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A NOVEL METHOD TO SYNTHESIZE O-ESTERS OF THIOCARBOXYLIC ACIDS

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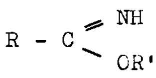
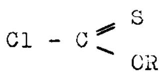
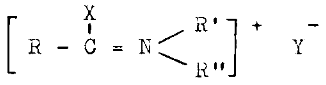
Esters of thiocarboxylic O-acids have previously been prepared by the reaction of imido ethers (Ia) with hydrogen sulfide, or by the reaction of Grignard reagents with chlorothiocarbonic acid O-esters (Ib) (1-4). An alternative method involves the reaction of immonium-type salts (II) with hydrogen sulfide (5). However, these compounds are usually so unstable that their preparations are accomplished only in low yields. Furthermore, the reaction of I or II with hydrogen sulfide is accompanied by some complications due to hydrolysis (6), and secondary reactions of resulting thioesters (7).



Ia



Ib



X = Cl, OR'''; Y = Cl, Br

II

In this letter the authors wish to report a novel and simple method to synthesize O-esters of thiocarboxylic acids by the reaction of orthoesters with hydrogen sulfide in presence of catalysts. Thus, into a flask which contained 20 g. of triethyl orthobenzoate (III) and 100 mg. of zinc chloride, dry hydrogen sulfide was bubbled gently for 40 hours at room temperature. Direct fractional distillation of the contents afforded pure O-ethyl thiobenzoate (n_D^{20} : 1.5889) in 80% yield; b.p. 88-89°C/3 mmHg (lit. (8) b.p. 112-120°C/11 mmHg). The infrared absorption spectrum entirely lacked carbonyl absorption at 1730 cm^{-1} which corresponds to ethyl benzoate. The nmr spectrum also confirmed the structure of this compound; τ = 1.90 (2H) multiplet, 2.68 (3H) multiplet, 5.36

(2H) quartet, and 8.51 (3H) triplet*.

p-Toluenesulfonic acid (IV) is less effective as catalyst than zinc chloride in this synthesis, i.e., 1.6 g. of IV in 10 g. of III gave the product in only 12% yield after 10 days and unchanged III was recovered nearly quantitatively.

The synthesis of O-ethyl thioacetate requires somewhat different conditions: the reaction with zinc chloride resulted in the formation of polymerized product. Into a mixture of triethyl orthoacetate (V) (14.3 g.) and ferric chloride (50 mg.), cooled with an ice-salt bath, dry hydrogen sulfide was bubbled for 42 hours. Direct fractional distillation gave pure O-ethyl thioacetate in 52% yield (n_D^{26} : 1.4579, b.p. 105-109°C). The nmr spectrum of the ester showed signals at τ = 5.58 (2H) quartet, 7.50 (3H) singlet, and 8.62 (3H) triplet*. No carbonyl absorption was detected in the infrared absorption spectrum. As regards the catalytic activity, ferric chloride is a stronger Lewis acid than zinc chloride (9), but the latter has strong affinity to the thiocarbonyl group (10) and causes the polymerization of relatively unstable O-ethyl thioacetate. Because of far low polarity of the reaction media, p-toluenesulfonic acid is not an effective catalyst although specific hydronium ion catalysis has been reported for the hydrolysis of triethyl orthoformate (11).

There are several advantages in this synthesis in comparison with previous ones. These include that the reactants, orthoesters, are stable compounds and easily obtained in a large amount (12); no noticeable side reaction takes place; and unreacted reactants can be recovered by fractional distillation.

The reaction conditions and yields are summarized in Table I. The reaction mechanism could be represented by the following equations,

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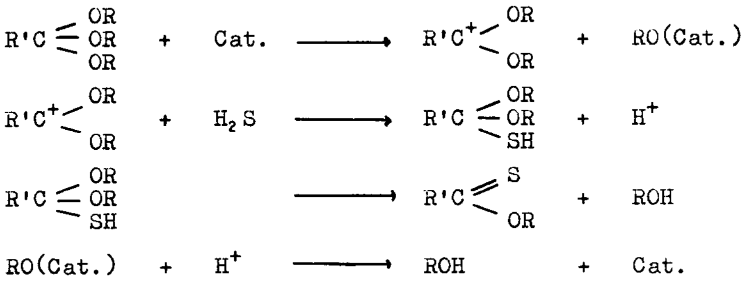
*It is worth noting that, in nmr spectra, the thiocarbonyl group exerts a larger anisotropic effect than its oxygen analog does. Thus, all protons in alkyl groups in these thioesters appear at lower field than those in the corresponding oxygen analogs, and systematic difference is observed in proton chemical shift between the thiocarbonyl compounds and the corresponding carbonyl compounds. Ethyl benzoate; τ = 2.02 (2H) multiplet, 2.60 (3H) multiplet, 5.70 (2H) quartet, and 8.67 (3H) triplet. Ethyl acetate; τ = 5.99 (2H) quartet, 8.05 (3H) singlet, and 8.77 (3H) triplet.



The formation of thioketones from the corresponding ketals by the reaction with hydrogen sulfide (13) may go through a similar reaction pathway.

TABLE I

Orthoesters	Catalyst	Temp.	Time, hr.	Yield, %
III	$ZnCl_2$	a	40	80
III	p-TsOH	a	240	12
V	$ZnCl_2$	b	30	1
V	$FeCl_3$	b	41.5	52

a) At room temperature. b) Cooled with an ice-salt bath.

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