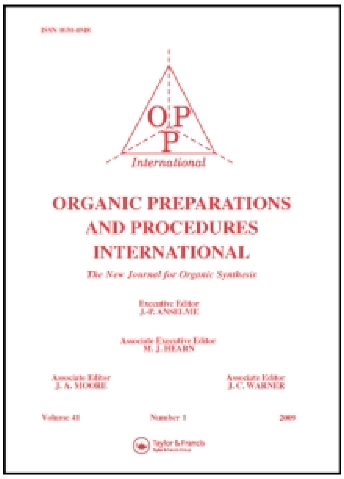

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DIMETHYL-2,4-THIOPHENEDICARBOXYLATE

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DIMETHYL-2,4-THIOPHENEDICARBOXYLATE

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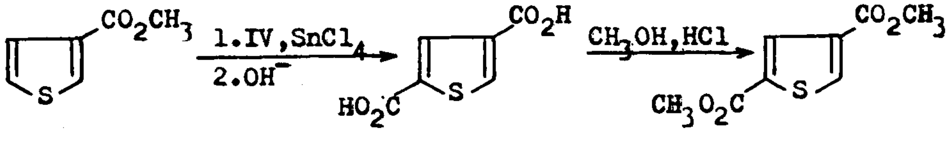

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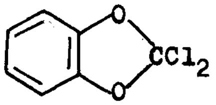

The title compound, dimethyl-2,4-thiophenedicarboxylate is a valuable intermediate to a variety asymetrically disubstituated thiophene derivatives. Previously reported [1-4] syntheses of III employed intermediates often difficult to prepare, and some of the steps in the multi-step procedures were of low yields. Pyrocatechol dichloromethylene acetal(IV) was used for the syntheses of aromatic and heterocyclic acids.[5,6] We obtained 75% and 85% yield of III after esterification when methyl-3-thiophenecarboxylate[7] was allowed to react with one and two equivalents of IV respectively. The analogous product (2,4-furandicarboxylic acid) was obtained from methyl-3-furancarboxylate in about

50% yield.

EXPERIMENTAL

Dimethyl-2,4-thiophenedicarboxylate. To a stirred solution of 1.4g(0.01mole) of methyl-3-thiophenecarboxylate and 1.9g(0.01mole) of pyrocatechol dichloromethylene acetal[5] in 25ml dry dichloromethane, was added 2.4g anhydrous tin(IV)-chloride. The mixture was heated under reflux for 2 hrs. Then 25ml of water was slowly added and the mixture was stirred for an additional 10 min. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phases were evaporated in vacuo, 20ml of 20% potasium hydroxide and 0.01g of sodium thiosulphate were added to the light yellow residue and the mixture heated under reflux for 30 min. The reaction mixture was then cautiously acidified with conc. HCl. After standing overnight, the crude acid was collected and weighed 1.7g(99%); it was refluxed with 100ml methanol saturated with dry hydrogen chloride for 4 hrs. Evaporation in vacuo yielded 1.6g(80%) of crude III. Recrystalization from *n*-heptane gave 1.5g (75% based on methyl-3-thiophenecarboxylate) of pure dimethyl-2,4-thiophenedicarboxylate, mp.118°, lit.[1] mp.120°. NMR ($CDCl_3$) δ 3.82 (s,3H), 3.86 (s,3H), 8.14 (d,1H, J=1.2Hz) 8.25 (d,1H, J=1.2Hz).

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