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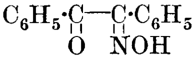
CCXCVIII.—*The Configurations of the Benzilmonoximes.*

By Thomas Weston Johns Taylor and Marcia Sarah Marks.

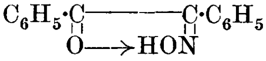
The configurations generally accepted at present for the benzilmonoximes are founded on the work of Meisenheimer and his co-workers on the oxidation of triphenyl*iso*oxazole and its derivatives (*Ber.*, 1921, **54**, 3206; 1924, **57**, 282) and on the Beckmann transformation (*ibid.*, 1924, **57**, 289). Convincing though this evidence is, difficulties in the stereochemistry of compounds showing this type of geometrical isomerism still remain (compare von Auwers, *Ber.*, 1929, **62**, 1320). Hence evidence as to the configurations of these substances, which in many respects form the keystone of the stereochemistry of all oximes, has been sought from an entirely different source.

In an earlier paper (Taylor and Ewbank, J., 1926, 2818), it was pointed out that the reactivity of the carbonyl group in the α-oxime and the absence of such reactivity in the β-oxime, together with the rough estimates of solubility that have been recorded, indicate that in the β-oxime the hydroxyl group and the carbonyl group are so situated in the molecule that co-ordination between the two can occur; this view leads to the configurations (I) and (II), which are the same as those of Meisenheimer.



$$C_6H_5\cdot\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle NOH}{\|}}{C}\cdot C_6H_5$$

(I) α-Oxime.



$$\begin{array}{lcr} C_6H_5\cdot C & \text{————} & C\cdot C_6H_5 \\ \quad\;\| & & \| \quad \\ \quad\;O & \longrightarrow & HON \end{array}$$

(II) β-Oxime.

If this view is correct, the α-oxime in physical properties should be a hydroxylic substance, while in the β-oxime the typical hydroxylic physical properties should disappear. The two compounds should behave very much as *o*- and *m*-nitrophenols behave, since in these substances the space arrangement of the groups in the meta-compound prevents the co-ordination of hydroxyl and nitro-groups which is responsible for the characteristically non-hydroxylic physical properties of the ortho-compound (Sidgwick and Callow, J., 1924, **125**, 527).

The solubilities of the two oximes in benzene have been measured and analysis of the results indicates clearly that the α-oxime does indeed behave as a hydroxylic compound, while the β-oxime does not, and thus Meisenheimer's configurations (I) and (II) receive further support.

The solubility measurements are plotted in Fig. 1. The solubility in benzene of a substance that forms " normal " mixtures with that

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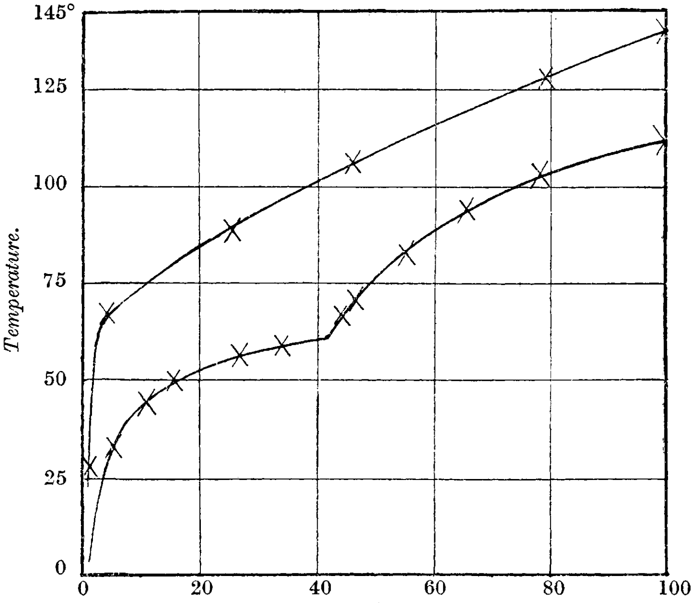
solvent can be calculated from the melting point and latent heat of fusion of the substance by means of the equation

$$-\log_e S = \frac{Q}{R} \cdot \frac{T_m - T}{T_m T}$$

where T_m is the melting point and Q the latent heat of fusion, R the gas constant, and S the solubility at temperature T, expressed as a molar fraction. If, however, the substance is hydroxylic, the solubility is known always to be less than the " natural " value and in many cases this leads to the formation of two liquid layers (see Sidgwick, " The Electronic Theory of Valency," 1927, p. 138 *et seq.*). Whether a substance is behaving normally as a solute or not can be most easily discovered by calculating from the solubility measurements, by means of a modified form of the above equation, the " nominal heats of solution " for decreasing values of the concentration of the solute (Sidgwick and Ewbank, J., 1921, **119**, 993; Sidgwick and Taylor, J., 1922, **121**, 1853). If the substance is normal, these values remain fairly constant, usually falling slightly; if, however, its solubility is markedly less than the natural, the values

Fig. 1.



Upper curve, solubility of α-benzilmonoxime in benzene.
Lower ,, ,, ,, β- ,, ,, ,, ,, .

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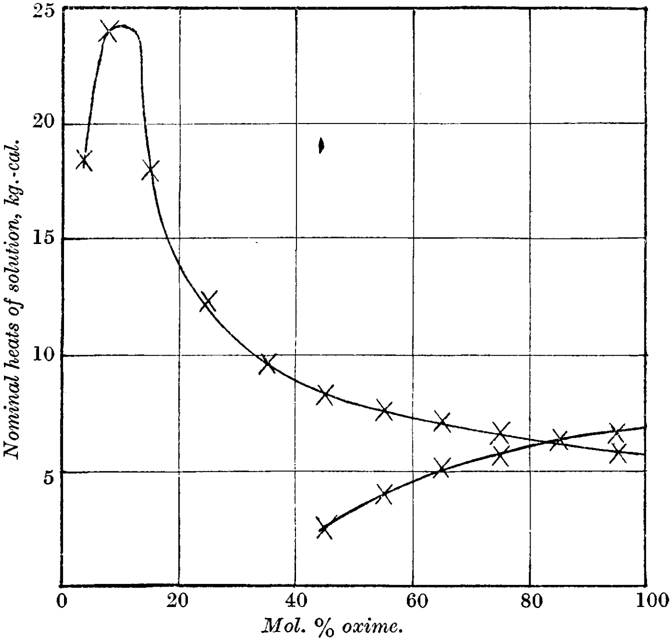
rise and pass through a maximum, which becomes infinity if actual separation into two liquid layers occurs.

The calculated values for the nominal heats of solution are plotted in Fig. 2, and it will be seen that the α-oxime is definitely a substance which shows the same type of abnormality as the *m*- or *p*-nitrophenols or the corresponding hydroxybenzaldehydes (Sidgwick and Aldous, J., 1921, **119**, 1001; Sidgwick and Allott, J., 1923, **123**, 2819), *i.e.*, substances whose solubility relationships are determined by the presence of a free hydroxyl group in the molecule. The curve for the β-oxime cannot be taken to low concentrations in solution because of the entry below 62° of a new solid phase containing benzene. Enough of the curve, however, can be obtained to show that there is no abnormality of the above kind and that the solubility of the β-oxime is more of the type of that of *o*-nitrophenol or hydroxybenzaldehyde, where the hydroxylic physical properties have disappeared because of co-ordination between the hydrogen atom of the hydroxyl group and a donor group in a suitable spatial position in the molecule. It is on this ground that the configurations (I) and (II) receive fresh support.

FIG. 2.



Nominal heats of solution in benzene : rising curve, α-oxime ; falling curve, β-oxime.

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As the concentrations of the β-oxime in the saturated solutions decrease, the values of the nominal heat of solution begin to fall off steeply; this is connected with the formation of the solid compound with the solvent (compare Sidgwick and Callow, *loc. cit.*, p. 1011).

Since the α-oxime in solution is known to change slowly into the β-oxime (von Auwers and V. Meyer, *Ber.*, 1889, **22**, 540) at 100° and above, there was a danger that the solubility measurements of the α-oxime would be vitiated by this change. It was, however, inappreciable during the time necessary for the determination, since, in the same sealed bulb, the temperature of complete solubility remained the same in a series of redeterminations, and the solubilities of the two forms are so widely different that any isomeric change would have been apparent.

EXPERIMENTAL.

Preparation of the Oximes.—All published methods are troublesome and uncertain; some give rise to mixtures of the two oximes which form slowly-solidifying oils very difficult to separate by recrystallisation. All these methods have been investigated in detail. The following directions make the preparation of both oximes in a state of purity easy and certain.

α-*Benzilmonoxime* (a modification of the method of von Auwers and Siegfeld, *Ber.*, 1893, **26**, 792, footnote). Benzil, which must be pure, is ground to a thin paste with a little alcohol, and hydroxylamine hydrochloride (1 equiv.) in concentrated aqueous solution is added. The whole is cooled to —5° (most conveniently by using a bath of crushed ice and concentrated hydrochloric acid) and caustic soda (3 equivs.) in 20% aqueous solution is added drop by drop with rapid mechanical stirring. The temperature must not rise above 0° and the stirring must be efficient. After about 1½ hours the mixture is diluted with water and the small quantity of unchanged benzil is removed on a sintered glass filter. The filtrate is acidified with the minimum of glacial acetic acid, and, after standing, the crude pinkish α-oxime is collected and recrystallised from aqueous alcohol (60 vol. % alcohol). Animal charcoal must not be used in the recrystallisations. The product is recrystallised from benzene twice and is then pure. 44 G. of benzil gave after the first recrystallisation 37 g. of oxime, m. p. 137°; the final yield was 28 g. of pure oxime, m. p. 140° (von Auwers and V. Meyer, *loc. cit.*, give 137—138°).

β-*Benzilmonoxime* is most conveniently obtained from the *pure* α-oxime by boiling it for 15 minutes with one-tenth of its weight of dried animal charcoal in a quantity of pure benzene just sufficient to dissolve the α-oxime at the boiling point (see Taylor and Marks, *Nature*, 1930, **125**, 636). The charcoal is removed and the pure

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compound, β-oxime + $\frac{1}{2}C_6H_6$, crystallises slowly on cooling; more can be obtained by evaporation of the mother-liquor. The melting point of our samples of pure β-oxime is 112°; the value 113—114° given by von Auwers and V. Meyer seems to be a little too high. Meisenheimer and Heim (*Annalen*, 1907, **355**, 280) were unable to obtain specimens which melted above the range 105—108°; their samples probably contained a little α-oxime, from which it is difficult to separate the β-oxime by recrystallisation. The pure β-oxime causes no colour change whatever in aqueous alcoholic solutions of copper acetate, while those contaminated with the α-oxime give a greenish colour.

Solubility Measurements.—The synthetic method was used, sealed bulbs containing known amounts of the oxime and of benzene (purified by freezing-out twice and then shaking with sulphuric acid) being heated in a bath with a thermo-regulator until the temperature of complete solubility was ascertained. All temperatures given are corrected for the emergent stem, and the thermometers used were checked against a standard. The observed temperatures were :—

α-Oxime.

Mol. %.	Temp.
0·45	28·6°
3·99	68·0
25·53	89·0
46·20	106·3
79·60	127·8

β-Oxime.

Mol. %.	Temp.	
5·27	33·5°	co-existing solid phase : β-oxime + $\frac{1}{2}C_6H_6$.
11·18	44	
15·74	50	
26·72	56	
34·06	59	
44·13	67	
46·38	71	
55·35	83	
65·83	94	
78·32	103	

The compound β-oxime + $\frac{1}{2}C_6H_6$ was first obtained by von Auwers and V. Meyer (*loc. cit.*), who stated that it melts " bei etwa 70° "; according to our results this compound has a non-congruent melting point, and the transition temperature, *i.e.*, that of incipient fusion, is 62°. Many samples of the compound have been prepared (Found : loss in weight on heating at 100°, 14·50, 14·67, 14·81. Calc., 14·78%) and all melt over a range of temperature beginning at 62—63°.

Nominal Heats of Solution.—The values obtained (see references above for calculation) were :—

α-Oxime, mol. % ...	95	85	75	65	55	45	35	25
Q, kg.-cal................	5·81	6·35	6·67	7·25	7·65	8·19	9·74	12·35
Mol. %	15	7·5	3·75					
Q	17·97	24·02	18·42					
β-Oxime, mol. % ...	95	85	75	65	55	45		
Q, kg.-cal.	6·80	6·56	5·60	5·12	3·98	2·65		

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Note by T. W. J. T.—In the earlier paper (Taylor and Ewbank, *loc. cit.*) a structure was proposed for the metallic derivatives of oximino-ketones, such as α-benzilmonoxime, which would involve a stereochemical change of the α- into the β-structure during the formation of the derivative. Such a change does not appear to take place, since the copper derivative of α-benzilmonoxime, R·Cu·OH, that we described can be easily decomposed by grinding it in the cold with dilute sulphuric acid, and the oxime so recovered is the α-oxime. Hence the structure proposed by Pfeiffer and Richarz (*Ber.*, 1928, **61**, 103) and supported by Hieber and Leutert (*Ber.*, 1929, **62**, 1839) and by Brady and Muers (this vol., p. 1599) is much more probable than ours. The cobalt derivative of α-benzilmonoxime resists all attempts to decompose it short of complete degradation.

Summary.

1. The solubilities in benzene of the two benzilmonoximes have been measured.

2. Analysis of the results indicates clearly that the stereochemical configurations of these oximes are those proposed by Meisenheimer, and thus supports the view that, in this case at least, the Beckmann transformation involves the groups in the *anti*-position to one another.

3. Improved methods for the preparation and purification of these oximes are described.

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