INTRAMOLECULAR DARZENS CONDENSATION OF 1,3-DIMETHYL-6-PHENYL-3-CHLOROACETOXY-4-PIPERIDONE

G. V. Pshenichnyi, A. P. Lugovskii,
and V. A. Mashenkov

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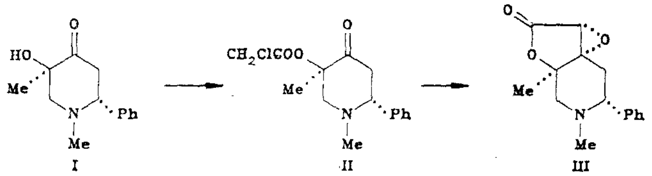
The Darzens condensation has been used extensively in organic synthesis [1]. Only a few instances of the intramolecular version of this reaction have, however, been reported [1, 2]. We have found that the 3-chloroacetoxy-4-piperidone (II) undergoes an intramolecular Darzens condensation in the presence of potassium tert-butoxide to give the epoxylactone (III).



1,3-Dimethyl-6-phenyl-3-chloroacetoxy-4-piperidone (II). To a solution of 21.9 g (0.1 mole) of the piperidone (I) [3] in 100 ml of dichloromethane was added 14.2 g (0.125 mole) of chloroacetyl chloride and 18.8 g (0.125 mole) of diethylaniline. The mixture was kept for 2 h at 20°C, washed with saturated sodium bicarbonate solution and water, dried over Na_2SO_4, the solvent removed, and the residue crystallized from benzene—hexane (1:1) to give 20.3 g (69%) of product, mp 66-67°C. IR spectrum (C_2Cl_4): 1745, 1775 cm^{-1}. PMR spectrum ($CDCl_3$): 1.77 (s, $3\text{-}CH_3$); 2.02 (s, $N\text{—}CH_3$); 2.57 (d.d, J = 16.2 and 3.5 Hz, $5\text{-}H_e$); 2.69 (d.d, J = 16.2 and 11.0 Hz, $5\text{-}H_a$); 3.02 (s, $2\text{-}CH_2$), 3.39 (d.d, J = 11.0 and 3.5 Hz, $6\text{-}H_a$); 4.06 and 4.10 (two d, J = 14.4 Hz, CH_2Cl); 7.22-7.35 ppm (m, C_6H_5).

6,8a,r-Dimethyl-2-oxo-5c-phenyl-3c,9c-epoxyfuro[2,3-c]piperidine (III). To a solution of 2.95 g (0.01 mole) of (II) in 15 ml of THF was added with stirring at 0-5°C a solution of 1.35 g (0.012 mole) of potassium t-butoxide in 20 ml of THF. The mixture was kept for one hour, neutralized with acetic acid, and diluted with water. The solid which separated was washed and dried to give 2.07 g (80%) of product, mp 124-125°C. IR spectrum (CCl_4): 1795 cm^{-1}. PMR spectrum ($CDCl_3$): 1.61 (s, $8\text{-}CH_3$); 1.73 (d.d, J = 14.1 and 3.3 Hz, $4\text{-}H_e$); 2.00 (s, $N\text{—}CH_3$); 2.21 (d, J = 11.5 Hz, $7\text{-}H_a$); 2.35 (d.d, J = 14.1 and 11.5 Hz, $4\text{-}H_a$); 3.11 (d.d, J = 11.5 and 3.3 Hz, $5\text{-}H_a$); 3.16 (d, J = 11.5 Hz, $7\text{-}H_e$); 3.68 (s, 3-H); 7.20-7.48 ppm (m, C_6H_5).

The elemental analyses of the products were in agreement with the calculated values.

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