action products were removed by distillation. The mixture was then worked up as in the preparation of pyridine III to give 0.12 g (17%) of pyridine XII with mp 136-137°. No melting-point depression was observed for a mixture of a sample of this product with an authentic sample.

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UTILIZATION OF IR SPECTROSCOPY FOR THE STUDY OF THE MECHANISM OF THE CYCLIZATION OF β-(2-CARBOXYARYLAMINO)PROPIONIC ACIDS

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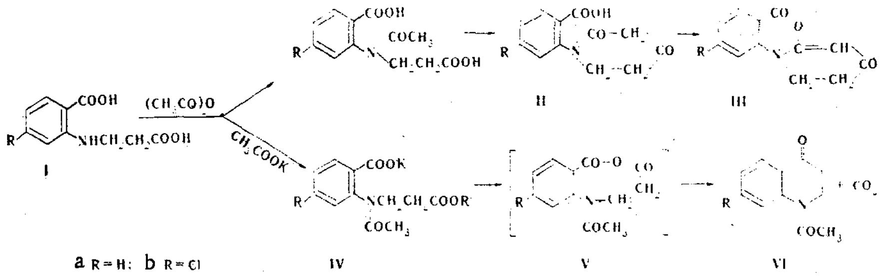
It was established by IR spectroscopy that the cyclization of β-(2-carboxylarylamino)propionic acids to 2,3-dihydroquinoline-4(1H)-ones in acetic anhydride in the presence of an alkali metal acetate proceeds through an intermediate step involving the formation of an eight-membered cyclic anhydride. In the case of β-(2-carboxy-5-chlorophenylamino)propionic acid the presence of an intermediate in the reaction mixture was established by the IR spectra of samples of the mixtures selected at various temperatures and was illustrated by the IR spectrum obtained by differential spectroscopy.

It has been previously shown [1, 2] that the cyclization of β-(2-carboxyarylamino)-propionic acids (I) in acetic anhydride may proceed in two directions, depending on the presence or absence of an alkali metal acetate in the reaction medium:



a R=H; b R=Cl

It has been established that in the presence of potassium acetate a reaction with splitting out of carbon dioxide leads to N-acetyl-2,3-dihydroquinolin-4(1H)-one (VI), and the acetyl derivative (IV) of the monopotassium salt of the starting acid was isolated as an intermediate. It was later assumed that the latter is converted to a cyclic anhydride (V), which undergoes decomposition to give carbon dioxide and a quinoline (VI).

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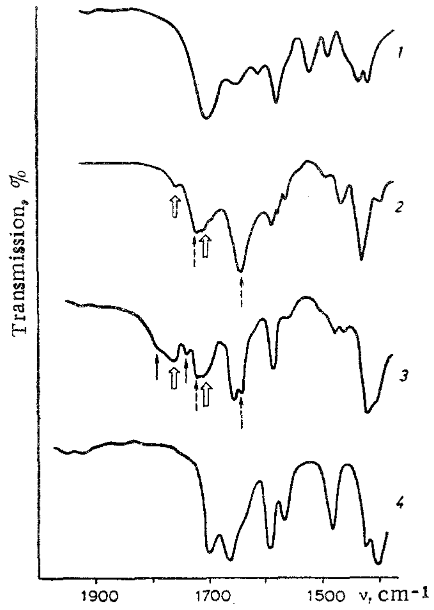

Fig. 1

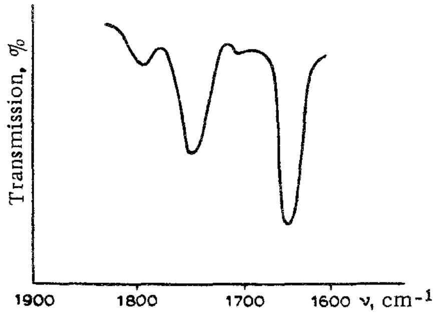

Fig. 2

Fig. 1. IR spectra: 1) β-(2-carboxy-5-chlorophenylamino)propionic acid; 2) reaction mixture at 100°C; 3) reaction mixture at 120-135°; 4) N-acetyl-2,3-dihydroquinolin-4(1H)-one [the absorption bands related to the monopotassium salt IV (→), lactone III (⇒), and cyclic anhydride V (→) are indicated on the spectra].

Fig. 2. IR spectrum of cyclic anhydride V obtained by differential spectrometry.

Previous attempts to isolate a cyclic anhydride from the reaction mixture, even at the beginning of the process when the first bubbles of carbon dioxide appear, were unsuccessful, and mainly monopotassium salt IV, quinolone VI, and a small amount of lactone [3] (III) were isolated.

In the present research we undertook spectral studies of the products of cyclization of I or IV directly in the reaction mixture. To avoid further reaction, the unchanged acetic anhydride was removed from the samples at high vacuum (5 · 10^{-3} mm) at 20°C. The IR spectra of KBr pellets of the solid phase were measured.

The previously established fact that monopotassium salt IV and a small amount of lactone III are formed when I or its N-acetyl derivative are heated to 100° in acetic anhydride in the presence of potassium acetate under conditions for which carbon dioxide is not yet evolved was spectroscopically confirmed. The characteristic bands for lactone III (1765 and 1647 cm^{-1}) are of low intensity. Absorption bands corresponding to the CO-O-CO grouping of cyclic mixed anhydride V, which, according to [4], should lie at 1800 and near 1745 cm^{-1}, are not observed in the spectra of samples selected at this stage of the reaction. Similar results were obtained by heating monopotassium salt IV only with acetic anhydride in the absence of potassium acetate.

Samples taken from the reaction mixture at higher temperatures (at which carbon dioxide evolution occurs) were then investigated. The intensity of the absorption bands of the starting compounds in the IR spectra of these samples decreases substantially, and bands characteristic for the final product (Fig. 1), the intensity of which increases in proportion to the heating time, appear. A certain increase in the intensity of the bands characteristic for lactone III occurs simultaneously, and bands related to the C=O vibrations in the cyclic anhydride molecule appear at 1797 and 1745 cm^{-1} [4].

Since the band at 1797 cm^{-1} is overlapped by the more intense band of the lactone (1765 cm^{-1}) and the band at 1745 cm^{-1} is overlapped by the band of monopotassium salt IV (1712 cm^{-1}), differential spectroscopy [5] was used for the reliable identification of the absorption bands of the cyclic anhydride. The differential spectrum (Fig. 2) showed that the intensity of the high-frequency band is substantially lower than that of the low-frequency band. According to [6], this is peculiar only to the IR spectra of cyclic anhydrides. Thus, the presence of cyclic anhydride V in the reaction mixture was observed by IR spectroscopy. The low intensity of the absorption bands corresponds to the low percentage of anhydride V in the reaction products. The changes in the intensities of the bands of anhydride V are insignificant in samples selected at reaction mixture temperatures from 120 to 135°. This makes it possible to assume that cyclic anhydride V is formed at approximately the same temperatures as quinolone VI and that the rate of formation of anhydride V evidently differs little from the rate of its conversion to quinolone VI.

EXPERIMENTAL

The IR spectra were measured with a UR-20 spectrometer. The cyclization reaction was carried out by the method described in [1-3]. The samples for the spectral studies were selected from the reaction mixture at temperatures from 80 to 145°; prior to the start of carbon dioxide evolution (<100°) and at 110-145°, initially every 10 min and then every 5 min. The 120-130° temperature range, over which the measurements showed that the intensity of the bands of the cyclic anhydride was at a maximum, was particularly thoroughly investigated. At these temperatures samples were selected from the reaction mixture every 2 min.

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STEREOCHEMISTRY OF THE QUATERNIZATION OF 2- AND 4-EPIMERIC trans-1-ALKYL-2-METHYL-4-ETHYNYLDECAHYDRO-4-QUINOLOLS WITH ALKYL HALIDES

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The quaternization of trans-1-alkyl-2-methyl-4-ethynyldecahydro-4-quinolols containing an equatorial 2-CH_3 group by means of methyl iodide proceeds with predominant axial incorporation of the methyl group, whereas quaternization of the corresponding trans-1,2-dimethyl-4-ethynyldecahydro-4-quinolols by means of ethyl and n-propyl iodide takes place with predominant equatorial incorporation of the alkyl group; the ratios of the stereoisomers in the products of forward and reverse quaternization are approximately identical. Methylation of amino alcohols with an axial 2-CH_3 group also leads to the predominant formation of epimers of the quaternary salts with an axial methyl group attached to the nitrogen atom, whereas the reverse quaternization of these amino alcohols proceeds nonstereoselectively to give an approximately equimolar mixture of the epimers of the quaternary salts.

In the case of quaternization of trans-1-alkyldecahydroquinolines [1] and trans-1-alkyl-4-ethynyldecahydro-4-quinolols [2] with alkyl halides it was found that the addition

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