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IMPROVED SYNTHESIS OF 6H,12H-DIBENZO[b,f][1,5]DITHIOCIN

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IMPROVED SYNTHESIS OF
6H,12H-DIBENZO[b,f][1,5]DITHIOCIN

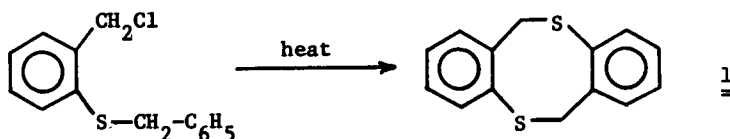
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The synthesis of 6H,12H-dibenzo[b,f][1,5]dithiocin (**1**) has been reported three times in the literature in yields ranging from trace amounts to 25%. In 1965 Stacy¹ obtained **1** in 25% yield by treating *o*-mercaptobenzyl chloride with either sodium cyanide in dimethyl sulfoxide or with sodium hydroxide in ethanol. Borovicka² reported the second synthesis of **1** by treating *o*-(thiobenzyl)benzyl alcohol with thionyl chloride in pyridine. The yield of **1** from this reaction was not reported. Finally, in 1970 Harpp³ obtained **1** in 7% yield by desulfurization of 3H-1,2-benzothiole with tris(diethylamino)phosphine.

We wish to report a new route to the synthesis of **1** which affords a greatly improved yield of pure product uncontaminated by polymeric material¹ or products resulting from side reactions.^{2,3}

Heating *o*-benzylmercaptobenzyl chloride¹ under reduced pressure for three hours affords a 38% yield of **1** as a pure solid. Since starting material can be recovered from the reaction mixture the effective yield of **1** is 56%.



EXPERIMENTAL

o-Benzylmercaptobenzyl Chloride.

This compound was prepared using the procedure of Stacy.¹

6H,12H-Dibenzo[b,f][1,5]dithiocin.

Into a 100 ml round bottomed flask equipped with a magnetic stirrer and an efficient Vigreux column attached to a distilling head connected to a vacuum pump, was placed 22 g (0.092 mole) of o-benzylmercaptobenzyl chloride and the solid heated to 190-200° under reduced pressure (5 mm), and held at this temperature for three hrs. The pressure was then reduced to 1 mm and the temperature held at 180°. At this point a fraction distilled over which was collected and proved to be the starting material, o-benzylmercaptobenzyl chloride. After this fraction had ceased to distil, the temperature rose to 200° and at this point the product began to distil and solidified as a white solid when cooled. After collecting all the product it was crystallized from 20 ml of 95% ethanol to give 4.3 g (0.0176 mole, 38%) of white crystals, mp 175-176° [lit¹ 174-176°]; nmr (CDCl₃) τ 5.6 (s, 4, CH₂) and 2.8 (m, 8, ArH).

Anal. Calcd for C₁₄H₁₂S₂: C, 68.80; H, 4.94; mol wt 244.

Found: C, 68.58; H, 4.78; mol wt 244 (mass spectrum)

The initial fraction distilled accounted for 7 g (0.029 mole) of recovered starting material. Thus the effective yield of \downarrow is 56%.

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