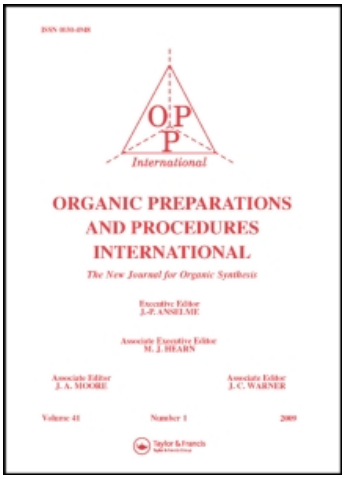

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AN IMPROVED METHOD FOR THE SYNTHESIS OF DISULFONYLMETHYL THIOLSULFONATES

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OPPI BRIEFS

AN IMPROVED METHOD FOR THE SYNTHESIS OF DISULFONYLMETHYL THIOLSULFONATES

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In 1970 we described reactions between thiophosgene and sulfinic acid salts[1] which, inter alia, produce disulfonylmethyl thiosulfonates (I).

$$CSCl_2 + 3\ RSO_2^- + H^+ \longrightarrow (RSO_2)_2CH\text{-}S\text{-}SO_2R + 2\ Cl^-$$

I

In our original study[1] no efforts were made to optimize the modest yields of I (~10%) obtained in a heterogeneous benzene/water medium. We have now found that changing to aqueous acetone as the solvent substantially improves the yields of I. Since I exhibits sulfenylating properties towards active methylene compounds,[2,3] including acetone, it is important that the reaction mixture be worked up immediately.

So far, we have been unable to prepare I where R contains an electron-withdrawing substituent R = $4\text{-}ClC_6H_4$, probably because of insufficient nucleophilicity of the corresponding sulfinate anion.

EXPERIMENTAL

S-[(Bisphenylsulfonyl)-methyl]benzenethiosulfonate (I, R = C_6H_5).- A stirred solution of 60 g (0.3 mole) sodium benzenesulfinate dihydrate and 100 ml water in 500 ml acetone is kept at 0°. A solution of 11.7 ml

(0.15 mole) thiophosgene in 50 ml acetone is added dropwise over 10 min. After stirring for another 30 min, the volatiles are removed by rotatory evaporation at room temperature, and the residue is triturated with water. Crude yields: 65-71%, mp. 168-170°. Recrystallization from acetonitrile raises the mp. to 170.5-173.4°, lit.[1] mp. 170.5-173.0°, (yield 43%). NMR ($CDCl_3$, TMS): δ 5.88 (s, 1H), 7.3-8.2 (m, 15H).

S-[(Bis-p-toluenesulfonyl)-methyl] p-toluenethiosulfonate (I, R = 4-MeC_6H_4).- From sodium p-toluenesulfinate dihydrate according to the preceding procedure. Crude yield: 90%, mp. 159-164.5°. Recrystallization as above yields 59% of pure product, mp. 165.9-168.0°. NMR ($CDCl_3$, TMS): δ 2.46 (s, 9H), 5.83 (s, 1H), 7.2-7.9 (m, 12H).

Anal. Calcd. for $C_{22}H_{22}O_6S_4$: S, 25.11. Found: S, 25.07

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SYNTHESIS OF dl-2-METHYL-2-(4-METHYL-3-PENTENYL) 5-OXYMETHYLENEMETHOXY-2H-BENZOPYRAN. A CANNABICHROMENE HOMOLOGUE

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The benzopyran ring system has previously been synthesized in the case of cannabichromene by the pyridine catalyzed reaction of olivetol with cit-