REARRANGEMENT OF 2,4,4-TRIMETHYL-5-PHENYL-4H-IMIDAZOLE 1-OXIDE TO 2,4,4-TRIMETHYL-1-PHENYL-2-IMIDAZOLIN-5-ONE

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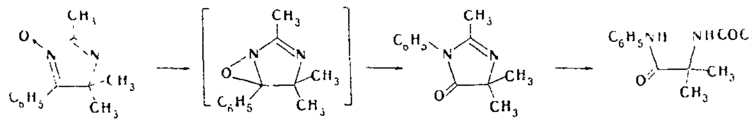
A compound with the composition $C_{12}H_{14}N_2O \cdot HCl$ (III, ~35%, mp 178-180°) is formed when solutions of 2,4,4-trimethyl-5-phenyl-4H-imidazole 1-oxide (I) or 5-ethoxy-2,4,4-trimethyl-5-phenyl-2-imidazolinium chloride 1-oxide (II) in anhydrous alcohol are refluxed in the presence of HCl for 5 h. An intense band of a C = O group (1790 cm^{-1}) appears in the IR spectrum of the product, and the band of a C = N group (1660 cm^{-1}) is retained. Absorption at 221 nm (log ε 4.09) is observed in the UV spectrum. The PMR spectrum of III contains the signals of protons of two equivalent methyl groups (1.66 ppm), a methyl group attached to a double bond (2.49 ppm), and the signal of protons of a phenyl ring. The presence in the C^{13} NMR spectrum of signals of three carbon atoms of methyl groups, carbon atoms of a phenyl ring, of carbon atoms in sp^2 and sp^3 hybrid states, and, particularly, of a carbon atom included in a carbonyl group at 177.9 ppm, together with other spectral characteristics, confirmed the 2,4,4-trimethyl-1-phenyl-2-imidazolin-5-one structure for III. Neutralization of hydrochloride III gave 2,4,4-trimethyl-1-phenyl-2-imidazolin-5-one [IV, $C_{12}H_{14}N_2O$, molecular weight (determined by high-resolution mass spectrometry) 202.1755 (calculated value 202.1753]; the absorption of the C = O (1755 cm^{-1}) and C = N (1650 cm^{-1}) groups is retained in its IR spectrum. Alkaline hydrolysis of imidazolone IV gave N-acetamido-α-aminoisobutyric acid anilide (V, mp 149-150°, IR spectrum: 1680, 1660, 1600, and 1550 cm^{-1}).

Thus the reaction consists in migration of the phenyl residue from the carbon atom to the adjacent nitrogen atom.

The reaction formally can be represented by a scheme including a step involving the formation of an oxaziridine ring (see [1]):



I IV V

We have not observed examples of a thermal rearrangement of this sort in the literature.

LITERATURE CITED

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