

STUDY OF THE TAUTOMERISM OF ACETYL- AND CARBETHOXY-SUBSTITUTED TETRAHYDROFURANONES

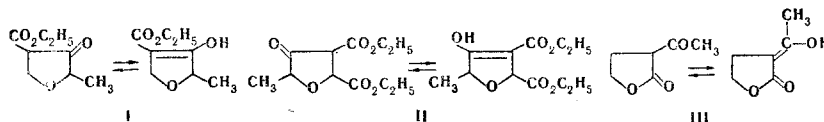
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The equilibrium position of 2-methyl-4-carbethoxytetrahydro-3-furanone, 2-methyl-4,5-dicarbethoxytetrahydro-3-furanone, and 3-acetyltetrahydro-2-furanone in acetonitrile, dioxane, and alcohols was determined. It was shown that the two Meyer equations are satisfied for these keto-enols paired with acetylacetone.

We have previously shown that heterocyclic β -ketoesters with five- and six-membered rings containing sulfur and nitrogen as the heteroatoms differ substantially in their tautomeric properties from the esters of 1-cyclopentanone- and 1-cyclohexanone-2-carboxylic acids [1-6]. Thus a considerable change in the equilibrium position is observed when the CH_2 group in the five-membered ring is replaced by an $>\text{S}$ and $>\text{NR}$ group [2,3]. The Meyer equation may not be satisfied for heterocyclic β -ketoesters because of dissimilar solvation of the heteroatoms of the ketone and enol forms as a consequence of the difference in their conformations [4,5]. In this paper, we have studied the tautomerism of heterocyclic β -ketoesters with five-membered rings containing oxygen as the heteroatom and of an α -acyllactone. α -Acyllactones are of interest in connection with a study [7] in which it was shown that these keto-enols contain the trans-enol together with the cis-enol in equilibrium.

The tautomerism of 2-methyl-4-carbethoxytetrahydro-3-furanone (I), 2-methyl-4,5-dicarbethoxytetrahydro-3-furanone (II), and 3-acetyltetrahydro-2-furanone (III) was studied by IR and UV spectroscopy.



The IR spectrum of liquid I contains intense bands at 1730 and 1775 cm^{-1} , which pertain to the keto form, and insignificant absorption at $\sim 1650\text{ cm}^{-1}$, which can be assigned to the enol form. The IR spectrum of liquid II contains intense bands at 1730 and 1775 cm^{-1} , which pertain to the keto form, and rather intense bands at 1650 and 1685 cm^{-1} , which are affiliated with the enol form. The absorption of the ester group in the 5 position lies at 1730 - 1775 cm^{-1} . There are intense bands at 1725 and 1775 cm^{-1} (keto form) and a band of average intensity at 1660 cm^{-1} (enol) in the IR spectrum of liquid III (see also [8]). Thus, according to the IR spectra, the keto form predominates in the liquid state in the equilibrium of I, while both forms are present in significant quantities in the equilibria of II and III. The UV spectra of I-III in water, alcohols, acetonitrile, dioxane, hexane, and in ethanol in the presence of alkali were recorded from 220 to 340 nm (Table 1). The absorption maximum of the enol form lies at $\sim 250\text{ nm}$. The contribution of the keto form to the absorption at the enol maximum is insignificant except for solutions of I in water and acetonitrile. As seen from Table 1, the absorption maximum of the enol form is shifted to longer wavelengths on passing from neutral to alkaline solutions. This is characteristic for β -dicarbonyl compounds [9]. In aqueous solution III is ionized. The problem of the rate of establishing equilibrium in solutions of I-III was solved as follows. The spectra of I-III in solution are completely reproduced 5 min, 1 day, 3 days, and 5 days after

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TABLE 1. UV Absorption and M_{TS} Values for I-III in Solution (nm)

Solvent	λ_{T_1}, nm	$\epsilon_{T_1, S}$	$M_{T_1, S}$	λ_{T_2}, nm	$\epsilon_{T_2, S}$	$M_{T_2, S}$	λ_{T_3}, nm	$\epsilon_{T_3, S}$	$M_{T_3, S}$
Water	240	465 ± 3	1,111 ± 0,002	240	760 ± 12	1,661 ± 0,047	280	1500 ± 20	1,704 ± 0,019
Acetonitrile	240	307 ± 5		240	930 ± 14	1,219 ± 0,004	252	363 ± 6	1,453 ± 0,003
Methanol	245	432 ± 7	1,125 ± 0,003	245	2060 ± 30	1,164 ± 0,003	252	1430 ± 17	1,106 ± 0,002
Ethanol	245	664 ± 10	1,078 ± 0,002	245	2620 ± 40	1,150 ± 0,003	252	1560 ± 20	1,081 ± 0,001
Isobutyl alcohol	246	910 ± 14	1,057 ± 0,003	245	2840 ± 40	1,370 ± 0,008	252	1990 ± 30	1,375 ± 0,008
Dioxane	246	410 ± 6	1,133 ± 0,003	244	1370 ± 20		252	550 ± 8	
Hexane	250	1660 ± 25		245	3100 ± 50		275	1700 ± 240	
Ethanol + NaOH	280	16000 ± 240						8100 ± 120	

preparation. This indicates either a very high or a very low rate of establishing equilibrium in solutions of I-III. It is known that the molar extinction coefficient of the enol form of keto-enols is only slightly dependent on the nature of the solvent [9, 10], and that the rate of establishing equilibrium is usually lowest in hexane. The considerable differences in the molar extinction coefficients of I-III in hexane solutions from the molar extinction coefficients in other solvents were therefore considered as proof of the high rate of establishing equilibrium in solutions of I-III.

We made a comparison of the effect of the solvent on the equilibrium of I-III with the effect of the solvent on the equilibrium of acetylacetone (IV), which is similar in this respect to acetoacetic ester. For this we used Eq. (1), which is equivalent to the Meyer equation:

$$\frac{\epsilon_{T_1, S_n}}{\epsilon_{T_1, S_n} - \epsilon_{T_1, S_1}} = \text{const} \frac{\epsilon_{T_2, S_n}}{\epsilon_{T_2, S_n} - \epsilon_{T_2, S_1}}, \quad (1)$$

where ϵ_{TS} is the molar extinction coefficient of tautomer T in solvent S. The satisfaction of Eq. (1) means that the Meyer equation is satisfied [11, 12]. The preference for Eq. (1) over the Meyer equation consists in the fact that the

$$M_{TS} = \epsilon_{TS_n} / (\epsilon_{TS_n} - \epsilon_{TS_1})$$

values are more accessible than the equilibrium constants. The molar extinction coefficients of I-III in the standard state were calculated from the equations presented in [12]. The molar extinction coefficients in the standard state in methanol-isobutyl alcohol (152), methanol-ethanol (125), and ethanol-isobutyl alcohol (202) (average value 150) were obtained for III paired with acetylacetone. (The molar extinction coefficient in the standard state was taken as 2300 [12].) The molar extinction coefficient in the standard state in methanol-ethanol (339) and methanol-isobutyl alcohol (398) (average value 370) was obtained for II paired with III. (The molar extinction coefficient in the standard state was taken as 150.) The molar extinction coefficient in the standard state in methanol-ethanol (51) and methanol-isobutyl alcohol (44) (average value 48) was obtained for I paired with II. (The molar extinction coefficient in the standard state was taken as 370.) The problem of finding the absorption of tautomers in the standard state is equivalent to the problem of drawing a line through the origin as close as possible to all of the points on the graph of $M_{T_1, S}$ versus $M_{T_2, S}$. It is therefore necessary to calculate the standard states for all of the possible combinations of solvents and to take the arithmetic-mean value. If the values for the various combinations of states differ markedly, this indicates that Eq. (1) is not satisfied for all of the combinations. In this case, it is necessary to select that value of the molar extinction coefficient of the tautomers in the standard state in such a way that it satisfies the maximum number of combinations. In the case of I-III, the absorption in the standard state for all combinations of solvents, including the participation of acetonitrile and dioxane, was calculated. However, the closest values proved to be the values for combinations of alcohol solvents, and their average was taken for the absorption of I-III in the standard state. A small error in determining ϵ_{TS_1} does not affect the satisfaction of Eq. (1), since it is included in all M_{TS} values.

TABLE 2. Ratios of the M_{TS} Values for I-IV in Solution

Solvent	M_{T_2S}/M_{T_1S}	M_{T_2S}/M_{T_3S}	M_{T_3S}/M_{T_1S}	M_{T_1S}/M_{T_4S}	M_{T_2S}/M_{T_4S}	M_{T_3S}/M_{T_4S}
Acetonitrile		0,975 ± 0,021				
Methanol	1,084 ± 0,006	1,057 ± 0,076	1,025 ± 0,005	0,784 ± 0,007	1,035 ± 0,027	0,942 ± 0,026
Ethanol	1,080 ± 0,005	1,052 ± 0,005	1,026 ± 0,005	0,778 ± 0,005	0,850 ± 0,008	1,244 ± 0,010
Isobutyl alcohol	1,088 ± 0,005	1,064 ± 0,004	1,023 ± 0,003	0,787 ± 0,009	0,840 ± 0,006	1,253 ± 0,009
Dioxane	1,209 ± 0,010	0,997 ± 0,015	1,214 ± 0,010	0,823 ± 0,008	0,856 ± 0,010	1,242 ± 0,013
					0,995 ± 0,013	1,001 ± 0,014

The M_{TS} values for I-III in solutions (Table 1) were calculated by means of the absorptions of I-III in the standard states. The satisfaction of Eq. (1) is characterized by the deviation of its constants from the average value. As seen from Table 2, the maximum deviation of the constant of Eq. (1) from the average value for I-IV in alcohols is equal to the error in the determination of the constants. Thus the Meyer equation is satisfied for various combinations of I-IV in alcohol solutions. However, Eq. (1) does not make it possible to solve the problem of the satisfaction of the Meyer equation in two of the solvents. On the basis of the data in Table 2, it can be stated that the Meyer equation that is satisfied in alcohols is not satisfied for I-IV in acetonitrile and dioxane. However, these results say nothing as to whether another Meyer equation is satisfied in acetonitrile and dioxane or whether no equation whatsoever is satisfied. The problem of the satisfaction of the Meyer equation for two solvents can be solved only by means of equilibrium constants.

The molar extinction coefficients of enols I-III (ϵ_{0T}) that are necessary for the calculation of the equilibrium constants were found from equations based on the Meyer equation [12, 13]. The ϵ_{0T} value for II was determined from Eq. (2):

$$\epsilon_{0T_1} = \frac{\epsilon_{T_1S_1} \epsilon_{T_1S_2} (K_{T_2S_2} - K_{T_2S_1})}{\epsilon_{T_1S_1} K_{T_2S_2} - \epsilon_{T_1S_2} K_{T_2S_1}}, \quad (2)$$

where ϵ_{TS} is the molar extinction coefficient of tautomer T in solvent S, and K_{TS} is the equilibrium constant of tautomer T in solvent S. The T_1 and T_2 values obey the Meyer equation, and ϵ_{T_1S} is not proportional to K_{T_2S} even in one solvent. Compound II was taken as T_1 , and acetylacetone (IV) was taken as T_2 . The equilibrium constants of IV were calculated from the molar extinction coefficients presented in [12], and ϵ_{0T_4} was 10,500 [12]. The ϵ_{0T_1} value for II was obtained as 4500 ± 300 .

The ϵ_{0T} value for I and III was determined from Eq. (3):

$$\epsilon_{0T_1} = \frac{\epsilon_{T_2S_1} \epsilon_{T_2S_2} (\epsilon_{T_1S_1} - \epsilon_{T_1S_2}) + n \epsilon_{T_1S_1} \epsilon_{T_1S_2} (\epsilon_{T_2S_2} - \epsilon_{T_2S_1})}{n(\epsilon_{T_1S_1} \epsilon_{T_2S_2} - \epsilon_{T_2S_1} \epsilon_{T_1S_2})}, \quad (3)$$

where ϵ_{TS} is the molar extinction coefficient of tautomer T in solvent S, ϵ_{0T} is the molar extinction coefficient of the absorbing and solvent-independent form of tautomer T, and $n = \epsilon_{0T_2}/\epsilon_{0T_1}$. The conditions and possibilities for the use of Eq. (3) and Eq. (2) were examined in detail in [14]. For pairs III-II, Eq. (3) has the form $\epsilon_{0T_1} = -(2600 \pm 240)/n + (6800 \pm 600)$ (T_1 is II). The error in Eq. (1) has the same sign in the coefficient and free term. The value for II (4500) was substituted into the equation, n was found, and an ϵ_{0T} value of 5200 ± 300 was found for III from $\epsilon_{0T_2} = n\epsilon_{0T_1}$. Equation (3) for the III-I pair has the form $\epsilon_{0T_1} = -(2000 \pm 70)/n + (6400 \pm 240)$. The ϵ_{0T} value for III (5200) was substituted into it, n was found, and the ϵ_{0T} value for I was found from $\epsilon_{0T_2} = n\epsilon_{0T_1}$. It was found to be 9000 ± 600 . Thus the ratio of the molar extinction coefficients of enols II and I is two. To verify this, Eq. (1) was written for the II-I pair, and $n = 2$ was substituted into it. The equation has the form $\epsilon_{0T_1} = -(568 \pm 30)/n + (4750 \pm 230)$. The ϵ_{0T} values obtained were 4500 ± 200 and 9000 ± 450 .

The molar extinction coefficients of the enols of keto-enols are often found from the results of UV spectra and bromometric titration. We titrated I and III in ethanol by an indirect method. Enol contents of $7.2 \pm 0.2\%$ and $9.2 \pm 0.4\%$ were obtained for I and III, respectively. In both cases, a modified method gave 100% enol, which indicates the easy reduction of the brominated enol. When I and III were titrated by an indirect method with a delay of 10 min, 58 and 56.8% enol, respectively, were obtained. These additional results would seem to indicate the satisfactory applicability of the indirect method for the determination of the enol content in alcohol solutions of I and III. The

TABLE 3. Equilibrium Constants of I-IV in Solution*

Solvent	K_{T_1S}	K_{T_2S}	K_{T_3S}	K_{T_4S}
Acetonitrile	0,035±0,001	0,26±0,01	0,075±0,001	1,4±0,1
Methanol	0,050±0,001	0,84±0,02	0,277±0,006	2,6±0,1
Ethanol	0,080±0,001	0,40±0,05	0,428±0,008	3,7±0,1
Isobutyl alcohol	0,112±0,002	1,71±0,07	0,620±0,015	6,0±1,1
Dioxane	0,048±0,001	0,44±0,01	0,118±0,002	4,0±0,4

* $\epsilon_{0T_3} = 5200$, $\epsilon_{0T_2} = 4500$, $\epsilon_{0T_1} = 9000$, and $\epsilon_{0T_4} = 10,500$.

TABLE 4. Ratios of the Equilibrium Constants of I-III to IV and of III to II in Solutions

Solvent	K_{T_1S}/K_{T_4S}	K_{T_2S}/K_{T_4S}	K_{T_3S}/K_{T_4S}	K_{T_3S}/K_{T_2S}
Acetonitrile	0,026±0,002	0,19±0,02	0,54±0,04	0,29±0,01
Methanol	0,019±0,001	0,32±0,03	0,06±0,08	0,33±0,02
Ethanol	0,022±0,001	0,38±0,03	1,17±0,06	0,31±0,02
Isobutyl alcohol	0,019±0,004	0,28±0,08	1,03±0,26	0,36±0,02
Dioxane	0,014±0,002	0,11±0,02	0,30±0,04	0,27±0,02

molar extinction coefficient of enol I, calculated on the basis of the UV spectra and the results of bromometric titration, is 9600 ± 600 . It is in good agreement with the value obtained above from Eq. (3). However, the molar extinction coefficient of enol III, obtained by this method, is $17,000 \pm 500$, which is certainly not in agreement with the value obtained from the equations and, from general considerations, seems unreal. Our data on the titration of III in ethanol are in agreement with the results in [7] for methanol. The rate of addition of bromine to the double bond of enol III is probably not very high.

Using the molar coefficients of the enols found from Eq. (3), we calculated the equilibrium constants of I-III in solution (Table 3). The equilibrium constants of acetylacetone (IV) are also presented in Table 3. The molar extinction coefficients of IV in solutions were taken from [12].

The ratios of the equilibrium constants of I-III to IV and of III to II are presented in Table 4.

It is apparent from Table 4 that the Meyer equation is satisfied for I-III paired with IV in alcohols within the limits of experimental error. The ratios of the equilibrium constants of I-III and IV in acetonitrile and dioxane are considerably lower than the ratios in alcohols. However, they are comparatively close to one another, and it can be assumed that the Meyer equation is also satisfied for I-III paired with IV in acetonitrile and dioxane. Thus two Meyer equations are satisfied for I-III and IV in the examined group of solvents. A condition for the satisfaction of the Meyer equation for the two tautomers is an identical change in the differences in their solvation on passing from one solvent to another. This is possible not only when the differences in the solvation of the two tautomers are the same in each solvent but also when the differences are dissimilar but differ by the same magnitude in each solvent. Several Meyer equations are therefore possible for two tautomers in a group of solvents [6]. In our case, the satisfaction of two Meyer equations for I-III and IV indicates that the differences in the solvation of I-III and IV are dissimilar and differ by a certain magnitude either in alcohols or in acetonitrile and dioxane or in both groups of solvents. We have previously shown [15] that one Meyer equation is satisfied in alcohols and acetonitrile for 4-cyano-3-thiophanone and 4-cyano-5-methyltetrahydro-3-furanone. This attests to the same effect of the solvent on the oxygen atom in the ketone and enol forms of 4-cyano-5-methyltetrahydro-3-furanone. The effect of solvents on I-II and III is also the same. The reason for the satisfaction of two Meyer equations for I-III and IV is therefore the change in solvation of the chelate ring in the enol form of I-III as compared with the enol form IV. The low molar extinction coefficients of enols I-III indicate great deformation of the chelate ring associated with ring strain. The satisfaction of the Meyer equation for the two cyano ketones mentioned above presupposes that the ring strain does not change the solvation of the carbonyl group in the ring. Thus the chemical type of I-III changes as a result of deformation of the chelate ring. The Meyer equation can be satisfied for two tautomers of different chemical types if the mechanism of solvation of the corresponding forms is the same. This is usually observed in a number of monotopic solvents. In our case also, the sol-

vents can be divided into two groups with respect to satisfaction of the Meyer equation for I-III and IV. Dioxane and acetonitrile are close with respect to their types, since they act as proton acceptors in solvation processes.

In contradiction to [7], we did not detect a cis-trans enol equilibrium for III. In [7], the equilibrium position of alkylactones was determined by bromometric titration. This method is apparently not applicable to this class of compounds because of the slow addition of bromine to the enol double bond. The same percentage of enol, which is apparently determined by the delay between the addition of bromine and β -naphthol, is obtained for III in methanol, ethanol, chloroform, and hexane.

We have previously shown that a sharp shift in the equilibrium position to favor the enol form is observed when the CH_2 group in the ring of 1-cyclopentanone-2-carboxylic acid is replaced by a >S group [2]. The CH_2 and >S groups have different bond lengths and angles and barriers to rotation about these bonds [16, 17]. Both differences may be reasons for the observed shift. The >O group has bond lengths and angles that are close to the bond lengths and angles of the $>\text{CH}_2$ group and a barrier to rotation about the bond that is close to the barrier to rotation about the bond of the >S group [16, 17]. The determination of the shift in the equilibrium position on passing from an ester of 1-cyclopentanone-2-carboxylic acid to 4-carbalkoxytetrahydro-3-furanone makes it possible to solve the problem of the relative magnitude of the bond angles and lengths and the barriers to rotation in tautomers with five-membered rings. As seen from Table 3 and the data in [2], the equilibrium position on passing from esters of 1-cyclopentanone-2-carboxylic acid to I is shifted to favor the keto form. The lengths and angles of the bond of the >S group are responsible for the high percentage of enol in the 4-carbalkoxy-3-thiophanones. Of course, in I there should be an effect of the methyl substituent on the equilibrium. However, in the case of 4-acetyl-3-thiophanones [18], we have observed that substitution leads to an increase in the percentage of enol in the equilibrium. A similar picture is observed on passing from I to II.

EXPERIMENTAL

2-Methyl-4-carbethoxytetrahydro-3-furanone (I). This compound was obtained in 42% yield by the method presented in [19] for 4-carbomethoxytetrahydro-3-furanone from ethyl lactate and ethyl or methyl acrylate; bp 61° (0.2 mm), $n_D^{19.5}$ 1.4470. Found: C 55.7; H 7.0%. $\text{C}_8\text{H}_{12}\text{O}_4$. Calculated: C 55.8; H 7.0%. The preparation of I by using methyl acrylate was of interest. We observed a similar exchange of radicals in the preparation of 1-butyl-4-carbethoxy-2,3-dihydropyrrolidine [10].

2-Methyl-4,5-dicarbethoxytetrahydro-3-furanone (II). This compound was obtained like I in 36% yields from ethyl fumarate and ethyl lactate with the difference that the solvent was benzene instead of dimethyl sulfoxide; bp 103° (0.3 mm), n_D^{22} 1.4480, d_4^{22} 1.1566. Found: C 53.8; H 6.7%; MR_D 56.57. $\text{C}_{11}\text{H}_{16}\text{O}_6$. Calculated: C 54.1; H 6.6%; MR_D 56.81 (enol); 55.76 (ketone).

3-Acetyltetrahydro-2-furanone (III). This was obtained by the method in [20] and had bp $115\text{-}116^\circ$ (15 mm); n_D^{18} 1.4585, and d_4^{18} 1.1740. Found: MR_D 28.82. Calculated: MR_D 29.89 (enol); 28.38 (ketone).

The UV spectra of $2 \cdot 10^{-3}$ M solutions were recorded with an SF-4A spectrophotometer at layer thicknesses of 0.02-0.05 cm. The spectra were recorded at definite time intervals until there were no longer changes in them. The error in determining the molar extinction coefficients is given as equal to the maximum instrument error. Ethanol solutions of I-III were titrated by modified and reverse methods. The mean-arithmetic value and mean-square error were calculated from a mixture of results. After preparation the solutions were allowed to stand for 15 min to 24 h. The time lags after the various operations were varied.

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