

Synthesis of Carboxylic Acids and their Methyl Esters from Alkyl Phenyl Sulphides

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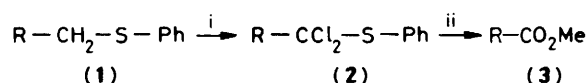
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Alkyl phenyl sulphides are converted with sulphuryl chloride and pyridine under controlled temperatures into 1,1-dichloroalkyl phenyl sulphides or 1-chloroalk-1-enyl sulphides; treatment of these intermediates with methanol-water (1% v/v) and mercury(II) acetate-formic acid gives, respectively, methyl carboxylic esters and carboxylic acids.

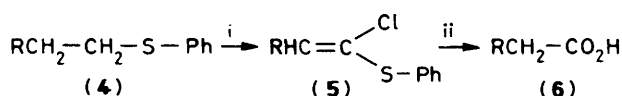
Several chlorination agents have been described which convert sulphides into 1-chloro-sulphides.¹ None of them, however, under the experimental conditions described, permits the controlled substitution of two 1-chlorine atoms in alkyl phenyl sulphides.^{2,3}

Halogenation with sulphuryl chloride at controlled temperatures and the addition of a base such as pyridine permit us to introduce two chlorine atoms at the 1-position of the sulphur atom of alkyl phenyl sulphides.

The dichlorides were synthesized by addition of SO₂Cl₂ (40 mmol) and pyridine (40 mmol) to the sulphides (1) (20 mmol) in 100 ml of CCl₄, maintained at -5 °C, under nitrogen. After 2 h the reaction mixture was allowed to warm to room temperature, washed with cold water, and dried over sodium sulphate. Evaporation of the solvent gave the crude dichloro-sulphide (2) which, without further purification, was treated with methanol-water (1% v/v) and sodium carbonate,⁴ at -5 °C for 30 min, to give the corresponding methyl carboxylic esters (3) in good yields (see Table 1).



i, SO₂Cl₂-pyridine, -5 °C; ii, MeOH-H₂O, -5 °C.



i, SO₂Cl₂-pyridine, room temp., then reflux for 1 h; ii, Hg(OAc)₂-HCO₂H, 3 h, 50 °C.

Hydrolysis of the dichloro-sulphides (2), assisted by Cu^{II} salts,⁵ led invariably to mixtures in which the 1-chloroalk-1-enyl sulphides (5) are the major products. The same compounds are obtained in good yields by performing the chlorination reaction under reflux (see Table 2). The 1-chloroalk-1-enyl sulphides (5) were converted into the corresponding carboxylic acids (6) by hydrolysis with mercury(II) acetate and formic acid⁶ for 3 h at 50 °C.

The above sequences represent a new method for the conver-

Table 1. Synthesis of methyl carboxylic esters (3).

R	Yield % ^a
C ₈ H ₁₇	76
C ₇ H ₁₅	70
C ₆ H ₁₁	70
Ph[CH ₂] ₂	41

^a Overall isolated yields.

Table 2. Synthesis of 1-chloroalk-1-enyl sulphides (5) and carboxylic acids (6) from (4).

R	B.p. of (5)/°C (mmHg)	Yield of (5)/% ^a	Yield of (6)/% ^b
C ₈ H ₁₈	129 (0.12)	74	71
C ₆ H ₁₁	131 (0.30)	70	62
Pr ⁿ	96-97 (0.60)	69	—
Pr ^t	104-105 (0.37)	72	—
Ph	decomp. at 152 (0.40)	86	26

^a Isolated yields. All these new compounds gave spectral data consistent with the proposed structures. ^b Yields based on starting sulphides.

sion of sulphides into methyl carboxylic esters and carboxylic acids.

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