REACTION OF PRIMARY AND SECONDARY ENAMINES WITH ANHYDRIDES OF UNSATURATED DICARBOXYLIC ACIDS

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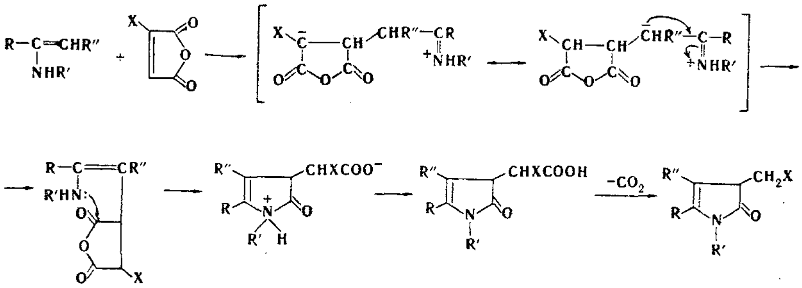
It was established that donor–acceptor complexes are formed in the reaction of some conjugated enamines with anhydrides of unsaturated dicarboxylic acids; in all likelihood, this constitutes evidence in favor of a scheme that includes nucleophilic addition of the enamine to the double bond. Addition of this type with subsequent intramolecular cyclization leads to the formation of Δ^2-pyrrolin-5-ones. In the case of citraconic anhydride it is shown (on the basis of data from the PMR and mass spectra) that nucleophilic attack is directed to the unsubstituted carbon atom of the ethylene bond.

We have previously shown that Δ^2-pyrrolin-5-one derivatives are formed in the reaction of enamines with various structures with maleic or citraconic anhydrides in the absence of a solvent (for example, see [1]). A scheme that includes the formation of an intermediate C-alkylated enamine and its intramolecular cyclization has been proposed for the reaction [1, 2].



In 1970 Robson and Markus [3] confirmed the formation of a Δ^2-pyrrolin-5-one derivative in the case of the reaction of maleic anhydride with N-methylaminocrotonic ester (in ether at room temperature).

In 1974 Szilagyi and Wamhoff [4] carried out the reaction of β-aminocrotonic ester with maleic anhydride in tetrahydrofuran (THF) with illumination with UV light and showed that despite their expectations, photocycloaddition does not occur, but 2-methyl-3-carbethoxy-4-carboxymethyl-Δ^2-pyrrolin-5-one is formed. The scheme proposed by the authors included N-acylation of the enamine as the first step. However, this pathway seems less likely to us, since one must take into account the fact that the β-carbon atom in N-acylenamines, in contrast to the enamines themselves, is less reactive [4], and this should undoubtedly hinder cyclization.

According to the scheme proposed by us [1] and Robson and Markus [3], the reaction includes nucleophilic addition of the enamine to the double bond of maleic anhydride (i.e., C-alkylation of the enamine).

According to the literature data, the formation of donor–acceptor complexes precedes nucleophilic addition to the double bond of electrophilic olefins, including maleic anhydride (for example, see [6, 7]).

We were able to establish that a yellow coloration, which vanishes rapidly, is observed in the reaction

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TABLE 1. UV Spectroscopic Data

Enamine	λ_{max}, nm (ε)		
	enamine	charge-transfer bands	
		with maleic anhydride	with citraconic anhydride
$CH_3C(NH_2)=CHCOOC_2H_5$	270 (108)	315 (67)	315 (72)
$CH_3C(NHCH_3)=CHCOOC_2H_5$	290 (145)	315 (60)	315 (75)
$CH_3C(NHCH_2C_6H_5)=CHCOOC_2H_5$	290 (140)	315 (60)	—
$CH_3C(NHCH_3)=CHCOCH_3$	290 (106)	325 (115)	315 (70)

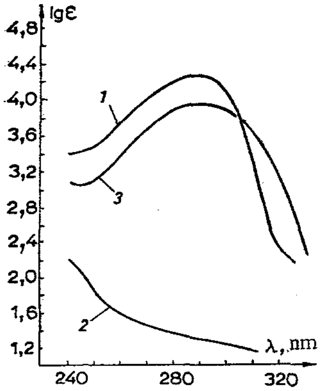


Fig. 1

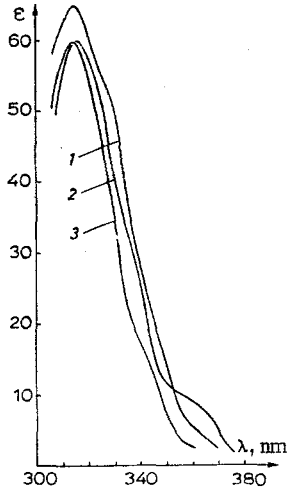


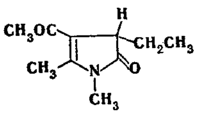
Fig. 2

Fig. 1. UV spectra of N-methylaminocrotonic ester (1), maleic anhydride (2), and 1,2-dimethyl-3-carbethoxy-Δ^2-pyrrolin-5-on-4-ylacetic acid (3).

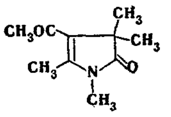
Fig. 2. UV spectra of donor–acceptor complexes formed from N-methylaminocrotonic (1), N-benzylaminocrotonic (2), and aminocrotonic (3) esters with maleic anhydride.

of acceptor conjugated enamines with maleic and citraconic anhydrides in chloroform. The formation of donor–acceptor complexs, which is observed visually, is confirmed by UV spectroscopic data. Thus an absorption band with λ_{max} 315 nm, which is absent in the spectra of the starting and final compounds (Figs. 1 and 2), was observed in the spectrum of a mixture prepared directly in the cuvette and consisting of different volumes of a 10^{-1} M solution of the anhydride and a 10^{-3} M solution of N-methylaminocrotonic ester. This band was assigned to the resulting πn–π complex [7]. We observed the formation of πn–π complexes in the reaction of various enamines with maleic and citraconic anhydrides.

Our data may consitute evidence in favor of a scheme that includes nucleophilic addition of the enamines to the double bond of the anhydrides of unsaturated dicarboxylic acids, since it is known that the first and fastest step in the nucleophilic addition is the formation of donor–acceptor complexes [6].



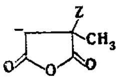
I



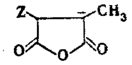
II

The data from a mass spectral analysis and the PMR spectra made it possible to solve the problem of the orientation of the nucleophilic attack of enamines on citraconic anhydride. One can imagine the formation of alternative structures I and II. However, an ($M-CH_2CH_3$) fragment ion with m/e 152 is observed in the mass spectrum, along with the molecular ion at m/e 181*, of the compound obtained by condensation of acetylacetone (N-methyl)enamine with citraconic anhydride. Fragmentation of this type provides evidence in favor of structure I.

Thus, probably because of the predominance of steric factors, nucleophilic attack in the case of citraconic anhydride is directed to the unsubstituted carbon atom of the ethylene bond, although according to the electronic factors, the intermediately formed carbanion A should be more stable, and addition of the enamine should consequently have taken place at the substituted atom of the ethylene bond.



A



B

EXPERIMENTAL

The UV spectra of the compounds were recorded with an SF-4A spectrophotometer (see Table 1 and Fig. 1). The λ_{max} values of the Δ^2-pyrrolin-5-ones are presented in [1]. The mass spectra were recorded with an MKh-1303 spectrometer (by direct introduction of the samples into the ionization region at 160° at an ionizing voltage of 50 V and an emission current of 1.5 mA). The PMR spectra of CCl_4 solutions of the compounds were recored with a Varian-60 spectrometer with tetramethylsilane as the internal standard.

Reaction of Acetylacetone (N-Methyl)enamine with Citraconic Anhydride. A mixture of 2.26 g (0.02 mole) of acetylacetone (N-methyl)enamine and 2.24 g (0.02 mole) of citraconic anhydride was heated in a Claisen flask at 150° for 15 h, after which it was vacuum fractionated. Refractionation gave 2.6 g (58%) of 1,2-dimethyl-3-acetyl-4-ethyl-Δ^2-pyrrolin-5-one [2] with bp 152-155° (1 mm). Found: C 66.0; H 8.2; N 7.6% $C_{10}H_{15}N_2O$. Calculated: C 66.3; H 8.3; N 7.7%. Mass spectrum: 181, 166, 152 (100 %), 138, 124, 110, 56. PMR spectrum, δ: 2 and 0.9 (q CH and s $C = C-CH_3$); 3 and 3.1 (t CH and s CH_3CO); 2.45 ppm (s $C = CCH_3$). The assignments were made from the integral intensities of the signals and comparison with the spectrum of 1,2-dimethyl-3-carbomethoxy-4-carboxymethyl-Δ^2-pyrrolin-5-one [3].

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