KETONIC AND ENOLIC MODIFICATIONS OF COMPOUNDS.

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A very important subject is that connected with the change from the ketonic to the enolic structure and vice versa. The results which have been obtained are different in most cases from those found by other writers. The following examples have been taken from data given by Smiles, *The Relations between Chemical Constitutions and Some Physical Properties*.

(1) Acetyl acetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$. M_a 27.45
Ketonic form Σnr_a 25.36

Enolic forms—

$\{ \text{CH}_3 : \text{C}(\text{OH}) - \text{CH}_2 - \text{C}(\text{CH}_3)\text{O} \dots \dots \dots$	26.27
$\{ \text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH} \curvearrowright \text{C}(\text{CH}_3)\text{O} \dots \dots \dots$	conj. + 0.55 26.93
$\{ \text{CH}_3 : \text{C}(\text{OH}) \curvearrowright \text{CH} : \text{C}(\text{OH})\text{CH}_3 \dots \dots \dots$	conj. + 1.06 28.34
$\{ \text{CH}_3 - \text{C}(\text{OH}) : \text{C} : \text{C}(\text{OH}) \cdot \text{CH}_3 \dots \dots \dots$	: 1.75 27.38

It is thus clear that acetyl acetone is the pure di-enolic form. The above result shows that the last di-enolic form is the correct one.

Smiles, M_a 27.45. Di-enolic 27.33 calc.

Perkin (molecular magnetic rotations), Keto-enol 80 per cent.

Enolic 20 „

(2) Methyl acetyl acetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{CH}_3) \cdot \text{CO} \cdot \text{CH}_3$. M_a 30.75

Ketonic form Σnr_a 29.96

Enolic forms—

$\text{O} : \text{C}(\text{CH}_3) - \text{CH}(\text{CH}_3) - \text{C}(\text{OH}) : \text{CH}_3 \dots \dots$	30.87
$\text{O} : \text{C}(\text{CH}_3) \curvearrowright \text{C}(\text{CH}_3) : \text{C}(\text{OH}) \cdot \text{CH}_3 \dots \dots$	conj. + 0.55 31.53
Di-enolic	31.98

The first formula seems to be the correct one.

Smiles, M_a 30.75. Mono-enol 30.89

Di-enol 31.90

Perkin (molecular magnetic rotations), Di-ketonic 46.4 per cent.

Keto-enol 53.6 „

The advantage of the above method is that it shows which of the mono-enols is the correct one.

(3) Ethyl oxalo-acetate, $C_2H_5 \cdot OOC \cdot CO \cdot CH_2 \cdot COOC_2H_5$. M_a 43'38

This is a class of compound which is very interesting, as its exact formula can be obtained by comparing it with a well-known substance.

Di-ethyl methyl maleate.

Hydroxy ethyl maleate.

Di-ethyl methyl maleate $46'48$

Less CH_2 $4'60$ } $-3'10$

Plus O' $1'50$ }

Σnr_a $43'38$

M_a $43'38$

[There is thus no anomaly. See No. 6.]

The substance is again the pure one, and is hydroxy di-ethyl maleate.

Smiles Σnr_a $43'46$

(4) Mesityl oxide oxalic ethyl ester—

Assuming that this compound is represented by the formula—

its refractivity would be

Σnr_a $51'86$

Ketonic form—

The β form is therefore ketonic.

The α form has an extraordinarily high value, which cannot be accounted for, even if the substance be considered to be tri-enolic Σnr_a $53'09$.

Also the manifestation or suppression of anomalies of compounds in solution cannot be accounted for, but a consideration of this question needs to be separate.

(5) Methyl cyano-aceto-acetate, $CH_3 \cdot CO \cdot CH(CN) \cdot CO_2CH_3$. M_a $33'80$.

Ketonic form—

Σnr_a .

Enolic—

$\Delta_1 + 0'58$ } $33'83$ M_a
 $\Delta_2 + 0'56$ } $33'80$

The anomaly for Δ_2 for $-\text{C} : \text{C} \begin{array}{c} \text{---} \end{array} \text{CN}$ is + 0.58. The propionyl compound possesses a refractivity of—

$$M_a \ 38.40 \quad \Sigma nr_a \ 38.32 \text{ (calc.)}$$

Smiles gives the following results : ketonic 35.97, enolic 36.98, and concludes that the substance is enolic.

(6) Acetyl malonic ester, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{CO}_2 \text{C}_2\text{H}_5)_2$. $M_a \ 48.60$.

Ketonic form Σnr_a
47.02

Enolic forms—

$\text{CH}_2 : \text{C}(\text{OH}) - \text{CH}(\text{CO}_2 \text{C}_2\text{H}_5)_2$ 47.79

$\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{C} \begin{array}{c} \text{---} \text{CO}_2 \text{C}_2\text{H}_5 \\ \text{---} \text{CO}_2 \text{C}_2\text{H}_5 \end{array}$ $\Delta + \frac{48.04}{0.56}$
48.60

The expected anomaly is + 1.10 for the conjugation of the two CO_2 etc. groups. There are cases which theoretically involve a double anomaly such as the above, but which nevertheless show a single one.

The following cases illustrate this :—

Ethyl maleate— M_a . Σnr_a . Δ .

$\text{CH} - \text{COOC}_2\text{H}_5$
 $\parallel$
 $\text{CH} - \text{COOC}_2\text{H}_5$ 42.23 41.85 + 0.43

Methyl citra-conate—

$\text{CH}_3 - \text{C} - \text{COOCH}_3$
 $\parallel$
 $\text{CH} - \text{COOCH}_3$ 37.84 37.21 + 0.63

Ethyl citra-conate—

$\text{CH}_3 - \text{C} - \text{COOC}_2\text{H}_5$
 $\parallel$
 $\text{CH} - \text{COOC}_2\text{H}_5$ 46.48 46.41 —

It is thus observed that the expected anomaly is reduced by half or disappears entirely. This is the most important point at present, since it shows that the diminution of the anomaly of acetyl malonic ester is not due to heterogeneity of substance, but to a similar cause to that which operates in methyl citra-conate, for instance. This leads us to conclude that acetyl malonic ester is homogeneous and possesses the formula already indicated.

(7) Ethyl acetone dicarboxylate CO_2 etc. $\cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \text{CO}_2$ etc. $M_a \ 47.64$
 CO_2 etc. $\cdot \text{CH}_2 \cdot \text{C}(\text{OH}) : \text{CN} \begin{array}{c} \text{---} \end{array} \text{CO}_2$ etc. $\Sigma nr_a \ 47.75 \ \Delta \ 0.53$ Smiles $\Sigma nr_a \ 49.04$
partially enotic.

Aromatic Derivatives.

In order to deal with the question, it will be necessary to calculate the anomaly shown by some simple benzene derivatives.

$\text{C}_6\text{H}_5 \begin{array}{c} \text{---} \end{array} \text{CH} : \text{CH}_2$ M_a . Σnr_a . Δ .
35.98 34.92 1.06
 $\text{C}_6\text{H}_5 \begin{array}{c} \text{---} \end{array} \text{CH} : \text{O}$ 31.77 30.67 1.10

(1) Oxymethylene phenyl acetic ether—

Formyl phenyl acetic ester (not known), possible formula for solid modification—

The calculated value of the first compound agrees with the observed value, a fact which confirms the formula attributed to it.

Smiles concludes that the form is enolic from—

Ketonic 51'07
Enolic 52'08

There is seen to be a considerable difference between M_a and Σnr_a .

(2) Acetate of α oxymethylene phenyl acetic ester—

The number shows that the formula is as stated. Smiles gives the value 61'50 without the anomalies.

The most important conclusion is that in cases where one or more keto or enol forms are possible, only one form really exists, and that pure substances result—never mixtures. The different isomers appear to be mutually exclusive.

NOTE.—Acetone oxalic ester.

$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2$ etc. M_a 39'08 Σnr_a 39'20. The substance is ketonic and not enolic as stated by Smiles.