

Easy Synthesis of 1,3-Dithiole-2-thione

By C. H. CHEN

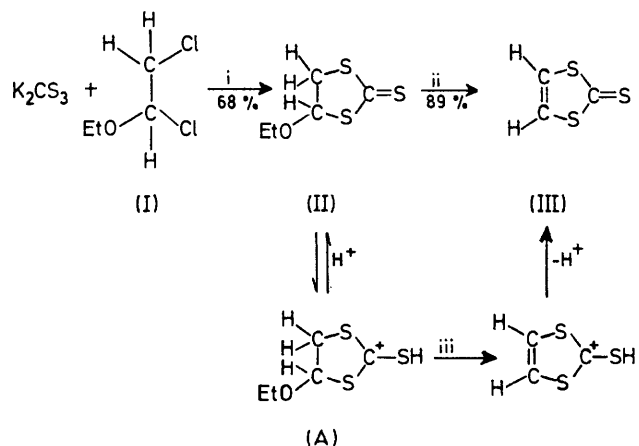
(Research Laboratories, Eastman Kodak Company, Rochester, New York 14650)

Summary Reaction of potassium trithiocarbonate and 1,2-dichloroethyl ethyl ether followed by elimination of ethanol with toluene-*p*-sulphonic acid affords 1,3-dithiole-2-thione in good yield.

TETRATHIAFULVALENE (TTF) has recently been the focus of much intense research because its tetracyanoquinodimethane (TCNQ) salt was found to form highly conducting charge-transfer complexes exhibiting interesting metallic properties.¹ A key intermediate in TTF synthesis is 1,3-dithiole-2-thione (III) which was prepared originally by a three-step synthesis using ethylene trithiocarbonate and dimethyl acetylenedicarboxylate as starting materials.² We report here an alternative synthesis of (III) in two steps with good overall yield (61%) starting from potassium trithiocarbonate and 1,2-dichloroethyl ethyl ether (I), both readily available commercial chemicals.† We believe this new approach offers advantages in simplicity, efficiency, and ease of operation, and suggests the potential use of (I) as a synthon for the incorporation of an 'ethylene' linkage in the syntheses of other heterocycles, since direct nucleophilic displacement of vinyl *cis*-1,2-dihalide often proves difficult.³

Thus, to a cooled, well stirred suspension of 16.5 g of K_2CS_3 in 100 ml of dimethylformamide (DMF) was added dropwise a solution of 13.5 g of (I) in 50 ml of DMF. After the usual work-up, distillation *in vacuo* gave 10.3 g (68%)

of pure 4-ethoxy-1,3-dithiolan-2-thione (II),‡ b.p. 112–114 °C at 0.03–0.04 mmHg. Slow azeotropic distillation



i, Dimethylformamide, ii, $MeC_6H_4SO_3H-p$ (1 equiv.), PhMe, heat; iii, H^+ , $-EtOH$.

of a toluene solution (50 ml) of 500 mg of (II) and 530 mg (1 equiv.) of anhydrous toluene-*p*-sulphonic acid (PTSA) in 3 h with intermittent removal of ethanol afforded *ca.* 400 mg of a brown solid which was recrystallized from

† Available from Ventron Corporation and Eastman Organic Chemicals.

‡ The structure was confirmed by i.r., n.m.r., and mass spectroscopy and elemental analysis.

hexane (cooled to -78°C) to give 330 mg (89%) of pure 1,3-dithiole-2-thione (III), m.p. $49-50^{\circ}\text{C}$ (lit.² $50-51^{\circ}\text{C}$).

The necessity of employing 1 equiv. of PTSA to effect smooth elimination of ethanol from (II) suggests a possible mechanism which is consistent with the expectation that initial protonation of (II) must have taken place on the thione group to give the carbonium ion (A) which would

then provide the driving force for the subsequent elimination of ethanol under acid catalysis.

The author thanks Dr. N. F. Haley of Kodak Research Laboratories for helpful discussions.

(Received, 9th August 1976; Com. 920.)

¹ J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Amer. Chem. Soc.*, 1973, **95**, 948.

² L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456.

³ J. March, 'Advanced Organic Chemistry,' McGraw-Hill, New York, 1968, p. 33.