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Short Communications

A Convenient Synthesis of Thieno [2,3-b]thiophene

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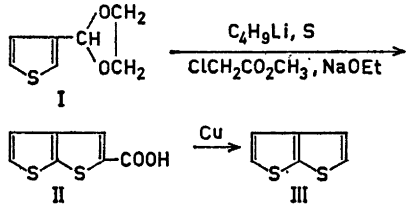
The chemistry of thieno[2,3-b]thiophene (liquid thiophthene) (III) is almost unknown, although this compound has been known since 1886, when it was obtained in low yield by heating either citric acid or 1,2,3-propane-tricarboxylic acid with phosphorus trisulphide.[1] Its formation in the reaction between acetylene and sulphur or hydrogen sulphide is not of preparative use.[2] Neither is the cyclization of 2-(2,2-diethoxyethylthio)-thiophene or of 2-thienylthioacetic acid [4] of any preparative value for obtaining the thieno[2,3-b]thiophene system; with the first-mentioned compound a low yield of III has been claimed, while in the latter case, a rearrangement yielding 2H,3H-thieno[3,2-b]thiophene-3-one was observed. This rearrangement has been found to occur also with some other 2-thienylthio-derivatives.[5,6] Recently, Goldfarb and Litvinov [7,8] have prepared some alkyl-substituted thieno[2,3-b]thiophenes through formylation or acetylation of 5-ethyl-2-thienylthioacetic acid ester, followed by Dieckman condensation to the alkylated thieno[2,3-b]thiophen-2-carboxylic acids, which then were decarboxylated.

We have now found a convenient synthesis which makes thieno[2,3-b]thiophene (III) easily available and permits a detailed study of its chemical reactions. 3-Thiophenealdehyde ethylene acetal (I) is metalated by butyllithium in the 2-position [9] and the intermediate thienyllithium derivative is made to react with sulphur and methyl chloroacetate. The crude methyl 3-formyl-2-thienylthioacetate obtained upon hydrolysis was treated with alcoholic sodium ethylate to yield 2-thieno-[2,3-b]thiophenecarboxylic acid (II) in 90 % yield. Decarboxylation with copper and quinoline then yielded 78 % of III.



Experimental. 2-Thieno[2,3-b]thiophenecarboxylic acid. 89 ml of 1.2 N ethereal butyl lithium was added dropwise under nitrogen to a stirred solution of 15.6 g (0.10 mole) of 3-thiophene aldehyde ethylene acetal [9] in 30 ml of ether and the mixture refluxed for 20 min. After cooling in ice-water, 3.2 g (0.10 mole) of dry sulphur was added in small portions. The mixture was refluxed for 1 h and cooled to room temperature, whereupon 10.9 g (0.10 mole) of methyl chloroacetate in 20 ml of ether was added dropwise. After standing overnight, the mixture was poured into ice-cold 2 N hydrochloric acid, the aqueous phase extracted with ether and the combined ether phases dried and added dropwise to a solution of 6.9 g of sodium in about 200 ml of ethanol. After refluxing for 5 h, the ether was distilled off, the residue poured into water and acidified with conc. hydrochloric acid, precipitating 17.3 g (94 %) of 2-thieno[2,3-b]thiophenecarboxylic acid. Recrystallization from acetic acid, which did not change the IR-spectrum, gave m.p. 242–244°. NMR[$(CD_3)_2SO$]: $\tau_3 = 1.97$ ppm, $\tau_{4 \text{ or } 5} = 2.24$ ppm, $\tau_{5 \text{ or } 4} = 2.56$ ppm, $J_{45} = 5.5$ c/s. (Lit.[10] m.p. 245°).

Thieno[2,3-b]thiophene. A mixture consisting of 9.2 g (0.050 mole) of crude 2-thieno[2,3-b]-thiophenecarboxylic acid, 5 g of copper powder, and 100 ml of freshly distilled quinoline was heated carefully and with efficient stirring to 180°. After being kept at that temperature for 2 h, the mixture was heated at 225–230° for 24 h, whereafter quinoline and liquid thiophthene were distilled off. The distillate was acidified with hydrochloric acid and the oil which separated was taken up in ether and dried. Fractionation yielded 5.4 g (78 %) of thieno[2,3-b]thiophene, b.p. 95°/10 mm Hg; picrate m.p. 135.5–136.5° after recrystallizations from methanol and ethanol. [Lit.[2], b.p. 98°/13 mm Hg, picrate m.p. 137–138°]. NMR (CCl_4): (Hard coupled AB-spectrum centered at 2.89 τ with a coupling of 5.4 c/s).

The NMR-spectra were obtained on a Varian A-60 NMR-spectrometer.

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Ternary Transition Metal Arsenides with the *anti*-$PbCl_2$ Structure

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The occurrence of a number of ternary transition metal phosphides crystallizing with the *anti*-$PbCl_2$-type structure was recently reported.[1] Isostructural compounds also occur in ternary silicide and germanide systems, and the representatives for this class of compounds have been denoted by the name of *E*-phases.[2,3] As mentioned in Ref. 1, crystal-chemical considerations indicate, that *E*-phases should occur also in ternary transition metal-arsenic systems. The results of the present investigation prove the correctness of this prediction, and crystallographic data for eight ternary arsenides crystallizing with the *anti*-$PbCl_2$-type structure are given in Table 1.

The ternary arsenides were prepared by heating the component elements in evacuated and sealed silica tubes at 1000°C. Attempts to prepare *E*-phases containing zirconium and hafnium were not successful. Different synthetic techniques were tried, involving both heat-treatment of mixtures of the elements and arc-melting of mixtures of zirconium or hafnium with the mono-arsenides of the iron group metals. The resulting alloys gave rather line-rich powder patterns, which could not be easily interpreted.

The lattice parameters as given in Table 1 were in each instance determined accurately (estimated relative accuracy 0.04 %). However, appreciable homogeneity ranges were observed for some of the compounds. Since deviations from the ideal composition may have occurred during the synthesis of the samples, the values in Table 1 should be regarded with some caution.

The *E*-type structure appears to have a quite widespread occurrence in ternary systems, the number of known *E*-phases is now approaching fifty. As regards the conditions for the formation of *E*-phases, the importance of the size-factor principle has already been stressed in the crystal-