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

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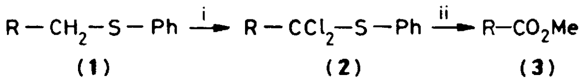
Alkyl phenyl sulphides are converted with sulphuryl chloride and pyridine under controlled temperatures into 1,1-dichloroalkyl phenyl sulphides or 1-chloroalk-1-enyl sulphides; treatment of these intermediates with methanol–water (1% v/v) and mercury(II) acetate–formic acid gives, respectively, methyl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

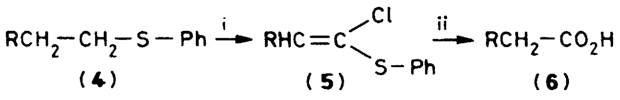
Several chlorination agents have been described which convert sulphides into 1-chloro-sulphides.[1] None of them, however, under the experimental conditions described, permits the controlled substitution of two 1-chlorine atoms in alkyl phenyl sulphides.[2,3]

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 SO_2Cl_2 (40 mmol) and pyridine (40 mmol) to the sulphides (**1**) (20 mmol) in 100 ml of CCl_4, 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, SO_2Cl_2–pyridine, −5 °C; ii, $MeOH–H_2O$, −5 °C.



i, SO_2Cl_2–pyridine, room temp., then reflux for 1 h; ii, $Hg(OAc)_2$–HCO_2H, 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 acid[6] 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_8H_{17}	76
C_7H_{15}	70
C_5H_{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 of (**5**)/%[a]	Yield of (**6**)/%[b]
C_6H_{13}	129 (0.12)	74	71
C_5H_{11}	131 (0.30)	70	62
Pr^n	96—97 (0.60)	69	—
Pr^i	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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