IMIDAZO[1,2-b]-1,2-BENZISOTHIAZOLES AND PYRIMIDO[1,2-b]-1,2-BENZISOTHIAZOLIUM SALTS

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We have shown that 3-amino-1,2-benzisothiazole, which was obtained in one step from ochlorobenzonitrile, sulfur, and ammonia [1], upon refluxing in alcohol for 4 or 2 h with α bromo ketones (the Chichibabin reaction) gives imidazo[1,2-b]-1,2-benzisothiazole hydrobromídes in 90 and 80% yields, from which the bases (Ia, b) were obtained by the action of ammonia.



I a R=Ph, b R=Me; II a, b R=Me, a A=CF₃CO_k, b A=ClO₄; c, d R=Ph; c A=CF_bCO_g, d A=ClO₄; III a R=H, A=ClO₄, b X₂=O, R=Me, A=CF₃CO₂

When 3-amino-1,2-benzisothiazole is maintained with acetylacetone or benzoylacetone in trifluoroacetic acid at room temperature for 3 days with subsequent precipitation of the products by means of ether, it is converted to trifluoroacetates IIa,c in 54 and 36% yields; IIa, c were converted to perchlorates IIb, c by the action of perchloric acid in acetic acid, Heterocyclic systems I and II were previously unknown; the closest analogs to them previously described are individual hydrogenated S,S-dihydroxy derivatives. The position of the phenyl group in salts IIc,d was determined from the PMR spectra, in which it gives two groups of bands with a distance of ~ 0.7 ppm between them; this is characteristic for the 2 position in condensed pyrimidinium salts with a nitrogen atom in common. The use of 1,1,3,3-tetraethoxypropane in this reaction leads to salt IIIa in 70% yield, whereas salt IIIb was obtained in 29% yield when 3-amino-1,2-benzothiazole 1,1-dioxide was heated with acetylacetone in trifluoroacetic acid. Compound Ia had mp 169-170°C (from CH₃CN); Ia.HBr had mp 208-210°C (CH₃CN); Ib had mp 179-180°C (CH₃CN); PMR spectrum [CF₃COOH, hexamethyldisiloxane (HMDS]: 2.03 (s, 3H, 2-CH₃), 6.62 (s, 1H, 3-H), 7.35 (d, 1H, 9-H, J₉₋₈ = 5 Hz), and 6.8-7.2 ppm (m, 3H, 6-H, 7-H, 8-H). Compound IIa had mp 75-76 $^{\circ}$ C (reprecipitated from CF₃COOH by means of ether); PMR spectrum: 2.60 (s, 3H, 2-CH₃), 2.65 (s, 3H, 4-CH₃), 7.25 (s, 1H, 3-H), 7.3-7.7 (m, 3H, 7-, 8-, 9-H), 8.20 (d, 1H, 10-H, J_{10,9} = 7 Hz); IIb had mp 149-151°C (from absolute ethanol); IIc had mp 94-95°C (after purification by the method used for IIa); PMR spectrum: 2.56 (s, 3H, 4-CH₃), 6.78 (s, 1H, 3-H), 7.0-7.5 (m, 3H, meta and para protons of $2-C_6H_5$), 7.6-7.8 (m, 3H, 7-H, 8-H, 9-H), 7.8-8.1 (m, 2H, ortho protons of $2-C_6H_5$), and 8.45 ppm (d, IH, 10-H, J₁₀, = 6.5 Hz); IId had mp 159°C (dec., CH₃NO₂); IIIa had mp 110°C (dec., absolute ethanol); IIIb had mp 263-264°C (CH₃CN); PMR spectrum: 2.48 (s, 6H, 2CH₃) and 7.0-7.7 ppm (m, 9H, ethylene and aromatic protons).

The results of elementary analysis of the compounds obtained were in agreement with the calculated values.

LITERATURE CITED

1. H. Fleig and H. Hagen, West German Patent No. 2609864; Chem. Abstr., 88, 6867 (1978).

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