DIAZOCARBONYL DERIVATIVES OF HETEROCYCLES.

6.* INTRAMOLECULAR REACTIONS OF 2-CARBOMETHOXY-3-DIAZOACETYLQUINOLINE

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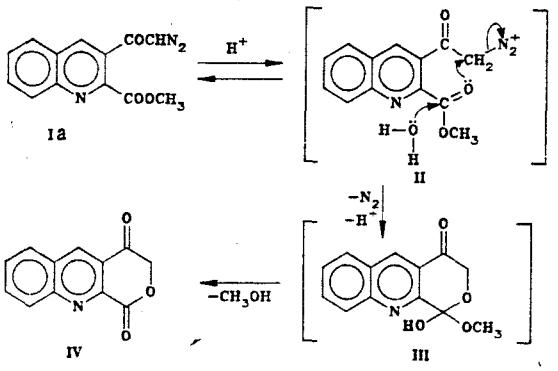
Treatment of 2-carbomethoxy-3-diazoacetylquinoline with mineral acids results in an intramolecular reaction leading to the formation of 6H-2,5-dioxopyrano-[3,4-b]quinoline; in the presence of bases the intramolecular condensation product is 2-diazo-1,3-dioxocyclopenteno[4,5-b]-quinoline. Treatment of 2-carbomethoxy-3-diazoacetylquinoline with sodium methoxide results in a reversible intramolecular rearrangement via migration of the diazomethine fragment and formation of the isomeric 3-carbomethoxy-2-diazoacetylquinoline.

ortho-Carbomethoxy derivatives of 3-diazoacetylpyridines react with mineral acids via an intramolecular cyclization pathway to form aza-analogs of isochroman-1,4-dione [2]; in the presence of base, in contrast, these compounds undergo intramolecular condensation reactions to give 2-diazo-4- or 5-azaindane-1,3-dione products [3]. Use of sodium methoxide as base led us to the discovery of a new type of ring-chain rearrangement reaction of o-carbomethoxy-diazoacetylpyridines, which leads to the formation of an equilibrium mixture of isomeric diazoketones [3].

In the present paper we have examined the intromolecular reactions of 2-carbomethoxy-3-diazoacetylquinoline (Ia).

Diazoketone Ia was prepared by acylation of diazomethane with the acid chloride derivative of 2-carbomethoxy-3-quinolinecarboxylic acid. Treatment of Ia with mineral acids (10% $CHlO_4$, 10% H_2SO_4, 10% HCl) has been demonstrated to lead to an intramolecular cyclization process, which generates 6H-2,5-dioxopyrano[3,4-b]quinoline (IV) as the reaction product.



The mechanism of this reaction probably involves initial protonation of the diazomethine carbon atom, intramolecular nucleophilic substitution of the diazonium group by the oxygen atom of the CO_2CH_3 carbonyl group, followed by subsequent conversion of intermediate III to compound IV via elimination of CH_3OH.

The IR spectrum of compound IV contains, in addition to the weak C=N and C=C stretching vibrations bands for the quinoline ring in the 1610-1583 cm^{-1} region, intense absorption bands at 1748 and 1703 cm^{-1}, corresponding to the C = O groups of the δ-lactone and ketone functional groups, respectively, [2]. The PMR spectrum (CF_3COOH) shows, in addition to the signals for the four aromatic protons of the quinoline ring, at 8.20-8.86 ppm, singlets for the two protons of the δ-lactone methylene group, at 5.64 ppm, and for the proton in the 4-position

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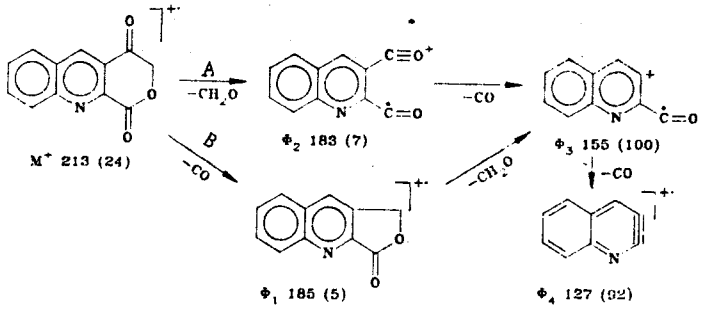
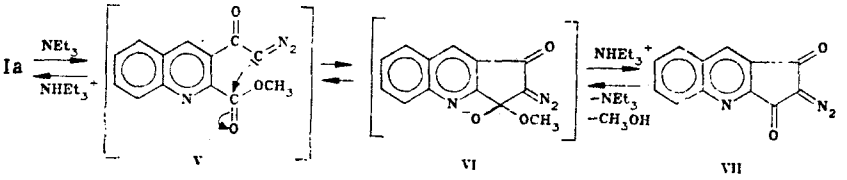
of the quinoline ring, at 9.96 ppm. The mass spectrum of compound IV exhibits an intense molecular ion peak at M^+ 213, whose further decomposition can take place via two pathways: path A, loss of a molecule of formaldehyde and formation of a Φ_2 ion (183), which can subsequently lose two molecules of CO to form Φ_4 ion (127); and path B, initial loss of a CO molecule and the formation of Φ_1 ion (185), with further cleavage of CH_2O (Φ_3 ion) and CO molecules (Φ_4 ion).

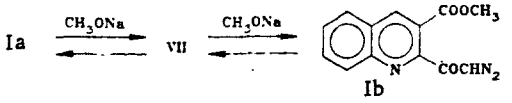


An investigation of the base-catalyzed intramolecular reactions of diazoketone I revealed that in the presence of triethylamine an intramolecular condensation reaction takes place, leading to the formation of 2-diazo-1,3-dioxocyclopenteno[4,5-b]quinoline (VII).



The first stage of this reaction probably involves deprotonation of the diazomethane fragment in Ia via reaction with triethylamine, which gives an intermediate carbanion V. Subsequent Dieckman-type intramolecular condensation and elimination of CH_3OH would lead to the formation of compound VII, whose IR spectrum shows intense absorption bands at 2105 (N≡N group) and 1700 cm^{-1} (C=O group). The PMR spectrum exhibits signals due only to the five aromatic protons of the quinoline ring. The mass spectra of compound VII contains an intense M^+ molecular ion peak at 223; fragmentation of the latter involves initial elimination of a N_2 molecule and accompanying Wolff rearrangement, followed by stepwise elimination of two CO molecules to give ions at (167) and (139). The overall scheme for mass spectral decompsition of compound VII is entirely consistent with the mass spectral fragmentation data for other known 2-diazo-1,3-dicarbonyl compounds [4].

It was also found that use of sodium methoxide as the base catalyst in the reaction of Ia caused the reaction to proceed further, and not to stop at the formation of 2-diazo-1,3-dicarbonyl compound VII, resulting in acyl cleavage of compound VII and the formation of an equilibrium mixture of starting diazoketone Ia and its isomeric derivative, 3-carbomethoxy-2-diazoacetylquinoline (Ib).



The mechanism of this reaction is probably analogous to the mechanism outlined previously for reversible equilibrium intramoleclar rearrangement of o-carbomethoxydiazoacetylpyridines [3]. The properties of diazoketone Ib agree with the literature data [5].

This study of the intramolecular reactions of 2-carbomethoxy-3-diazoacetylquinoline has allowed us to broaden the scope of the class of o-carbomethoxydiazoacetylazine derivatives which conform to the general principles of intramolecular interaction of the diazocarbonyl fragment and the ester functional group, under conditions of both acid- and base-catalyzed reactions.

EXPERIMENTAL

IR spectra were recorded on a Specord 75-IR spectrophotometer using vaseline mulls; UV spectra were obtained on a Specord UV-Vis spectrophotometer using methanol solutions. The PMR spectra of compounds Ia and VII were obtained on a Tesla BS-497 spectrometer (100 MHz) using $CDCl_3$ solutions, while the spectrum of compound IV was measured on a Varian FT-80 spectrometer for a CF_3COOH solution. TMS was used as internal standard. Mass spectra were obtained on an MX-1303 spectrometer with direct sample introduction to the ionizing stream, and at an electron energy of 50 eV, 150 μamp emission current, and temperatures of 70-140°C. Silica gel L 40/100 was used for column chromatography. The purities of substances were assessed by TLC using a benzene–ethyl acetate eluent system on Silufol UV-254 plates. The starting material, 2-carbomethoxy-3-quinolinecarboxylic acid, was prepared according to [6].

2-Carbomethoxy-3-diazoacetylquinoline (Ia). A mixture of 2.3 g (10 mmole) of 2-carbomethoxy-3-quinolinecarboxylic acid and 10 ml thionyl chloride was refluxed for 4 h. Excess thionyl chloride was evaporated at reduced pressure, and the residue was suspended in 20 ml dry ether. The resulting suspension was added in small portions to a cooled (–10°C) solution of diazomethane in ether with stirring; the latter solution had been obtained from 10 g nitrosomethylurea in 90 ml ether. The reaction temperature was raised to 20°C and stirring was continued for another 30 min. Nitrogen was bubbled through the solution to remove excess diazomethane, the solvent was removed by evaporation at reduced pressure, and the residue was chromatographed on a silica gel column. Yield 2.17 g (85%), mp. 95-96°C (benzene–hexane), R_f 0.34 (benzene–ethyl acetate, 4:1). IR spectrum: 2110 (N≡N), 1725, 1620 (C=O), 1600 cm^{-1} (C=N, C=C). UV spectrum: λ_{max} (log ε): 247 (3.91), 294 nm (3.37). PMR spectrum: 4.14 (3H, s, CO_2CH_3) 5.98 (1H, s, CHN_2); 7.66-8.33 (4H, m, C_6H_4); 8.39 ppm (1H, s, 4-H. Mass spectrum, m/e (I/I_{max}, %): 227 (29), 214 (19), 186 (17), 156 (47), 143 (16), 140 (21), 137 (14), 129 (37), 128 (100), 127 (29).

6H-2,5-Dioxopyrano[3,4-b]quinoline (IV). A solution of 0.51 g (2 mmole) diazoketone Ia in 10 ml methanol was treated with 0.5 ml 10% H_2SO_4 (10% $HClO_4$, 10% HCl). The reaction mixture was maintained at 20°C for 6 h, the methanol was evaporated at reduced pressure, and the residue was stored at 5°C for 8 h. The resulting precipitate was removed by filtration and recrystallized from benzene–hexane. Yield 0.31 g (72%), mp 197-198°C. IR spectrum: 1748, 1703 (C=O), 1610, 1585 cm^{-1} (C=N, C=C). UV spectrum, λ_{max} (log ε): 245 (4.59), 263 sh (4.11), 294 nm (3.67). PMR spectrum: 5.64 (2H, s, CH_2), 8.20-8.86 (4H, m, C_6H_4), 9.96 ppm (1H, s, 4-H).

2-Diazo-1,3-dioxocyclopenteno[4,5-b]quinoline (VII). A solution of 0.51 g (2 mmole) diazoketone Ia in 5 ml methanol was treated with 0.2 ml triethylamine. The reaction mixture was stirred at 20°C for 2 h; the resulting precipitate was removed by filtration and recrystallized from benzene–hexane. Yield 0.31 g (70%), mp 240-242°C, R_f 0.59 (benzene–ethyl acetate, 4:1). IR spectrum: 2105 (N≡N), 1700 (C=O), 1600, 1570 cm^{-1} (C=N, C=C). UV spectrum, λ_{max} (log ε): 273 (3.95), 307 nm (3.39). PMR spectrum: 7.66-8.50 (4H, m, C_6H_4); 8.64 ppm (1H, s, 4-H).

Rearrangement of Diazoketone Ia. To a solution of 0.064 g (0.25 mmole) diazoketone Ia in 1 ml methanol was added 0.2 ml (0.26 mmole) of a 5% solution of sodium methoxide in anhydrous methanol. The reaction mixture was maintained at 20°C for 48 h; the solution was then chromatographed on Silufol UV-254 plates and the bands due to diazoketones Ia, VII, and Ib were removed from the plates, eluted with methanol, and the UV spectra of the resulting solutions were measured in order to determine the molar concentrations of the rearrangement products (R_f, λ_{max}, and log ε values for Ib are given in [5]). The ratios of diazoketones Ia, VIII, and Ib were 26, 37, and 37%, respectively. Each experiment was carried out three times. The reproducibility of the results was ±0.5%.

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