Tetrahedron Letters No. 27, pp 2461 - 2462, 1973. Pergamon Press. Printed in Great Britain.

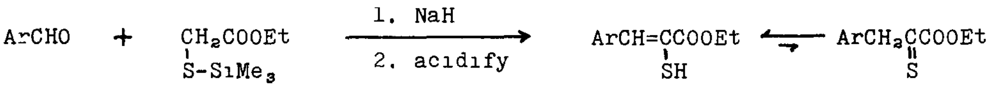
A Novel Synthesis of α-Thionic Esters

Toshio Hayashi and Hiroshi Midorikawa

The Institute of Physical and Chemical Research, Wako-Shi, Saitama, 351, Japan

(Received in Japan 12 May 1973; received in UK for publication 25 May 1973)

Although preparation of an equilibrium mixture of α-mercaptoacrylic acids and α-thionic acids via hydrolysis of aldehyde or ketone condensates of rhodanine was reported by Granacher[1] and other several workers[2], the corresponding esters have still remained unknown. We wish to report here a simple, one-step synthesis of α-mercaptoacrylic esters (2α) or α-thionic esters (2β) with the use of trimethylsilylthioacetic ester (1).

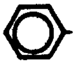
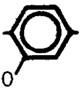


$$\mathrm{ArCHO} + \underset{\mathrm{S{-}SiMe_3}}{\mathrm{CH_2COOEt}} \xrightarrow[\text{2. acidify}]{\text{1. NaH}} \underset{\mathrm{SH}}{\mathrm{ArCH{=}CCOOEt}} \rightleftharpoons \underset{\mathrm{S}}{\mathrm{ArCH_2CCOOEt}}$$

1 2α 2β

Reaction of 1 with an aromatic aldehyde in the presence of sodium hydride led to the formation of 2 in good yield, together with small amounts of α-mercapto-β-hydroxydihydrocinnamic ester (3) and cinnamic ester (4). The results were listed in Table 1. Reaction time was 3 hours for aldehydes having an electron-attractive substituent, while 5 hours were taken for aldehydes having an electron-donating substituent. Shorter reaction time might lead to an increase in the yield of 3, whereas longer reaction time might increase the yield of 4 at the expence of 3. The use of glyme as a solvent instead of THF also increased the yield of 3 at the expence of 2. The IR spectra of 2 showed the SH stretching band at 2550-2580 cm^{-1}. The NMR signal of the SH proton ($CDCl_3$) was located between δ 4.60 and 4.80 ppm. However, the benzylic proton signal due to the tautomeric form 2β was not detected. This means that the equilibrium between 2α and 2β is extremely shifted to the left.

Table 1

Ar-	Yield of 2 (%)	bp (mp) °C /mm
	63	132 /4
Cl	65	139 /3
 Cl	80	98 /$1.1x10^{-2}$
CH_3O	48	154 /3.5
CH_3O CH_3O	65	(60-61)

General Procedure— To a mixture of 1 (0.030 mol) and an aldehyde (0.033 mol) in 40 ml of tetrahydrofuran (THF) was added slowly sodium hydride (0.032 mol) with stirring at room temperature under nitrogen atmosphere. After being stirred for 3 to 5 hr., the mixture was poured into 300 ml of ether and allowed to stand for 30 min. The resulting precipitates which contained almost only sodium salt of 3 were collected on a filter. The filtrate was extracted repeatedly with distilled water and the aqueous layer was acidified with hydrochloric acid. The resulting oil was taken into ether and then subjected to fractional distillation or column chromatography.

References

1) C Granacher, Helv. Chim. Acta, 3, 152 (1920).
2) E. Camaigne, Chem. Rev., 39, 20 (1946).