CCCCXX.—*Studies of Dynamic Isomerism. Part XXVIII. Absorption Spectra of the Ketonic and Enolic Forms of an α-Diketone.*

By Thomas Martin Lowry, Henri Moureu, and Charles Alexander Hamilton MacConkey.

In the preceding paper of this series (this vol., p. 1333), the statement of Morton and Rosney (J., 1926, 706) that "the isomeric forms of benzoylcamphor give bands of the same wave-length, but of unequal intensity" was shown to be incorrect, since the absorption bands actually occur at different wave-lengths, although they are of very similar intensity, when examined before isomeric change has taken place. Since the preceding statement was used as evidence in support of the general proposition "that enolic and ketonic modifications possess the same wave-length of maximum absorption," it was of interest to see whether this proposition could be substantiated in other cases. In the present investigation, therefore, we have taken advantage of the separation by one of us (Moureu, *Compt. rend.*, 1928, **186**, 380) of the ketonic and enolic forms, (I) and (II), of benzylmethylglyoxal, in order to repeat with an α-diketone the tests that had already been carried out on a typical β-diketone.

$$\underset{\text{(I; ketonic form.)}}{C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}CH_3} \rightleftharpoons \underset{\text{(II; enolic form.)}}{C_6H_5{\cdot}CH{:}C(OH){\cdot}CO{\cdot}CH_3}$$

The labile ketonic form (I) of benzylmethylglyoxal can be separated in a pure state as a yellow liquid by distillation in presence of a trace of sodium carbonate. Under these conditions, a reversible reaction is produced in the liquid phase, but the more volatile isomeride (which resembles the *o*-quinones in this property) escapes and becomes fixed in the vapour phase by the elimination of the non-volatile catalyst. It therefore distils as a homogeneous product, b. p. 104°/10 mm., and when frozen melts sharply at 17°. On the other hand, when an alkali or a nitrogenous base is added to the liquid, the enolic form (II) crystallises in a pure state, since it is the stable solid phase at all temperatures up to its m. p. at 70°. In the absence of a catalyst, the enol also can be distilled without change, boiling at 134°/10 mm.

The structures of the two isomerides were established by the fact that the yellow quinone-like ketonic form gave no reaction with bromine, reacted but slowly with ferric and antimonous chlorides, and gave only an 18% yield of methane when acted on by the Grignard reagent, whereas the colourless enolic form immediately fixed one molecular proportion of bromine, formed a brown salt with ferric chloride and a crystalline derivative with antimonous chloride, and gave an 80% yield of methane with the Grignard reagent (*Compt. rend.*, 1928, **186**, 503).

The measurements set out below show that the absorption bands of the ketonic and enolic forms of the α-diketone differ even more widely than in the case of the stable and labile forms of the β-diketone. In particular, the two adjacent carbonyl groups in the α-diketone displace the familiar ultra-violet band of the simple ketones into the visible region, exactly as in the case of camphorquinone (Lowry and French, J., 1924, **125**, 1921), but without increasing its intensity, whereas the conjugated double bond of the enolic isomeride gives rise to an enormous increase of intensity, but without any important change of wave-length, exactly as in the case of benzylidenecamphor (*ibid.*). The inequality of wave-length is therefore twice as great as in the case of benzoylcamphor, and is accompanied by a difference of intensity in the ratio of about 600 to 1.

The structures assigned to the two isomerides are largely irrelevant to the present discussion, since the general proposition cited above implies that, if a series of isomerides can be converted into one another by successive keto-enol transformations, the wave-length of the absorption bands must remain constant throughout, whatever structure may be assigned to individual members of the series. If, therefore, two isomeric enols can be produced from a given ketone, or if two stereoisomeric enols can be converted into one another through an intermediate ketonic form, as might conceivably occur in the case of benzoylcamphor (*loc. cit.*, p. 1334), the absorption bands of both enols must be at the same wave-length as that of the ketone, and must therefore be identical in wave-length with one another. In the present instance, however, the quinone-like colour of the liquid diketone and the absence of quinonoid characters in the solid isomeride provide an ocular vindication of the structures deduced from the chemical diagnosis recorded above, and make it obvious that we are dealing with a typical keto-enol isomerism.

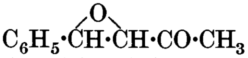
In view of their close relation to the α-diketone, we have also included in our programme the measurement of the absorption spectra of the compounds set out below.

$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \rightleftharpoons C_6H_5{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3$$

(III; Benzoylacetone, ketonic form.) (IV; Benzoylacetone, enolic form.)

$$C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$$

(V; Benzylideneacetone.)



$$C_6H_5{\cdot}\overset{\quad O \quad}{CH{\cdot}CH}{\cdot}CO{\cdot}CH_3$$

(VI; Acetylphenylethylene oxide.)

Benzoylacetone is a structural isomeride of the α-diketone which forms the main subject of the present investigation. It exhibits the dual reactivity of a tautomeric compound, yielding derivatives of the ketone (III) and of the enol (IV); but, unlike the isomeric α-diketone, it is only known in one form, to which the structure (IV) is conventionally assigned. The unsaturated ketone (V) has been examined on account of its close relationship to the isomeric enols (II) and (IV). The ethylenic oxide (VI) is a compound of fixed structure, which is isomeric with the labile α- and β-diketones (I) and (III), and the enols (II) and (IV), to which it is related in the same symmetrical manner as the olefin from which it is derived.

FIG. 1.

Molecular extinction coefficients of benzoylacetone. (a) *In alcohol;* (b) *in* cyclo*hexane.*

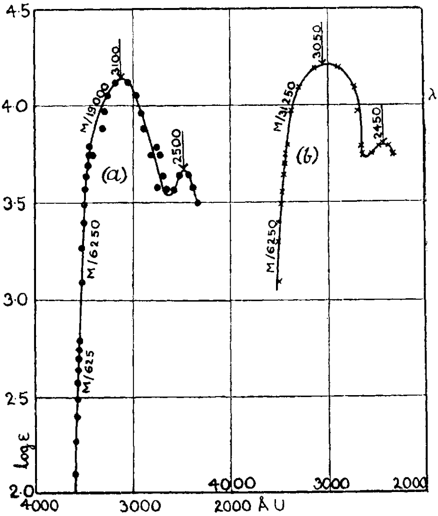
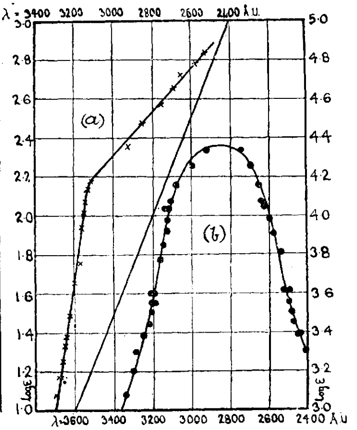


FIG. 2.

(a) *Molecular extinction coefficients of acetylphenylethylene oxide.*
(b) *Molecular extinction coefficients of benzylideneacetone.*



1. *Benzoylacetone.*—The absorption spectrum of benzoylacetone has been examined by Baly and Desch (J., 1905, **87**, 766) and by Morgan and Moss (J., 1913, **103**, 78), who recorded the presence of a single absorption band. Our own measurements, with alcohol as the solvent [Fig. 1 (*a*)], gave two maxima

$$\log \varepsilon = 4{\cdot}15 \text{ at } 3100; \quad \log \varepsilon = 3{\cdot}66 \text{ at } 2500 \text{ Å.U.},$$

which we had no difficulty in identifying with the characteristic bands of the two forms of benzoylcamphor, *viz.*, $\log \varepsilon = 4{\cdot}27$ at 3140; $\log \varepsilon = 4{\cdot}21$ at 2420 Å.U. No change was observed in the absorption spectrum when examined ½ hour after the preparation of the solution and again on the following day. A similar pair of maxima

$$\log \varepsilon = 4{\cdot}26 \text{ at } 3050; \quad \log \varepsilon = 3{\cdot}80 \text{ at } 2450$$

was observed when the experiment was repeated with a freshly-prepared solution in *cyclo*hexane [Fig. 1 (*b*)], the measurements being completed in the course of about 80 minutes.

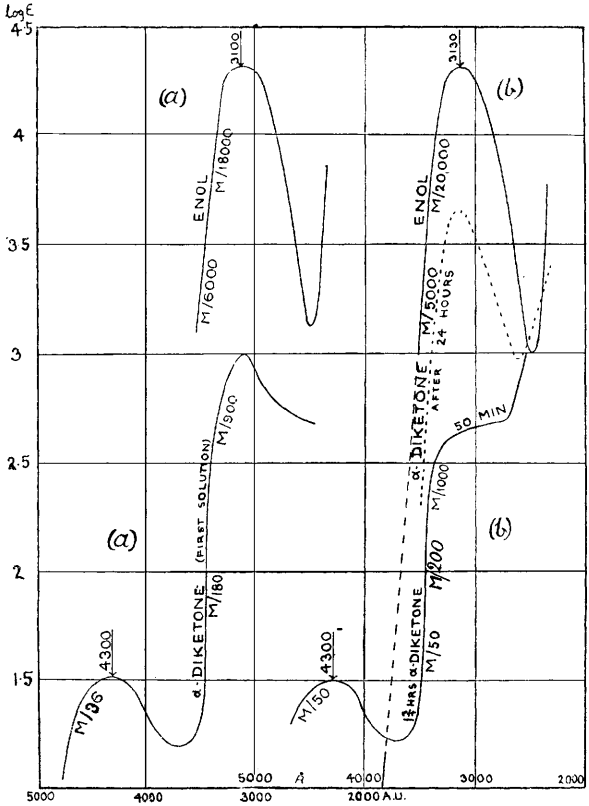
Since the only known form of benzoylacetone gives an immediate coloration with ferric chloride, it has generally been supposed to have an enolic structure, and the band observed by Baly and Desch, and by Morgan and Moss at 3100 Å.U., has been regarded as a characteristic of the isomeride (IV). If no other information were available, it might be supposed that the two bands shown in Fig. 1 (*a*) and (*b*) were both due to the same isomeride, since we have not been able to observe them separately. On the other hand, the close agreement of the wave-lengths of the bands of Fig. 1 (*a*) with those of alcoholic solutions of the two forms of benzoylcamphor leads us to conclude that in this case also the bands are due to two isomeric forms of the β-diketone; our failure to separate them can then be attributed to catalysis, since we do not yet know of any certain method of arresting isomeric change in these very sensitive prototropic compounds. This conclusion is confirmed by the fact that, whilst the intensity of the bands given by the two pure forms of benzoylcamphor is greater than those of the two bands of benzoylacetone, the latter agree quite well with the intensities of the bands ($\log \varepsilon = 4{\cdot}10$ and $3{\cdot}90$) in an equilibrium mixture of the two forms of benzoylcamphor. According to this view, the crystals of benzoylacetone, melting at 61°, may be regarded as a homogeneous solid phase, probably corresponding in structure with the stable form of benzoylcamphor, but reverting with even greater readiness to an equilibrium mixture in solution.

2. *Benzylideneacetone and Acetylphenylethylene Oxide.*—The absorption spectrum of benzylideneacetone (V) is shown in Fig. 2 (*b*). As might be expected, it gives a maximum, $\log \varepsilon = 4{\cdot}36$ at 2850 Å.U., in close agreement with the maximum ($\log \varepsilon = 4{\cdot}32$ at 2900 Å.U.) already recorded for an alcoholic solution of benzylidenecamphor (Lowry and French, J., 1924, **125**, 1921). The close agreement in the position and intensity of the two bands shows that the influence of the camphor nucleus is not very great, and suggests that the observations made with camphorquinone, benzoylcamphor, and other compounds of the camphor group may be expected to reappear almost unchanged in the corresponding open-chain compounds of the present series.

The absorption spectrum of acetylphenylethylene oxide is shown Fig. 2 (*a*). Unlike the preceding compound, it does not give an absorption band, but only a rapid " step-out " at wave-lengths less than 3100 Å.U. Since one of the ketonic groups remains intact when we pass from the labile α- or β-diketone to the fixed oxide, it is remarkable that this oxide does not give the familiar ketonic band at about 3000 Å.U. An explanation may perhaps be found in the view that, in the absence of a conjugated double bond, the " ether " oxygen atom becomes interlocked with the ketonic oxygen, in much the same way as in the esters, so that the oxide may be regarded as an analogue of benzyl acetate rather than of acetophenone.

FIG. 3.

Molecular extinction coefficients of benzylmethylglyoxal in alcohol.
(a) *First series ;* (b) *second series.*

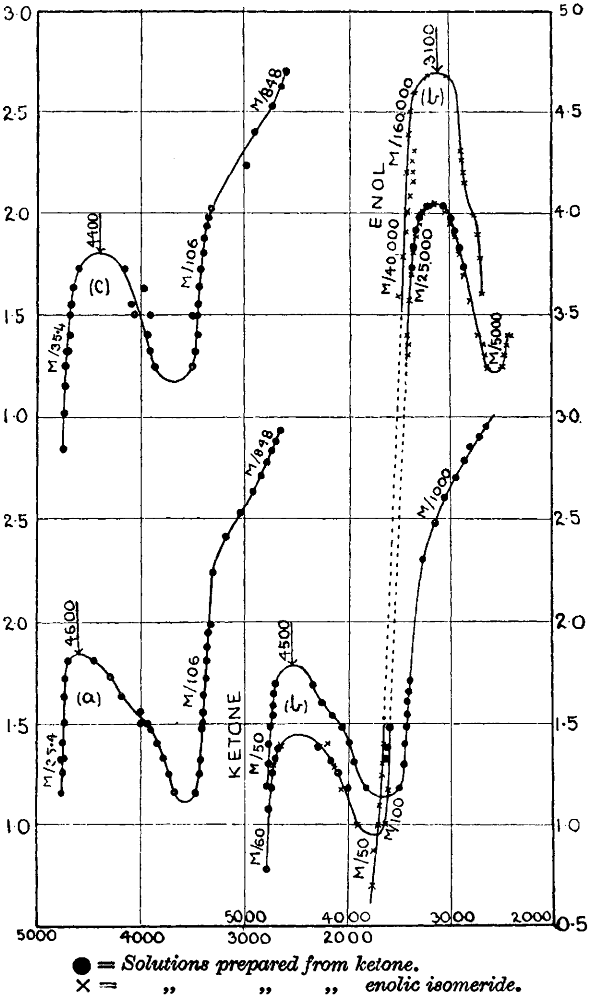


3. *Benzylmethylglyoxal and its Enolic Isomeride.*—(a) *Solid form.* The molecular extinction coefficients of the crystalline form of the α-diketone in alcoholic solution are set out in Fig. 3. Unlike the

isomeric β-diketone (benzoylacetone), this compound gives only a single *maximum*, log ε = 4·3 at 3100 Å.U., corresponding closely with that of the stable form of benzoylcamphor, whilst a very strong

FIG. 4.

Molecular extinction coefficients of benzylmethylglyoxal. (a) *In* cyclo*hexane* (*first series*) ; (b) *in* cyclo*hexane* (*second series*) ; (c) *in chloroform.*



● = *Solutions prepared from ketone.*
× = ,, ,, ,, *enolic isomeride.*

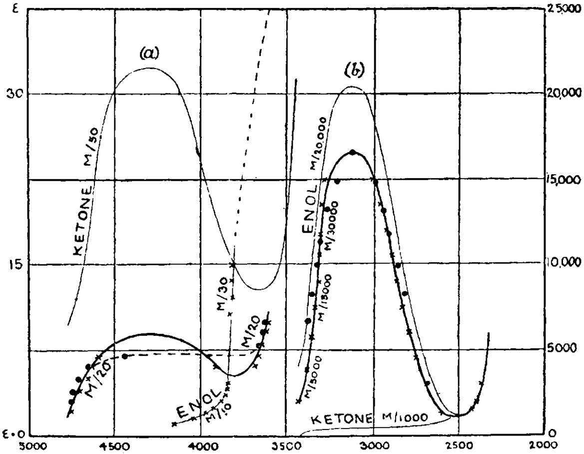
minimum, log ε = 3·2 at 2480 Å.U., appears at the wave-length of the absorption band of the labile form of the latter compound. A duplicate determination gave a similar maximum, log ε = 4·3 at

3130 Å.U., but a slightly deeper minimum, extending to log ε = 3. Since the solid and its freshly prepared solutions were quite colourless, it is clear that the enolic form does not give an absorption band in the visible spectrum; but this was also shown by direct observations at concentrations of $M/10$ and $M/30$, which are plotted at the foot of Fig. 5 (*a*).

A solution in *cyclo*hexane [Fig. 4 (*b*)] showed an even stronger maximum, log ε = 4·7 at 3100 Å.U., but the curve was not followed as far as the minimum, which occurs at 2500 Å.U. in the equilibrium mixture (see below). On the other hand, the absence of an absorption band in the visible region was again established by direct observations, since an $M/50$-solution showed an extinction coefficient which was already less than 5 (log ε = 0·7) at 3750 Å.U., and the absorptive power of the solution was then still diminishing according to an almost linear law as the wave-length was increased.

FIG. 5.

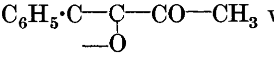
Equilibrium of ketonic and enolic forms of benzylmethylglyoxal in alcohol.
(a) *Ketonic band ;* (b) *enolic band.*



● = *Solutions prepared from ketone.*
× = ,, ,, ,, *enolic isomeride.*

It is of interest to compare the bands at about 3100 Å.U. of the enolic forms of the α- and β-diketone with the bands of benzylideneacetone at 2850, and of benzylidenecamphor at 2900 Å.U. It appears certain that we are dealing throughout with the same band, but that it is displaced to a slightly longer wave-length by the introduction of the hydroxyl radical, in just the same way as the ketonic band of camphor is displaced towards the visible region by the introduction of a halogen in the α- or α′-position (Lowry and

Owen, J., 1926, 606; compare also Grossmann, Z. *physikal. Chem.*, 1914, **109**, 329, 337). This band, although it is given by two isomeric enols, is in no sense a characteristic " enolic " band, since it is equally well developed in benzylideneacetone and benzylidenecamphor, although the hydroxyl group of the enol is absent in these two compounds; it appears, indeed, to be merely the ketonic band reinforced by conjugation of the carbonyl double bond with an olefinic double bond, exactly as in methylenecamphor (Lowry and French, J., 1924, **125**, 1921).

(b) *Liquid form.* The liquid form of the diketone reverts very easily to the crystalline form, since the yellow liquid solidifies almost immediately in the presence of a trace of a nitrogenous base. We were therefore less confident of securing an independent record of the ketonic band, especially in view of the very remarkable absorptive power of the isomeric enol. From analogy with camphorquinone, we anticipated that this band would be found in the blue region of the spectrum at about 4700 Å.U., and at a relatively high concentration, say, $\log \varepsilon = 1{\cdot}8$. We therefore made our first measurements with an $M/35{\cdot}4$-alcoholic solution, and observed the expected maximum, $\log \varepsilon = 1{\cdot}5$ at 4300 Å.U. [Fig. 3 (*a*)]. On diluting the solution, however, we found that a second maximum had already been developed in the ultra-violet at 3120 Å.U., although its intensity, $\log \varepsilon = 2{\cdot}97$, was 20 times weaker than in the case of the pure enol. We therefore repeated the experiment, taking much greater care in order to complete our observations before isomeric change had begun. The results of the second experiment, in which the exposures were completed in 50 minutes from the time when the solution was prepared, are shown in Fig. 3 (*b*). The curve no longer shows a maximum in the ultra-violet, but only a " step-out," $\log \varepsilon = 2{\cdot}6$ to $2{\cdot}8$ at 3300 to 2700 Å.U. This step-out is probably a genuine characteristic of the pure α-diketone, since it is very similar to one that had already been recorded in the case of camphorquinone (Lowry and French, J., 1924, **125**, 1921), where enolisation would appear to be impossible (Bredt, *J. pr. Chem.*, 1918, **97**, 1; *Annalen*, 1924, **437**, 1), since it would involve bending all the four bonds of the carbon atom (4) in the direction of the carbon atom (10) of the camphor nucleus. The step-out can also be compared with the one now recorded in the isomeric acetylphenylethylene oxide (VI), and may perhaps be attributed to the skeleton  $C_6H_5{\cdot}\underset{\text{—O}}{\text{C—C}}\text{—CO—CH}_3$ which is common to both isomerides.

Confirmation of these results was obtained by making use of solutions in *cyclo*hexane, for which molecular extinctions are plotted in Fig. 4 (*a*). The curves again show a maximum ($\log \varepsilon = 1{\cdot}85$ at

4600 Å.U.) in the visible spectrum, a minimum (log ε = 1·2 at 3600 Å.U.), and a step-out at wave-lengths on either side of 3000 Å.U. A duplicate series of observations, which are plotted in Fig. 4 (*b*), gave a precisely similar curve, although the numerical values are not quite the same in the two series. The two curves agree, however, in suggesting that the band in the visible spectrum is unsymmetrical, since each curve rises almost vertically on the side of longer wave-lengths, but spreads out on the side of shorter wave-lengths, as if there were a second characteristic frequency at about 4000 Å.U.

The molecular extinction coefficients of a solution of the α-diketone in chloroform, which are set out in Fig. 4 (*c*), show the same essential characteristics, *viz.*, a maximum (log ε = 1·8 at 4400 Å.U.) in the visible spectrum, followed in the ultra-violet by a minimum (log ε = 1·2 at 3700 Å.U.), and a step-out at wave-lengths on either side of 3000 Å.U., but without any indication of a maximum at 3100 Å.U.

The principal interest of these observations is the complete separation, which has again been realised, of the characteristic absorption bands of the enolic and ketonic isomerides. Thus, on the one hand, the colourless enol is completely transparent in the region covered by the visible absorption band of the α-diketone; on the other hand, it shows no sign of the band of shorter wave-length, which is given by the labile form of benzoylcamphor, and which appears again in the absorption spectrum of benzoylacetone. Conversely, the liquid diketone, which owes its yellow colour to the presence of a characteristic quinonoid band in the blue region of the spectrum, has been dissolved in three different solvents without developing a second maximum in the ultra-violet. Each isomeride therefore retains its individuality in solution and gives rise to an absorption band of characteristic wave-length, in close agreement with the wave-length predicted from the study of compounds of analogous structure.

4. *Equilibrium Mixtures.*—On account of the remarkable absorptive power of the enolic isomeride, special care had to be used in preparing solutions of benzylmethylglyoxal, in order to avoid the development of an ultra-violet maximum, resulting from incipient enolisation of the α-diketone. Nevertheless, the pure compound is much more stable than the majority of substances in which prototropic change is liable to take place, since the yellow liquid can be kept in hard-glass tubes for many weeks without showing any signs of solidification,* although this can be induced immediately by the addition of a basic catalyst. The stability of the α-diketone

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* Measurements of refractive index show that a slow transformation takes place even in hard-glass tubes.

and its enolic isomeride is indeed much greater than that of the two forms of benzoylcamphor, although these have been selected repeatedly for experiments on reversible isomeric change on account of the readiness with which the two isomerides can be prepared and kept. It was, however, only when we tried to prepare equilibrium mixtures of identical properties from the enolic and ketonic forms of benzylmethylglyoxal that we discovered with what difficulty the transformation is brought about in solution.

In the first instance, solutions of the two isomerides were allowed to stand for several days, since this had always proved sufficient to produce a condition of equilibrium in the case of benzoylcamphor. When dissolved in *cyclo*hexane, however, the α-diketone and its enolic isomeride had the same intensities of selective absorption even after the solution had been kept for several days. A trace of piperidine was then added, by stirring the solution of the enol with a platinum wire which had been dipped into the liquid base and drained against the side of the vessel; but even this deliberate addition of a catalyst produced no alteration in the absorptive power of the solution. Solutions of the two isomerides in *cyclo*hexane were next prepared, containing 1 mol. of piperidine for every 100 mols. of the organic compound. After 20 hours, a slight decrease was observed in the absorptive power of the ketonic form in the visible region. In the meanwhile, the enolic form had developed an absorption band in the visible spectrum at λ 4500, of intensity $\varepsilon = 12{\cdot}5$, as contrasted with $\varepsilon = 60$ for the pure ketone and $\varepsilon = 30$ for the equilibrium mixture finally obtained; but the absorptive power of this solution was unchanged after a further period of 5 days, although the ketonic and enolic solutions were still far removed from equality in this respect. These two solutions were then kept in a thermostat at 28° for 24 hours, but a glance showed that they were still of quite different depths of colour. In order to provide an amphoteric catalyst, a solution of *p*-cresol in *cyclo*hexane was now added to each solution, in quantity such that the molar concentrations of piperidine and *p*-cresol were equal in the resulting mixture. The maximum absorptive power of the ketonic solution in the visible spectrum at λ 4500 fell to $\varepsilon = 30$, but that of the enol at the same wave-length was not altered by this addition of cresol, but remained constant at λ 12·5. When diluted, the solution of the enol gave $\varepsilon = 5000$ at λ 3150, whilst the solution of the ketone gave $\varepsilon = 60$, but in neither case was a definite absorption band developed.

Equilibrium mixtures which gave identical extinction coefficients were finally obtained by adding 1 mol. % of piperidine to the dissolved ketone or enol and keeping the solutions for 20 hours in closed flasks at 50°. The equality of visual colour of the two solutions was confirmed by measurements with a Kletz colorimeter against a solution of camphorquinone. The results were as follows :

In *cyclo*hexane :

$$\frac{\text{Camphorquinone, } M/60}{\text{Ketonic solution, } M/20} = 1{\cdot}88,\ 1{\cdot}92. \quad \text{Mean} = \mathbf{1{\cdot}90}.$$

$$\frac{\text{Camphorquinone, } M/60}{\text{Enolic solution, } M/20} = 1{\cdot}81,\ 1{\cdot}92. \quad \text{Mean} = \mathbf{1{\cdot}87}.$$

In ethyl alcohol :

$$\frac{\text{Camphorquinone, } M/180}{\text{Ketonic solution, } M/20} = 0{\cdot}96,\ 0{\cdot}99,\ 0{\cdot}96,\ 1{\cdot}03. \quad \text{Mean} = \mathbf{0{\cdot}98}.$$

$$\frac{\text{Camphorquinone, } M/180}{\text{Enolic solution, } M/20} = 1{\cdot}00,\ 0{\cdot}88,\ 0{\cdot}97,\ 0{\cdot}94. \quad \text{Mean} = \mathbf{0{\cdot}95}.$$

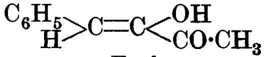
The equilibrium mixture in *cyclo*hexane has therefore rather more than one-sixth of the intensity of colour of camphorquinone, whilst in ethyl alcohol the ratio is rather more than one-ninth ; but, since this ratio depends on the width of the bands, as well as on their intensity, it cannot be used to deduce the ratio of the maximum extinction coefficients, as measured with a spectrophotometer.

Quantitative data for the molecular extinction coefficients of solutions in *cyclo*hexane are shown in Fig 4 (*b*), and those of alcoholic solutions are shown in Fig. 5, where different scales of intensity are used for the visual region of the ketonic band and for the ultra-violet region of the enolic band. In each case the circles represent values recorded for solutions of the ketone itself, and crosses are used for solutions prepared from the enolic isomeride. The two series of data can be represented by a single curve for each solvent, the largest deviation being at the ketonic band of Fig. 5 (*a*), where the solution of the enol showed a shallow maximum and minimum, whereas the solution prepared from the ketone gave only a step-out ; the points on either side of the loop can, however, be plotted on a single curve.

The circumstances in which these experiments were made were not suitable for deducing the equilibrium proportions of the ketonic and enolic forms, since the conditions of equilibrium were not well defined, and the dilutions at which the ketonic and enolic bands were observed differed very widely. It is therefore not surprising that the proportion of ketone (about $\frac{1}{2}$) in *cyclo*hexane at a dilution of $M/60$ and of enol (about $\frac{1}{4}$) in the same solvent at a dilution of $M/25{,}000$ do not add up to unity. In the case of the alcoholic solutions, the proportions of ketone and enol deduced from the extinction coefficients at the wave-lengths of the two maxima are roughly $\frac{1}{4}$ and $\frac{4}{5}$ at dilutions of $M/20$ and $M/30{,}000$, respectively;

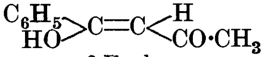
in this solvent, therefore, there appear to be 3 or 4 parts of enol to one of ketone, but this ratio also is rendered uncertain by the widely different concentrations at which the proportions of ketone and enol were determined, and by deviations from Beer's law, which are shown by the varying width of the absorption bands as observed in solutions of different concentrations. Attention should also be directed to the fact that at the wave-length λ 3800, at which the enol and the ketone have the same extinction coefficient, $\varepsilon = 15$, in alcoholic solutions, the equilibrium mixture has an absorption coefficient which is only about half as great. This anomaly throws doubt on the validity of the additive law as applied to mixtures of the α-diketone and its enolic isomeride, and suggests that they may perhaps unite with one another (like quinol and quinone) to form an unstable complex in solution.

Although the proportions of the isomerides cannot be deduced with certainty from the absorption curves for the equilibrium mixtures, these curves provide very important evidence as to the qualitative composition of these mixtures. Thus, if the two absorption bands of benzoylacetone, or of the two forms of benzoylcamphor, were characteristic of a pair of stereoisomeric enols, it would be difficult to exclude the possibility of a similar stereoisomerism in the enolic form of the α-diketone, as may be seen by comparing the formulæ



$$\begin{matrix}C_6H_5\\H\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}OH\\CO\cdot CH_3\end{matrix}$$

and



$$\begin{matrix}C_6H_5\\HO\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}H\\CO\cdot CH_3\end{matrix}$$

a-Enol. *β*-Enol.

Actually, however, the absorption curves for equilibrium mixtures of the two forms of benzylmethylglyoxal give no indication of the maximum at λ 2450, which is characteristic of the labile form of benzoylcamphor, and which is also seen in the absorption spectrum of benzoylacetone. On the contrary, the curves for solutions in alcohol and in *cyclo*hexane actually pass through a *minimum* in this region of the spectrum. The band at λ 2450 must therefore be associated with a structure which is not only different from those of the two known forms of benzylmethylglyoxal, but is not produced from either of them by isomeric change in presence of a catalyst. Such a form cannot be a mere stereoisomeride, although it might conceivably be a co-ordinated enol, containing a 6-atom ring which could not be produced from an α-diketone.

Summary.

Benzylmethylglyoxal, $C_6H_5\cdot CH_2\cdot CO\cdot CO\cdot CH_3$, shows an absorption band in the visible spectrum, with a maximum $\log \varepsilon = 1{\cdot}5$ at 4300 in alcohol, or $\log \varepsilon = 1{\cdot}85$ at 4600 in *cyclo*hexane, but only a " step-out " in the ultra-violet at about 3000 Å.U. The enolic isomeride, $C_6H_5{\cdot}CH{:}C(OH){\cdot}CO{\cdot}CH_3$, on the other hand, is colourless, but has a strong absorption band in the ultra-violet with a maximum $\log \varepsilon = 4{\cdot}3$ at 3100 in alcohol, or 4·7 at 3100 in *cyclo*hexane. Both bands are given by solutions in which the two isomerides are in equilibrium.

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