A STUDY OF THE TAUTOMERISM OF THE N-BUTYL-4(2)-METHOXYCARBONYL-PYRROLID-3-ONES AND THEIR HYDROCHLORIDES

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The tautomerism of N-butyl-2-methoxycarbonyl-4-methylpyrrolid-3-one (I), N-butyl-4-methoxycarbonylpyrrolid-3-one (II), N-butyl-4-methoxycarbonyl-2-methylpyrrolid-3-one (III), N-butyl-4-methoxycarbonylpyrrolid-3-one hydrochloride (IV), and N-butyl-4-methoxycarbonyl-2-methylpyrrolid-3-one hydrochloride (V) has been studied by UV and IR spectroscopy. It has been found that the esters I-V are highly ionized in aqueous and ethanolic solutions at concentrations of 10^{-2}–10^{-3}M. On passing from methyl cyclopentran-1-one-2-carboxylate to the esters II and III the position of the equilibrium in heptane and CCl_4 shifts in the direction of the keto form. On passing from the esters II and III to the esters IV and V, the position of the equilibrium shifts in the direction of the enol. Meyer's relationship is not satisfied for the esters II and III, while it is satisfied for the esters IV and V. Hypotheses have been put forward on the causes of the phenomena mentioned.

Although heterocyclic β-ketoesters are cis-fixed ketoenols they do not necessarily satisfy Meyer's equation. Deviations are possible, in the first place, because of the dissimilar solvation, and, consequently, the dissimilar change in solvation on passing from one solvent to another, of the heteroatoms of the ketonic and enolic forms. Causes for dissimilar solvation may be the presence of conjugation with the heteroatom in one form and its absence in the other, or a difference in the conformations of the tautomers. In the second place, deviations from Meyer's equation are possible because of intermolecular interactions of the tautomeric forms with one another. We have shown [1] that Meyer's equation is not satisfied in the case of the N-alkyl-3-methoxycarbonylpiperid-4-ones because of the dissimilar solvation of the heteroatoms of the ketonic and enolic forms due to a difference in their conformations. In view of what has been said above, it appeared of interest to study the influence of the solvent on the tautomerism of the N-alkyl-4(2)-methoxycarbonylpyrrolid-3-ones and their hydrochlorides.

We have previously [1] established that at a concentration of 5×10^{-3}M, the N-alkyl-3-methoxycarbonylpiperid-4-ones exhibit appreciable ionization in the UV spectra only in aqueous solutions, while their hydrochlorides show no appreciable ionization even in aqueous solutions at a concentration of 5×10^{-5}M. Ethyl cyclohex-1-one-2-carboxylate has a pK value in water of 12.8 [2] and the considerable ionization of the N-alkyl-3-methoxycarbonylpiperid-4-ones in aqueous solution is apparently due to the basic properties of the tertiary amino group. A small capacity for ionization could have been expected in the N-alkyl-4(2)-methoxycarbonyl-pyrrolid-3-ones since the N-alklpiperidines are generally only slightly more basic than the N-alkylpiperidines [3,4] and ethyl cyclopentan-1-one-2-carboxylate has a pK value in water of 10.7 [2]. Amine hydrochlorides do not possess basic properties and the absence of appreciable ionization in the UV spectra for the hydrochlorides of the N-alkyl-4-methoxycarbonylprrolid-3-ones even in aqueous solutions at concentrations of 5×10^{-5}M could have been expected.

We have also observed previously [5] that on passing from methyl cyclopentan-1-one-2-carboxylate to methyl tetraphdrothiophen-3-one-4-carboxylate the postion of the equilibrium shifts strongly in the direction of the enolic form. This is apparently due to dissimilar changes in the torsional strain in the tautomeric forms on replacing a C—C bond by a C—S bond (barriers to rotation about the bonds 2.9 and 1.3 kcal//mole, respectively [6]). Torsional strain has a great influence on the properties of compounds with five-membered rings. In cyclopentane, for example, it leads to a bending of the ring and in consequence of this to a change in the frequencies of some basic vibrations, to the appearance of a new vibration connected with the motion of the atoms of the ring perpendicular to its plane, and to the appearance of pseudorotation, which makes corresponding contributions to the entropy and enthalpy [7,8]. The existing methods of calculating thermodynamic functions [9] do not permit an evaluation of the change in the contribution from the torsional strain to the entropy of the tautomeric forms of methyl cyclopentan-1-one-2-carboxylate when a CH_2 group of the ring is replaced by S-atom. However, a simple empirical method [10] permits an evaluation of the change in the contribution of the torsional strain to the enthalpies of the forms. Since the barrier to rotation round a C—S bond is less than round a C—C bond, this contribution will decrease in both forms, but to a smaller extent in the nonplanar keto form [11] than in the more planar enol form [12]. The shift in the position of the equilibrium in the enol direction expected from this difference on passing from methyl cyclopentan-1-one-2-carboxylate to methyl tetrahydrothiophene-3-one-4-carboxylate corresponds to the observed difference.

There should be a similar influence of the change in torsional strain on the equilibrium on passing from methyl cyclopentan-1-one-2-carboxylate to a N-alkyl-4-methoxycarbonylprrolid-3-one, since the barrier to rotation round a C—N bond (1.9 kcal/mole [6]) is less than round a C—C bond. The actual shift will also depend on the van der Walls interactions of the alkyl radical on the nitrogen atom. The atomic distances of the $=CH_2$ and $=NR$ groups are similar [13]. The steric requirements of the free electron pair of a nitrogen atom are not greater than those of a hydrogen atom [1, 14].

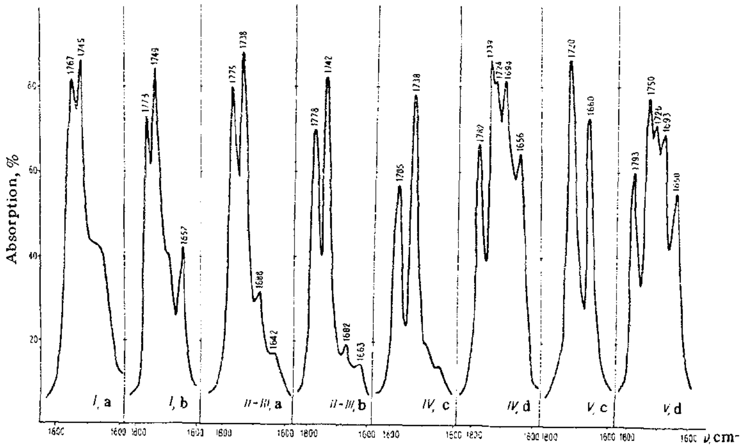


Fig. 1. IR spectra of the esters I–V: a) in the liquid state; b) in CCl_4; c) in the solid state; d) in isobutanol.

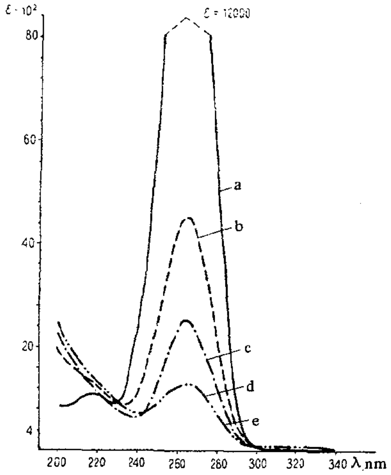


Fig. 2. UV spectra of the ester I: a) in water (c 3.3×10^{-3} M); b) in methanol (c 9.4×10^{-3} M); c) in ethanol (c 8.5×10^{-3} M); d) in isobutanol (c 2.1×10^{-3} M); e) in heptane (c 2.2×10^{-3} M).

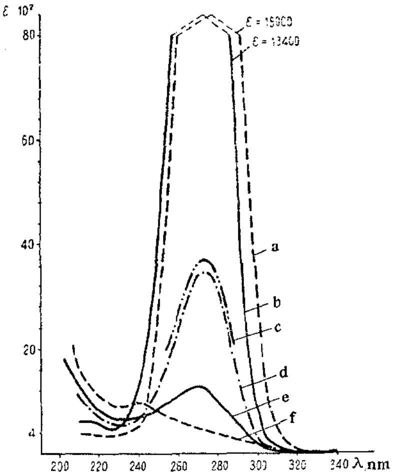


Fig. 3. UV spectra of the ester II: a) in 0.0014 N caustic soda solution (c 1.4×10^{-3} M); b) in water (c 1.4×10^{-3} M); c) in methanol (c 3.5×10^{-3} M); d) in ethanol (c 7×10^{-2} M); e) in isobutanol (c 1.8×10^{-2} M); f) in heptane (c 1.5×10^{-2} M).

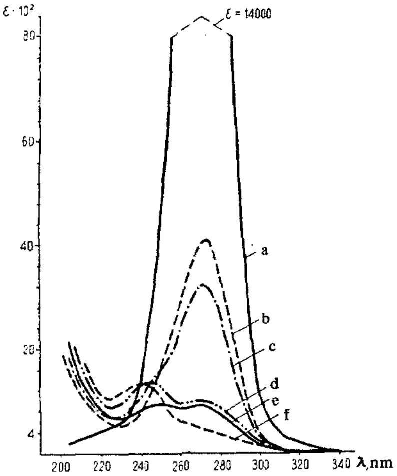


Fig. 4. UV spectra of the ester III: a) in water (c 1.6×10^{-3} M); b) in methanol (c 3.4×10^{-3} M); c) in ethanol (c 4×10^{-3} M); d) in isobutanol (c 4.8×10^{-3} M); e) in isobutanol (c 4×10^{-3} M); f) in heptane (c 6.7×10^{-3} M).

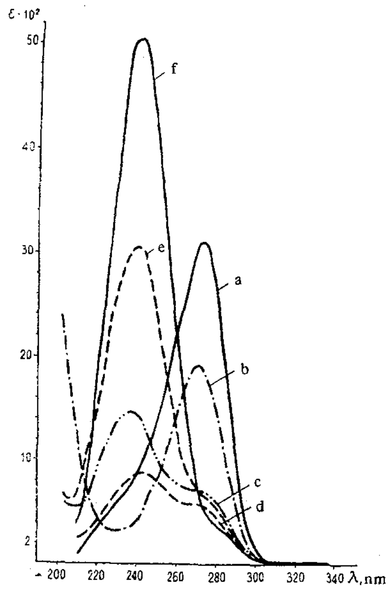


Fig. 5. UV spectra of the ester IV: a) in water (c 2.6×10^{-3} M); b) in methanol (c 3×10^{-3} M); c) in methanol (c 1.6×10^{-2} M); d) in 0.00064 N HCl solution (c 6.4×10^{-4} M); e) in ethanol (c 3×10^{-3} M); f) in isobutanol (c 2.6×10^{-3} M).

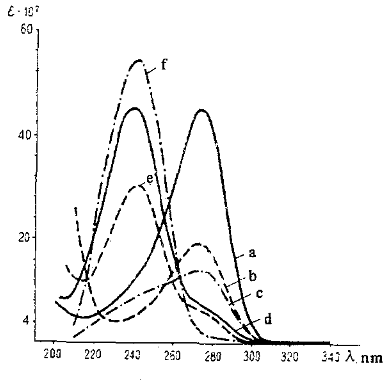
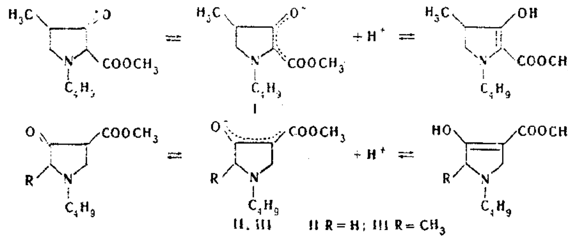


Fig. 6. UV spectra of the ester V: a) in water (7.5×10^{-4} M); b) in methanol (c 1.3×10^{-3} M); c) in water (c 1.3×10^{-2} M); d) in methanol (c 1.5×10^{-2}) e) in ethanol (c 1.3×10^{-3} M); f) in isobutanol (c 1.3×10^{-3} M).

The tautomerism of N-butyl-2-methoxycarbonyl-4-methylpyrrolid-3-one (I), N-butyl-4-methoxycarbonylpyrrolid-3-one (II), N-butyl-4-methoxycarbonyl-2-methylpyrrolid-3-one (III), N-butyl-4-methoxycarbonylpyrrolid-3-one hydrochloride (IV), N-butyl-4-methoxycarbonyl-2-methylprrolid-3-one hydrochloride (V) has been studied by UV and IR spectroscopy


I

II, III   II R = H; III R = CH_3

The UV spectra of the esters I–V were recorded in water, alcohols, and heptane. Solutions of the esters I–III were prepared from the liquid substances in the equilibrium of which the keto form predominates, solutions of the ester IV from the solid ketone form, and solutions of the ester V form the solid enol (according to the IR spectra, see Fig. 1). The high values of the molar extinction coefficients in the UV spectra of the above-prepared solutions of the esters I–IV in water and in alcohols (15–45 min after preparation) show the high rate of establishment of equilibrium in these solutions. These values, like those for the ester V, are reproduced in the spectra of solutions after they have stood for 3 hr and in the spectra of solutions prepared anew (apart from the values for the spectra of methanolic solutions of the esters II and V). Consequently, apart from the exceptions mentioned, they may be considered as the equilibrium values. The values of the molar extinction coefficients and the spectra of heptane solutions of the esters I–III taken one hour and 24 hr after the preparation of the solutions are similar and may also be taken as the equilibrium values. The intensities of the absorption of the solutions of esters I–V decrease on standing.

Ester I has λ_{max} 266 nm (Fig. 2) and the esters II–V λ_{max} about 240 and 275 nm (Figs. 3–6). The relative intensities of the shortwave and long-wave absorption of the esters II–V depend on the nature of the solvent and the concentration of the solute. When the polarity of the solvent is increased and the concentration of the solute is decreased, the intensity of the band at about 240 nm decreases, while the intensity of the band at 275 nm increases. An alkaline solution of the ester II absorbs at 279 nm (Fig. 3). An alkaline solution of ester I absorbs at 269 nm (the intensity of the absorption rapidly falling). When an aqueous solution of the ester IV is acidified, the intensity of absorption at 242 nm increases and the intensity of absorption at 275 nm decreases (Fig. 5).

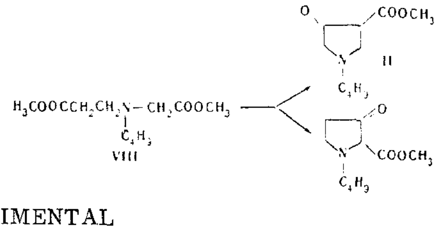
The changes observed in the UV spectra permit the conclusion that dissociation takes place in solutions of esters I–V. The band at about 240 nm relates to the absorption of the undissociated enol (247 nm in 4-methoxycarbonyl-3-oxotetrahydrothiophene, and 257 nm in the esters of cyclopentan-1-one-2-carboxylic acid [5]), and the band at 275 nm in the esters II–V and at 266 nm in the ester I to the absorption of the anion (281 nm in 4-methoxycarbonyl-3-oxotetrapydrothiophene and 286 nm in ethyl cyclopentan-1-one-2-carboxylate [15]). Changes analogous to ours have been observed in the UV spectra of a series of trans-fixed β-diketones and have been explained by their dissociation [16]. The esters II and III (molar extinction coefficient of the anion 15,000) contain the following percentages of the anion: in water 89 and 93, in methanol >24 and 27, in ethanol 23 and 21, and in isobutanol 8.6 and 5.3, respectively. The ester I is ionized even in heptane. The esters IV and V contain >10.3 and >14.3%, respectively of the anion in water (the maximum possible value of 30,000 was taken as the molar extinction coefficient [15]), and they exhibit absorption of the anion in alcoholic solutions (Figs. 5 and 6).

Thus, the capacity for ionization of the esters I–III proved to be considerably greater than expected and considerable ionization was detected in the esters IV and V (pK in water on the basis of the law of mass action <4.5). This complicated the determination of the keto-enol equilibrium in solutions of the esters I–V from their UV spectra. However, it can be seen from the spectra that for the esters IV and V (Figs. 5 and 6) Meyer's relationship is satisfied (the content of enol in the equilibrium increases with a decrease in the polarity of the solvent), while for the esters II and III it is not satisfied on passing from isobutanol solution to a solution in heptane (Figs. 3 and 4). According to the IR spectra, Meyer's relationship is not satisfied for the esters I–III on passing from the liquid state to solution in CCl_4 (Fig. 1). According to the UV spectra, in heptane there is less of the enolic forms in the equilibria of the esters II and III (ε of the enol in heptane 800–1200) than in the ester of cyclopentan-1-one-2-carboxylic acid (ε of the enol in heptane 4300 [15]) and in 4-methoxycarbonyl-3-oxotetrahydrothiophene (ε of the enol in hexane 7900). This conclusion is confirmed by a comparison of the IR spectra of the esters II and III (Fig. 1), of the esters of cyclopentan-1-one-2-carboxylic acid, and of 4-methoxycarbonyl-3-oxotetrahydrothiophene [5] in CCl_4. On passing from the esters II and III to the esters IV and V the position of the keto-enol equilibrium shifts in the direction of the enolic form, i. e., just as on passing from N-alkyl-3-methoxycarbonylpiperid-4-ones to their hydrochlorides [1].

The question of the assignment of the frequencies in the 1800–1600 cm^{-1} region in the IR spectrum of β-keto-esters with 5-membered rings has not been answered in the literature [17]. On passing from the esters of cyclopentan-1-one-2-carboxylic acid [5] to the esters I–V, the 1740 cm^{-1} band is retained and the 1760 cm^{-1} band is shifted to 1780 cm^{-1}. Under these conditions it is most probably the frequency of the stretching vibrations of the cyclic carbonyl group that undergoes change. It is considered [18] that the frequency of the stretching vibrations of a cyclic carbonyl group depends on the size of the valence angles at it. In our examples, the change of valence angles can be explained only by a change in the strain of the molecule and therefore the high frequency of the stretching vibrations of the cyclic carbonyl shows the greater strain in the keto form of the esters I–V than in the keto form of an ester of cyclopentan-1-one-2-carboxylic acid. The frequency of the stretching vibrations of an ester group in a chelate ring is connected with the strength of the chelate hydrogen bond [19]. The increase in the frequency of these vibrations in the enolic form of the esters I–V as compared with the enolic forms of the esters of cyclopentan-1-one-2-carboxylic acid indicates a weakening of the chelate hydrogen bond, which can only be a consequence of the deformation of the cyclopentene ring due to high strain. A splitting of the 1730 cm^{-1} band in the IR spectra of isobutanol solutions of esters of cyclopentan-1-one-2-carboxylic acid has been observed previously [5]. This splitting is found still more distinctly in the spectra of isobutanol solutions of the esters I–III and, particularly, IV and V (Fig. 1). The nature of the splitting is obscure. In the 2500-3700 cm^{-1} region of the IR spectra, the esters I–III have the following absorption bands, cm^{-1}: I) 2815, 2882, 2940, 2960; II) 2750, 2810, 2870, 2930, 2950; III) 2752, 2820, 2875, 2932, 2941.

The features of the IR spectra show the existence of strains in the tautomeric forms of esters I–V. The most probable cause of strain is van der Waals interactions with the participation of the butyl radical on the nitrogen atom. These interactions cause a deformation of the rings of the tautomeric forms, while in the enolic form the deformation of the cyclopentene ring leads to a deformation of the chelate ring and, because of this, to a decrease in conjugation. The decrease in conjugation in the enolic form evidently explains the shift in the position of the equilibrium in the direction of the keto form on passing from methyl cyclopentan-1-one-2-carboxylate to the esters II and III, and the high acidities of the enols of the esters I–V. The high acidity of the keto forms of the esters I–V may be connected with the greater possibilities for van der Waals interactions of the methyl radical on the nitrogen atom in the keto form than in the anion. It must be mentioned that the acidity of the forms in aqueous and alcoholic solutions may be affected by the dissimilar obstructions to the solvation of the nitrogen atom in the tautomeric forms and in the anion. The nonfulfillment of Meyer's equation for the esters II and III in the cases mentioned above is apparently due to intermolecular interactions of the tautomeric forms with one another.

The esters I and III were obtained by the cyclization of butyl(methoxy-carbonylmethyl)(β-methoxycarbonylpropyl)amine (VI) and butyl(α-methoxycarbonyl-ethyl)(β-methoxycarbonylethyl)amine (VII), respectively. In these cases condensation can take place only in one direction [20, 21], and the structure of the reaction products does not give rise to doubt. The cyclization of butyl(β-methoxycarbonylethyl)(methoxycarbonylmethyl)amine (VIII) may take place in two directions, and the question of which has not been answered in the literature [20]. On comparing the properties of the esters I (2-methoxycarbonyl isomer) and III (4-methoxycarbonyl isomer), we found that they differ considerably. Unlike, the ester I, the ester III, when hydrogen chloride is passed through an ethereal solution, forms a solid hydrochloride in quantitative yield and with exceptional ease. In the UV spectra, the absorption maximum of the anion is at 266 nm for the ester I and at 275 nm for the ester III. The product of the Dieckmann condensation of compound VIII forms a solid hydrochloride in quantitative yield when hydrogen chloride is passed through an ethereal solution, and its UV spectrum has the absorption maximum of the anion at 275 nm. Thus, it is the 4-methoxycarbonyl isomer (the ester II).



EXPERIMENTAL

Methyl β-butylaminopropionate. This was obtained by a method similar to that given by Leonard et al. [22]. At 20–25° C, 13 g (0.15 mole) of freshly distilled methyl acrylate was added to 10 g (0.14 mole) of butylamine in 100 ml of methanol. After being stirred for 2 hr, the solution was slowly heated to 60° C. The alcohol and the unchanged starting materials were driven off in vacuum, and the residue was distilled. Yield 12.4 g (57%), bp 106° C (14 mm) n_D^{21} 1.4290; d_4^{21} 0.9268. Found, %: N 8.52. Calculated for $C_8H_{17}NO_2$, %: N 8.79.

Butyl (β-methoxycarbonylethyl)(methoxycarbonylmethyl)amine (VIII). This was obtained by a method similar to that given by Clemo et al. [23]. A mixture of 11.5 g (0.07 mole) of methyl β-butylaminopropionate, 7.7 g (0.07 mole) of methyl chloroacetate, and 25 g of anhydrous potassium carbonate was heated in the water bath for 18 hr. Then water was added, the oil was extracted with ether, and the ethereal extract was dried over $MgSO_4$. The ether was driven off in vacuum and the residue was distilled. Yield 10.8 g (64.7%), mp 142° C (15 mm); n_D^{22} 1.4439; d_4^{22} 1.0219. Found, %: N 6.06. Calculated for $C_{11}H_{21}NO_4$, %: N 6.06.

N-Butyl-4-methoxycarbonylpyrrolid-3-one (II). In drops, 17.3 g (0.075 mole) of VIII was added to a suspension of 4.4 g (0.08 mole) of sodium methoxide in 100 ml of absolute benzene. The solution was stirred for 2 hr and was slowly heated to 60° C, and then it was cooled to 10° C, and 50 ml of water was added. The benzene layer was separated off and the aqueous layer was neutralized with acetic acid extracted with benzene. The benzene was evaporated off from the extract in vacuum, and the residue was distiled. Yield 5.1 g (32%), bp 92–94° C (1 mm); n_D^{20} 1.4653; d_4^{20} 1.0538. Found, %: N 7.03; MR_D 52.29. Calculated for $C_{10}H_{17}NO_3$, %: N 7.03; MR_D 52.83 (enol), 51.78 (keto form).

N-Butyl-4-methoxycarbonylpyrrolid-3-one hydrochloride (IV). Dry hydrogen chloride was passed through a solution of 5 g (0.025 mole) of the ester II in 60 ml of absolute ether. Colorless crystals of the hydrochloride began to deposit immediately and after four recrystallizations from acetone and ether they had mp 116–117° C. Yield 5.4 g (92%). Found, %: N 6.04; Cl 15.17. Calculated for $C_{10}H_{17}NO_3 \cdot HCl$, %: N 5.94; Cl 15.07.

Butyl(α-methoxycarbonylethyl)(β-methoxycarbonylethyl)amine (VII). This was obtained in a similar manner to the amine VIII from methyl β-butylaminopropionate and methyl α-bromopropionate. Yield 61%. Mp 143–144° C (10 mm); n_D^{20} 1.4429; d_4^{20} 1.0008. Found, %: N 6.00. Calculated for $C_{12}H_{23}NO_4$, %: N 5.71.

N-Butyl-4-methoxycarbonyl-2-methylpyrrolid-3-one (III). This was obtained in a similar manner to the ester II from the amine VII. Yield 34.7%. Bp 94–96° C (1 mm); n_D^{20} 1.4590; d_4^{20} 1.0270. Found, % N 6.57; MR_D 56.77. Calculated for $C_{11}H_{19}NO_3$, %: N 6.67; MR_D 56.40 (keto form); 57.45 (enol).

N-Butyl-4-methoxycarbonyl-2-methylpyrrolid-3-one hydrochloride (V). This was obtained in a similar manner to the hydrochloride IV.

Yield 93%, mp 101.5–102° C. Found, %: N 5.56; Cl 13.99. Calculated for $C_{11}H_{19}NO_3 \cdot HCl$, %: N 5.61; Cl 14.20.

Methyl β-butylaminobutyrate. To 12 g (0.16 mole) of butylamine in 100 ml of absolute methanol was added 17 g (0.17 mole) of freshly distilled methyl methacrylate. The reaction mixture was left for 48 hr. The alcohol and the unchanged starting materials were driven off in vacuum, and the residue was distilled. Yield 12.8 g (45%), bp 89° C (12 mm); n_D^{20} 1.4320; d_4^{20} 0.9170. Found, %: N 8.19. Calculated for $C_9H_{19}NO_2$, %: N 8.09.

Butyl(methoxycarbonylmethyl)(β-methoxycarbonylpropyl)amine (VI). This was obtained in a similar manner to the amine VIII from methyl β-butylaminobutyrate and methyl chloracetate. Yield 50%, bp 142–143° C (15 mm); n_D^{20} 1.4425; d_4^{20} 1.0076. Found, %: N 6.00. Calculated for $C_{12}H_{23}NO_4$, %: N 5.71.

N-Butyl-2-methoxycarbonyl-4-methylpyrrolid-3-one (I). This was obtained in a similar manner to the ester II from the amine VI. Yield 22%, bp 117° C (2 mm); n_D^{22} 1.4633; d_4^{22} 1.0246. Found, %: N 6.42; MR_D 58.77. Calculated for $C_{11}H_{19}NO_3$, %: N 6.57; MR_D 57.45 (enol), 56.40 (keto form).

The IR spectra in the 1900–700 cm^{-1} region were recorded on a Hilger H-800 spectrophotometer and in the 2500–3700 cm^{-1} region on an IKS-14 spectrophotometer. The UV spectra were recorded on a Unicam SP-500 spectrophotometer.

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