Novel Rearrangement of *N*-Chloroacetylamines

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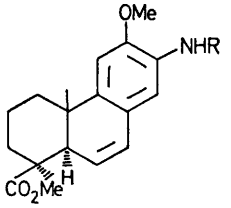
Summary *N*-Chloroacetylamines on photolysis in methanol give the rearranged *N*-substituted glycine esters along with the unrearranged methyl ethers.

Witkop *et al.*[1] and Yonemitsu *et al.*[2] have utilized the photochemical cyclization of *N*-chloroacetyl derivatives of various amines for the syntheses of ten- and six-membered

heterocycles. We were interested in the cyclization of a chloroacetyl derivatives of an oestrogenic amine (Ia) obtained from podocarpic acid,[3] in order to obtain a heterosteroidal system and thus undertook the photolysis of (Ia) (125 W mercury arc lamp, immersion type quartz reactor, 0·01 M solution in methanol, irradiated for 1 h).

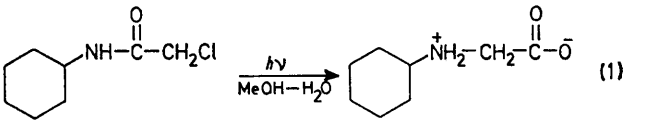


(I)

a; R = $C(O)CH_2Cl$
b; R = $C(O)CH_2OMe$
c; R = $CH_2C(O)OMe$

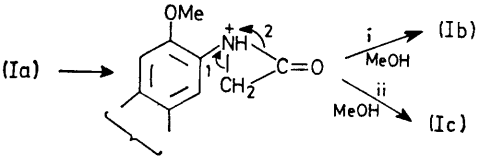
Two compounds, (Ib), m.p. 182 °C and (Ic), m.p. 162—163 °C, were isolated in 40 and 30% yields, respectively, after the removal of the solvent under reduced pressure and repeated fractional crystallizations from methanol. No cyclized product was isolated. Structures of compounds (Ib) and (Ic) have been confirmed by their n.m.r. spectra.

N-Chloroacetylcyclohexylamine (m.p. 116 °C) in MeOH–H_2O (8:2) as solvent under the same conditions of photolysis gave *N*-cyclohexylglycine, m.p. 232 °C (lit.[4] m.p. 229 °C), in *ca.* 20% yield [equation (1)].



(1)

The amino-acid exists in the dipolar, *i.e.* zwitterionic form as evidenced by the appearance of bands in its i.r. spectra, ν (KBr) 6·17 and 6·34 (carboxylate anion) and 3·15 and 3·28 ($-NH_2-$) μm.[5]



SCHEME

The mechanism for these reactions has not been established, but one possibility involving an α-lactam (Scheme) is supported by our recent finding that ionic intermediates are formed in the photolysis of *N*-chloroacetyl derivatives in alcohols.[6]

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