PYRYLIUM[2,3-b]INDOLE SALTS

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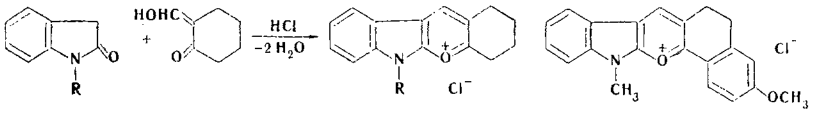
UDC 547.756.816

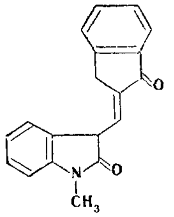
2-Ketoindoline and 1-methyl-2-ketoindoline condense with hydroxymethylene ketones in the presence of hydrogen chloride to give pyrylium[2,3-b]indole chlorides, which can be converted to 5-(3-oxindolyl)-Δ^2-pyrazolines by reaction with phenylhydrazine and to 5-(3-oxindolyl)-Δ^2-isoxazolines by reaction with hydroxylamine.

It is known [1] that the condensation of hydroxymethylene ketones with methyl or methylene ketones in the presence of perchloric acid results in the formation of pyrylium salts. In the present research it was demonstrated that, in the oxindole series, this reaction makes it possible to obtain the previously undescribed pyrylium[2,3-b]indole salts. The reaction is carried out in analogy with the recently described reaction of thiooxindole with β-diketones [2]: a methanol solution of equimolecular amounts of the reagents is cooled with ice and saturated with dry hydrogen chloride, as a result of which colored, crystalline products that generally retain solvent molecules are obtained. We obtained this sort of compound (I-III) by the reaction of 2-hydroxymethylenecyclohexanone with oxindole (2-ketoindoline) and 1-methyloxindole (1-methyl-2-ketoindoline) and also by the reaction of 2-hydroxymethylene-6-methoxy-1-tetralone with 1-methyloxindole. Intense absorption bands with maxima at 1640, 1590, and 1570 cm^{-1}, which are characteristic for the stretching vibrations of the C=C bonds of the pyrylium ring [3,4], appear in the IR spectra of I-III, but the carbonyl group band is absent.

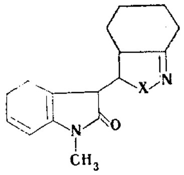


I R=H; II R=CH_3 III

However, the product of condensation of 1-methyl-2-ketoindoline with 2-hydroxymethylene-1-indanone does not cyclize to a pyrylium salt. A dark-red substance, to which we assign the 2-(1-methyl-2-ketoindolinyl-3-methylene)-1-indanone (IV) structure on the basis of the results of elementary analysis and IR spectroscopy, was isolated in good yield.



IV



V, VI

V X=NC_6H_5, VI X=O

In the case of 1-oxonium-2,3-tetramethylene-9-methylcarbazole chloride (II), we studied the reaction of the pyrylium[2,3-b]indole salts with some nucleophilic agents. When II is refluxed with excess ammonium acetate in acetic acid, it gives a complex mixture of products, from which the corresponding α-carboline could not be isolated by chromatography with a column filled with aluminum oxide. It is known [5] that

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Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1030-1032, August, 1972. Original article submitted May 25, 1971.

chromylium salts, which contain a benzene ring condensed with the pyrylium ring, are not converted to pyridine bases. Refluxing of II with excess phenylhydrazine in alcohol gives a colorless derivative, the IR spectrum of which contains the intense absorption band of a carbonyl group with a maximum at 1705 cm^{-1}, while NH group absorption is absent. The UV spectra contain absorption maxima at 283 nm (log ε 3.89) (in alcohol) and at 219 and 267 nm (log ε 3.00 and 2.99) (in alcoholic alkali solution), which closely recalls the UV spectra of 1-methyl-2-ketoindoline in the same solvents. We were unable to acetylate this product with a mixture of acetic anhydride and pyridine; when it is refluxed in acetic acid, it is cleaved to 1-methyl-2-ketoindoline and 2-phenyltetrahydroindazole. On the basis of these data and the results of elementary analysis, we assigned the 1-phenyl-3,4-tetramethylene-5-(1-methyl-2-keto-3-indolinyl)-Δ^2-pyrazoline (V) structure to the compound obtained.

Compound II reacts similarly with hydroxylamine, as a result of which 3,4-tetramethylene-5-(1-methyl-2-keto-3-indolinyl)-Δ^2-isoxazoline (VI), the structure of which was also proved by IR and UV spectroscopy and elementary analysis, is formed.

EXPERIMENTAL

1-Oxonium-2,3-tetramethylenecarbazole Chloride (I). A solution of 2.66 g (0.02 mole) of 2-ketoindoline and 2.52 g (0.02 mole) of 2-hydroxymethylenecyclohexanone in 10 ml of methanol was cooled with ice and saturated with dry hydrogen chloride, after which the mixture was diluted with an equal volume of absolute ether and allowed to stand in a refrigerator for several hours. The resulting crystalline precipitate was removed by filtration and washed thoroughly on the filter with absolute ether to give 82% of I with mp 190-192°. Found: C 64.8; H 5.5; Cl 12.6; N 5.2%. $C_{15}H_{14}ClNO \cdot H_2O$. Calculated: C 64.9; H 5.8; Cl 12.8; N 5.0%. IR spectrum (in completely fluorinated paraffin), cm^{-1}: 3400 (NH, broad band), 1640, 1590, and 1570 (pyrylium ring C=C).

1-Oxonium-2,3-tetramethylene-9-methylcarbazole Chloride (II). This compound was similarly obtained in 96% yield from 1-methyl-2-ketoindoline and 2-hydroxymethylenecyclohexanone and had mp 141°. Found: C 61.8; H 6.7; Cl 11.2; N 5.2%. $C_{16}H_{16}ClNO \cdot 2H_2O$. Calculated: C 62.0; H 6.5; Cl 11.4; N 4.5%. IR spectrum (in completely fluorinated paraffin), cm^{-1}: 3400 (NH, broad band), 1640, 1590, and 1570 (pyrylium ring C=C). UV spectrum* (in water): λ_{max} 253, 284, and 344 nm (log ε 3.28, 3.18, and 3.56).

3-Methoxy-12-methyl-5,6-dihydro-13-oxoniumindolo[3,2-b]phenanthrene (III). This compound was similarly obtained in 37% yield from 1-methyl-2-ketoindoline and 2-hydroxymethylene-6-methoxy-1-tetralone and had mp 236°. Found: C 70.2; H 5.6; N 3.6%. $C_{21}H_{18}ClNO_2 \cdot \frac{1}{2}C_2H_5OH$. Calculated: C 70.5; H 5.6; N 3.7%. IR spectrum (in completely fluorinated paraffin), cm^{-1}: 3400 (NH, broad band), 1635, 1600, and 1550 (pyrylium ring C=C).

2-(1-Methyl-2-keto-3-indolinylmethylene)-1-indanone (IV). This compound [2.4 g (83%)] was similarly obtained from 1.47 g (0.01 mole) of 1-methyl-2-ketoindoline and 1.49 g (0.01 mole) of 2-hydroxymethylene-1-indanone. The dark-red product had mp 151° (from alcohol). Found: C 78.6; H 5.4; N 4.8%. $C_{19}H_{15}NO_2$. Calculated: C 78.9; H 5.2; N 4.8%. IR spectrum (in mineral oil), cm^{-1}: 1670, 1580, 1530, 1250, 940, 780, and 730. UV spectrum (in methanol): λ_{max} 212, 258, and 399 nm (log ε 4.37, 4.14, and 4.02).

1-Phenyl-3,4-tetramethylene-5-(1-methyl-2-keto-3-indolinyl)-Δ^2-pyrazoline (V). A 1.3-g (12 mmole) sample of phenylhydrazine was added to a solution of 1.9 g (6 mmole) of II in 20 ml of methanol, and the mixture was refluxed for 1 h and poured into 100 ml of water. The aqueous mixture was filtered, and the solid was crystallized from methanol to give 1.4 g (74%) of V with mp 232°. Found: C 76.3; H 6.8; N 12.4%. $C_{23}H_{22}N_3O$. Calculated: C 76.5; H 6.7; N 12.2%.

3,4-Tetramethylene-5-(1-methyl-2-keto-3-indolinyl)-Δ^2-isoxazoline (VI). A solution of 0.9 g (3 mmole) of II in 10 ml of methanol was refluxed for 1 h with 0.4 g (6 mmole) of $NH_2OH \cdot HCl$ in the presence of 0.5 g (6 mmole) of sodium acetate to give 0.8 g (100%) of VI with mp 144°. Found: N 10.3%. $C_{16}H_{18}N_2O_2$. Calculated: N 10.3%. IR spectrum (in mineral oil), cm^{-1}: 1700, 1610, 1495, 1355, 1130, 1090, 860, 770. UV spectrum (in methanol): λ_{max} 283 nm (log ε 3.00).

Cleavage of Pyrazoline V. Pyrazoline V, obtained by treatment of 2.2 g (7 mmole) of pyrylium salt II with phenylhydrazine, was refluxed without purification in 20 ml of acetic acid for 1 h. The mixture was poured into water, and the product was extracted with chloroform. The extract was washed thoroughly with water, concentrated to a small volume, and passed through a column packed with aluminum oxide to

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*Recorded with a Specord spectrophotometer.

give 1.3 g (93%) of 2-phenyltetrahydroindazole with mp 49°. The picrate had mp 126° [6]. Also obtained were 0.45 g (50%) of 1-methyl-2-ketoindoline and 0.3 g of an unidentified substance with mp 126°. Found (for the latter): C 66.4; H 6.9; N 18.2%. $C_{21}H_{27}N_5O_2$. Calculated: C 66.1; H 7.0; N 18.3%. We did not, however, study this compound.

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