SYNTHESIS OF 3-(IMIDAZO[1,2-a]BENZIMIDAZOL-3-YL)PROPIONIC ACIDS AND THEIR DERIVATIVES

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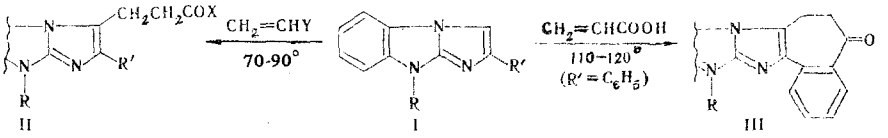
We have established that imidazo[1,2-a]benzimidazol-3-ylpropionic acids and their derivatives (II) are formed as a result of the substitutive addition of acrylic acid and its ester and nitrile to 2,9-disubstituted imidazo[1,2-a]benzimidazoles (I) in the 3 position. Particularly good results are obtained when the reaction is carried out in polyphosphoric acid (PPA) at 70-90°C; simultaneous saponification of the nitrile group to an amide group occurs in the case of acrylonitrile.

The use of PPA makes it possible to employ 1-alkyl-3-acylmethyl-2-iminobenzimidazolines, which readily undergo cyclization under the reaction conditions to give imidazo[1,2-a]benzimidazole derivatives I, for the synthesis of II.



R=CH_3, C_2H_5, C_3H_7; R'=CH_3, C_6H_5; X=OH, OCH_3, NH_2; Y=COOH, $COOCH_3$, CN

The results of elementary analysis of II were in agreement with the calculated values. Characteristic bands of dimerized carboxy groups appear in the IR spectra of acids II (X = OH) in mineral oil at 1690-1705 (CO) and at 920 and 2400-2800 cm^{-1} (OH); the spectrum of ester II (X = OCH_3) contains bands at 1735 (CO) and at 1050 and 1250 cm^{-1} (C-O-C). Two bands of moderate intensity at 3300 and 3150 cm^{-1} (NH), as well as a band of stretching vibrations of a CO group at 1690 cm^{-1}, are observed in the IR spectrum of amide II (X = NH_2). Signals of methylene protons of a propionic acid residue and residues of propionic acid derivatives appear in the PMR spectra of II (CF_3COOH) in the form of two triplets at 2.55-2.6 and 3.2-3.3 ppm with equal integral intensities.

When 2-phenylimidazol[1,2-a]benzimidazoles are heated with acrylic acid in PPA at 110-120°C, the reaction does not stop with the formation of acids II; the latter undergo further intramolecular cyclodehydration in the ortho position of the phenyl ring in the 2 position to give 6,7-dihydro-5-oxocycloheptено[5',6':4,5]imidazo[1,2-a]benzimidazoles III. IR spectrum ($CHCl_3$): 1682-1685 cm^{-1} (C=O). The signal at 3.15 ppm (q, 4H) in the PMR spectrum (CF_3COOH) can be assigned to the protons of the CH_2CH_2 group.

The following compounds were obtained [R, R', and X, melting points (°C), and yields (%) given]: II, CH_3, C_6H_5, OH, 270-271, 99; II, C_2H_5, C_6H_5, OH, 255-256, 100; II, CH_3, CH_3, OH, 251-252, 97; II, CH_3, C_6H_5, OCH_3, 132-133, 80; II, CH_3, C_6H_5, NH_2, 229-230, 99; III, CH_3, 227-228, 97; III, C_3H_7, 153, 95.

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