

Studies in Heterocyclics: Synthesis of 7-Substituted 3-Phenyl-1*H*-imidazo[1,2-*a*]benzimidazoles

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Abstract

Some new 7-substituted 3-phenyl-1*H*-imidazo[1,2-*a*]benzimidazoles have been synthesized by the thermal rearrangement of 3-(*o*-amino-substituted phenyl)-2-imino-4-phenyl-4-thiazoline. A mechanism of formation of the products is suggested.

In a previous communication we have described the synthesis of hydroxybenzimidazoles¹ and benzothiazines.² This paper describes the novel and unambiguous synthesis of some new 7-substituted 1*H*-imidazo[1,2-*a*]benzimidazoles (1) (Table 1). These compounds are of interest, because of their structural similarity to the benzimidazole moiety [5,6-dimethyl-1-(α -D-ribofuranosyl)benzimidazole] of vitamin B₁₂.³

Compounds (1) have been obtained by the thermal rearrangement of 3-(*o*-amino-substituted phenyl)-2-imino-4-phenyl-4-thiazoline in dry toluene.

Table 1. 7-Substituted 3-phenyl-1*H*-imidazo[1,2-*a*]benzimidazoles (1)

R in (1)	M.p. (°C)	Molecular formula	Found (%)			Required (%)		
			C	H	N	C	H	N
H	246	C ₁₅ H ₁₁ N ₃	77.1	4.7	18.0	77.2	4.7	18.0
Me	237	C ₁₆ H ₁₃ N ₃	77.6	5.1	17.1	77.7	5.2	17.0
OMe	216	C ₁₆ H ₁₃ N ₃ O	72.8	4.8	15.8	73.0	4.9	15.9
OEt	208	C ₁₇ H ₁₅ N ₃ O	73.4	5.3	15.0	73.6	5.4	15.1
Br	264	C ₁₅ H ₁₀ BrN ₃	51.4	3.1	13.3	51.6	3.2	13.4
OH	197	C ₁₅ H ₁₁ N ₃ O	72.1	4.2	16.7	72.2	4.4	16.8

The infrared spectrum of (1) falls in three regions: 760–880 cm⁻¹ (imidazole ring), 1550–1620 cm⁻¹ (aromatic C–N and C=C bond), 2600–3200 (associated NH bond). The broad absorption band at 3200–2600 cm⁻¹ is attributed to the internal vibration which became intense by a Fermi-type interaction with the fundamental NH stretching vibration.⁴ Bands at 1680–1600 and 1585–1500 cm⁻¹ have been

¹ Soni, R. P., and Saxena, J. P., *Bull. Chem. Soc. Jpn*, 1979, **52**, 2033; 3096.

² Soni, R. P., and Jain, M. L., *Tetrahedron Lett.*, 1980, **21**, 3795.

³ Eggers, H. J., and Tamm, I., *J. Exp. Med.*, 1961, **113**, 657.

⁴ Bassignana, P., Cogrisi, C., Gandino, M., and Merli, P., *Spectrochim. Acta*, 1965, **21**, 605.

assigned to ring vibration.⁵ The n.m.r. spectrum ($(\text{CD}_3)_2\text{SO}$) of (1; $\text{R} = \text{H}$) shows signals at δ 6.5–7.7 (10H, m, ArH) and 8.20 (1H, s, flat peak NH). The mass spectrum⁶ of (1a) shows the molecular ion at m/e 233 (100%). In the mass spectrum prominent peaks also appeared at m/e 232 (40), 206 (83) and 179 (76), resulting by successive loss of H, HCN and 2HCN. Other ion peaks obtained were at m/e 205 (65), 152 (32), 142 (25), 117 (35), 116 (37), 115 (39), 91 (24), 90 (39). This fragmentation is consistent with the proposed structure.

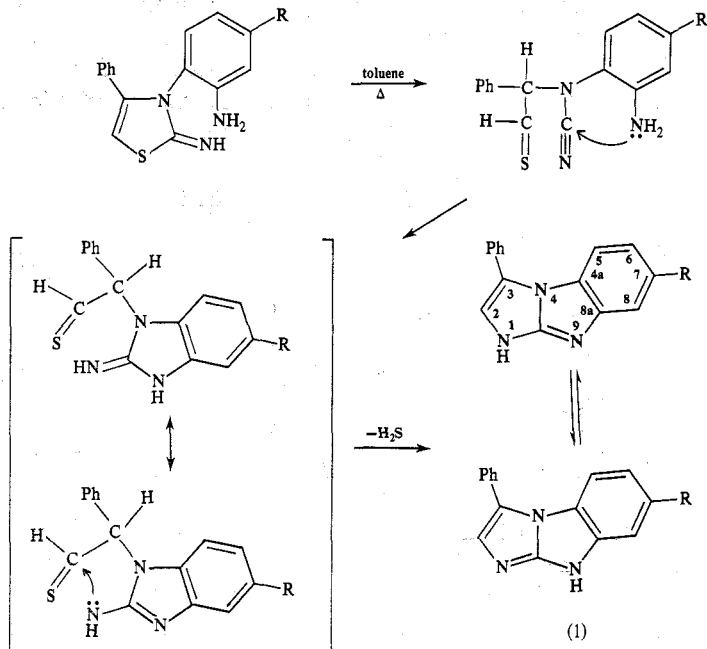
The absorption spectra of (1) (Table 2) shows a close resemblance with the structural related compounds.⁷

Table 2. Ultraviolet spectra

R	λ_{max} (nm)	$\log \epsilon$
H	244, 272, 279	3.74, 3.71, 3.79
Me	241, 273, 277	3.70, 3.72, 3.75
OMe	245, 271, 284	3.62, 3.84, 3.92
OEt	248, 269, 281	3.67, 3.77, 3.87
Br	250, 265, 275	3.69, 3.81, 3.95
OH	249, 270, 286	3.76, 3.77, 3.65

Reaction Mechanism

The mechanism of Scheme 1 is suggested for the formation of 3-phenyl-1*H*-imidazo[1,2-*a*]benzimidazoles.



Scheme 1

⁵ Bellocq, A. M., Perchard, D., Novak, A., and Josien, M., *J. Chim. Phys. Phys.-Chim. Biol.*, 1965, **62**, 1334.

⁶ Porter, Q. N., and Baldas, J., 'Mass Spectrometry of Heterocyclic Compounds' (Interscience: New York 1971).

⁷ Steck, E. A., Nachod, F. C., Ewing, G. W., and Gorman, N. H., *J. Am. Chem. Soc.*, 1948, **70**, 3406.

Experimental

General

All the melting points have been determined on a Kofler instrument and are uncorrected. The u.v. absorption spectra were recorded on a Beckman DU-2 spectrophotometer in quartz cells of 1 cm path length. Infrared spectra were run in KBr wafers on a Perkin-Elmer Infracord-137 spectrophotometer; n.m.r. spectra were recorded on a Varian HA-100 spectrometer, and mass spectra were recorded on a Varian MAT CH7 instrument.

7-Substituted 3-Phenyl-1H-imidazo[1,2-a]benzimidazoles (I)

3-(o-Amino-substituted phenyl)-2-imino-4-phenyl-4-thiazoline⁸ (0.01 mol) in dry toluene (50 ml) was heated under reflux for 24 h, by which time evolution of H₂S had ceased. The solvent was removed under reduced pressure. The solid residue obtained was filtered, washed with benzene and dried. It was recrystallized from toluene/ethanol. The compounds were obtained in 45–60% yields.

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⁸ Vasudeva, S. K., Mahajan, M. P., and Ralhan, N. K., *Indian J. Chem.*, 1973, **11**, 1204.