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THE PHOSPHORIC ACID HYDROLYSIS OF 4-AMINOBENZO [b] THIOPHENE

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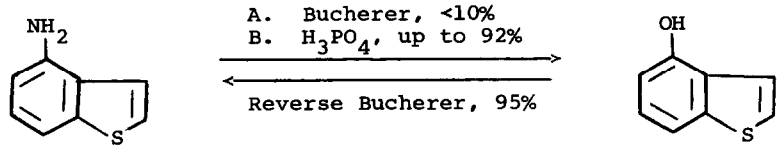
The replacement of the amino by the hydroxyl group through acid hydrolysis is limited practically to naphthalenes (1,2), acridines (3), highly reactive monocyclic amines such as 1,3,5,-triaminobenzene (4), and in heterocyclics to systems where hydrolysis can lead to a tautomerically stable carbonyl compound (5). We wish to report preliminary results of the acid hydrolysis of 4-aminobenzo-[b] thiophene (I), an amine falling outside of the above classifications.

Attempts to convert I to 4-hydroxybenzo[b] thiophene (II) via a Bucherer reaction failed. Surprisingly, the converse reaction produced I in 95 percent yield[6].



I II

Compound I is readily acetylated (6) and has been diazotized to prepare 4-nitrobenzo[b] thiophene (6) and 4-hydroxybenzo[b] thiophene [7].

The hydrolysis was conducted in sealed glass tubes which were agitated and heated in a rocking autoclave. The conversion of I to II was accompanied by the formation of trace amounts of benzo[b] thiophene and upon opening the reaction tubes, an odor of hydrogen sulfide was generally detected. No secondary amine was formed.

The optimum conditions for hydrolysis include employing the highest concentration of phosphoric acid, and the lowest acid to amine equivalence ratio without formation of by-products. All experiments in Table 1 gave 100% recovery

of material (I+II). The percentage yield of II was inversely proportional to the amine concentration through an acid to amine equivalence ratio of 10. Further dilution of amine showed no advantage in yield.

TABLE 1

Hydrolysis of 4-Aminobenzo[b]thiophene in 15% H_3PO_4 (6 Hrs. at 250°)

	Equivalence; Acid/Amine			
	2	5	10	15
II, % Yield	42	83	92	91

Increasing the phosphoric acid concentration beyond 15 percent in experiments at 250°, resulted in an ether insoluble, unidentifiable tar-like material (Table 2). Lowering the hydrolysis temperature to 200° allowed use

TABLE 2

Hydrolysis of 4-Aminobenzo[b]thiophene at Equivalence Ratio of 5

H_3PO_4, %	Recovery, % 6 Hrs at 200°		Recovery, % 6 Hrs at 250°	
	(I+II)	II	(I+II)	II
15	--	--	100	83.0
20	100	52.0	85	63.0
40	100	58.0	77	56.2
60	90.5	46.5	13	8.7

of 40 percent phosphoric acid while maintaining a 100 percent recovery of material, although the yield of II decreased.

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