetal (1b) [m.p. 41°; lit.[6] 42-43°] was produced in 98% yield from (3b)[7], whilst (3c)[7] gave (1c) [m.p. 73-74°; lit.[6] 71°] in 92% yield, under the same conditions. For the preparation of (1a), the yield was only slightly reduced if the intermediate (3a) was used without rigorous purification; experimental details are given below[8].

A possible mechanism for this reaction is shown below; the transformation is an interesting new application of the use of alumina for transformations in synthetic chemistry.[9]



We wished to see if this sequence could be used to prepare the potentially useful synthon[10] (4a). Chlorination of ethyl thiophenylacetate (5) with sulphuryl chloride gave (6) in 90% yield. The alumina-catalysed rearrangement in this case occurred only on heating under nitrogen at 120° for 24 hr., (4a) being isolated in 50% yield, along with 29% of the acid (4b).



$$PhSCH_2CO_2Et \longrightarrow PhS\underset{\underset{Cl}{|}}{C}H-CO_2Et \longrightarrow (PhS)_2CHCO_2R$$

(5) (6) (4a) R = Et

(4b) R = H

References and Notes

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8. Bis[phenylthio]methane (1a):- To a refluxing solution of thioanisole (2a) (2.48g, 0.02 mol) in dichloromethane (5 ml) was added sulphuryl chloride (2.9g, 0.025 mol) in dichloromethane (5 ml). After 1 h at reflux, the mixture was washed with sodium bicarbonate solution until the washings were alkaline, and then with water. After drying ($MgSO_4$) and evaporation, the residual oil [p.m.r.: δ 4.8, 2H, s; δ 7.0-7.5, 5H, m] was added to neutral alumina (B.D.H., 20g), and warmed at 50-55° for 0.25h. Thorough elution with dichloromethane, evaporation and low temperature crystallisation from methanol gave (1a) (2.2g, 95%); m.p. 38° (lit.[4] 38-40°).
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