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α-ACETOXY AND α-HALOMETHYLKETONES FROM ACYLOXOSULFONIUM YLIDES

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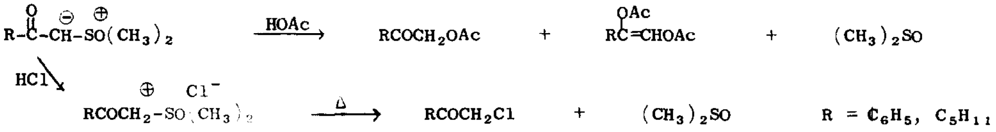
The selective preparation of α-halo and α-acyloxymethyl ketones by reaction of halogen acids or organic acids with α-diazoketones is well known. Since the diazoketones are usually obtained by the reaction of diazomethane with appropriate acid chlorides this method is not very appealing for larger-scale preparations. We wish to report a new method based on the action of acids on dimethyl acyloxosulfonium ylides.

Dimethyl β-benzoyloxosulfonium ylide(1) was refluxed with glacial acetic acid for 8 hours to afford a mixture of phenacyl acetate (20%), b.p. 91-93°/0.25 mm. (identical to authentic material) and α β-diacetoxystyrene (16%), b.p. 100-101°/0.25 mm. (lit.,(2) 118-120°/2 mm.); n.m.r., τ 2 61 (5H, doublet, phenyl), 3.82 (1H, singlet, vinyl H), 7.75 (3H, singlet, acetate), 7.83 (3H, singlet, acetate). Similarly, dimethyl β-hexanoyloxosulfonium ylide, m.p. 79-80.5°, gave 1-acetoxy-2-heptanone (30%)(3) and 1,2-diacetoxy-1-heptene (20%); n.m.r., 5.05 τ 1H, triplet, vinyl H), 7.50 (6H, singlet, acetate). The formation of the diacetoxy vinyl products is difficult to account for, however, phenacyl acetate was unaffected by prolonged treatment with hot acetic acid.



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\ominus}{C}H\text{-}\overset{\oplus}{S}O(CH_3)_2 \xrightarrow{HOAc} RCOCH_2OAc + R\overset{OAc}{C}{=}CHOAc + (CH_3)_2SO$$

$$\downarrow HCl$$

$$RCOCH_2\text{-}\overset{\oplus}{S}O(CH_3)_2\ Cl^- \xrightarrow{\Delta} RCOCH_2Cl + (CH_3)_2SO \qquad R = C_6H_5,\ C_5H_{11}$$

Treatment of a chloroform solution of the benzoyl ylide with hydrogen chloride precipitated a hygroscopic chloride salt, which when heated at 120° for a few minutes decomposed to phenacyl chloride and dimethyl sulfoxide. The mixture was partitioned between hexane and water and the phenacyl chloride (identical to authentic sample) was obtained in a 68% yield after removal of the hexane, followed by distillation *in vacuo*. An analogous reaction with the hexanoyl ylide gave 1-chloro-2-heptanone in a 45% yield. The liquid was identical with material prepared from hexanoyl chloride and diazomethane followed by treatment of the diazoketone with dry hydrogen chloride. The corresponding bromo ketones were similarly obtained, but in poor yields, accompanied by considerable decomposition.

We also found that trimethyl sulfoxonium bromide could be obtained by reaction of dimethyl sulfoxide and methyl bromide at 80-90° for 48 hours in a sealed tube. This was more convenient than preparation of the chloride salt,(4) thus the bromide was used for formation of the acyl oxosulfonium ylides.

Refereneces

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