Tetrahedron, 1957, Vol. 1, pp. 317–327. Pergamon Press Ltd., London

TAUTOMERIC EQUILIBRIUM OF KETONIC AND *CIS*- AND *TRANS*-ENOLIC FORMS OF β-DICARBONYL COMPOUNDS IN SOLUTION*

M. I. KABACHNIK, S. T. YOFFE and K. V. VATSURO
Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

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Abstract—In this paper the tautomeric equilibrium of ketonic and *cis*- and *trans*-enolic forms of β-dicarbonyl compounds is considered as an acid-base protolytic one. The application of the Brønsted–Izmaylov theory has enabled to suggest a general equation $K_{TS} = \mathscr{E}\mathscr{L} + \mathscr{E}_1$ for keto–enol equilibrium constants, depending on the solvent, the well known Meyer's equation being included in it as a particular case. Equilibrium constants have been bromometrically determined in a number of solvents of keto–enols of three types, i.e. "*cis*-fixed", "*trans*-fixed" and that involving both stereoisomeric forms. A method for quantitative determination of *cis-trans*-enol equilibrium had been proposed.

THE application to problems of tautomerism of the theory of protolytic acid-base equilibrium proposed by Brønsted[1,2] and recently further developed by Izmailov,[3,4,5], has been the subject of previous papers by the present authors[6–9] in which a quantitative interpretation of the ionic theory of tautomerism has been discussed.

This theory was first put forward by Wislicenus,[10] and in recent years Lapworth, Lowry, Ingold *et al.* and Baker[11–14] have studied the qualitative aspect of the theory starting from the concept of the formation of a "common ion" (by ionic dissociation of tautomeric forms) which is capable of recombination with oppositely charged ions at two points of the molecule.

Similar ideas were formulated by Arndt and Eistert,[15,16] who investigated the

$$\mathrm{p}k_{AS_1} = \mathrm{p}k_{AS_2} + \text{const.}$$

relation between the structure of keto-enols, acidity, solvation and enolisation. The

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* Translated by A. L. Pumpiansky, Moscow.

[1] Y. N. Brønsted *Chem. Rev.* **5**, 291 (1928).

[2] Y. N. Brønsted *Z. Phys. Chem.* A **169**, 32 (1934).

[3] N. A. Izmailov *Zh. Phys. Khim. SSSR* **23**, 639, 643 (1949).

[4] N. A. Izmailov *Zh. Phys. Khim. SSSR* **24**, 321 (1950).

[5] N. A. Izmailov *Proceedings of the Kharkov University, U.S.S.R. Chemical Research Institute* Vol. 10, p. 5 (1953).

[6] M. I. Kabachnik *Dokl. Akad. Nauk. SSSR* **83**, 407, 859 (1952).

[7] M. I. Kabachnik and S. T. Yoffe *Dokl. Akad. Nauk. SSSR* **91**, 833 (1953).

[8] M. I. Kabachnik Problems of organic reaction mechanism. *Proceedings of the Kiev Conference held on* 2–5 *June*, 1952 p. 126. Kiev (1954).

[9] M. I. Kabachnik *Usp. Khim. SSSR* **25**, 138 (1956).

[10] W. Wislicenus Über Tautomeric. *Ahrenssammlung chem. u. chem. techn. Vorträge* **2**, 230 (1898).

[11] A. Lapworth and A. O. Hann *J. Chem. Soc.* **81**, 1512 (1902).

[12] T. Lowry *J. Chem. Soc.* 2557 (1927).

[13] C. Ingold, C. Shopee and J. F. Thorpe *J. Chem. Soc.* 1477 (1926).

[14] J. Baker *Tautomerism.* London (1934).

[15] F. Arndt, B. Eistert *Ber. Dtsch. Chem. Ges.* **74**, 423 (1941).

[16] F. Arndt, L. Loewe and R. Ginkök *Rev. Fac. Sci. univ. Istanbul* A **11**, 147 (1946)

relation between acidity and enolisation has proved to be of great importance to this problem, and in this connection the investigations of Schwarzenbach[17–20] should be mentioned.

We have based our investigation on the following concept. If the tautomeric equilibrium is an ionic one and consists in the transfer of a proton from one point of the molecule to another by proton transferring particles then, irrespective of the kinetics of this transfer, the conditions for tautomeric equilibrium should be determined by the equilibrium of the ketonic and enolic forms as acids with the corresponding ions, in the simplest case—with their common enolate—anion and solvated hydrogen ions. The tautomeric keto-enol equilibrium should then obey the laws of equilibrium exhibited by ordinary acids and bases. Experiments show this to be the case.

According to Pedersen,[21] keto-enol equilibrium can be represented as a triple buffer system:

$$KH + S \rightleftarrows E^- + HS^+ \rightleftarrows EH + S$$

(with KH-ketone, EH-enol, E^--enolate-anion, S and HS^+-solvent and respective cation). Tautomeric equilibrium constant can then be designated in terms of the acidity constants.

$$\frac{EH}{KH} = \mathrm{K}_{TS} = \frac{k_{KS}}{k_{ES}} = \frac{k_K}{k_E} \cdot \frac{f_{KS}}{f_{ES}}.$$

where k_K and k_E are thermodynamic acidity constants of ketone and enol, f_{KS} and f_{ES} are the respective activity coefficients. The activities being referred to a standard common to all solvents, k_K and k_E do not depend on the medium. This relationship is a general one and is applicable to any prototropic ionic tautomeric system such as lactim-lactams, thione-thiols and others. The factor k_K/k_E denotes the enolisability of the keto-enol as such. It may be termed "the thermodynamic tautomeric equilibrium constant":

$$\frac{k_K}{k_E} = \mathrm{K}^t = \frac{a_E}{a_K}$$

This factor shifts the equilibrium to the form with the smaller thermodynamic acidity constant. The factor f_{KS}/f_{ES} refers to the influence of solvation on the equilibrium ratio shifting it to the more solvated form. If the thermodynamic constant of the tautomeric equilibrium is either very large or small, the change in the factor f_{KS}/f_{ES} does not essentially effect the equilibrium ratio, which is shifted to one side practically in all media (α-pyridon,[22] carbostyril,[23] α-aminopyridine,[24] nitromethane[25] and others).

The effect of the solvent on the tautomeric equilibrium ratio can be represented in

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[17] G. Schwarzenbach *et al.* *Helv. Chim. Acta* **23**, 1147, 1162 (1940).

[18] G. Schwarzenbach *et al.* *Ibid.* **27**, 1049, 1701 (1944).

[19] G. Schwarzenbach *et al.* *Ibid.* **30**, 656, 669 (1947).

[20] G. Schwarzenbach *et al.* *Ibid.* **34**, 1954 (1951).

[21] K. J. Pedersen *J. Phys. Chem.* **37**, 751 (1933).

[22] G. Gustafson *Suom Kemist* B **18**, 11 (1945).

[23] M. I. Kabachnik, S. T. Yoffe and Yu. N. Sheinker *Zh. Obschei Khim. SSSR* **26**, 2025 (1956).

[24] S. J. Angyal and C. L. Angyal *J. Chem. Soc.* 1461 (1952).

[25] D. Turnbull and S. Maron *J. Amer. Chem. Soc.* **65**, 212 (1943).

terms of the Brønsted equation[1,2] which gives the following linear relationship between the logarithms of the ionisation constants in two solvents, S_1 and S_2:

$$pk_{AS_1} = pk_{AS_2} + \text{const.}$$

This relationship with $tg\alpha = 1$ has been repeatedly checked experimentally. As formulated by Izmailov, the value of the constant C remains the same for acids of one chemical type such as carboxylic acids, phenols, sulphonic acids, etc. For ketones and enols being acids of different chemical types, two simultaneous equations are required:

$$pk_{KS_1} = pk_{KS_2} + \text{const.}_1$$

$$pk_{ES_1} = pk_{ES_2} + \text{const.}_2$$

Hence, tautomeric equilibrium constants in two solvents, S_1 and S_2 must also display a linear relationship:

$$p\mathrm{K}_{TS_1} = p\mathrm{K}_{TS_2} + C \tag{1}$$

This relationship has been confirmed for a large number of keto-enols in various solvents. It is also of a general nature. Thus, for example, the linear relationship with $tg\alpha = 1$ is also observed for tautomeric equilibrium constants of acylaminopyridines and acylaminothiazoles.[26]

Meyer's empirical relation[27]

$$\mathrm{K}_{TS} = \mathscr{E}\mathscr{L}$$

can readily be deduced[6] from equation (1).

At the same time there are instances in the literature where Meyer's relation does not hold, such as ethyl formylphenylacetate in hydroxylic solvents, "the *trans*-fixed" enols of Eistert.[28] This for example, in the case of ethyl formylphenylacetate is due to the formation of hydrates or hemiacetals, and in other more general cases to steric peculiarities of the enolic structure. Accordance with and deviation from Meyer's equation depend in general on the stereoisomerism of enolic forms. The present investigation is devoted to the fundamental and experimental investigation of this point.

Bromometrical determination of the keto-enol equilibrium constant actually results in the sum of *cis*- and *trans*-enolic concentrations. The tautomeric equilibrium constant

$$\mathrm{K}_{TS} = \frac{[E_{cis}H] + [E_{trans}H]}{[KH]}$$

can be represented as the sum of constants:

$$\mathrm{K}_{TS} = \mathrm{K}_{(cis\text{-enol/ketone})s} + \mathrm{K}_{(trans\text{-enol/ketone})s}$$

Applying the Brønsted-Izmailov theory to the acid-base equilibrium under consideration, one has to bear in mind that the three forms, ketonic and *cis*- and *trans*-enolic refer to acids of different chemcial types and accordingly the relation between

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[26] Yu. N. Sheinker *Dokl. Akad. Nauk. SSSR* **113**, 5 (1957).

[27] K. Meyer *Ber. Dtsch. Chem. Ges.* **47**, 826 (1914).

[28] B. Eistert and W. Reiss *Ber. Dtsch. chem. Ges.* **87**, 92, 108 (1954).

their ionisation constants in any two solvents should be represented respectively as:

for ketone: $pk_{KS_1} = pk_{KS_2} + C'_1$

for *cis*-enol: $pk_{E_{cis}S_1} = pk_{E_{cis}S_2} + C'_2$

for *trans*-enol: $pk_{E_{trans}S_1} = pk_{E_{trans}S_2} + C'_3$

Hence we have two equations:

$$pk_{(cis\text{-enol/ketone})S_1} = pk_{(cis\text{-enol/ketone})S_2} + C_1 \qquad (2)$$

$$pk_{(trans\text{-enol/ketone})S_1} = pk_{(trans\text{-enol/ketone})S_2} + C_2 \qquad (3)$$

Applying the same reasoning as used by one of use in deriving Meyer's equation for the equilibrium of two forms (ketonic and only one enolic),[6] we obtain two different equations

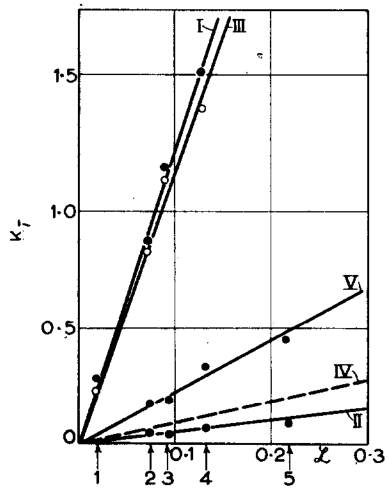


Fig. 1 The dependence of the tautomeric equilibrium constant on solvent used for "*cis*-fixed" and acyclic keto-enols.
I ethyl *cyclo*hexanonecarboxylate in 67 per cent methanol
II ethyl cyclopentanonecarboxylate in methanol.
III benzoylcamphor in chloroform.
IV ethyl acetoacetate in ethanol.
V ethyl benzoylacetate in benzene.

for keto-*cis*-enol equilibrium: $k_{(cis\text{-enol/ketone})S} = \mathscr{E}\mathscr{L}$

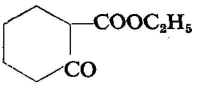
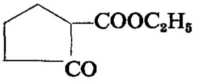
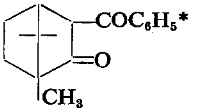
for keto-*trans*-enol equilibrium: $k_{(trans\text{-enol/ketone})S} = \mathscr{E}'\mathscr{L}'$

Hence, for overall keto-enol equilibrium

$$k_{TS} = \mathscr{E}\mathscr{L} + \mathscr{E}'\mathscr{L}'$$

This equation differs from that of Meyer by an additional term $\mathscr{E}'\mathscr{L}'$ referring to *trans*-enolisation. As in Meyer's relation, the value $\mathscr{E}$ refers to enolisability of the keto-enol to *cis*-enol, and $\mathscr{E}'$ to enolisability of the keto-enol to *trans*-enol. $\mathscr{L}$ and $\mathscr{L}'$ denote the enolising capacity of the solvent to *cis*- and, respectively, *trans*-enol. For each solvent, the values $\mathscr{L}$ and $\mathscr{L}'$ are equal to the equilibrium constants of two chosen keto-enols taken as standard for *cis*- and *trans*-enolisation. Constants $\mathscr{E}$ and

TABLE 1. ENOL CONTENT IN "*cis*-FIXED" AND ACYCLIC KETO-ENOLS (PER CENT)

Keto-enols	Solvents					
	67% CH_3OH	CH_3OH	$CHCl_3$	C_2H_5OH	C_6H_6	C_6H_{14}
$CH_3COCH_2COOC_2H_5$	2·0	7·1	8·7	11·4	18·3	54·3
	22·2	45·1	54·5	61·7	74·8	—
	2·0	4·0	3·7	5·9	8·2	—
$C_6H_5COCH_2COOC_2H_5$	(4·6)	(14·5)	(15·2)	(24·2)	(30·0)	(68·7)
	18·5	45·2	53·9	59·0	71·7	—

* G. A. Baluyeva (Private communication).

$\mathscr{E}'$ do not depend on the solvent and are determined by the structure of the keto-enol, constants $\mathscr{L}$ and $\mathscr{L}'$ depending solely on the solvent and being common to all keto-enols.

To prove experimentally the suggested equation and to work out a method for determining the content of *cis*- and *trans*-enolic forms in solution it was necessary to choose standard keto-enols for *cis*- and, respectively, *trans*-enolisations.

Meyer is known to have applied as standard keto-enol ethyl acetoacetate. There were good reasons to believe enolisation of ethyl acetoacetate to be predominantly *cis*.[29,30] To prove this the equilibrium constants of ethyl acetoacetate in different solvents were compared with those cyclic β-keto-carboxylic esters, i.e., ethyl *cyclo*pentanone and ethyl *cyclo*hexanone-carboxylates. On purely structural grounds these substances can provide only *cis*-enolic forms, the *trans*- position being occupied by the ring. Such substances have been named by Eistert as "*cis*-fixed" enols. Determinations were carried out using Meyer's bromometrical back titration method[31] and directly, following Hesse and Krehbiel[32] with 1 per cent solution containing 0·06–0·08 mole/l., at 20°C. Data obtained are listed in Table 1 with some comparative literature values given in parentheses.

By plotting, as shown in Fig. 1, the ethyl acetoacetate equilibrium constant in different solvents (Meyer's $\mathscr{L}$ constant) against that of other keto-esters listed in the

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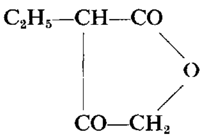
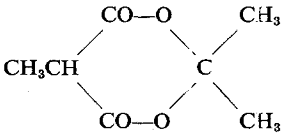
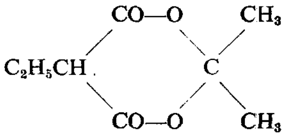
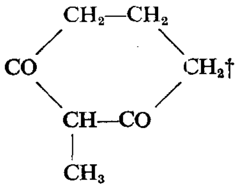
[29] N. V. Sidgwick *J. Chem. Soc.* **127**, 907 (1925).
[30] P. Nachod *Z. Phys. Chem.* **A182**, 208 (1938).
[31] K. Meyer *Ber. Dtsch. Chem. Ges.* **45**, 2846 (1912).
[32] G. Hesse and G. Krehbiel *Liebigs Ann.* **593**, 35 (1955).

Table, it will be seen that the results obtained are in agreement with Meyer's original equation, all straight lines passing through the origin there being a satisfactory linear relationship. As two of the cited cyclic keto-enols lead only to "fixed" *cis*-enols and there also exists evidence about *cis*-enol being formed in benzoylcamphor, it may be concluded that, within the accuracy of the bromometrical method, it is possible to consider ethyl acetoacetate and ethyl benzoylacetate as substances forming only or almost exclusively *cis*-enols. This, of course, refers to all keto-enols which agree well with Meyer's formula.

Ethyl acetoacetate can this be retained as the standard substance for *cis*-enolisation. As standard substance for *trans*-enolisation any "*trans*-fixed" enol described by Eistert and Reiss can be used. These authors proposed as "*trans*-fixed" enols cyclic β-dicarbonyl compounds, which, for steric reasons can produce only *trans*-enolic forms. In the investigation mentioned above Eistert and Reiss found that the enol content of their compounds decreased from water to hexane being the converse of that found by Meyer. But, as the authors state, their bromometrical data were neither reproducible

Table 2. Enol content in "*trans*-fixed" enols (per cent)

Keto-enols	Solvents				
	67% CH_3OH	CH_3OH	$CHCl_3$	C_2H_5OH	C_6H_6
	96·1	96·5	96·1	96·1	not dis.
	—	55·7	60·8	61·2	58·9
	—	71·5	73·5	73·3	70·8
	95·6	96·6	not dis.	93·8	not dis.

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* The enol content in a polar solvent was determined by the authors from ultra-violet absorption spectra of methanol solutions acidified with HCl after exposure for 24 hr. Such conditions lead to enols producing methyl ethers, spectra of the latter being rather similar to those of enols.

† The sample has been kindly supplied by S. I. Zaviyalov.

nor exact owing to the rapid re-enolisation of bromo-ketones during the bromometrical determination. Their spectroscopic data is also doubtful.* We have therefore determined the enol content in various solvents of such "*trans*-fixed" enols, which do not undergo re-enolisation in the course of bromometrical determination. In Table 2 the bromometrical data of the enol content are given for such keto-enols, using the direct method.

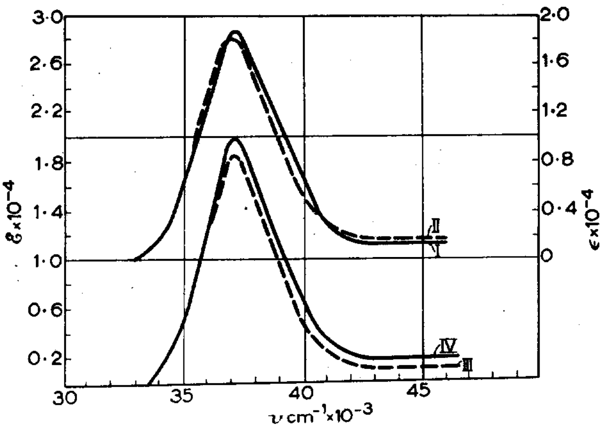

FIG. 2. Ultra-violet spectra of cyclic *iso*propylidene alkylmalonates.
I *iso*propylidene methylmalonate in methanol.
II *Idem* in ethanol.
III *iso*propylidene ethylmalonate in methanol.
IV *Idem* in ethanol.

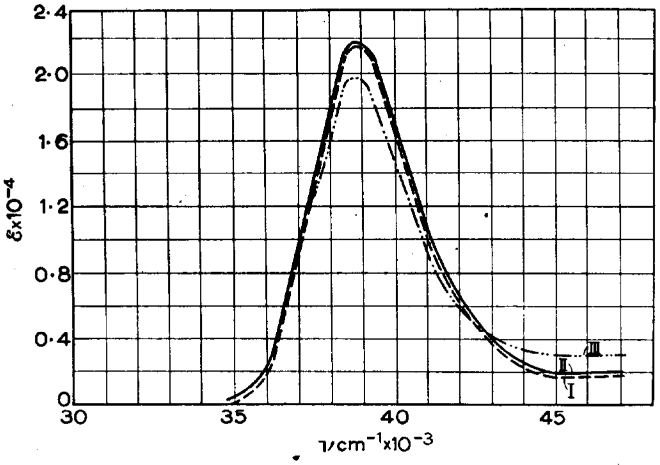

FIG. 3. Ultra-violet spectra of ethyltetronic acid
I in water
II in methanol.
III in ethanol.

The consistency of tautomeric equilibrium constants of ethyl tetronic acid in water, methanol and ethanol and cyclic *iso*propylidene aklylmalonates in alcohols is substantiated by ultra-violet spectra (Figs. 2 and 3).*

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* The spectra were supplied by the Optical laboratory of the Institute of Organo-element compounds, headed by I. V. Obreimov.

It follows from the data obtained that $\mathscr{L}'$ is independent of the solvent and the following equation can be derived for keto-enols.

$$K_{TS} = \mathscr{E}\mathscr{L} + \mathscr{E}_1 \tag{4}$$

If the keto-enol produces only a *cis*-enolic form then $\mathscr{E}_1 = 0$ corresponding to the usual Meyer formula (linear relationship between K_{TS} and $\mathscr{L}$; the straight line passes through the origin). If only *trans*-enol is formed, then $\mathscr{E} = 0$ and the equilibrium constant does not depend on the type of solvent used. Finally, if in the tautomeric equilibrium both enolic forms are present together with the keto form, the relationship between K_{TS} and $\mathscr{L}$ must remain linear, but the straight line cuts on the axis Y an intercept $\mathscr{E}_1$. Having determined the keto-enol equilibrium constant in a number of solvents with a known $\mathscr{L}$, the *cis*-and *trans*-form ratio can be calculated.

This has been checked on keto-enols known to contain *cis*- and *trans*-enolic forms, such as α and γ-substituted acetoacetic esters, studied by Henecka.[33] Whilst α-methyl or α-ethyl substituted compounds readily form brightly coloured iron complexes, α-*iso*propyl derivatives as well as, according to our data, α-secondary butyl derivatives fail to react with ferric chloride or react very sluggishly. At the same time, as shown by bromometrical evidence, all these substances contain a definite amount of enol, enough for the coloured reaction to take place. The introduction of branched radicals into α-position and, to a somewhat smaller extent, into γ-position is thus seen to hinder the formation of the chelated salt. It is of importance to note, that this does not depend on the total enol content. In interpreting these results Henecka regards keto-enols that give no colour reaction with ferric chloride as *trans*-enols and it is necessary to conclude, that in these substances the formation of *cis*-enol with a planar six-ring hydrogen bonded cycle is hindered. Spectroscopic investigations carried out by Shigorin[34,35,36] substantiate that these α-alkylacetoacetic esters can only *trans*-enolise.

We have studied the effect of the solvent on the keto-enol equilibrium in several α-substituted esters of this series, the results obtained being listed in Table 3.

TABLE 3. ENOL CONTENT IN α-SUBSTITUTED ACETOACETIC ESTERS (PER CENT)

$CH_3COCHCOOC_2H_5$ | R	67% CH_3OH	CH_3OH	C_2H_5OH	C_6H_6
R = C_2H_5	0·9	1·8	2·8	4·2
R *n*-C_3H_7	1·9	3·0	4·2	5·6
R *iso*-C_3H_7	2·6	3·0	3·1	3·6
R *n*-C_4H_9	3·4	4·3	5·4	6·2
R sec.-C_4H_9	10·5	10·6	10·6	10·8
R = H	2·0	7·1	11·4	18·3

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[33] H. Henecka *Chemie der β-dicarbonylverbindungen* S. 122. Springer-Verlag (1950).
[34] D. N. Shigorin *Zh. Phys. Khim. SSSR* **23**, 505 (1949).
[35] D. N. Shigorin *Ibid.* **24**, 924, 932 (1950).
[36] D. N. Shigorin and A. P. Sholdinov *Ibid.* **24**, 954 (1950).

As seen from Fig. 4, by plotting $\mathscr{L}$ against K_{TS} the straight lines pass above the origin. The equilibrium of these keto-enols is thus represented by equation (4). From the data obtained one calculates the *cis*-enol content in the enolic fraction of the keto-enol.

$$cis\text{-enol} = \frac{100\,\mathscr{E}\mathscr{L}}{\mathscr{E}\mathscr{L} + \mathscr{E}_1} \quad \text{(per cent)}$$

the results calculated being given in Table 4.

One can also propose another way to calculate *cis*-*trans*-enolic equilibrium. One has first to determine the equilibrium constants for $k_{(cis\text{-enol}+trans\text{-enol/ketone})S}$ in two selected solvents for three groups of substances: (a) "*cis*-fixed" enols (b) "*trans*-fixed" enols and (c) keto-enols under investigation. Then one finds from the data for the two former groups the values of C_1 and C_2 constants in equations (2) and (3). Finally considering C_2 for "*trans*-fixed" enols to be 0, one calculates for the keto-enols in question the *cis*-to *trans*-from ratio as follows:

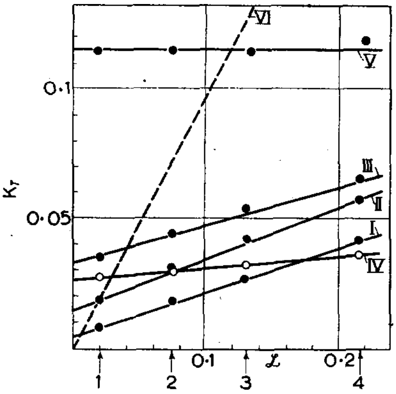

FIG. 4. The dependence of the tautomeric equilibrium constant on solvent used for α-substituted ethyl acetoacetates, $CH_3CO\underset{\mathrm{R}}{\underset{|}{C}}H\cdot COOC_2H_5 \rightarrow CH_3CO\underset{\mathrm{H}}{\underset{|}{C}}HCOOC_2C_5$. I—R = C_2H_5, II—R = C_3H_7, III—R = C_4H_9. IV—R = *iso*-C_3H_7, V = secondary—C_4H_9. VI—R = H. Solvents: I. 67 per cent methanol; II. methanol; III. ethanol; IV. benzene.

$$\frac{[E_{cis}H]_{S_1}}{[E_{trans}H]_{S_1}} = \frac{k_{TS_1} - k_{TS_2}}{k_{TS_2} - \alpha\, k_{TS_1}}$$

$$\frac{[E_{cis}H]_{S_2}}{[E_{trans}H]_{S_2}} = \frac{k_{TS_2} - k_{TS_1}}{k_{TS_1} - \dfrac{1}{\alpha} k_{TS_2}}$$

with $\alpha = 10^{C_1}$. In Fig. 5 are plotted pK_{TS_1} against pK_{TS_1} for the keto-enols of the first group where $S_1 = 67$ per cent CH_3OH and $S_2 = C_6H_6$. Hence: $C_1 = 1{\cdot}0$ and $\alpha = 10$.

The results calculated using this method are to be found in parentheses in Table 4.

It will be seen, that the keto-enols which are sterically hindered do contain much of the *trans*-enolic form and the most hindered secondary butyl acetoacetate contains very little of the *cis*-form. As was to be expected the relative *cis*-*trans* ratio is strongly dependent on the solvent used.

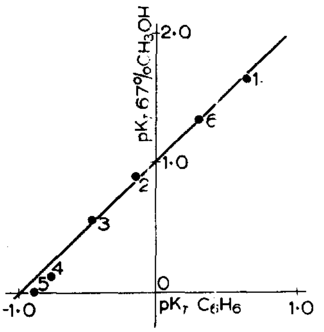

FIG. 5. The relationship between the tautometic equilibrium constants of "cis-fixed" and cyclic keto-enols in 67 per cent methanol and benzene.
1. ethyl acetoacetate.
2. ethyl 2-methyl*cyclo*hexanonecarboxylate.
3. ethyl *cyclo*hexanonecarboxylate.
4. acetylacetone (K. Meyer).
5. acetylacetone.
6. ethyl benzoylacetate.

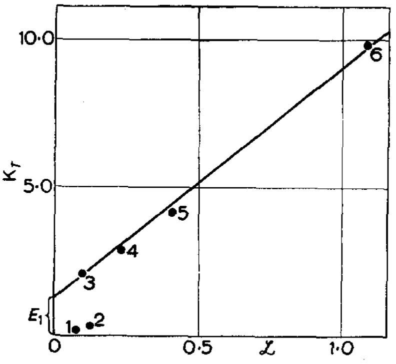

FIG. 6. The defendence of the tautomeric equilibrium constant of ethyl formylphenylacetate on the solvent used.
1. methanol.
2. ethanol.
3. chloroform.
4. benzene.
5. ether.
6. hexane.

TABLE 4. *Cis*-ENOL CONTENT IN THE ENOL FRACTION OF THE α-SUBSTITUTED ETHYL ACETOACETATES (PER CENT)

$CH_3COCHCOOC_2H_5$ (R = H)	$\mathcal{E}$	$\mathcal{E}_1$	Solvents			
			67% CH_3OH	CH_3OH	C_2H_5OH	C_6H_6
R = C_2H_5	0·177	0·005	46·6 (43·2)	74·8	83·1	89·5 (88·4)
R *n*-C_3H_7	0·201	0·015	25·1 (23·4)	51·1	63·4	75·0 (75·0)
R *iso*-C_3H_7	0·050	0·026	4·6 (4·1)	13·0	19·9	30·1 (30·1)
R *n*-C_4H_9	0·156	0·033	10·6 (9·3)	26·9	37·9	51·5 (52·6)
R sec.-C_4H_9	0·019	0·116	0·4 (0·4)	1·3	2·1	3·5 (3·7)

By making use of this method, we have also determined the *cis*-enol content in the enol fraction of ethyl formylphenylacetate in chloroform, benzene, ether and hexane. As seen from Fig. 6 there is in these solvents a linear relationship between K_{TS} and $\mathcal{L}$ (points 3, 4, 5 and 6). The intersect $\mathcal{E}_1$ is characteristic of the presence of the *trans*-form. Points 1 and 2 on the plot, referring to methanol and ethanol do not obey the general relationship, in agreement with findings of Wislicenus[37] that ethyl formylphenylacetate forms hemiacetals in alcoholic solutions.

In Table 5 are presented the values of total enol content and *cis*-enol content in the enol fraction.

[37] W. Wislicenus *Liebigs Ann.* **413**, 21 (1917).

TABLE 5. *CIS*-ENOL CONTENT IN THE ENOL FRACTION OF ETHYL FORMYLPHENYL ACETATE ($\mathscr{E} = 7{\cdot}253$, $\mathscr{E}_1 = 1{\cdot}208$) (PER CENT)

Solvent	Total enol content	*Cis*-enol content in the enol-fraction
Chloroform	66·4	35·3
Benzene	73·2	57·3
Ether	80·4	71·1
Hexane	90·8	87·7

CONCLUSIONS

(1) The principal regularities of the protolytic acid-base equilibrium have been shown to be applicable to the tautomeric equilibrium of a complex system, involving ketonic and *cis-trans*-enolic forms.

(2) A general equation $K_{TS} = \mathscr{E}\mathscr{L} + \mathscr{E}_1$ for the tautomeric ketonic-*cis-trans*-enolic equilibrium constant in different solvents has been derived, the well known Meyer's equation being included in it as a particular case.

(3) A method of quantitative determination of *cis*- and *trans*-enol content in solutions has been proposed and exemplified on α-substituted acetoacetates and ethyl formylphenylacetate.