REACTIONS OF 1-ARYLPYRIDINIUM IONS WITH ANIONS OF METHYL ACETOACETATE, CYANOACETATE AND MALONATE

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1,4-Dihydropyridine derivatives are the main primary products of the reaction of arylpyridinium salts with anions of methyl acetoacetate and malonate. Rate constants of formation and reverse reactions of the substituted dihydropyridines have been determined. In the case of 1-(4-nitrophenyl)pyridinium bromide with methyl cyanoacetate, mechanism and kinetics of subsequent reactions have been studied in detail. Base-catalyzed opening of the substituted 1,2-dihydropyridine ring results in formation of 1-cyano-1-carbmethoxy-6-(4-nitrophenyl)amino-1,3,5-hexatriene. This compound reacts with anion of methyl cyanoacetate to form sodium salt of 1,7-dicyano-1,7-dicarbmethoxy-1,3,5-heptatriene, the reaction being catalyzed by sodium methoxide. Decreasing σ constant of substituent in the benzene ring makes the oxidation of the substituted 1,2-dihydropyridine into 1-subst. phenyl-2-cyanocarbomethoxymethylene-1,2-dihydropyridine more significant.

1-Substituted pyridinium ions react with nucleophiles to form 1,2- and 1,4-dihydropyridine derivatives[1]. If the reaction of arylpyridinium ions is carried out with hydroxyl ions or primary and secondary amines as nucleophiles, 1,2-dihydropyridines undergo rapid base-catalyzed ring opening to form glutaconic dialdehyde derivatives. Concentration of the 1,2-dihydropyridines is so low that it cannot be determined even spectrometrically[2-5]. The presence of a hydrogen atom at α-atom of the nucleophile is necessary for the ring opening in this case. Substituted 1,2-dihydropyridine is the final product in the reaction with methoxide and ethoxide ions. The situation is different in the case of reactions with carbanions. Substituted 1-vinyl- resp. 1-alkylpyridinium ions give the substituted 1,2- and 1,4-dihydropyridines on reaction with carbanions[6-8], this being the case even when there is a labile proton at α-carbon atom. (On the contrary, pyridine-N-oxide reacts with sodium acetylide[9] and phenylmagnesium bromide[10] to give hepta-2,4-diene-6-inal oxime and 5-phenyl-2,4-pentadiene-6-inal oxime, respectively. The ring opening of the primary 1,2-dihydropyridine is defined, in these cases, as electrocyclic reaction.) Arylpyridinium ions react with acetone and cyclohexanone anions to give mixtures of 1,2- and 1,4-dihydropyridines[11]. 1,2-Dihydropyridines undergo ring opening in strongly basic medium, but the products formed are unstable in the reaction medium and could not be isolated and identified.

The present paper describes a study of reaction of 1-(4-methyl-, 4-bromo-, 4-nitrophenyl) pyridinium ions $Ia-c$ with anions of methyl acetoacetate, cyanoacetate and malonate $IIa-c$. The opening of 1,2-dihydropyridine ring should proceed under far milder conditions in these cases than in the reactions with acetone and

cyclohexanone. The aim of this work was to determine the rates and equilibrium constants of formation of the dihydropyridines and their structure, the structure of products of subsequent reactions and their mechanism and kinetic equations.

EXPERIMENTAL

Preparation of 1-(4-methyl-, 4-bromo-, 4-nitro-phenyl)pyridinium chlorides resp. bromide *Ia—c* and of methyl acetoacetate, cyanoacetate and malonate *IIa—c* was described elsewhere[2,12]. The other chemicals used were commercial reagents of *p.a.* purity grade.

1-(4-Methylphenyl)-2-cyanocarbmethoxymethylene-1,2-dihydropyridine (VIIa): 2·75 g (13·5 mmol) *Ia* dissolved in 8 ml methanol was treated with 1·15 ml (13 mmol) *IIb* and 3·2 ml 4M sodium methoxide. After 25 minutes 6·5 ml 2M-HCl in methanol was added. Yield 1·8 g *VIIa* (50·5%). After crystallization from methanol the substance melted at 242—243°C. For $C_{16}H_{14}$.N_2O_2 (266·3) calculated: 72·16% C, 5·30% H, 10·52% N; found: 72·06% C, 5·43% H, 10·24% N. NMR spectrum: H_3 — a pair of doublets 3·05τ; H_4, H_5 — a multiplet about 1·8τ; H_6 — a pair of doublets 1·70τ; aromatic H — 2·4 to 2·7τ; OCH_3 — 6·37τ; $ArCH_3$ — 7·62τ; $J_{3,4} = 8·0$ Hz; $J_{5·6} = 7·5$ Hz; $J_{3,5} = 2·5$ Hz; $J_{4,6} = 2·0$ Hz.

1(4-Bromophenyl)-2-cyanocarbmethoxymethylene-1,2-dihydropyridine (VIIb): 2·7 g (10 mmol) *Ib* in 12 ml methanol was treated with 0·80 ml (9 mmol) *IIb* and 9 ml 2M sodium methoxide. After 10 minutes the mixture was filtered to give 0·9 g (27%) raw product. This was washed with 50 ml hot ethanol and crystallized from n-butanol. M.p. 288—289°C. For $C_{15}H_{11}BrN_2O_2$ (331·2) calculated: 54·40% C, 3·35% H, 8·46% N; found: 54·65% C, 3·53% H, 8·44% N.

1-Cyano-1-carbmethoxy-6-(4-bromophenyl)amino-1,3,5-hexatriene (IXb): After filtration of *VIIb* the mother liquor was acidified with 9 ml 2M-HCl, and the precipitated substance *IXb* (0·8 g, 24%) was filtered off and washed with methanol. M.p. 169—170°C. For $C_{15}H_{13}BrN_2O_2$ (333·1) calculated: 54·09% C, 3·93% H, 8·41% N; found: 54·19% C, 3·69% H, 8·29% N. NMR spectrum (50°C, dimethyl sulphoxide): $H_{2(6)}$ — a doublet 2·23τ; $H_{6(2)}$ — a doublet 2·16τ; H_4 — a triplet 2·60τ; $H_{3(5)}$ — a triplet 4·02τ; $H_{5(3)}$ — a triplet 3·72τ; aromatic H — 2·45 to 2·95τ; OCH_3 — 6·30τ; $J_{n,n+1} = (12·7 \pm 0·5)$ Hz.

1-Cyano-1-carbmethoxy-6-(4-nitrophenyl)amino-1,3,5-hexatriene (IXc): 0·93 g (3·3 mmol) *Ic* and 0·26 ml (3 mmol) *IIb* were mixed with methanol, and 3 ml 1M sodium methoxide was added within 3 minutes drop by drop. After five minutes the compound *IXc* was filtered off and washed with methanol. Yield 0·7 g (77%). M.p. 199—200°C. For $C_{15}H_{13}N_3O_4$ (299·2) calculated: 60·21% C, 4·38% H, 14·05% N; found: 59·91% C, 4·08% H, 14·15% N.

Sodium salt (X) *of* 1,7-dicyano-1,7-dicarbmethoxy-1,3,5-heptatriene (XI): Mixture of 2·7 g (10 mmol) *Ib* and 1·59 ml (18 mmol) *IIb* in 8 ml methanol was treated with 5·5 ml 4M sodium methoxide. After 15 minutes the reaction mixture was diluted with tetrachloromethane, and the sodium salt was filtered off, washed with methanol, digested with water and methanol. Yield 2·4 g (85%). M.p. 291—293°C. NMR spectrum: $H_{2,6}$ — a doublet 2·46τ; H_4 — a triplet 2·69τ; $H_{3,5}$ — a triplet 4·12τ; OCH_3 — 6·40τ; $J_{n,n+1} = (12·7 \pm 0·5)$ Hz.

Solutions of the substituted dihydropyridines for NMR *spectra measurements*: Solution of 2·2 mmol *I* in 2 ml methanol was treated with 2 mmol *II* and 2 ml 1M sodium methoxide. About 5 seconds after the mixing 50 ml tetrachloromethane was added. The mixture was concentrated *in vacuo* to 1/3 of the original volume, and the non-soluble portions were filtered off. The filtrate was concentrated to about 2 ml *in vacuo* and used for the measurements of spectra. In the case

of product of the reaction of *Ic* and *IIa* the filtrate was evaporated and 1 ml deuteriochloroform was added to the dry residue.

NMR spectra of reaction products of *IIa* with *Ia*, *Ib* and *Ic*, respectively: aromatic H — 2·90 to 3·30; 2·50 to 3·40; 1·75 to 3·15τ; $H_{2,6}$ — 3·68; 3·68; 3·39τ (a broadened doublet); $H_{3,5}$ — 5·44; 5·40; 5·09τ (multiplet); H_4 — 6·30; 6·33; 6·14τ (a multiplet); H_α — 6·68; 6·49; 6·37τ (a doublet); OCH_3 — 6·31; 6·35; 6·26τ (a singlet); $COCH_3$ — 7·72; 7·86; 7·76τ (a singlet); $J_{2,3}$ — 8·0; 8·0; 7·7 Hz; $J_{3,4}$ — 4·1; 4·0; 4·0 Hz; $J_{4,\alpha}$ — 8·2; 8·0; 8·0 Hz.

NMR spectrum of the reaction product of *IIc* with *Ib*: aromatic H — 2·60 to 3·30τ; $H_{2,6}$ — 3·65τ (a broadened doublet); $H_{3,5}$ — 5·35τ (a multiplet); H_4 — 6·35τ (a multiplet); H_α — 6·68τ (a doublet); OCH_3 — 6·35τ (a singlet); $J_{2,3}$ — 8·2 Hz; $J_{3,4}$ — 4·0 Hz; $H_{4,\alpha}$ — 6·0 Hz.

Equilibrium constants measurement and kinetic experiments. Equilibrium constants of the compounds *IXb* and *IXc* with methoxide ion were determined spectrometrically at 480 nm by measurements in sodium methoxide solutions using a Zeiss VSU-2P spectrophotometer. pK_a value of the substance *XI* was determined spectrophotometrically by measuring the absorbances at 550 nm of the solutions of the compound *X* in diluted hydrochloric acid. As the compound *XI* is decomposed during the measurements, the absorbance values were extrapolated to zero time.

The reaction rates of pyridinium salts with carbanions were measured with the use of a Durrum Stopped-Flow Spectrophotometer model D 110 in methanol at 405 nm at 25°C; the ionic strength 0·01 was adjusted with sodium chloride. One syringe contained a mixture of the pyridinium salt and C-acid, the other contained a buffer 4-bromophenol-4-bromophenolate (for the reaction of *IIb* and *IIc*) resp. sodium methoxide (*IIa*). The reaction half-lives were read from the screen of the apparatus, and the rate constants were calculated from the relation $k_{obs} = 0·693/t_{1/2}$. Each measurement was repeated twice at least. The rate of formation of *IXc* was measured by a similar method at 513 nm (the isosbestic point of *IXc* and *X*). Sodium methoxide was used instead of buffer (concentration 0·04—0·20M). Rate of formation of the compound *X* was measured with the Zeiss VSU-2P at 25°C. The solution of *IXb* resp. *IXc* was injected into 1 cm cell containing methanolic solution of methyl cyanoacetate, sodium methoxide and sodium chloride to adjust the ionic strength at 0·05, whereafter the absorbance increase at 550 nm was measured. The rate constants were calculated from the relation $k_{obs}t = -\ln(A_\infty - A_t) + \text{const}$.

RESULTS AND DISCUSSION

The reaction course of pyridinium salts with carbanions is represented in Scheme 1 for the reaction of arylpyridinium salts with the anion of methyl cyanoacetate. The main products of additions of anions of methyl acetoacetate and malonate to arylpyridinium ion are substituted 1,4-dihydropyridines (structure of the products were determined in solutions of tetrachloromethane resp. deuteriochloroform; the attempts to measure the spectra in methanol failed). The chemical shifts and coupling constants are very similar to those found for 1-substituted-phenyl-4-acetonyl-1,4-dihydropyridines[11]. The presence of 1,2-dihydropyridines in CCl_4 resp. $CDCl_3$ solutions could not be proved by NMR spectra. Their existence in the reaction mixture is inferred from the isolation of products *VII* and *IX* which can only be formed from 1,2-dihydropyridines. NMR spectra of the addition products of arylpyridinium salts with anion of methyl cyanoacetate could not be measured, because the subsequent reactions were very fast.
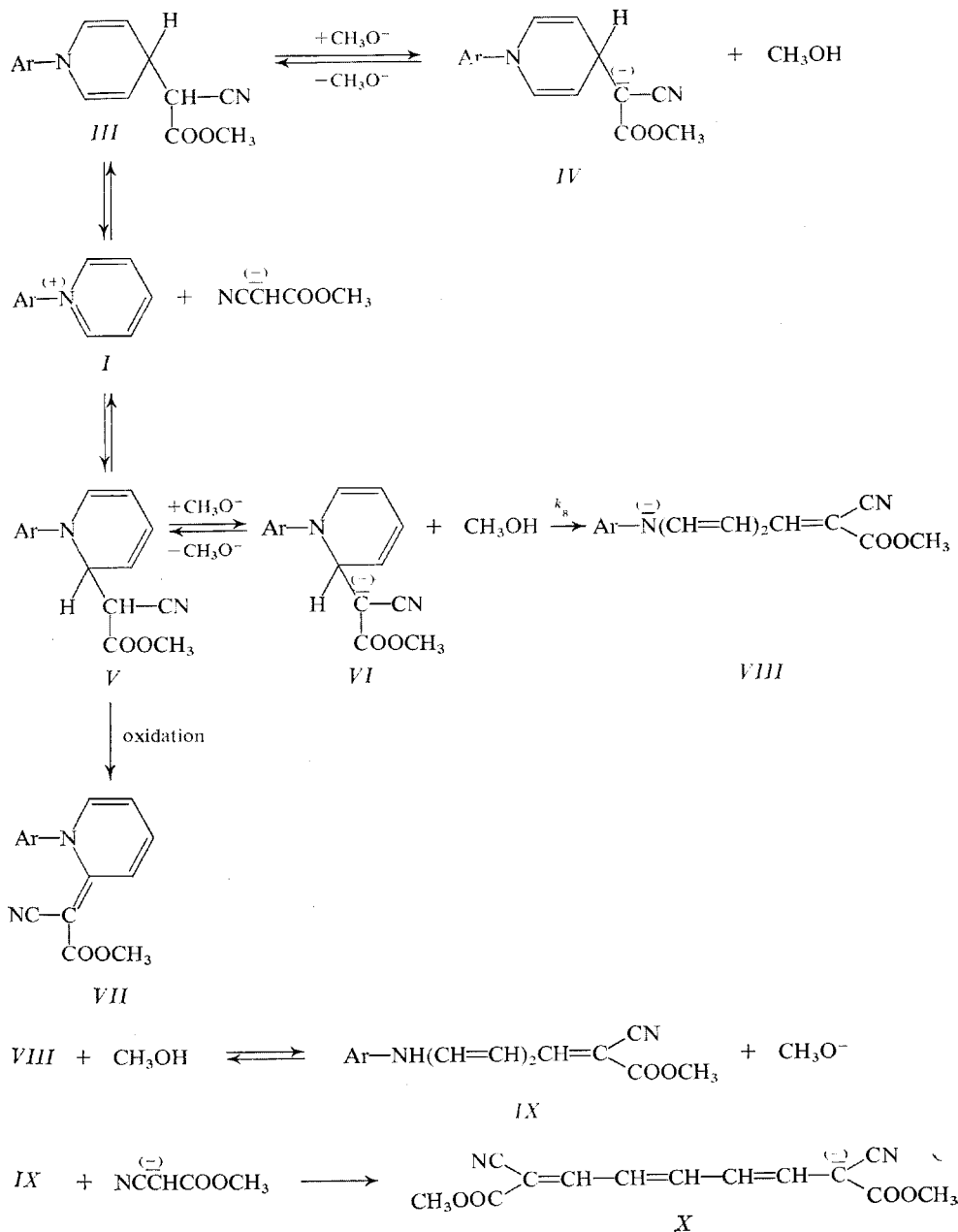
Ar = subst. phenyl

SCHEME 1

The rate constants of formation and reverse reaction of dihydropyridines (Table I) were measured with all the three carbanions in the case of *Ic*. The corresponding reactions of *Ia* and *Ib* could not be followed spectrophotometrically, because the absorbances of the dihydropyridines being formed are superposed by far greater absorbances of the carbanions. Concentrations of the carbanions were calculated from the equilibrium constants of reactions of the compounds *IIa — c* with methoxide ion[12] and from the concentration of methoxide ion (in the case of *IIa*), or from the composition of the 4-bromophenolate buffer, pK_{CH_3OH} and pK_a of 4-bromophenol in methanol[14] (in the cases of *IIb* and *IIc*). The time dependence of absorbance changes was exponential in all the cases. In the reaction with methyl cyanoacetate anion the initial absorbance was zero; the rate constants of formation and reverse reaction of dihydropyridines were calculated from the relation $k_{obs} = k_1[\overset{(-)}{NCCH}.COOCH_3] + k_{-1}$. In the reactions with anions of methyl acetoacetate and malonate the effective concentration of methoxide ions was greater, and, therefore, rapid pre-equilibrium of *Ic* with methoxide ion was significant[5]. The rate constants were calculated from the relation $k_{obs} = k_1[\text{carbanion}][Ic]/[Ic]_{anal} + k_{-1}$. The ratio $[Ic]/[Ic]_{anal}$ was calculated from the measured initial absorbance and from absorbance of the reaction product of *Ic* with methoxide ion only.

In the reaction with anion of acetoacetate the initial absorbance value was roughly twice as high as that calculated[5] for the reaction product of *Ic* with methoxide ion. One possible explanation is a rapid formation of substituted 1,2-dihydropyridine. That is why the value of the rate constant k_1 is less reliable than those of reactions with anions of methyl cyanoacetate and malonate.

Logarithms of equilibrium constant values of formation of dihydropyridines (Table I) and those of equilibrium constants of reactions of *IIa — c* with methoxide

TABLE I

Values of k_1 (l mol^{-1} s^{-1}), k_{-1} (s^{-1}) and K_1 (l mol^{-1}) for the Reaction of *Ic* with *IIa — c*

Compound	$k_1 . 10^{-3}$	k_{-1}	$K_1 . 10^{-2}$	K^a
IIa	4·75	20	2·38	4·8
	(5·50)^b	(470)^b	(0·117)^b	—
IIb	184	26	71	54
	(103)^b	(62)^b	(16·6)^b	—
IIc	210	0·85	2 400	0·5
	(250)^b	(20·5)^b	(122)^b	—

^{a} The values of equilibrium constants of reactions of *IIa — c* with methoxide ion (l mol^{-1}), ref.[12].
^{b} For the reactions of *IIa — c* with trinitrobenzene, ref.[13].

ion show practically the same changes but in opposite directions. The rate constant values of formation and reverse reaction of *Ic* with methyl cyanoacetate anion are greater than it corresponds to acidity of methyl cyanoacetate, which is typical for the C-acids activated by a cyano group[15]. The found rate and equilibrium constants are similar to the corresponding constants of the reaction of these carbanions with 1,3,5-trinitrobenzene (Table I), which is especially true for the reactions with cyanoacetate. In the case of anions of acetoacetate and malonate the reverse reactions are faster by more than one order of magnitude, which can be due to higher sterical requirements of these carbanions as compared with methyl cyanoacetate anion.

Consecutive reactions of dihydropyridines were studied in more detail in the case of anion of methyl cyanoacetate. In this reaction it was possible to follow separately the individual reaction steps, and all the reaction products were isolated and identified. Preparative experiments using 2 equivalents of methyl cyanoacetate anion gave mainly the sodium salt of *X* in the reaction with *Ib* and *Ic*, whereas with *Ia* a mixture of *X* and *VIIa* was formed. When using one equivalent of methyl cyanoacetate anion and one equivalent of sodium methoxide, the compound *VIIa* was the main reaction product from *Ia*, whereas a mixture of *VIIb* and *IXb* was formed from *Ib*. Practically pure *IXc* was obtained from *Ic*. On the basis of NMR spectra the structure *VIIa* was ascribed unambiguously to oxidation product of the 1,2-dihydropyridine formed from *Ia*. Character of spectrum of *VIIb* was analogous. The compound *IX* is a primary product of opening of dihydropyridine ring, and analogous substances were obtained and identified in the reaction of 1-(2,4-dinitrophenyl)pyridinium chloride with hydroxyl ion[16] and piperidine[4]. In the case of 4-bromo derivative the structure was verified by NMR spectra. Character of spectra of the 4-nitro derivative was similar, but the chemical shifts and coupling constants could not be precisely determined due to low solubility.

Elemental analysis of the compound *X* gave lower values for carbon and nitrogen (1 to 1·5% difference from theory). However, the suggested structure is supported by the following facts: The compound *X* is formed by reaction with methyl cyanoacetate anion from the compound *Ib* as well as from *Ic*; an analogous substitution proceeds also in the reaction of 5-piperidino-1-(2,4-dinitrophenyl)-2,4-pentadienylideneiminium chloride with piperidine giving glutaconic dialdehyde dipiperidyl hydrochloride[4]. Character of the NMR spectra agrees perfectly with the structure suggested.

Conjugated acid *XI* of the compound *X* is a relatively strong C-acid; pK_a value found in water is $1·78 \pm 0·05$. The compound *XI* is unstable in acid medium and undergoes further rapid reactions. Attempts of its isolation by acidification of the solution of *X*, extraction in benzene and evaporation of the solvent failed, giving only waxy products.

Kinetics of formation of the compound *IX* was studied with 4-nitro derivative, because in this case it was possible to determine the overall concentration of dihydro-

pyridines (*III* and *V*). The kinetic experiments were carried out under the conditions when practically all the pyridinium salt was transformed into mixture of dihydro-pyridines. The reaction rate was independent of concentration of methyl cyano-acetate anion and increased non-linearly with methoxide ion concentration, until it was independent of methoxide ion concentration (at its highest concentrations). This suggests that the reaction is subject to specific base catalysis. The both dihydro-pyridines and their anions are in a rapid antecedent equilibrium, and the rate-limiting step consists in the opening of the dihydropyridine ring of the compound *V* (Scheme 1). As it is impossible to determine separately the equilibrium constants of the com-pounds *III* (K_3) and *V* (K_5) with methoxide ion, the kinetic equation (*1*) was derived with the presumption that the both constants are the same $(K_{3,5})$. Character of the dependence is not changed by this presumption, and the kinetic equation is much simpler. Dependence of $1/k_{obs}$ on $1/[CH_3O^-]$ was linear in accord with the equation (*1*). From the intercept and slope the values $k_8/(K + 1) = 0.56 \text{ s}^{-1}$ and $K_{3,5} = 200 \text{ l/mol}$ were determined, respectively, the latter being four times as high as that for methyl cyanoacetate.
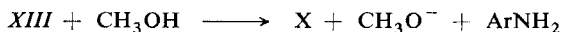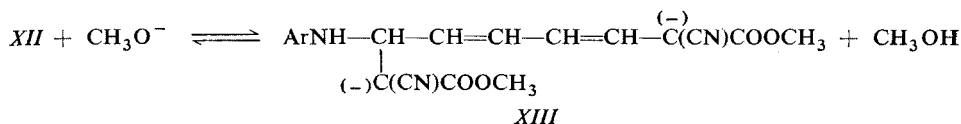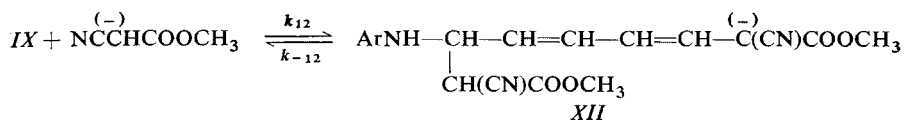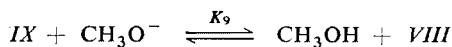
$$k_{obs} = \frac{k_8}{K + 1} \frac{K_{3,5}[CH_3O^-]}{1 + K_{3,5}[CH_3O^-]}, \qquad (1)$$

$K = [III]/[V].$

The rate of formation of the anion *X* is directly proportional to concentrations of the undissociated compound *IXb* resp. *IXc* and methyl cyanoacetate anion. The dependences found are in accordance with the reaction mechanism given in Scheme 2 and kinetic equation (*2*). K_9 is 2.74 and 2.81 for *IXb* and *IXc*, respectively. At low methoxide ion concentrations the decomposition of the dianion *XIII* is rate

$$k_{obs} = \frac{1}{1 + K_9[CH_3O^-]} \frac{k_{12}[\overset{(-)}{NCCHCOOCH_3}] K_{12}k_{10}[CH_3O^-]}{k_{-12} + k_{10}K_{12}[CH_3O^-]} =$$
$$= k_{corr}/(1 + K_9[CH_3O^-]) \qquad (2)$$

limiting, whereas at higher concentrations the addition of methyl cyanoacetate anion to the compound *IX* is rate limiting. The dependence of $[\overset{(-)}{NCCHCOOCH_3}]/k_{corr}$ on $1/[CH_3O^-]$ was linear for the both derivatives (Fig. 1). The values $k_{12} = 8.3$ and $11.2 \text{ l mol}^{-1} \text{ s}^{-1}$ (for *Ib* and *Ic*, respectively) were calculated from the inter-cept, and the values $k_{-12}/K_{12}k_{10} = 1.66 \cdot 10^{-2}$ and $4.76 \cdot 10^{-3} \text{ mol l}^{-1}$ (for *Ib* and *Ic*, respectively) were calculated from the slope, the latter two values expressing the rate constants ratio of conversion of the intermediate *XII* into the starting substance *IX* and product *XI*. For the 4-bromo derivative this ratio is 3.5 times greater,

$$IX + CH_3O^- \underset{}{\overset{K_9}{\rightleftharpoons}} CH_3OH + VIII$$

$$IX + \overset{(-)}{NCCHCOOCH_3} \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} ArNH-CH-CH=CH-CH=CH-\overset{(-)}{C(CN)}COOCH_3$$
$$\underset{\underset{XII}{CH(CN)COOCH_3}}{|}$$

$$XII + CH_3O^- \rightleftharpoons ArNH-CH-CH=CH-CH=CH-\overset{(-)}{C(CN)}COOCH_3 + CH_3OH$$
$$\underset{\underset{XIII}{(-)C(CN)COOCH_3}}{|}$$

$$XIII + CH_3OH \longrightarrow X + CH_3O^- + ArNH_2$$

Ar = substituted phenyl

SCHEME 2

because the addition complex $XIIb$ decomposes easily into IXb, and, on the contrary, the transformation into the compound X is more difficult than with the 4-nitro derivative. Small differences in the values of constants k_{12} and values of equilibrium constants K_9 are surprising. The reason could be in that the 4-nitro derivative is present partially in the form of the tautomer XIV which cannot react with methyl cyanoacetate anion, and the influence of substituent in the benzene ring on the dissociation of the proton is small. The presence of this tautomer could not be proved from NMR and IR spectra due to very low solubility.
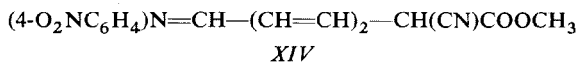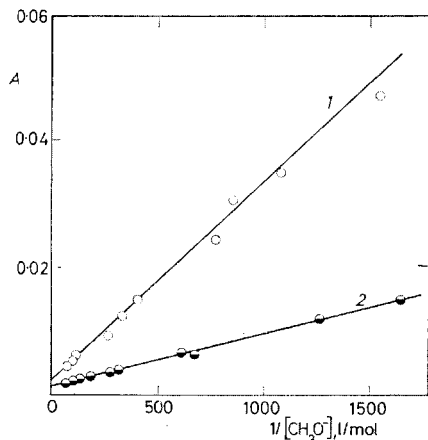
$$(4-O_2NC_6H_4)N=CH-(CH=CH)_2-CH(CN)COOCH_3$$
$$XIV$$

FIG. 1

Dependence of $[\overset{(-)}{NCCHCOOCH_3}]/k_{corr}$ (A, mol s l^{-1}) on $1/[CH_3O^-]$ (1 mol^{-1}) for the Reaction of IXb 1 resp. IXc 2 with IIb in Methanol at 25°C

Mechanism of the reaction of 1-(subst. phenyl)pyridinium ions with methyl cyano-acetate anion is analogous to that of the reaction of 1-(2,4-dinitrophenyl)pyridinium chloride with primary and secondary amines[3,4]. The main difference consists in that the complexes of arylpyridinium ions with methyl cyanoacetate anion are far more stable than those with neutral amines, and opening of the 1,2-dihydropyridine ring is subject to specific base catalysis. In the case of the reaction of 1-(2,4-dinitrophenyl)-pyridinium chloride with amines the opening of the 1,2-dihydropyridine ring is subject to general base catalysis[3,17].

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