SYNTHESIS OF NEW FLUORO DERIVATIVES OF MONOTHIO-β-DIKETONES

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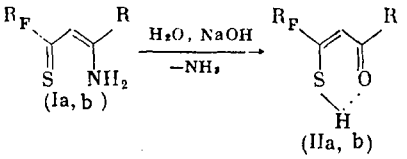
Alkaline hydrolysis of fluorine-containing β-aminovinylthiones (I) was the first reported synthetic method for monothio-β-diketones (IIa, b) with gem orientation of the fluoroalkyl and mercapto group which are isomeric to compounds obtained previously by the reaction of fluorinated β-diketones with hydrogen sulfide [1, 2]:



$R_F = HCF_2CF_2$, R = Me (a); $R_F = CF_3$, R = Ph (b)

The IR and PMR spectra of (IIa) and (IIb) indicate that they exist as mixtures of the enol and enethiol forms, which are yellow-green oils unstable upon storage and undergo decomposition upon distillation.

1,1,2,2-Tetrafluoro-3-mercapto-4-hexen-4-one (IIa). A solution of 0.7 g (3.5 mmoles) 1,1,2,2-tetrafluoro-5-amino-4-hexen-3-thione in 5 ml methanol was added to a solution of 0.14 g (3.5 mmoles) NaOH in 10 ml water. The reaction was monitored by thin-layer chromatography. Stirring was stopped after 15-20 min and the reaction mixture was acidified to pH 7 and extracted with 5-6 portions of benzene. The benzene solution was dried and the solvent was distilled off. The residue was subjected to chromatography on a silica gel column with $CHCl_3$ eluant (R_f 0.8). The solvent was distilled off to yield 0.5 g (71%) (IIa). Found: C 36.13; H 3.07; S 16.01%. Calculated for $C_6H_7F_4OS$: C 35.65; H 2.99; S 15.86%. IR spectrum (ν, cm^{-1}): 3280 (O–H), 1650 (C=O). PMR spectrum (δ, ppm): 2.30 s (CH_3), 6.06 t.t (HCF_2CF_2), 6.82 s (=CH–), 14.07 s (O-H...S).

By an analogous procedure (but with heating the reaction mixture for 10-15 min at reflux), we obtained 1-phenyl-4,4,4-trifluoro-3-mercapto-1-buten-1-one (IIb) in 76% yield. Found: C 52.05; H 3.04; S 13.81%. Calculated for $C_{10}H_7F_3OS$: C 51.72; H 3.04; S 13.81%. IR spectrum (ν, cm^{-1}): 2400 (S–H), 1705 (C=O). PMR spectrum (δ, ppm): 7.44 s (=CH–), 7.7 m (Ph), 14.51 s (O...H–S).

LITERATURE CITED

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