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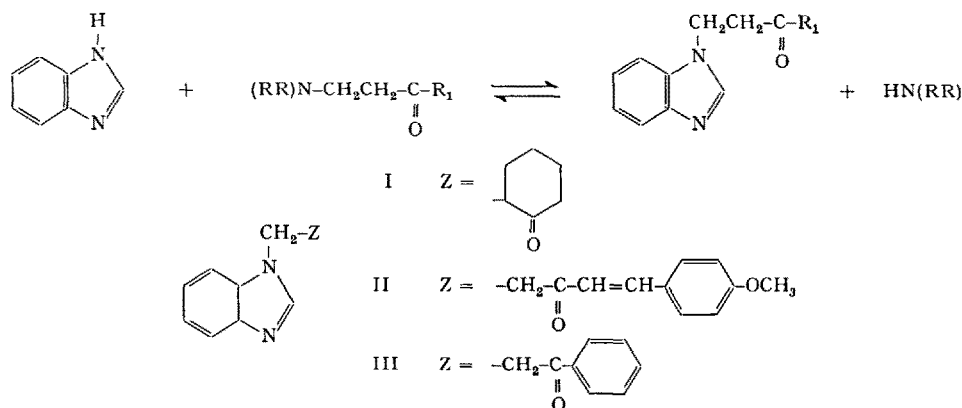
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β -Keto N-Substituted Benzimidazoles

We wish to report on the synthesis of new benzimidazoles, involving the addition of benzimidazole to α,β -ethylenic ketones. As a source of alkylating agent, we used Mannich bases which, under relatively mild conditions, suffer amine elimination to form a conjugated unsaturated system: the latter condenses with the benzimidazole. The reaction proceeds according to the Mannich-Robinson modification of the Michael condensation. Benzimidazole (0.04 mole) reacted with the appropriate dimethyl or diethylamino Mannich base (0.05 mole) in ethanol (50 ml) under reflux. The reaction was followed by observation of the elimination of the volatile amine.

1-(2-methylcyclohexanone)-benzimidazole (I). With 2-dimethylaminomethylcyclohexanone¹ the reaction time was

line residue was recrystallized from acetone-petrol ether to give a product, m.p. 129–131°C, yield 60%. Found: N 11.19; C₁₆H₁₄ON₂ requires N 11.20. UV λ_{max}^{EtOH} m μ (log ϵ): 249 (4.25). IR (KBr) 1670 cm⁻¹ (C=O), 3030, 770, 750, 690 cm⁻¹ (aromatic). *Oxime*, m.p. 138–142°. Found: N 15.69; C₁₆H₁₆ON₃ requires N 15.84. (B) In order to test the direct Michael condensation, benzimidazole (0.06 g, 0.05 mole) and phenyl-vinyl-ketone⁴ (0.66 g, 0.05 mole) were made to react 1 h in toluene (2 ml) under reflux and with *Triton B* as a catalyst. After cooling, the crystalline precipitate was collected and recrystallized from acetone-petrol ether to give a product, m.p. 126 to 128°, yield 51%. Identity with compound obtained from the Mannich base was confirmed by mixed melting point and mixed melting point of the oximes, UV- and IR-spectra⁵.



40 h. After concentration of the solvent, the viscous residue was chromatographed on silicic acid (Merck). Elutions from benzene-chloroform 3:1 and 1:1 gave a product which crystallized from benzene-petrol ether, m.p. 83–87°, yield 18%. Found: C 73.55, H 7.11, N 12.53; C₁₄H₁₆ON₂ requires C 73.65, H 7.06, N 12.27. UV λ_{max}^{EtOH} m μ (log ϵ): 255 (4.016). IR (KBr) 1705 cm⁻¹ (C=O), 3050, 740 cm⁻¹ (aromatic). *Oxime*, m.p. 190–192°. Found: N 17.21; C₁₄H₁₇ON₃ requires N 17.28.

1-(5p-anisyl 4-penten 3-one)-benzimidazole (II). With 1-diethylamino 5p-anisyl 4-penten 3-one² the reaction time was 17 h. After concentration of the solvent the viscous residue was chromatographed on aluminium oxide (Merck, neutral), and elutions from ether-benzene 1:1 gave a product which crystallized from benzene, m.p. 131–134°, yield 9%. Found: N 8.86; C₁₉H₁₈O₂N₂ requires N 9.14. UV λ_{max}^{EtOH} m μ (log ϵ): 236 (4.09), 325 (4.26). IR (KBr) 1680 cm⁻¹ (C=O), 1640, 960 cm⁻¹ (C=C), 3030, 765, 740 cm⁻¹ (aromatic). *Phenylhydrazone*, m.p. 125–127°. Found: N 14.34; C₂₅H₂₄ON₄ requires N 14.13.

1-(3-phenylpropane 3-one)-benzimidazole (III). (A) With β -dimethylaminopropiophenone³ the reaction time was 72 h. After concentration of the solvent, the crystal-

Résumé. L'addition nucléophile du benzimidazole aux cétones α,β -éthyléniques a été réalisée par la réaction de Michael modifiée selon Mannich-Robinson, utilisant les bases de Mannich comme source de cétones éthyléniques. La réaction a permis d'obtenir des dérivés N-substitués comportant une fonction cétone en position β .

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