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A CONVENIENT PREPARATION OF SULPHINIC ESTERS FROM SULPHINYL CHLORIDES AND CHLOROSULPHITES USING HEXAMETHYLDISILOXANE AS CHLORIDE ANION ACCEPTOR

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Sulphinic esters can be obtained in high yields by the reaction of sulphinyl chlorides with chlorosulphites in the presence of hexamethyldisiloxane and catalytic amount of dimethyl sulphoxide.

A variety of silicon derivatives have been used in the past years as synthetic mediators.[1)] Here we wish to report a novel means of preparing sulphinic esters 1 in which hexamethyldisiloxane (HMDSO) 2 is used as chloride anion acceptor.

When sulphinyl chlorides 3 are allowed to react with chlorosulphites 4 and hexamethyldisiloxane 2 in the presence of catalytic amount of sulphoxide sulphinic esters 1 are cleanly produced. Trimethylchlorosilane and sulphur dioxide are formed as by products.

$$\underset{\underline{3}}{\text{R-S(=O)-Cl}} + \underset{\underline{4}}{\text{R}^1\text{O-S(=O)-Cl}} + \underset{\underline{2}}{(\text{Me}_3\text{Si})_2\text{O}} \xrightarrow{\text{R}''_2\text{SO}} \underset{\underline{1}}{\text{R-S(=O)-OR}^1} + 2\text{Me}_3\text{SiCl} + \text{SO}_2$$

Typically a few drops of dimethyl sulpoxide is added to an equimolar mixture of sulphinyl chloride 3, chlorosulphite 4, and hexamethyldisiloxane 2, and the reaction(without any solvent)is allowed to proceed at room temperature. The progress of the reaction was conveniently followed by ^{1}H-NMR spectroscopy, the singlet for trimethylchlorosilane increased at the expense of the singlet for HMDSO. After completion of the reaction, trimethylchlorosilane was removed[2)] and sulphinic esters 1 were purified by distillation.

TABLE I. Preparation of Sulphinic esters 1

R	R^1	Time(hr)	Yield(%)[a]	Bp(°C)/mmHg[b] Found	Reported
CH_3	C_3H_7	6	73	68-70/18	67-68/17[3]
n-C_3H_7	C_2H_5	7	78	82-84/20	80-81/18[3]
n-C_4H_9	CH_3	6	81	80-81/20	72-73/10[3]
C_6H_5	CH_3	8	86	83-84/0.1	88-89/0.3[3]
C_6H_5	C_2H_5	10	83	87-88/0.3	79-80/0.1[3]
p-CH_3-C_6H_4	CH_3	8	84	85-86/0.1	86-88/0.4[3]
p-CH_3-C_6H_4	C_2H_5	10	80	90-92/0.15	76-78/0.1[4]
p-CH_3-C_6H_4	i-C_3H_7	14	87	90-92/0.1	91-93/0.1[4]

[a] All compounds exhibited consistent spectral data. [b] 1 mmHg=400/3 Pa.

The procedure presented here constitutes a simple, convenient, and mild method for the synthesis of sulphinic esters in neutral conditions. The mechanism of this reaction is not clear at present and needs further investigations. Preliminary exeriments showed that the rate of the reaction is strongly dependent on the basicity of sulfoxide used as catalyst. This is consistent with the assumption that the sulphonium salt 5 is a reactive intermediate. The reaction of salt 5 with another charged intermediate 6 will lead to the final reaction products.

$$\underset{5}{R\text{-}\overset{\overset{O}{\|}}{S}\text{-}O\text{-}\overset{+}{S}R''_2}\ \ Cl^- + \underset{6}{R^1O\text{-}\overset{\overset{O}{\|}}{S}\text{-}O(SiMe_3)_2Cl^-} \longrightarrow \underset{1}{R\text{-}\overset{\overset{O}{\|}}{S}\text{-}OR^1} + 2Me_3SiCl + SO_2 + R''_2SO$$

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