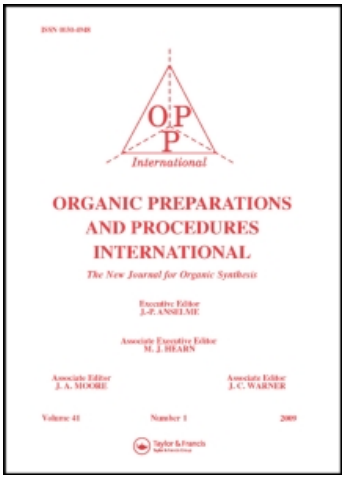

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IMPROVED SYNTHESIS OF 6H,12H-DIBENZO[b,f][1,5]DITHIOCIN

Abdullatif K. Youssef[a]; Michael A. Ogliaruso[a]
[a] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

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

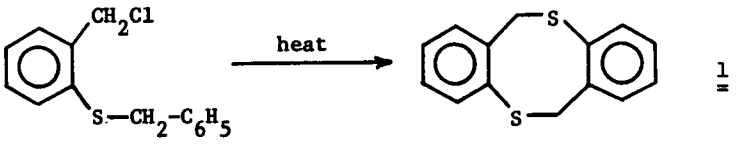
Abdullatif K. Youssef and Michael A. Ogliaruso*

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

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 Stacy[1] obtained 1 in 25% yield by treating o-mercaptobenzyl chloride with either sodium cyanide in dimethyl sulfoxide or with sodium hydroxide in ethanol. Borovicka[2] 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 Harpp[3] 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 material[1] or products resulting from side reactions.[2,3]

Heating o-benzylmercaptobenzyl chloride[1] 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%.



1

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° [lit[1] 174-176°]; nmr ($CDCl_3$) τ 5.6 (s, 4, CH_2) and 2.8 (m, 8, ArH).

Anal. Calcd for $C_{14}H_{12}S_2$: 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 1 is 56%.

REFERENCES

1.- G. W. Stacy, F. W. Villaescusa and T. E. Wollner, J. Org. Chem., 30, 4074 (1965).

2.- M. Borovicka, F. Kvis, J. Chromik and M. Protiva, Coll. Czech. Chem. Comm., 32, 1738 (1967); C. A. 67, 2849 (1967).

3.- D. N. Harp and J. G. Gleason, J. Org. Chem., 35, 3259 (1970).

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