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REACTIONS OF ACETAL-CONTAINING α-CHLOROKETONES WITH ETHANOLAMINE AND MERCAPTOETHANOL

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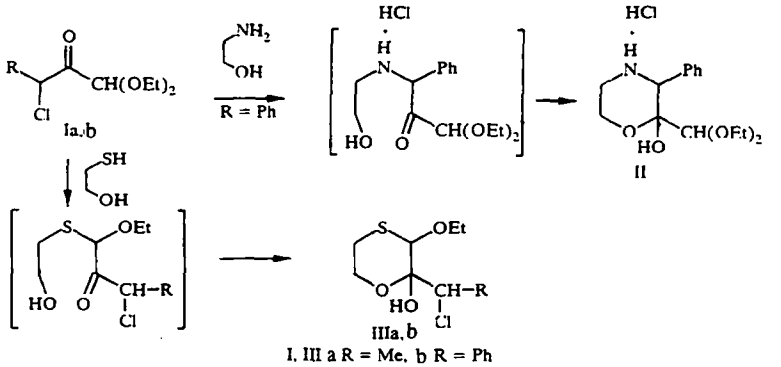
Polyfunctional ketones I react with binucleophiles at different reaction centers. For example, the chloroketone Ib reacts with ethanolamine by nucleophilic displacement of the chlorine atom to give an intermediate aminoketone, which subsequently undergoes heterocyclization to give the acetal-containing product II. On the other hand, compounds Ia and Ib react with mercaptoethanol initially at the acetal group which leads to synthesis of oxathiine derivatives via the intermediate O,S-acetals.



I, III a R = Me, b R = Ph

2-Hydroxy-2-diethoxymethyl-3-phenyl-2,3,5,6-tetrahydrooxazine-1,4 Hydrochloride (II). A solution of ethanolamine (0.48 g, 7.8 mmol) in methanol (10 cm^3) was added dropwise at room temperature to a solution of chloroketone Ib (2 g, 7.8 mmol) in absolute methanol (20 cm^3). The reaction mixture was stirred for 10 h. The solvent was removed in vacuum and the resulting white crystals were washed with acetone and dried in vacuum. Yield 2.12 g (85%). M.p. 162-164°C. IR spectrum (Nujol mull): 3420 cm^{-1} (OH). ^1H NMR spectrum (DMSO-D_6): 1.10 (6 H, t, $OCH_2\underline{CH_3}$), 2.85 (2 H, m, NCH_2), 3.55 (2 H, m, OCH_2), 3.90 (1 H, s, CH), 4.37 (4 H, m, $O\underline{CH_2}CH_3$), 6.80 (1 H, s, $\underline{CH}Ph$), 7.35 (3 H, m, Ph), 7.62 (2 H, m, Ph), 8.13 (1 H, br s, OH), 10.00 ppm (2 H, br s, NH_2^+). ^{13}C NMR spectrum (DMSO-D_6): 14.95 and 15.12 (t, $\underline{CH_3}CH_2O$), 55.39 (t, NCH_2), 57.41 (t, OCH_2), 61.12 (d, NCH), 62.64 and 64.67 (t, $CH_3\underline{CH_2}O$), 95.43 (s, C−OH), 101.95 ppm (d, CHO_2). Found, %: N 4.65, Cl 11.54. Calc. for $C_{15}H_{23}NO_4 \cdot HCl$, % N 4.41, Cl 11.18.

2-Hydroxy-2-(α-chloroethyl)-3-ethoxy-2,3,5,6-tetrahydrooxathiin-1,4 (IIIa) was obtained analogously from chloroketone Ia (3 g, 15.3 mmol) and mercaptoethanol (1.24 g, 15.3 mmol) in absolute methanol at room temperature for 5 h. Yield 2.8 g (80%). IR spectrum (Nujol mull): 3490 cm^{-1} (OH). ^1H NMR spectrum (DMSO-D_6): 1.12 (3 H, t, $\underline{CH_3}CH_2O$), 1.45 (3 H, d, $\underline{CH_3}CH$), 2.81 (2 H, m, SCH_2), 3.47 (2 H, m OCH_2), 4.00 (2 H, m, $\underline{CH_3}CH_2O$), 4.41 (1 H, s, OH), 5.61 (1 H, br s, OH). ^{13}C NMR spectrum (DMSO-D_6): 17.45 (q, $\underline{CH_3}CHCl$), 20.52 (q, $\underline{CH_3}CH_2O$), 23.17 (t, SCH_2), 62.93 (d, CHCl), 63.94 (t, OCH_2), 66.65 (t, $CH_3\underline{CH_2}O$), 81.26 (d, OCHS), 96.90 ppm (s, COH). Found, %: Cl, 15.85, S 14.13. Calc. for $C_8H_{15}ClO_3S$, %: Cl 15.67, S 14.15.

2-Hydroxy-2-chlorobenzyl-3-ethoxy-2,3,5,6-tetrahydrooxathiine-1,4 (IIIb) was obtained by an analogous method. Yield 51%. M.p.123-125°C. IR spectrum (Nujol mull): 3485 cm^{-1} (OH). ^1H NMR spectrum (DMSO-D_6): 1.25 (3 H, t, $\underline{CH_3}CH_2O$), 2.95 (2 H, m, SCH_2), 3.51 (2 H, m, $CH_3\underline{CH_2}O$), 4.52 (1 H, s, CH), 5.20 (1H, s, OH), 7.85 (3 H, m, Ph), 7.47 ppm (2 H, m, Ph). Found, %: Cl 12.65, S 11.15. Calc. for $C_{13}H_{17}ClO_3S$, %: Cl 12.31, S 11.09.

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