ANTHRAQUINONEISOIMIDAZOLES

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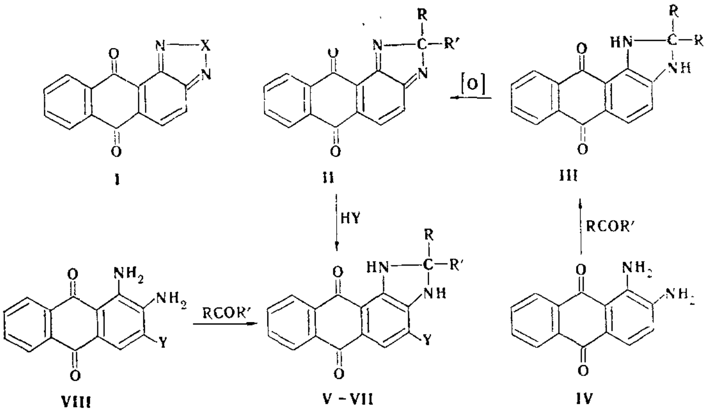
UDC 547.673'785.5

Heterocyclic anthraquinone derivatives of the I type readily undergo nucleophilic addition reactions that are not characteristic for compounds of the anthraquinone series owing to partial localization of the diene system in the ring adjoining the heteroring [1]. The same effect might have been expected in the case of the previously unknown anthraquinoneisoimidazoles (II), bearing in mind that the recently synthesized 2,2-pentamethylenebenzisoimidazole has clearly expressed unsaturated character [2].

EXPERIMENTAL

2,2-Dialkylanthra[1,2-d]imidazoline-6,11-diones (III). These compounds were obtained by heating 10 mmole of 1,2-diaminoanthraquinone (IV) with 20 mmole of cyclohexanone or acetone and 0.2 g of sulfuric acid in 10 ml of dimethylformamide at 50°C for 2 h. The yields ranged from 85 to 92%. Compound IIIa had mp 190-190.5°; λ_{max}, nm (log ε): 268 (4.66), 567 (4.21); ν_{CO} 1629, 1650 cm^{-1}. Compound IIIb had mp 229-230°; λ_{max}, nm (log ε): 268 (4.63), 570 (4.16); ν_{CO} 1630, 1648 cm^{-1}. Lead dioxide or manganese dioxide was added to a solution of 10 mmole of imidazoline III in 100 ml of dioxane at room temperature until the color changed from red–violet to brown–yellow (5-10 min) to give 2,2-dialkylanthra]1,2-d]isoimidazole-6,11-diones (II) in 70-75% yields. Compound IIa had mp 190° (decomp.), λ_{max}405 nm (log ε 3.36), and ν_{CO} 1670 cm^{-1}. Compound IIb had mp 195° (decomp.), λ_{max}, nm (log ε): 315 (3.76, shoulder), 405 (3.36); ν_{CO} 1679 cm^{-1}.



I X=O, S, Se, NAr; a RR′=$(CH_2)_5$, b R=R′=CH_3; V Y=Cl; VI Y=Br; VII Y=$C_6H_5SO_2$

Anthraquinoneisomidazoles II are distinguished by their high reactivities and they actively add various nucleophilic agents to give 4-substituted anthraquinoneimidazolines. Thus when a solution of 2 mmole of hydrochloric, hydrobromic, or benzenesulfonic acid in 3 ml of dioxane was added to a solution of 1 mmole of II in 10 ml of dioxane at room temperature, the red–violet coloration of imidazolines V-VII, respective tively, appeared immediately. The yields of V-VII ranged from 88 to 93%. Compound Va had mp 193.5-

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Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 855-856, June, 1974. Original article submitted July 25, 1973; revision submitted October 26, 1973.

194°; λ_{max}, nm (log ε): 270 (4.67), 552 (4.15); ν_{CO} 1640, 1659 cm^{-1}. Compound VIa had mp 199-199.5°; λ_{max}, nm (log ε): 271 (4.63), 550 (4.11); ν_{CO} 1635, 1659 cm^{-1}. Compound VIIa had mp 231-232°; λ_{max}, nm (log ε): 273 (4.68), 523 (4.15); ν_{CO} 1640, 1661 cm^{-1}. The structure of 4-substituted imidazolines V-VII was confirmed by alternative synthesis from the corresponding 3-substituted 1,2-diaminoanthraquinones (VIII).

The products were isolated by dilution of the solutions with water and were purified by chromatography of chloroform solutions on aluminum oxide with subsequent crystallization from alcohol (imidazolines) or benzene–hexane (isoimidazoles); the results of elementary analysis were in satisfactory agreement with the calculated values. The electronic absorption spectra were obtained from alcohol solutions of the imidazolines and from dioxane solutions of the isoimidazoles. The IR spectra were obtained from KBr pellets of the compounds.

LITERATURE CITED

1. M. V. Gorelik, in: Chemistry of Anthraquinone [in Russian], Khimiya, Moscow (1969), p. 5.
2. D. W. S. Latham, O. Meth-Cohn, and H. Suchitzky, Chem. Commun., 1040 (1972).