# KETO-CIS-TRANS-ENOL-EQUILIBRIUM OF 3-ALKYLACETYLACETONES

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Abstract—The effect of solvents on the position of keto-*cis-trans*-enolic equilibrium of a series of 3-alkylacetylacetones has been studied. The bromometric and IR evidence for 1% solutions gives a sound qualitative picture but owing to insufficient dilution does not elucidate pertinent quantitative regularities. The latter was achieved by studying UV spectra with dilution down to  $10^{-4}$  m/l. As a measure of concentration of tautomeric forms integral densities of absorption bands assigned to *cis*-and *trans*-enolic forms were used. The data obtained led to the conclusion that *cis*-enolization of 3-alkylacetylacetones follows Meyer's rule whereas *trans*-enolization is independent of the nature of the solvent. The overall enolization is expressed as  $K_T = EL + E_1$ . The specificity of  $\beta$ -dicarbonyl compounds as a particular chemical type in terms of the Brønsted–Izmailov theory is discussed.

#### **1. GENERAL CONSIDERATIONS**

In previous work<sup>1,2</sup> it has been shown that the solutions of  $\alpha$ -alkylacetoacetates exhibit three forms in tautomeric equilibrium: ketonic, *cis*-enolic and *trans*-enolic forms. *Trans*-enolization of these substances was found to be essentially independent of the solvent whilst *cis*-enolization obeyed the well known Meyer's rule.<sup>3</sup>

$$K_{T (trans)} = \frac{(trans-enol)}{(ketone)} = Const = E_1$$
 (1)

$$K_{T (cis)} = \frac{(cis-enol)}{(ketone)} = EL$$
<sup>(2)</sup>

In this equation E is the *cis*-enolizability of the keto-enol, equal to the relationship between the constant of the keto-*cis*-enol equilibrium and that of the constant of keto-enol equilibrium of ethyl acetoacetate in the same solvent, L is the *cis*-enolizing

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- <sup>2</sup> M. I. Kabachnik, S. T. Yoffe, E. M. Popov and K. V. Vatsuro, Tetrahedron 12, 76 (1961).
- <sup>a</sup> K. H. Meyer, Ber. Dtsch. Chem. Ges. 45, 2846 (1912).

capacity of the solvent, equal to the keto-enol equilibrium constant of ethyl acetoacetate in the particular solvent.\*

The general tautomeric equilibrium constant is equal to the sum of particular constants.

$$K_T = K_{T (cis)} + K_{T (trans)} = \frac{(cis-enol) + (trans-enol)}{(ketone)} = EL + E_1$$
(3)

The dependence of  $K_T$  on L is expressed by a straight line that cuts on the ordinate an intercept  $E_1$  characteristic of *trans*-enolization.<sup>†</sup> The applicability of Meyer's rule to *cis*-enolization of  $\alpha$ -alkylacetoacetates indicates that *cis*-enolic forms of these substances belong to acids of one chemical type (as implied by the theories of Brønsted,<sup>6,7</sup> and Izmailov<sup>8,9,10</sup>). Their molecules involve a six-ring hydrogen bonded cycle which determines their general character of polarity and their solvation changes in passing from one solvent to another. With these substances, increased polarity of solvent results in decrease of enolization.

It has been shown<sup>11</sup> that, with tautomeric acids of the type to which the Brønsted-Izmailov equation applies, the tautomeric equilibrium constants in solvents  $S_1$  and  $S_2$  are in a linear relationship.

$$pK_{TS_1} = pK_{TS_2} + Const$$
(5)

(where  $pK_{TS}$  are tautomeric equilibrium constants in solvent S) directly leading to Meyer's rule.

The solvent effect on *trans*-enolization is generally more involved. Experimental evidence obtained by  $us^{1,2}$  and Eistert *et al.*<sup>12,13</sup> indicates that solvents affect the *trans*-enolization of various keto-enols differently. For "*trans*-fixed" cyclic  $\beta$ -diketones such as dimedone, the solvent effect on *trans*-enolization is opposite to that due to Meyer:

\* Thus ethyl acetoacetate is taken as a standard for *cis*-enolization. The enolic form of ethyl acetoacetate does indeed have *cis*-configuration.<sup>4,5</sup> Trans-enolization of  $\alpha$ -alkylacetoacetates is due to steric hindrances opposing the formation of the *cis*-enolic form.<sup>1,18</sup>

 $\dagger$  Equation (3) is a particular case of a more general form (4) derived previously for the tautomeric equilibrium of three acids involving common anions.<sup>1</sup>

$$K_T = EL + E'L' \tag{4}$$

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- <sup>18</sup> H. Henecka, Chem. Ber. 81, 179, 192 (1948).

enolization increasing with increasing polarity of the solvent. In "*trans*-fixed" cyclic ketolactones, such as  $\alpha$ -alkyltetronic acids, enolization is independent of the solvent.<sup>1,2,14,15</sup> "*Trans*-fixed" cyclic acylals of malonic acid, such as "Meldrum's acid" fail to enolize in solutions.<sup>2,16</sup> Finally, the dependence of the enolization of  $\beta$ -cyano-ketones obeys equation (4) only when the standard substance has been suitably chosen.<sup>2,17</sup>

The independence of keto-*trans*-enol equilibrium constants of the solvent observed for alkyltetronic acids and  $\alpha$ -alkylacetoacetates denotes similar changes in the free solvation energy of ketonic and *trans*-enolic forms with the change of solvent, a net result of many factors, not necessarily applicable to *trans*-enols of other chemical types.

In this connection it was of great interest to study the effect of solvents on *trans*enolization of various keto-enols and to elucidate the general rules concerning this phenomenon. This paper deals with the enolization of 3-alkylacetylacetones which can have three tautomeric forms, namely, ketonic, *cis*-enolic, and *trans*-enolic.



The enolic form of acetylacetone itself (R=H) has a *cis*-configuration with strong intramolecular hydrogen bonding.

As in the case of  $\alpha$ -alkylacetoacetates the introduction of branched substituents should create steric hindrances opposing *cis*-enolization and resulting in a *trans*-enolic form, the concentration of which will be higher the greater the forces of steric hindrance. Qualitatively these relations can be followed by observing the action of copper acetate on an alcoholic solution of keto-enols. This reaction is, in principle, similar to the well known Henecka test<sup>18</sup> with ferric chloride which led to the discovery of *trans*-enolization in  $\beta$ -dicarbonyl compounds with branched alkyl radicals. 3-Alkylacetylacetones with primary alkyl groups (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>, iso-C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) as well as the unsubstituted acetylacetone readily form peculiar light blue precipitates with copper acetate. On the other hand, 3-alkylacetylacetones with secondary radicals (R = iso-C<sub>3</sub>H<sub>7</sub>, sec-C<sub>4</sub>H<sub>9</sub>) do not react with copper acetate.

As the substances in question all contain in alcoholic solution a sufficiently high percentage of enol, (see below) the absence of any reaction with copper acetate points to *trans*-enolization.\*

In order to obtain quantitative evidence use has been made of the bromometrical method as well as a study of IR and UV spectroscopy.

• Steric hindrance during the formation of chelate copper salt must be greater than intramolecular hydrogen bonding. Therefore, the failure to react with copper acetate does not exclude the presence of some *cis*-form in equilibrium. Similarly, a positive reaction with copper acetate does not necessarily mean the absence of a *trans*-form in equilibrium.

# 2. BROMOMETRICAL EVIDENCE

3-Alkylacetylacetones, CH<sub>3</sub>CO--CH-COCH<sub>3</sub>, have been investigated involving the following substituents:

$I R = CH_3$	$IV \ R = C_4 H_9$	VII $R = iso-C_3H_7$
If $R = C_2 H_5$	$V R = iso-C_4H_9$	VIII $R = sec-C_4H_9$
$III R = C_3H_7$	$VI R = C_6H_5CH_2$	IX $R = cyclo-C_5H_9$

As solvents, 67% methanol, methanol, chloroform, ethanol, benzene, ethyl ether, carbon tetrachloride, and hexane were used. The percentage of enolic forms in 1% solutions of keto-enols was evaluated by direct bromemetric determination. The results are summarized in Table 1 with solvents given in order of increasing enolization of most substances.

Table 1. Tautomeric equilibrium constants in 1% solutions of 3-alkylacetylacetones  $CH_3$ ·CO·CH—CH·CH<sub>8</sub> (bromometric evidence)

		R						
(Solvent) R	СН₃	C₂H₅	C₃H,	C₄H9	i <b>so-C₄H</b> ,	C <sub>6</sub> H₅CH₂	iso-C <sub>8</sub> H <sub>7</sub>	sec-C₄H,
67% methyl alcohol	0.19	0.15	0.24	0.24	0.27	0.36	0.44	0.26
methyl alcohol	0.41	0.29	0.43	0-36	0.26	0.63	0.45	0.26
chloroform		0.46	0.50	0.57	0.70	<b>0</b> ·76	_	
benzene	0.61	0.46	0.57	0.50	0.67	0.68	0-42	0.26
carbon tetrachloride	0.64	0.46	0.61	0.55	0.55	0.68	0.46	<b>0·2</b> 7
ethyl alcohol	0.66	<b>0</b> ∙46	0.61	0.65	0.54	0.99	0.43	0.27
ether	0.69	0.74	0.81	0.63	0.65	0.76	0.48	0.26
hexane	0.65	0.71	0.66	1.53	1.27	0.83	0.20	0.29

From data in Table I it will be seen that enolization of 3-isopropyl and 3-sec butylacetylacetone (VII and VIII) does not depend on the nature of the solvent. This is to be correlated with the fact that these substances fail to react with copper acetate, a reaction characteristic of *cis*-enolization, and that secondary radicals introduce greater steric hindrance to the formation of a *cis*-enol with a planar six-ring hydrogen bonded cycle. Hence, these substances give in all solvents *trans*-forms and their *trans*enolization is not affected by the nature of the solvent, as we have previously shown for alkyl  $\alpha$ -alkylacetoacetates.

It is also noteworthy, that contrary to other 3-substituted derivatives, 3-cyclopentylacetylacetone (IX) does not enolize in all solvents. All the other derivatives studied (I–VI), follow, in general, Meyer's rule, namely, the enolization increases with decreasing polarity of the solvent. However, Meyer's rule does not strictly hold and the dependence of the keto-enol equilibrium constant on L, say for 3-butylacetylacetone (IV), Fig. 1, is not linear. At the same time, substances I–VI undergo specific reactions with copper acetate and ferric chloride, thus pointing to their *cis*-enolization that would be expected to follow Meyer's rule. The reason for such a divergence is seen from the dependence of the enolization of these substances upon concentration. It was found that the 1% solutions of these ketones are not sufficiently dilute for the equilibrium constant to be independent of concentration. Thus for 3-butylacetylacetone the 10 and 50 fold dilution markedly affects the percentage of the enolic form (Table 2).



FIG. I. Dependence of the tautomeric equilibrium constant ( $K_T$ ) on the solvent (constant L) for 3-butylacetylacetone (IV). Solvents: 1-67% methanol, 2-methanol, 3- chloroform, 4-ethanol, 5-benzene, 6-ether, 7-carbontetrachloride, 8-hexane.

0.1 AND	0.02% сон	CENTRATION	4S
	Percentag	ge of the en	olic form
Solvent	In 1% solution	In 0.1 % solution	In 0.02 % solution
67% methanol	19	27-33	41-50
ethanol	40	38-45	56–70
hexane	61	100	

TABLE 2. THE PERCENTAGE OF THE ENOLIC FORM\* OF 3-BUTYLACETYLACETONE IN VARIOUS SOLVENTS AT 1, 0.1 and 0.02% concentrations

\* The evaluation was carried out following Dieckman's modified procedure.<sup>19</sup>

Meyer<sup>20</sup> has dealt with the dependence of enolization on the concentration of ethyl acetoacetate in different solvents. His data show that in alcoholic and benzene solutions of 5% and less, enolization is not affected by dilution. In carbon bisulphide this range is even lower, amounting to about 2% and with hexane it is not reached even in 1% solution. As seen, with 3-alkylacetylacetones this range is attained only at much greater dilutions. This is possibly due to a higher percentage of enolic forms in the solutions of these substances. Use of more dilute solutions (0.02%) leads, however, to a sharp decrease in precision and reproducibility of bromometric data. Therefore, though giving a correct qualitative picture of *cis-trans*-enolization of these substances, the bromometric method does not permit the necessary quantitative calculations.

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<sup>&</sup>lt;sup>20</sup> K. H. Meyer and P. Kapelmeier, Ber. Disch. Chem. Ges. 44, 2724 (1911).

### 3. INFRA-RED DATA

The vibrational spectra of acetylacetone and its 3-substituted derivatives has been examined by Kohlraush.<sup>21</sup> Bawn,<sup>22</sup> Shigorin and Skoldinov<sup>23a</sup> and Mecke and Funck.<sup>23b</sup> The IR spectrum of acetylacetone, which is essentially in the *cis*-enolic form, revealed in the range of double bond vibrations characteristic absorption bands at 1600 and 1650 cm<sup>-1</sup> accounted for by the vibrations of molecules in the enolic form. These bands, tentatively assigned to C—C and C—O... H vibrations, are characteristic of the vibrations of the cycle with intramolecular hydrogen bonding. The ketonic form of acetylacetone is revealed in the spectrum by two absorption bands at 1700–1730 cm<sup>-1</sup> assigned to the symmetrical and asymmetrical C—O stretching vibrations.

3-alkylacetylacetones exhibit in equilibrium not only ketonic and *cis*-enolic but also *trans*-enolic forms, due to steric hindrance precluding the formation of a planar six membered hydrogen bonded cycle.<sup>18,23</sup>

The IR spectra of the substances investigated over the range of 1500–1800 cm<sup>-1</sup> (Fig. 2, I–V and VII–1X) revealed bands at 1700–1725 cm<sup>-1</sup>, which coincide in position and intensity with the symmetrical and asymmetrical stretching vibrations of the C=O groups, 3,3-dimethylacetylacetone (X) (Fig. 2, X), and the ketonic form of acetyl-acetone. Substances I–V also show in this range bands at 1585 and 1615 cm<sup>-1</sup>. The spectra of keto-enols having "cis-fixed" enolic forms, ethyl cyclohexanone- and cyclopentanone-carboxylates<sup>24</sup> as well as acetylacetone reveal similar bands, undoubtedly due to the vibrations of cis-enols. Thus the bands at ~1585 and 1615 cm<sup>-1</sup> in the spectra of 3-alkylacetylacetones are due to the vibrations of molecules of cis-enolic form.

The spectra of  $\alpha$ -alkylacetoacetates with branched substituents<sup>2</sup> and those of ketoenols with "*trans*-fixed" enolic forms (alkyltetronic acids, 2-alkyldihydroresorcinols, dimedon<sup>25</sup>) show that the absorption bands over the range concerned and characteristic of the vibrations *trans*-enolic form have their maxima at ~1620 and 1700 cm<sup>-1</sup>. The former is mainly due to the C=C stretching vibrations, the latter is assigned to the stretching vibration of the C=O group responsible for intermolecular hydrogen bonds.

The spectra of 3-isopropyl- and 3-sec-butylacetylacetones (Fig. 2, VII, VIII) show no bands of the *cis*-enolic form but reveal bands at  $\sim$ 1580 and 1680 cm<sup>-1</sup> characteristic of *trans*-enolic forms, and those at 1700 and 1720 cm<sup>-1</sup>, characteristic of ketonic forms.

Thus, the IR spectra of 3-alkylacetylacetones reveal that the compounds with primary substituents display keto-*cis*-enol tautomeric equilibrium whilst those with secondary substituents point to keto-*trans*-enol equilibrium. In the spectrum of 3-cyclopentylacetylacetone (Fig. 2, IX), only the bands of C=O stretching vibrations of the ketonic form at 1700 and 1725 cm<sup>-1</sup> could be observed, in accordance with bromometrical evidence on the absence of any marked enolization of this substance.

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- 240 R. D. Campbell and H. M. Gilow, J. Amer. Chem. Soc. 82, 5426 (1960).
- <sup>26</sup> R. E. Rasmussen, D. D. Tunnicliff and R. R. Brattain, J. Amer. Chem. Soc. 71, 1069 (1949).



FIG. 2. Infra-red spectra of 3-alkylacetylacetone CH<sub>3</sub>COCHRCOCH<sub>4</sub> (in substance) I. R = CH<sub>3</sub>, II. R = C<sub>8</sub>H<sub>5</sub>, III. R = n-C<sub>8</sub>H<sub>7</sub>, IV. R = n-C<sub>4</sub>H<sub>9</sub>, V. R-iso-C<sub>4</sub>H<sub>9</sub>, VII. R = iso-C<sub>8</sub>H<sub>7</sub>, VIII. R = sec-C<sub>4</sub>H<sub>9</sub>, IX. R = cyclo-C<sub>6</sub>H<sub>9</sub>, X. 3,3-dimethylacetylacetone.

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The IR data on enolization of 3-alkylacetylacetones confirm the bromometric evidence. They are, however, also only of qualitative value, the solutions under investigation being insufficiently dilute (1%).

## 4. ULTRA-VIOLET DATA

UV spectra enable dilute solutions to be investigated thus avoiding the limitations of the bromometric and IR methods and the use of quantitative relationships of the theory of tautomeric equilibrium.



FIG. 3. Ultra-violet spectra of 3-methylacetylacetone (I) --- hexane, --- ether, --- ethanol, --- dioxane, --- abs. methanole, --- 85% methanol,  $-\cdots$  75% methanol,  $-\times-\times$  67% methanol

The UV spectra of 3-alkylacetylacetones were studied in 67, 75 and 85% methanol, absolute methanol, ethanol, dioxane, ether, and hexane at  $5 \cdot 10^{-4}$  m/l concentration.

The electronic spectra of 3-alkylacetylacetones with primary substituents essentially differ from those of substances with secondary radicals in that the former show an absorption band at ~290 m $\mu$  and the latter at ~260 m $\mu$  (Table 3, Figs 3-9). As, according to the electronic spectrum of 3,3-dimethylacetylacetone (X, Fig 10), the absorption of the molecules of the ketonic form in this range is negligible, the absorption bands observed in the spectra of 3-alkylacetylacetones should be assigned to the electronic transition in the enolic molecular forms, namely, the 290 m $\mu$  band is to be referred to the *cis*-form and the 260 m $\mu$  band to the *trans*-form.

Substance					λ.	mμ				
				cis-Enol			tra	ins-Enol		
CH3COCHREOCH3	67% Methanol	Ethanol	Dioxane	Ether	Hexane	67% Methanol	Ethanol	Dioxane	Ether	Hexane
$R = CH_3$	292	291	289	288	287			_	_	
$\mathbf{R} = \mathbf{C}_{\mathbf{s}}\mathbf{H}_{\mathbf{s}}$	293	292	290	286	286	_	_			
$R = n - C_{3}H_{7}$	300	294	294	292	292	264	260	257	252	253
$\mathbf{R} = \mathbf{n} - \mathbf{C}_{\mathbf{q}} \mathbf{H}_{\mathbf{q}}$	300	294	293	289	288	265	260	257	252	252
$\mathbf{R} = \mathbf{iso-C_4H_9}$	295	294	294	293	292	262	260	257	253	252
$\mathbf{R} = \mathbf{iso-C_8H_7}$		_		_	_	263	259	256	252	251
$R = sec - C_4 H_9$	_	-	_			264	262	256	253	253

TABLE 3. WAVE LENGTHS OF ELECTRONIC ABSORPTION BANDS OF TAUTOMERIC ENOLIC FORMS IN 3-ALKYLACETYLACETONES



FIG. 4. Ultra-violet spectra of 3-ethylacetylacetone (II) — hexane, — — ether, — O — ethanol, — · — · — dioxane, — · · — · — abs. methanol, ----85% methanol, — · · — · · — 75% methanol, — × — × — 67% methanol.



FIG. 5. Ultra-violet spectra of 3-propylacetylacetone (III) — hexane, — — ether,  $-\bigcirc -\bigcirc -\bigcirc$  ethanol,  $-\cdot - \cdot -$  dioxane,  $-\times -\times -$  67% methanol.



FIG. 6. Ultra-violet spectra of 3-butylacetylacetone (IV) — hexane, — — ether,  $-\bigcirc-\bigcirc-$  ethanol,  $-\cdot$  —  $\cdot$  — dioxane,  $-\times$  —  $\times$  —  $\times$  67% methanol.





Fig. 8. Ultra-violet spectra of 3-isopropylacetylacetone (VII) — hexane, — — ether, — · — · — dioxane, — · · — · abs. methanol, — - - 85% methanol, — · · — · · - 67% methanol, — O — O — cthanol



FIG. 9. Ultra-violet spectra of 3-sec-butylacetylacetone (VIII) — hexane, — ether, — dioxane,  $-\bigcirc -\bigcirc$  methanol,  $-\times -\times -\times -$  67% methanol

In the spectra of 3-alkylacetylacetones with primary alkyl substituents (Figs. 3-7), the band at 290 m $\mu$  displays a pronounced asymmetry of the contour and the spectra of the solutions of some compounds (III-V) in 67% aqueous methanol distinctly exhibit absorption bands of *trans*-enolic forms (260 m $\mu$ ).



FIG. 10. Ultra-violet spectrum of 3,3-dimethylacetylacetone in ethanol

In the spectra of other solutions the absorption band of the *cis*-form at 290 m $\mu$  is so intensive that the band at 260 m $\mu$  only distorts its contour or is seen as its shoulder. On resolving the doublet into separate components on the assumption of the individual components being symmetric, the bands at 260 m $\mu$  in the spectra of solutions with different solvents were found practically coinciding with the corresponding absorption bands of *trans*-forms of isopropyl- and secbutyl acetylacetones (VII and VIII, Table 3).

It thus follows from the comparison of UV and IR data that the solutions of 3-alkylacetylacetones with primary radicals exhibit tautomeric equilibrium of three forms, of the ketone and the *cis*- and *trans*-enols, whilst in solutions of substances with secondary radicals there exists a tautomeric equilibrium of two forms, of the ketone and *trans*-enol.

If one considers the solvent effect on the magnitude of the molar absorption coefficient as sufficiently small, then one can take the integral intensities of absorption bands (estimated in terms of the area of the absorption band in the cm<sup>-1</sup> frequency range) as a measure of the concentration of tautomeric forms. As within the investigated range of electronic spectra of 3-alkylacetylacetones there are absorption bands of only *cis*- and *trans*-enolic forms and no marked absorption of the ketonic form, the integral intensity values cannot be used to derive the constants of tautomeric equilibrium. It is, however, possible to come to a definite conclusion in terms of an equation, describing the tautomeric equilibrium of keto-enols.

Substance					$J \cdot 10^6 \frac{1}{\text{cm}^3 \cdot \text{m}}$	ol				
				cis-Enol	· ·		tra tra	uns-Enol		
	67% Methanol	Ethanol	Dioxane	Ether	Hexane	67% Methanol	Ethanol	Dioxane	Ether	Hexane
$R = CH_{3}$	6.7	23.0	22.9	40.9	44.8	_				
$\mathbf{R} = \mathbf{C}_{\mathbf{s}}\mathbf{H}_{\mathbf{s}}$	5∙0	14.6	13.8	21.6	24.8	4.0	5.7	3.9	4.2	5-9
$\mathbf{R} = \mathbf{n} - \mathbf{C}_{3} \mathbf{H}_{7}$	4.0	14.5	14.0	18.8	21.3	9.9	9.9	9.4	8.9	9.4
$\mathbf{R} = \mathbf{n} - \mathbf{C}_{\mathbf{t}} \mathbf{H}_{\mathbf{t}}$	3-1	15.3	13.7	23.9	24·1	10.1	10-1	8.7	8∙4	8·9
$R = \sec - C_4 H_1$	6.0	14.7	12.6	21.4	25.1	9.9	10-2	8.8	7.7	<b>8</b> ∙0
$R = iso-C_3H_7$	_	_			—	27.8	<b>28</b> ·8	23.8	23.4	23.3
$R = \sec - C_4 H_1$		-	_	—	_	17.6	16·6	14.7	16.0	12.5

### TABLE 4. INTEGRAL INTENSITIES OF ELECTRONIC ABSORPTION BANDS OF ENOLIC FORMS IN 3-ALKYLACETYLACETONES

With  $R = CH_a$  cis-enol in 75% Methanol 8.6, in 85% Methanol 10.1, in abs. Methanol 14.4 With  $R = C_aH_b$  cis-enol in 75% Methanol 6.1, in 85% Methanol 7.4, in abs. Methanol 9.3

Table 4 gives the integral intensities of *cis*- and *trans*-absorption of 3-alkylacetylacetones in different solvents. In considering the results in Table 4 and their accuracy one should bear in mind the errors that could be introduced when measuring integral intensities owing to the division of the complex absorption band into two bands at 290 and 260 m $\mu$  and those due to the solvent effect.

An analysis of the electronic spectra indicates that *trans*-enolization of 3-alkylacetylacetones and of a number of other keto-enols with an open chain studied previously,<sup>1,2</sup> is not affected by the solvent. Regarding *cis*-enolization, analysis of the data in Table 4 should take into account that the constant of the tautomeric equilibrium *cis*-enol-ketone may be expressed by integral intensities. That is to say, if the concentrations of the *cis*- and *trans*-forms are denoted by  $C_e$  and  $C_t$ , the corresponding integral intensities by  $J_e$  and  $J_t$  and the molar absorption coefficients by  $\varepsilon_e$  and  $\varepsilon_t$ respectively, then the following expression for the keto-enol-equilibrium constant  $(K_T (cis))$  may be derived:

$$K_{T (cis)} = \frac{C_{o}}{C_{k}} = \frac{J_{c}/\varepsilon_{c}}{C - (J_{c}/\varepsilon_{c} - J_{t}/\varepsilon_{t})}$$
(6)

where C is the overall keto-enol concentration. It may be shown that if the *cis*-enols under study follow Meyer's rule  $K_T = EL$ , with ethyl acetoacetate being the standard substance and *trans*-enolization not depending on the solvent (in all solvents  $J_t = const$ ), then with a constant overall concentration C, the reciprocal values of integral intensities of the *cis*-band  $(1/J_c)$  in different solvents of the keto-enol in question and the value of 1/L must be in a linear relationship.

$$1/J_c = A - B(1/L)^* \tag{7}$$

In Fig. 11  $10^{-5}/J_c$  is plotted against 1/L for 3-methyl and 3-ethylacetylacetones (I and II). It will therefore be evident that *cis*-enolization of 3-alkylacetoacetones follows Meyer's rule.

As the percentage of *trans*-enol in each of the keto-enols studied is constant and *cis*-enolization obeys Meyer's rule it is possible to come to the conclusion that the overall enolization of the substances involved follows equation (3).

#### EXPERIMENTAL

3-Alkylacetylacetones were produced by alkylating sodium acetylacetonate with alkyl halides. 3-cyclopentylacetylacetone has not been reported in the literature. The properties of the substances investigated are given in Table 5.

3-Cyclopentylacetylacetone. Sodium acetylacetonate (92 g, 0.75 mole) and cyclopentyl iodide (147.5 g, 0.75 mole) were heated 4 hr at 160° in sealed ampoules. The resulting dark red liquid (freed from the precipitated sodium bromide) and ether used to wash the precipitate was dried (Na<sub>2</sub>SO<sub>4</sub>), the ether removed and the remainder fractionated *in vacuo* to yield a fraction b.p. 89.7–90°/5 mm;  $n^{20}_{\rm D}$  1.4641;  $d^{20}_{\rm A}$  0.9918, yield 9.4 g (7.4%). (Found: C, 71.3, 71.3; H, 9.5, 9.6. Calc. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.4; H, 9.6%)

Alkaline scission of 3-cyclopentylacetylacetone. 3-cyclopentylacetylacetone (5 g) was refluxed for 10 hr in 7% solution of potassium hydroxide (50 ml). The mixture steam distilled and the distillate ether extracted. The ethereal extract was dried ( $Na_2SO_4$ ) and after removal of ether and distillation

• Here 
$$A = \frac{\varepsilon_i}{\varepsilon_i \varepsilon_c C - J_i \varepsilon_c}$$
 and  $B = \frac{\varepsilon_i}{E(\varepsilon_i \varepsilon_c C - J_i \varepsilon_c)}$ 

It can be assumed that the molar absorption coefficients  $\varepsilon_e$  and  $\varepsilon_i$ , are independent of the solvent. The constancy of  $J_i$  follows from experimental data. Hence, for each of the substances under study (the overall concentrations C being constant) A and B are constant.

	TABLE	5. PROPER	TIES OF 3-A	<b>LKYLACETYLACETONES</b>				
R in CH <sub>s</sub> COCHRCOCH <sub>s</sub>	b.p. (pressure in mm)	°"	d 4	Literature data	Found	Calc.	Found	Calc.
CH3	46.5-48.5° (8)	1-4420	0-9760	b.p. 86° (60 mm) 1-4455 <sup>26</sup>	63-3	63·1	0.6	6.8
				4	63-4		6.8	
C <sub>2</sub> H <sub>6</sub>	65° (14) 83–85° (35)	1·4415	0-9549	b.p. 77·5° (15 mm) 1·4408 <sup>27</sup>	65.4	65.6	9.4	9.4 4
					65-5		9.5	
n-C <sub>3</sub> H,	87·5-89° (17)	1-4463	I	1-4437 <sup>28</sup>	67-8	67-6	6.6	6.6
					67-8		6.6	
iso-C <sub>3</sub> H,	82–83° (20)	1-4420	0-9311	b.p. 183–185° (750)29	67·1	67-6	10.0	6-6
				82–86° (20 mm)	67-3		6-6	
n-C <sub>4</sub> H <b>,</b>	96-96·5° (12)	1.4480	0-9278	b.p. 105–106° (20 mm) <sup>29</sup>	0-69	69-2	10-4	10-3
				•	69-1		10-5	
iso-C <sub>4</sub> H,	96-5 (19)	1-4465	0-9234	b.p. 93–94° (10 mm) <sup>30</sup>	0-69	69-2	10-2	10·3
					68.9		10·2	
sec-C <sub>4</sub> H,	56° (3)	1-4429	0-9321	b.p. 109–111° (13 mm) <sup>31</sup>	0.69	69·2	10-5	10-3
				4	69-1		10-4	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	144-5145-5	1-5270	1.0602	b.p. 143–146° (10 mm) <sup>82</sup>	75.6	75-8	7-5	7-4
				•	75.4		7-5	
cyclo-C <sub>s</sub> H <sub>s</sub>	89.7-90 (5)	1-4641	0-9918	]	71-3	71-4	9.5	9.6
					71-3		9.6	
			;					

<sup>26</sup> R. Y. Kelso, K. W. Greenlee, I. M. Decfer and C. E. Boord, J. Amer. Chem. Soc. 77, 1751 (1955).

K. Auwers, Liebigs. Ann. 416, 194 (1918).
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<sup>32</sup> J. Sprague, L. Beckham and H. Adkins, J. Amer. Chem. Soc. 56, 2667 (1934).



FIG. 11. Dependence of reciprocal integral intensities (10<sup>-6</sup>/J) of 3-methylacetylacetone (I) and 3-ethylacetylacetone (II) upon Meyer's 1/L.

*in vacuo* resulted in a fraction yield 2.7 g (72%); b.p. 48-50°/6 mm;  $n_{20}^{20}$  1.4442. For cyclopentylacetone, lit b.p. 84-86°/63 mm,  $n_{20}^{23.5}$  1.4432.<sup>33</sup> 2,4-Dinitrophenylhydrazone, m.p. 83-84° (from alcohol), lit m.p. 84°.<sup>33</sup>

3,3-Dimethylacetylacetone was synthesized according to a known procedure,<sup>34</sup> b.p. 54/8 mm;  $n_D^{30}$  1·4311;  $d_4^{50}$  0·9577. (Found: C, 65·4, 65·1; H, 9·4, 9·5; Calc. for C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>: C, 65·6; H, 9·4%) Lit b.p. 175-177°,<sup>34</sup> m.p. 21-22°,  $n_D^{37.8}$  1·426;  $d_4^{28}$  0·9494<sup>35</sup>.

Bromometric titration of 1% solutions was carried out according to Hesse and Krehbiel<sup>53</sup> with alcoholic bromine solution and that of 0.1 and 0.02% solutions by Diekman's procedure.<sup>30</sup>

The IR spectra were taken on a double beamed spectrometer UR-10, the UV spectra on spectrometer SF-4.

#### DISCUSSION

The application of Meyer's rule, as well as equations (3) and (4) are subject to the same limitations as the equations of the theory of acid-base equilibrium by Brønsted and Izmailov<sup>6-10</sup> from which they are derived. One of the main implications of this theory is known to be the linear dependence  $pK_{AS_1} = pK_{AS_1} + \text{Const.}$  (8) of the ionization  $pK_{AS}$  (or of protolysis) constants of acids in two solvents  $S_1$  and  $S_2$  with a slope of 45°. Such a linear dependence is observed for all acids of one chemical type. Brønsted's theory included in one chemical type all acids with like charges (all uncharged acids were involved in another type). It was then experimentally proved that this is not the case. Thus, carboxylic acids were found to belong to one type, sulfonic

<sup>&</sup>lt;sup>33</sup> W. Herz, J. Amer. Chem. Soc. 78, 1485 (1956).

<sup>34</sup> Yu. S. Zalkind, Zh. Russ. Phyzi. khim. Obsch. 37, 491 (1905).

<sup>&</sup>lt;sup>35</sup> K. Auwers, Liebigs. Ann. 415, 224 (1918).

<sup>&</sup>lt;sup>20</sup> G. Hesse and G. Krehbiel, *Liebigs. Ann.* 593, 35 (1955).

acids to another, phenols to a third type, etc.\* From this point of view all ketonic forms of  $\beta$ -dicarbonyl compounds involve one chemical type whilst their corresponding enolic forms belong to another.<sup>11</sup> Accordingly, Meyer's rule postulated ethyl aceto-acetate as one standard substance for all keto-enols. Later it turned out that *cis*- and *trans*-enolic forms must be referred to as acids of different chemical types and when applying equation (4) two standard substances should be used, one for *cis*-enolization and another for *trans*-enolization.

In the course of the present investigation it became apparent that the notion of a chemical type is still more specific. Thus, *cis*-enolic forms of  $\beta$ -keto-esters and  $\beta$ -di-ketones with an open chain belong to one chemical type, whilst their ketonic forms belong to another type (though also common to  $\beta$ -keto-ester and  $\beta$ -diketones). Hence applying Meyer's rule to *cis*-enolization of these substances one and the same standard substance may be used (ethyl acetoacetate). As far as *trans*-enolization is concerned, three types may at present be identified: (1) dimedon whose *trans*-enolization decreases with decreasing polarity of the solvent (the kind of quantitative dependence has in this case not yet been determined), (2) keto-enols of the type "Meldrum's acids" that are practically not enolized and (3) a large group of keto-enols whose *trans*-enolization does not in the first approximation depend on the nature of the solvent. The last group involves some alkyltetronic acids,  $\alpha$ -alkylacetoacetates and 3-alkylacetones.

As mentioned above, the independence of *trans*-enolization of the solvent, as far as this group of substances is concerned, is due to similar changes in the solvation energies of ketonic and *trans*-enolic forms with the change of solvent. The constancy of *trans*-enolization under study holds, of course, only in the first approximation. On closer consideration, slight but constant deviations can be observed.

Thus, in the case of the group of alkyltetronic acids the enolization in solvents of an ethereal type (ether, dioxane) is somewhat increased, undoubtedly due to the fact, that only the enolic (*trans*) form can form hydrogen bonding with the oxygen atom of ether. In the group of 3-alkylacetylacetones *trans*-enolization in solvents containing hydroxyls is somewhat higher than in those lacking hydroxyls (Table 4).<sup>†</sup> These deviations from the constancy are however small and can in no case be compared with the effect of the solvent on *cis*-enolization. In the case of *cis*-enolization the solvation energies of ketonic forms and cyclic hydrogen bonded *cis*-enolic forms change differently with the change of the solvent. The nature of such a change is expressed by Meyer's rule.

• These types differ also in the intercept cut off by the straight line corresponding to equation (8) on the ordinate. Physically, the assignment of a group of acids to one chemical type is based on similar changes in solvation energy both of ions and, correspondingly, undissociated molecules with the change of solvent.<sup>37</sup>

† The slight increase in integral intensities of the *trans*-band in 67% methanol and ethanol, as compared to dioxane, ether and hexane might, however, be here due to the changes in the molar absorption coefficient rather than concentration. We do not think that the increase in the integral intensity in hydroxyl-containing solvents can result from the dissociation to ions, 3-alkylacetylacetones being very weak acids. Thus,  $pK_A$ , for 3-isopropylacetylacetone in water is 12.85<sup>38</sup>. When diluted to 10<sup>4</sup> their dissociation in a neutral solvent is not recorded by spectral evidence.

<sup>87</sup> N. A. Izmailov, *Electrochemistry of solutions*, p. 629. Kharkov University (1959).

<sup>&</sup>lt;sup>38</sup> M. R. Rumpf and R. La Riviére, C. R. Akad. Sci. Paris. 244, N7, 902 (1957).