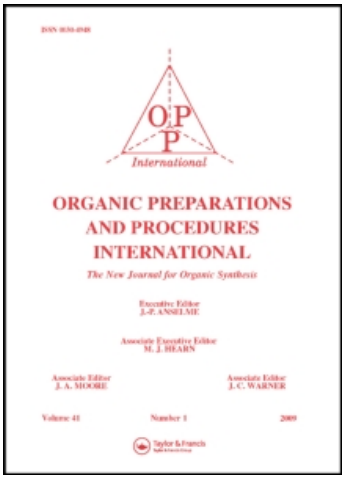

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A BRIEF PREPARATION OF THIAN-4-CARBOXYLIC ACID 1,1-DIOXIDE

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7. Experiments by Mssrs. L. A. Dolan and M. Frey.

8. Purchased from General Metallic Oxides Co., Jersey City, N. J. as "Manganese Hydrate 37."

9. In larger runs,[7] an ice-water bath was employed to control the exotherm.

10. This is a maximum reaction time (ca. 10 min after all the DDHQ has gone into solution). Our experience indicates that longer stirring times lead to lower yields of darker product and to more water-soluble by-products.

A BRIEF PREPARATION OF THIAN-4-CARBOXYLIC ACID 1,1-DIOXIDE

Submitted by E. Carlon, R. W. Draper and R. Friary*
(3/18/77)

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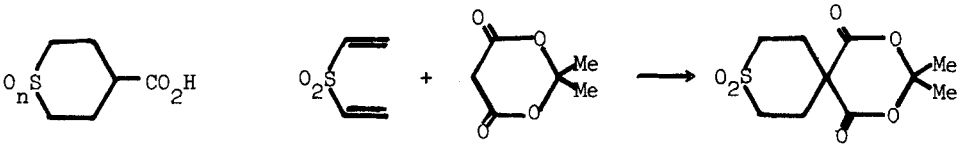
Thian-4-carboxylic acid 1,1-dioxide (I), which may be prepared by oxidation of thian-4-carboxylic acid (II), was needed for amidation of aromatic amines.[1] Since Prelog's seven-step synthesis of II was unduly long, a brief preparation of I or a suitable derivative was sought.[2-4]



I (n = 2) V III IV

II (n = 0)

By analogy to Meldrum's acid (III) which converts aniline to acetanilide, the spirocyclic compound IV expected from Michael reaction of III and divinyl sulfone (V), seemed a likely starting material for the required amidation.[5] When a solution of Meldrum's acid, divinyl sulfone, and a little potassium hydroxide in t-butyl alcohol was boiled, pure crystals of

IV precipitated. As desired, IV amidated amines when heated in a high-boiling solvent and could be hydrolyzed and decarboxylated with hot dilute sulfuric acid to thian-4-carboxylic acid 1,1-dioxide (I).

EXPERIMENTAL

3,3-Dimethyl-2,4-dioxa-9-thiaspiro[5,5]undecane-1,5-dione-9,9-dioxide (IV).- A solution of Meldrum's acid (500 mg, 3.48 mmoles), divinyl sulfone (410 mg, 3.48 mmoles) and potassium hydroxide (20 mg, 0.36 mmole) in t-butyl alcohol (25 ml) was heated under refluxed (N_2) for 6 hrs. The mixture was cooled and filtered; the colorless crystals of IV were washed with t-butyl alcohol and with ether. There was obtained 621 mg (68%) of IV, mp. 225-228° (gas evolution), of analytical purity.

IR: ν_{max} (KBr) 2960, 1750, 1710, 1380, 1310, 1130 cm^{-1}; NMR: δ (DMSO-d_6) 3.50-3.15 (envelope, 4H), 2.80-2.35 (envelope, 4H), 1.72 (s, 6H) ppm; MS: m/e 262 (M^+).

Anal. Calcd. for $C_{10}H_{14}O_6S$: C, 45.99; H, 5.38; S, 12.23.
Found: C, 45.62; H, 5.41; S, 12.08.

Thian-4-carboxylic acid 1,1-dioxide (I).- A mixture of IV (1.00 g, 3.81 mmoles) and 20% sulfuric acid (100 ml) was heated to reflux for 4 hrs, cooled, saturated with salt, and extracted with ethyl acetate. The extract was dried over sodium sulfate and concentrated to give 284 mg (42%) of compound I, mp. 190-194°, lit.[1] mp. 192-193°.

NMR: δ (DMSO-d_6) 12.51 (br s, 1H), 3.13 (envelope), 2.19 (envelope) ppm; MS: m/e/ 178 (M^+)

Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66
Found: C, 40.57; H, 5.83

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and mass spectra.

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AN EFFICIENT SYNTHESIS OF 4-HYDROXYBENZOTRIFLUORIDE

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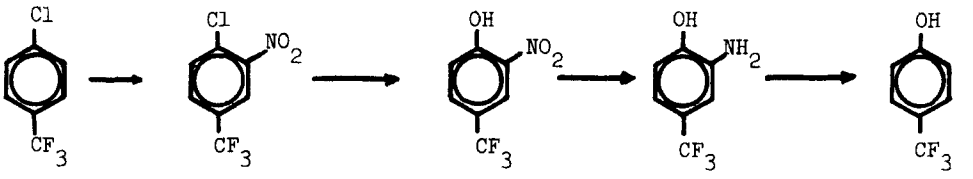
The relatively high cost of 4-hydroxybenzotrifluoride (V) is a limiting factor in its use as a chemical intermediate. Additionally, literature methods[1] for its preparation are cumbersome and not easily adapted to large scale operations. An improved synthesis of V from readily available, inexpensive 4-chlorobenzotrifluoride (I) in four steps is described.



I II III IV V