192. *Absorption Spectra in Relation to the Constitution of Keto–enols.*
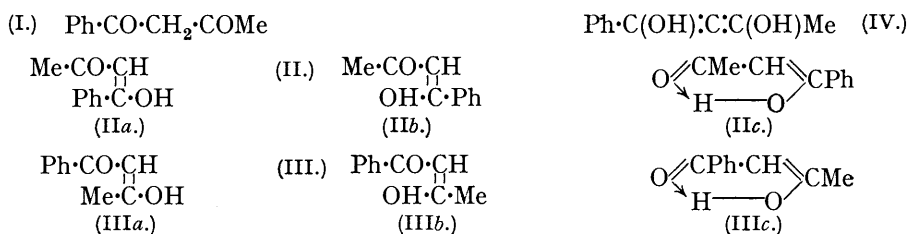
By R. A. Morton, Ali Hassan, and T. C. Calloway.

The evidence concerning the constitution of the enolic forms of many β-diketones and β-keto-esters is very conflicting. Well-tried physical criteria and diagnostic methods lead to mutually incompatible results, and the inconsistencies serve to emphasise the need for caution in the choice of a structural formula for every component in labile systems.

Benzoylacetone provides a test case because the terminal groups are markedly different. Apart from the diketonic structure (I), enolisation of either the benzoyl or the acetyl group or both may be postulated. Stereoisomerism in the mono-enols may occur, and in addition some form of chelation is plausible for the stereoisomerides in which the enolic hydroxyl and the unaltered carbonyl group are not well separated in space. Hence, if one dienolic form is included, there are eight possible formulations :

(I.) $Ph \cdot CO \cdot CH_2 \cdot COMe$ $Ph \cdot C(OH) \colon C \colon C(OH)Me$ (IV.)

$$Me \cdot CO \cdot \overset{|}{\underset{|}{C}}H$$
$$Ph \cdot C \cdot OH$$
(IIa.)

(II.)
$$Me \cdot CO \cdot \overset{|}{\underset{|}{C}}H$$
$$OH \cdot C \cdot Ph$$
(IIb.)

$$O \underset{\diagdown H \text{———} O}{\overset{\diagup CMe \cdot CH}{\diagdown}} CPh$$
(IIc.)

$$Ph \cdot CO \cdot \overset{|}{\underset{|}{C}}H$$
$$Me \cdot C \cdot OH$$
(IIIa.)

(III.)
$$Ph \cdot CO \cdot \overset{|}{\underset{|}{C}}H$$
$$OH \cdot C \cdot Me$$
(IIIb.)

$$O \underset{\diagdown H \text{———} O}{\overset{\diagup CPh \cdot CH}{\diagdown}} CMe$$
(IIIc.)

From Meyer's bromine absorption data (*Annalen*, 1911, **380**, 212; *Ber.*, 1912, **45**, 2849) and Hieber's data (*Ber.*, 1921, **54**, 902) based on the copper acetate method, the solid cannot contain more than 1% of diketone (I) and is almost certainly entirely enolic, but aqueous solutions at equilibrium contain only 32·5% of enol, so (I) evidently exists in solution. The products obtained upon alkaline hydrolysis support Claisen's view that enolisation occurs at the acetyl group, but Meyer, having observed in related compounds an increasing tendency towards enolisation of acyl groups in the order

$$CO_2Et < COMe < COPh < CO \cdot CO_2Et,$$
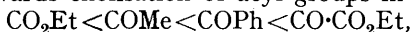
concluded that benzoylacetone enolises at the benzoyl group.

Scheiber and Herold (*Annalen*, 1914, **405**, 295) found that decomposition of benzoyl-acetone ozonide yielded benzoic acid and methylglyoxal, the former in a yield corresponding to 97·5% of that expected for β-hydroxystyryl methyl ketone; the solid was considered to be homogeneous (II), but a little of (III) and (IV) were postulated for solutions at equilibrium. Michael and Ross (*J. Amer. Chem. Soc.*, 1931, **53**, 2399), however, have pointed out that, as ozonisation is a slow process, it does not provide an unequivocal means for deciding between two alternative enolic structures. The evidence for dienolisation rested upon the process

$$> C{=}C{=}C < \xrightarrow[2H_2O]{2O_3} 2 > CO + CO_2 + 2H_2O_2,$$
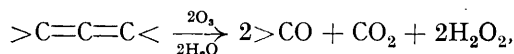
but the proportions of (III) and (IV) could not apparently have been other than very small. Realising that alkali fission of (II) should yield benzoic acid and acetone, whereas acetic acid and acetophenone are in fact formed, Scheiber and Herold suggested that the activated double bond of (II) might be less reactive than that of (III) or that sodium benzoylacetone might be derived from (III). The evidence of Claisen (*Ber.*, 1926, **59**, 144) concerning the reactivity of benzoylacetone with sodium hydroxide, ammonia, hydroxylamine, and aniline indicates greater reactivity at the acetyl group and is regarded (Michael and Ross, *loc. cit.*) as favouring the constitution (III). The same authors found that sodium benzoylacetone reacts (to the extent of at least 85%) with methyl chloroformate as if it possesses the structure $Ph \cdot CO \cdot CH \colon C(ONa) \cdot Me$. Nevertheless, Michael and Ross agree that, since the benzoyl group is decidedly more negative than the acetyl group, the sodium derivative should exist largely as $Ph \cdot C(ONa) \colon CH \cdot COMe$, although in all energetic reactions the alternative sodium derivative reacts preferentially.

Sidgwick (*J.*, 1925, **127**, 907; see also Pfeiffer, *Annalen*, 1913, **398**, 137; Lowry and Burgess, *J.*, 1923, **123**, 2111, for earlier suggestions on co-ordinated hydrogen) has argued

3 N

that a chelate ring, in which hydroxyl takes part, occurs in the enolic forms of β-diketones and β-keto-esters. Open-chain enols, being hydroxylic, would be expected to show higher boiling points than the corresponding ketones and to be more soluble in hydroxylic solvents and less soluble in hydrocarbons; chelated enols, on the other hand, would not be associated, and would exhibit lower boiling points, smaller solubilities in water, and greater solubilities in non-polar solvents than the ketones. The data for many keto-enols led Sidgwick to conclude that the enolic modifications were mainly, if not wholly, chelated. Sidgwick and Brewer (J., 1925, **127**, 2379) considered that the metallic derivatives of β-diketones might be either salts or covalent chelated compounds; *e.g.*, lithium benzoylacetone, on account of its insolubility in toluene and other properties, is regarded as a salt, whilst the potassium analogue behaves as a chelated compound. Anhydrous sodium benzoylacetone seems to be a salt, but on recrystallisation from 96% alcohol it is converted into a dihydrate, which, being soluble in toluene, appears to be chelated.

Sugden (J., 1929, 316), from the parachor of benzoylacetone, obtained evidence of an open-chain structure, the experimental data showing " that free β-diketones have but little tendency to form the chelate ring." The observed parachor was 382·4, as against 381·1 calculated for the open-chain compound and 364 for a chelated enol formulated on the basis of co-ordinated singlets. The conceptions of chelation held by Sidgwick and Sugden must be noted. The latter (" Parachor and Valency," 1930, p. 149) rejects the formulation (V), since the association of more than two electrons with the hydrogen atom in the K level violates Pauli's principle, and adopts the singlet formula (VI). It will be observed that
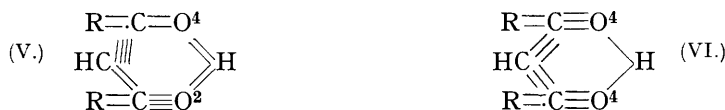
this formulation abolishes the distinction between the chelated forms CPh(OH):CH·COMe and COPh·CH:C(OH)Me, whereas in Sidgwick's formulation [cf. (V)] the distinction persists. Sugden submits very strong evidence that in the metallic derivatives of β-diketones, the residual valency is best written as a singlet rather than a duplet linkage, giving a symmetrical formula which makes every atom in the molecule neutral.

The recent work of von Auwers (*Ber.*, 1933, **66**, 955) on the dispersion of benzoylacetone and its ethers is indecisive as regards the constitution of the enolic form, but doubt is cast upon the evidence in favour of the existence of the dienol (IV).
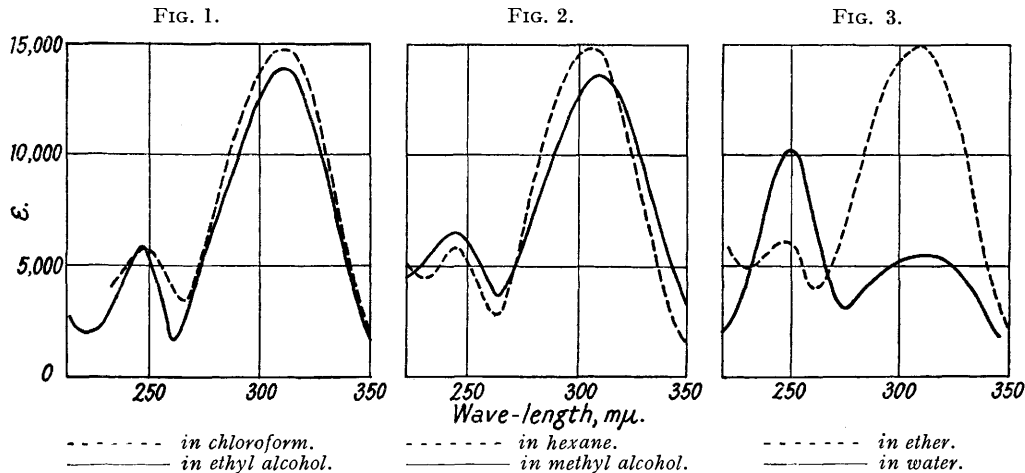
The situation is but little clearer in the case of the simpler compound acetylacetone. Apart from the fact that Sidgwick's criteria again indicate chelation of the enol, and the parachor supports an open-chain formula rather than an enol involving co-ordinated singlets, there is an additional complication in that Henri and Bielecki (*Compt. rend.*, 1914, **158**, 1022) adopted the formula CH₃·CO·CH₂·C(OH):CH₂ on the basis of spectrographic evidence, although von Auwers (*Ber.*, 1917, **50**, 937) considered the more usual formulation CH₃·CO·CH:C(OH)·CH₃ to be in much better accord with the refractometric as well as the chemical evidence, a conclusion in harmony with the ozonisation experiments of Scheiber and Herold, who found, however, evidence of some dienolisation.

Even with the β-keto-esters the position is unsatisfactory. The difficulty in choosing between chelated and open-chain enols persists, and in addition Henri and Bielecki (*Compt. rend.*, 1914, **158**, 866) and Grossmann (*Z. physikal. Chem.*, 1924, **109**, 305) postulate enolisation at the carbethoxy-group, although the equilibria studied by Meyer and the ozonide decompositions studied by Scheiber and Herold indicate strongly that for ethyl acetoacetate the formula CH₃·C(OH):CH·CO₂Et is to be preferred. The decomposition of ethyl benzoylacetate ozonide is likewise, it would seem, inconsistent with enolisation at the carbethoxy-group.

Equally equivocal are the published spectrographic data upon benzoylacetone. Early workers up to Shibata (*Acta Phytochim.*, 1927, **3**, 296) recorded one maximum near 310 mμ for M/10,000-solutions. Lowry, Moureu, and McConkey (J., 1928, 3167) observed two maxima :

Solvent.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$	Solvent.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
Ethyl alcohol	310	14,100	*cyclo*Hexane	305	18,200
	250	4,600		245	6,300

and on the basis of earlier work on benzoylcamphor isomerides (prototropic forms) it was stated " that in this case also the bands are due to isomeric forms of the diketone." Now, from the work of Meyer, the amount of diketone in alcoholic solutions is about 5% and in hydrocarbon solvents about 1%. It is easy to see that if the 245 mμ maximum, by analogy with benzoylcamphor, is due to the ketonic form, the molecular extinction coefficient of pure (I) must reach the impossibly high value of about 600,000.

The plan of the present work may now be outlined. The percentage of enolic benzoyl-acetone at equilibrium in various solvents is known from the work of Meyer; the relative intensities of the absorption bands in different solvents can be ascertained, and it should be possible to correlate extinction coefficients with data based on bromine absorption. This will not necessarily throw any light on the constitution of the enolic material : it will only fix its selective absorption. The constitutional aspect of the problem may be attacked by determining the relation between structure and spectral absorption for related compounds of fixed constitution, prepared as far as possible by unequivocal methods.

The two types of O-ether $CPh(OR){:}CH{\cdot}COMe$ (B-ether) and $COPh{\cdot}CH{:}C(OR)Me$ (A-ether) may help to differentiate between the enols (II) and (III), whilst methylbenzoyl-acetone, which exists in distinct and fairly stable ketonic and enolic forms, may throw light on the absorption spectra of both these forms of the parent substance. C-Dimethyl-benzoylacetone cannot enolise, and its spectral absorption should settle the general characteristics of the absorption of the diketone (I). Styryl methyl ketone, phenyl styryl ketone, and phenyl β-hydroxystyryl ketone should also offer relevant evidence. The absorption spectra of chelated metallic derivatives were also determined so that comparison could be made with the enolic forms.

Weygand (*Ber.*, 1925, **58**, 1473) obtained the methyl B-ether by the action of sodium methoxide on styryl methyl ketone dibromide and also by the steps

$$CPh{:}CH \longrightarrow CPh{:}CNa \xrightarrow{\text{AcCl}} CPh{:}C{\cdot}COMe \xrightarrow{\text{MeOH}} CPh(OMe){:}CH{\cdot}COMe.$$

The same ether can be isolated from the products of interaction of diazomethane and benzoylacetone, but a mixture of the A- and the B-ether is obtained by the action of methyl sulphate on sodium benzoylacetone (Claisen). The ethers obtained by the action of ortho-formic esters on benzoylacetone in the presence of ferric chloride as catalyst appear to be derived as follows :

$$CPh(OH){:}CH{\cdot}COMe + HC(OR)_3 \longrightarrow CPh(OH){:}CH{\cdot}CMe(OR)_2 + H{\cdot}CO_2R$$
$$\downarrow$$
$$COPh{\cdot}CH{:}CMe{\cdot}OR + ROH$$

Indeed, Claisen (*Ber.*, 1907, **40**, 3909) obtained such an ether and thence an *iso*oxazole of m. p. 42°, whilst the isomeric ether gave an *iso*oxazole of m. p. 68°.

C-Methylbenzoylacetone, $COPh{\cdot}CHMe{\cdot}COMe$, may be prepared by the action of methyl iodide on sodium benzoylacetone, and the pure mono-enol is obtained by pouring a cooled solution of the diketone in excess of sodium ethoxide into dilute sulphuric acid (Dieckmann, *Ber.*, 1912, **45**, 2686 ; 1922, **55**, 2479).

Absorption-spectra Data.—Very similar absorption curves are shown by acetophenone and benzaldehyde in alcohol :

Benzaldehyde.				Acetophenone.		
$\lambda_{max.}$, mμ	244	280·5	328	$\lambda_{max.}$, mμ......	241·5	278·5	320
$\epsilon_{max.}$	16,250	1,640	20	$\epsilon_{max.}$............	16,250	1,150	54

The curves are so different from those of aliphatic aldehydes and ketones and also from that of benzene that it is not unreasonable to ascribe the entire curve with its three distinct regions of absorption to the benzoyl group. This assumption will be justified later in this paper. Absorption-spectra determinations upon benzoylacetone dissolved in a variety of solvents (Figs. 1, 2, 3) show that two absorption bands occur, the maxima being near 247 and 310 mμ, and the respective intensities differing from solvent to solvent. As is usual for keto-enol equilibria, the percentage of diketone is much higher in water than in other solvents, and this is reflected in an abnormally low extinction coefficient at 310 mμ

and a correspondingly high extinction coefficient at 247 mμ. The two maxima may thus be associated *provisionally* with enolic and ketonic forms respectively. The intensity of the 310 mμ maximum in the different solvents varies linearly with the total enol content, but although the percentage of ketonic form exceeds 60 in water and is less than 1 in pentane, yet the 246 mμ maximum is only about twice as intense in water as in pentane. Enolic material must therefore contribute substantially to the absorption at that point. In C-methylbenzoylacetone, the ketonic form is very stable, and in the dimethylbenzoylacetone

FIG. 1.   FIG. 2.   FIG. 3.

Wave-length, mμ.

- - - - - - *in chloroform.*   - - - - - - *in hexane.*   - - - - - - *in ether.*
——— *in ethyl alcohol.*   ——— *in methyl alcohol.*   ——— *in water.*

there is naturally no enolisation. The absorption spectra for these two substances are shown in Figs. 4 and 7 and the maxima are given in Table I. The curves for the unenolised dike-

TABLE I.

Solvent.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$.
	Benzoylacetone.			
EtOH	245·5	6,000	310·5	13,800
MeOH	244·5	6,400	310·5	13,450
Et_2O	245	6,000	309	14,700
C_5H_{12}	245	5,800	306	14,600
C_6H_{14}	246	5,700	306	14,800
$CHCl_3$	249	5,750	311	14,650
CCl_4	(Solvent interferes)		311	14,200
H_2O	249·5	10,300	310	5,500
	C-Methylbenzoylacetone (ketonic form).			
EtOH	247	11,600	310	200
	284	1,500		
	C-Methylbenzoylacetone (enolic form).			
EtOH	228	4,500	309	12,200
	(inflexion)			
	C-Dimethylbenzoylacetone.			
EtOH *	236·5	14,500	310 *ca.*	100
	280·5	1,050		
	274	1,050		
	* MeOH and C_6H_{14} give similar curves.			
	Ethyl benzoylacetate.			
EtOH	242·5	9,600	285	4,700
MeOH	244·5	9,800	284	2,900
Et_2O	242	7,100	286	8,200
H_2O	249	10,500	285	1,275
NaOH (in excess)	(No definite band)		301	11,600
Alc. NaOEt (in consider-able excess)	230	10,300	306	12,000

FIG. 4.

Methylbenzoylacetone.

Wave-length, mμ.

——— *Ketonic form in alcohol.*
- - - - - - *Enolic form in hexane.*
-o-o-o-   ,,   ,,   *in 5 equivs. of* NaOEt.
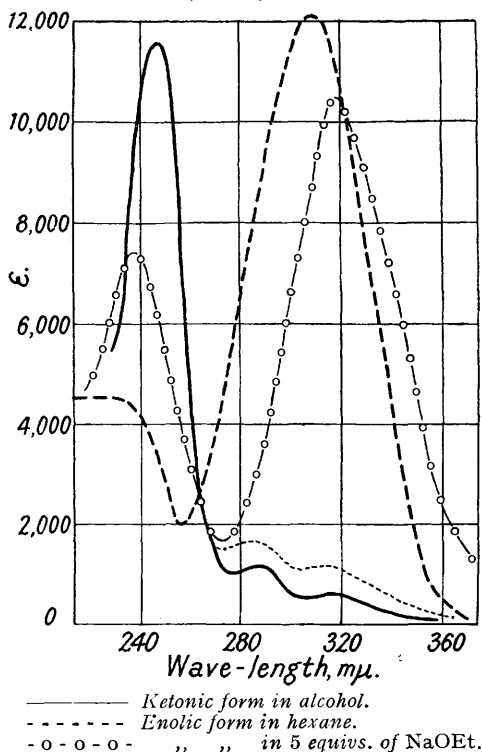
tones are very similar to those of acetophenone and benzaldehyde, and the ε values for the three bands, proceeding from longer to shorter wave-lengths, are of the order 50, 1,000, and 12,000 respectively. From this it must be concluded that all three bands belong to the benzoyl group, and that the ketonic form of benzoylacetone (I) must have a closely similar absorption curve. A serious difficulty at once arises over the absorption spectra of benzoyl-acetone in hydrocarbon solvents. As will be seen from Table II and Figs. 2 and 3, the enol content exceeds 99% and yet the 247 mμ band occurs at about half the intensity characteristic of the diketones in the pure state. In pentane and hexane, this band must therefore be due to an enolic form. The 310 mμ maximum is also definitely due to an enolic modification since its intensity provides a trustworthy measure of the total enol content in different solvents. There are three possible explanations : (i) The equilibria

Fig. 5.
Benzoylacetone methyl ether,
$C_6H_5 \cdot C(OMe){:}CH \cdot CO \cdot CH_3$ (*in hexane*).

Fig. 6.
Benzoylacetone ethyl ether,
$C_6H_5 \cdot CO \cdot CH{:}C(OEt) \cdot CH_3$ (*in hexane*).

Wave-length, mμ

Fig. 7.
Dimethylbenzoylacetone.

Wave-length, mμ.

——— *in alcohol.* - - - - - *with* 10 *equivs.* NaOEt.
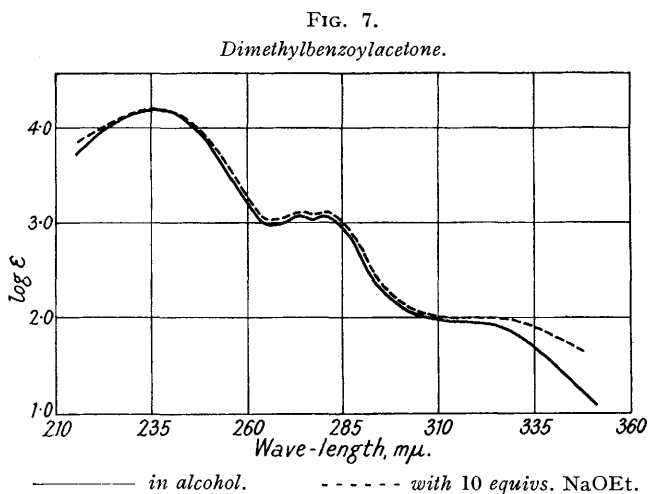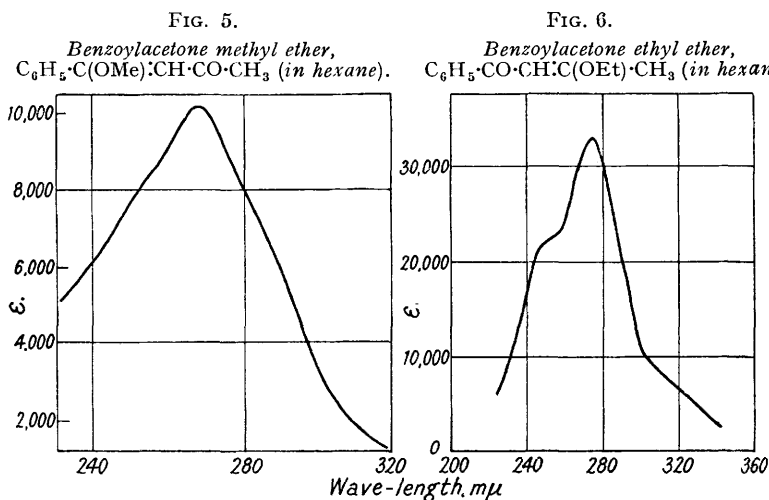
occurring at the somewhat high dilutions necessary for spectrographic studies are very different from those obtaining at the dilutions needed for the bromine-absorption titrations of Meyer. (ii) A single enolic form may occur and possess two clear maxima, the intensities of which would be given very nearly correctly in the pentane and hexane solutions which contain over 99% of enol. (iii) Two enolic forms may occur, and on this basis the 310 mμ maximum would have to be a property of both, whilst the 247 mμ band would only be shown by one enol [*e.g.*, (III) in which the benzoyl group is intact].

Against (i) is the fact that over a range of concentrations of about 20 : 1 Beer's law is

valid for all the solvents for which detailed observations were possible; this is not consistent with a radical change in the nature of the equilibrium. Further, the agreement between the percentages of enol in different solvents as determined by Meyer and those based on the intensity of absorption at 310 mμ provides good evidence that objections resting on (i) cannot be sustained.

The assumption that a single enolic form gives rise to both the 247 mμ and the 310 mμ maximum can be tested by accepting the extinction coefficients in hydrocarbons as representing the enol, and comparing the calculated ε values in different solvents with those observed by Meyer. Before applying this test as in Table II, it is necessary to justify the underlying principle. The main assumption in the table is that the absorption spectrum of a given isomeride is substantially independent of the solvent as regards both the spectral location and the extinction coefficients of the maxima. Perhaps the best evidence is that afforded by Scheibe's measurements (*Ber.*, 1926, **59**, 2620) on acetophenone, the nearest related product of fixed constitution :

Solvent.	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$.	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$.	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$.
Hexane	235	12,590	277	708	320	45
Ethyl alcohol	241	12,590	277	1,000	inflex.	50
Water	245	12,590	inflex.	1,400	inflex.	50

The above data, together with those on mesityl oxide and phorone, show no serious solvent effects on the well-defined 240 mμ band, although some of the ε values are a little lower than those observed by other workers. This comparative independence of the absorption on the solvent has, of course, many exceptions (cf. benzophenone and phorone in sulphuric acid; Scheibe, *loc. cit.*), but the evidence justifies the extension of the same principle to the ketonic form of benzoylacetone. As far as the enolic form is concerned, perhaps the strongest evidence is the extremely good agreement between Meyer's values and those based on absorption spectra for ethyl acetoacetate, acetylacetone, and benzoylacetone itself. Hence it is reasonable to make the above assumption.

TABLE II.

Benzoylacetone.

			Absorption at 247 mμ.			
		Enol, %, calc.	Calculated.			
Solvent.	Obs. (Meyer).	from ε values at 310 mμ.	Enol.	Keto.	Total.	Obs.
EtOH	94	92	5150	780	5,930	6,000
MeOH	90	89·7	5040	1300	6,340	6,400
Et$_2$O	98·1	98	5490	260	5,750	6,000
C$_5$H$_{12}$ and C$_6$H$_{14}$	99·2	98	5540	130	5,670	5,800
CHCl$_3$	92·8	97·5	5220	650	5,870	5,750
H$_2$O	32·5	36·7	2055	8230	10,285	10,300

100% Keto, $\varepsilon_{max.}$ at 247 mμ = 13,000.
100% Enol, $\varepsilon_{max.}$ at 247 mμ = 5,600; at 310 mμ = 15,000.

Ethyl benzoylacetate.

		Absorption at 242 mμ.				Absorption at 285 mμ.			
	Enol, %	Calculated.				Calculated.			
Solvent.	(Meyer).	Enol.	Keto.	Total.	Obs.	Keto.	Enol.	Total.	Obs.
EtOH	29·2	1752	7,505	9,257	9,600	850	3796	4646	4700
MeOH	16·1	966	8,894	9,860	9,800	1007	2093	3100	2900
Et$_2$O	52·5	3150	5,035	8,185	7,100	570	6825	7395	8200
H$_2$O	1·0	60	10,494	10,554	10,500	1188	130	1318	1275

100% Keto, $\varepsilon_{max.}$ at 242 mμ = 10,600; at 285 mμ = 1,200.
100% Enol, $\varepsilon_{max.}$ at 242 mμ = 6,000; $\varepsilon_{max.}$ at 285 mμ = 13,000.

As will be seen from the calculations in Table II, the assumption that the diketone (I) has a maximum at 247 mμ of approximately the same intensity as the corresponding band of acetophenone, benzaldehyde, and dimethylbenzoylacetone accounts for the whole of the extinction-coefficient data if, in addition, a single enolic isomeride with two bands is postulated. These bands must occur at 246 mμ and 310 mμ with intensities ε 5,600 and

15,000 respectively. It is significant that the 247 mμ band which has already been associated with the intact benzoyl group appears in the absorption of the enol, but the fall in extinction coefficient from over 10,000 in acetophenone to about half precludes a facile conclusion that the enol has the constitution (III). This raises the possibility mentioned earlier under (iii). In order to secure formal agreement between Meyer's titrations and the extinction coefficients in various solvents, we may make the alternative set of assumptions : (*a*) enol (II) has negligible absorption at 247 mμ, whilst (III) has a maximum at $\varepsilon = 11,000$; (*b*) both enols have a maximum at 310 mμ, $\varepsilon_{max.} = 15,000$; (*c*) enols (II) and (III) occur in equal proportion.

There is nothing intrinsically improbable in (*a*) and (*b*); (*c*) is far more difficult to entertain, but merits careful investigation. If it be supposed that the solid benzoylacetone is homogeneous and that the hexane solution contains equal parts of (II) and (III), the absorption spectra of absolutely fresh solutions might be expected to differ from those of solutions which had been allowed to reach equilibrium. A very careful series of tests showed, however, that the 246 mμ maximum was well defined for solutions in hexane photographed within 10 minutes of dissolution, and that the $\varepsilon_{max.}$ values were independent of time and concentration, $M/600$—$M/24,000$, at $5,700 \mp 300$. The minimum at 260 mμ, $\varepsilon_{min.}$ 3,600, and the maximum at 306 mμ were likewise constant within experimental error. Equilibrium must therefore be reached very rapidly. So far, therefore, it has not been possible to find any decisive evidence in favour of heterogeneity in the enolic material occurring when benzoylacetone is dissolved in hydrocarbon solvents. Now, the enolic form of benzoylcamphor shows a maximum near 312 mμ, which clearly corresponds with the 310 mμ band of benzoylacetone, but there is no sign of a 247 mμ maximum. Lowry, Moureu, and McConkey (*loc. cit.*) found that the enolic form of benzylmethylglyoxal, CHPh:C(OH)·COMe, exhibits one maximum at 310 mμ, $\varepsilon_{max.}$ 20,000, but instead of a maximum at 247 mμ a very deep minimum is shown. This compound is chromophorically so closely akin to CPh(OH):CH·COMe that the two might be expected to have the same absorption spectrum. It seems impossible to avoid one or other of the following conclusions : *either* the enolic form of benzoylacetone is homogeneous and is not (II) but (III), *or* benzoylacetone enolises in solution in hydrocarbon solvents to give equal parts of (II) and (III). A decision between these two alternatives must be deferred until the discussion has been carried further.

Benzoylacetone O-Methyl Ether (B-*ether*), CPh(OMe):CH·COMe.—Weygand's methods of preparation (*Ber.*, 1925, **58**, 1478) were followed with some modifications. The dibromide, m. p. 125—126°, from styryl methyl ketone was treated in boiling methyl alcohol with potash, and potassium bromide was deposited in quantity. Carbon dioxide was passed into the cooled solution for 12 hours to neutralise the excess alkali; the solution was then filtered, the alcohol distilled off, and the residue fractionated under reduced pressure. The main fraction, b. p. 150°/17 mm., agreed with Weygand's yellow oil in properties. Retreatment with methyl-alcoholic potash resulted in a product (A) which after fractionation still contained bromine. Accordingly, a larger quantity of crude oil was refluxed with methyl-alcoholic potash for 4 hours, and a smell resembling that of acetylphenylacetylene then became noticeable. This material was worked up as before, and after being shaken many times with sodium hydroxide to remove benzoylacetone, yielded three fractions, the main one, b. p. 135°/3 mm., being a pale yellow oil (B). Retreatment with potash gave a similar product (C) which appeared from the spectrographic examination to be somewhat richer in the *B*-ether than (B). The lower-boiling fraction was much more transparent and appeared to be CPhH(OMe)·CHBrAc, since it yielded the ether on distillation after standing over solid potash for 24 hours. Spectrographic examination of the various fractions in alcohol disclosed in all cases a single broad unresolved absorption band extending from 230 to 315 mμ with a maximum at 274·7 mμ. The maximum molecular extinction coefficient was, however, variable : preparation (A) 3,600; (B) 4,300 and 4,200; (C) 5,800; (D), a very dilute solution of (B) warmed with a little potassium hydroxide, 5,700. It is concluded that the product consists very largely of the *O*-methyl ether, but that a small quantity of more diactinic material may have been present even in (C).

Another method used by Weygand was studied. Acetylphenylacetylene unites with methyl alcohol to give the ether, but this reaction proceeded much more slowly than would

be inferred from his work. Careful repetition of the preparation according to his details gave a product which was found spectrographically to contain much unchanged acetyl-phenylacetylene. The best results were obtained by refluxing a methyl-alcoholic solution containing 3 times as much sodium as recommended by Weygand for one hour. After fractionation under reduced pressure a product, b. p. 148—153°/15 mm., 120°/2 mm., was obtained which no longer showed the absorption bands of acetylphenylacetylene. This material gave a single broad unresolved absorption band extending from 230 to 315 mμ with a maximum at 274·5 mμ in ethyl alcohol, and at 268 mμ in hexane, the extinction coefficient at the maximum being 10,000—10,300 in each case (see Fig. 5).

Hence, as regards spectral absorption, the two preparations of the *B*-ether are qualitatively identical, the location of absorption being very nearly independent of the solvent. Both methods of synthesis are unequivocal in the sense that the acetyl group must be intact. There is no evidence of enolisation in the presence of excess alkali since the absorption remains unchanged. Stereoisomerism about the double bond is, however, a possibility which may account for the difference in $\varepsilon_{max.}$ for the two preparations, since it is well known that *cis-trans*-isomerides exhibit qualitatively similar absorption differing in intensity over a range of about 2 : 1.

No absorption band in the region 268—275 mμ is shown by benzoylacetone itself, and it would seem that the fixed *B*-ether does not immediately throw any light on the problem of the constitution of the enolic form of the parent substance. It is, however, curious that the 274·5 mμ maximum corresponds almost exactly with the enolic band of acetylacetone.

Benzoylacetone O-Ethyl Ether (A-*ether*), COPh·CH:C(OEt)·CH$_3$.—This was prepared according to Weygand's directions (*loc. cit.*), following Claisen, from benzoylacetone by the action of ethyl orthoformate, as a colourless oil, b. p. 147—148°/13 mm. The absorption spectrum in ethyl alcohol showed a maximum at 284 mμ, $\varepsilon_{max.}$ 33,000 (275 mμ in hexane), and a pronounced inflexion near 250 mμ (see Fig. 6).   There can be no doubt that the two *O*-ethers are sharply differentiated by their absorption spectra. The inflexion at 250 mμ recalls the 247 mμ band present in benzoylacetone, but there is no band at 284 mμ in the parent substance. The intensity of absorption is rather more than twice that shown by benzoylacetone. The 284 mμ maximum appears to be the 280 mμ band of acetophenone vastly enhanced in intensity.

Neither the *A*-ether nor the *B*-ether resembles benzoylacetone in its absorption spectrum sufficiently closely to make a ready choice justifiable, but the implications of the two alternatives may be considered. Obviously, chelation of the enols may result in a difference in absorption, but as this question itself is still *sub judice*, the argument cannot be used at this stage.   In the *B*-ether there is only one band, and that occurs at a position intermediate between the two bands for benzoylacetone. On the other hand, the *A*-ether has two bands, the longer-wave band being about twice as intense as the shorter-wave band, as in the parent substance. The band near 250 mμ appears to be due to the intact benzoyl group in both cases. If it be accepted that the *A*-ether shows a closer similarity to benzoyl-acetone than does the *B*-ether, it must be concluded that if the enol has the structure (III), replacement of H by CH$_3$ results in an appreciable shift of one band from 284 to 310 mμ, accompanied by a 50% decrease in intensity of absorption. The study of the *O*-ethers therefore supports the presence of (III) but does not finally exclude that of the enol (II).

C-Methylbenzoylacetone, COPh·CHMe·COMe *and* CPh(OH):CMe·COMe (?).—This was studied as diketone, b. p. 126—128°/3 mm., and as pure enol, m. p. 50° after recrystallisation from hexane. The equilibrium mixture is very rich in diketone, and the solid enol, although stable for several weeks, finally became liquid at room temperature. The diketone showed absorption similar to that of acetophenone, whilst the enol, which was examined in hexane (because of the high enolising tendency of the solvent), exhibited a single broad absorption band with a maximum at 309 mμ, $\varepsilon_{max.}$ 12,100 (see Fig. 4).   The curve showed a minimum at 257 mμ, $\varepsilon_{min.}$ 2,000, and an inflexion from 220 to 230 mμ, ε *ca.* 4,500. The 247 mμ band of benzoylacetone was indubitably absent. Here, again, we have definite evidence that *either* the enolic material in benzoylacetone is not homogeneous *or* the enol in the methyl derivative and that in the parent substance are structurally different.

C-Dimethylbenzoylacetone, COPh·CMe$_2$·COMe.—Crystalline enolic methylbenzoylacetone (5·03 g.) was dissolved in absolute methyl alcohol in which sodium (0·375 g.) had previously been dissolved. Methyl iodide (12·87 g.) was then added and the mixture refluxed for 4 hours until the alkaline reaction had disappeared. The alcohol was distilled off, and the residue extracted with ether and washed several times with water. The dried ethereal extract on fractional distillation yielded a main fraction, b. p. 84°/2 mm., in good yield as a colourless oil (Found : C, 75·6; H, 7·3. Calc. : C, 75·8; H, 7·4%).

The data on this substance show three maxima, one of the bands being resolved into two subsidiary bands (see Table I and Fig. 7). The absorption of the benzoyl group is vastly stronger than that of the acetyl group, and it is interesting that the three bands occur at wave-lengths, *ca.* 235, 280, and 310 mμ, which also appear in the maxima due to enols. The intensities are, however, much greater for the two longer-wave bands in the enols. The comparison with benzoin (see Table IV) and the complete absence of any change in the presence of alkali are interesting, but not unexpected.

Phenyl β-Hydroxystyryl Ketone (Dibenzoylmethane), CPh(OH)ːCH·COPh.—In order to simplify the discussion, the experiments have been extended to include this compound, where the possibilities of enolisation are less numerous than in benzoylacetone. The substance was prepared from dibromobenzylideneacetophenone by the method of Allen (" Organic Syntheses," **8**, 60). Slow recrystallisation from ethyl alcohol gave large prisms, m. p. 78°, whilst rapid recrystallisation from more concentrated solutions gave needles, m. p. 71° (Dufraisse and Gillet, *Ann. Chim.*, 1926, **6**, 295, describe an α-form, m. p. 70—71°, and a β-form, m. p. 77—78°). Hartley and Dobbie (*Brit. Assoc. Rep.*, 1901, 201) studied the absorption spectra of " β-hydroxybenzalacetophenone " and " dibenzoylmethane," the latter, from its method of preparation, being probably phenyl β-ethoxystyryl ketone. The hydroxy-compound showed two maxima at 337 and 248 mμ approx., both bands being of considerable intensity. The ethoxy-compound (m. p. 77—78°) showed two maxima, at 304 and 248 mμ. Shibata (*Acta Phytochim.*, 1927, **3**, 303) records a maximum at 345 mμ in " dibenzoylmethane " with an inflexion near 250 mμ, the intensities appearing to correspond with ε values of about 25,000 and 15,000 respectively. Our own data are shown in Table III and Fig. 8.

TABLE III.

Solvent.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$	$\lambda_{min.}$, mμ.	$\epsilon_{min.}$
Phenyl Styryl Ketone.				
EtOH	310	26,100	246	6,000
Phenyl β-Hydroxystyryl Ketone (" Dibenzoylmethane ").				
Needles in EtOH {	344·3	23,000	276	4,330
	251·5	8,330	234	7,000
Prisms in EtOH {	345	22,500	278	4,300
	251	8,600	233	6,900
„ in C$_6$H$_{14}$	339	24,300	274	3,700
	250	9,500	233	7,600
„ in EtOH with 10 equivs. NaOEt {	351	23,000	285	1,700
	238·5	13,700		
„ in H$_2$O (containing 2% EtOH) {	357·5	11,750	307	5,500
	254	12,500		
Phenyl β-Methoxystyryl Ketone.				
EtOH	298	10,750	271	8,800
inflexion	250	10,500		
Phenyl β-Ethoxystyryl Ketone (m. p. 62°).				
EtOH	297	11,150	270	9,200
inflexion	250	10,600		

Phenyl β-Methoxy- and β-Ethoxy-styryl Ketones, CPh(OR)ːCH·COPh.—Unequivocal syntheses have been effected by Dufraisse and Gillet (*loc. cit.*) from benzoylphenylacetylene. The same products are obtained from phenyl αβ-dibromo-β-phenylethyl ketone by the methods of Ruhemann and Watson (J., 1904, **85**, 546) but better yields are obtained by the action of sodium alkoxide (Reynolds, *Amer. Chem. J.*, 1910, **44**, 305) ; the alkoxide (2
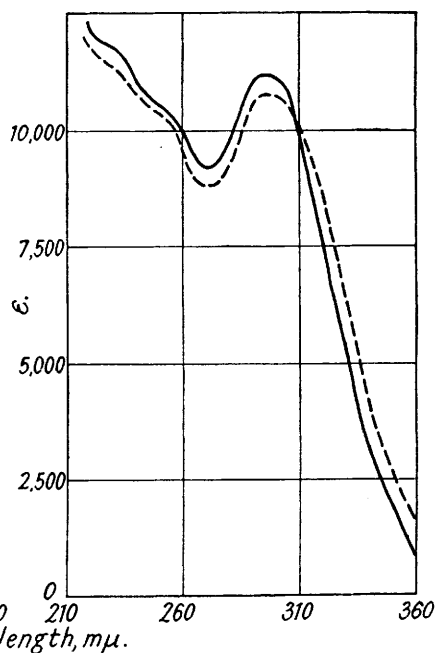
mols.) in alcohol is kept vigorously boiling under reflux while the dibromide (1 mol.) is added in small amounts; refluxing is continued for $\frac{1}{2}$ hour, and the cooled solution is filtered, the sodium bromide washed with a little alcohol, and the liquid, after being freed from solvent, is distilled under reduced pressure (b. p.'s : methyl ether, 195°/3 mm.; ethyl ether, 208°/3 mm.). The methyl ether could not be induced to crystallise in spite of repeated fractional distillation, but the ethyl ether crystallised in prisms, m. p. 62°. The latter exhibits polymorphism; Weygand and Hennig (*Ber.*, 1926, **59**, *B*, 2249) describe three forms, γ, m. p. 63°; β, m. p. 78°, and α, m. p. 81°. Dufraisse and Gérald (*Compt. rend.*, 1921, **173**, 985) record m. p. 60—61° and Sluiter (*Rec. trav. chim.*, 1905, **24**, 368) m. p. 61°. Weygand and Hennig also state that the lower-melting is spontaneously transformed into the higher-melting form, but we have not observed this effect. Dufraisse and Gillet (*loc. cit.*) obtained needles, m. p. 77—78°, and massive plates, m. p. 74—75°, but not the lower-melting form.

FIG. 8.

Dibenzoylmethane.

FIG. 9.

Wave-length, mμ.
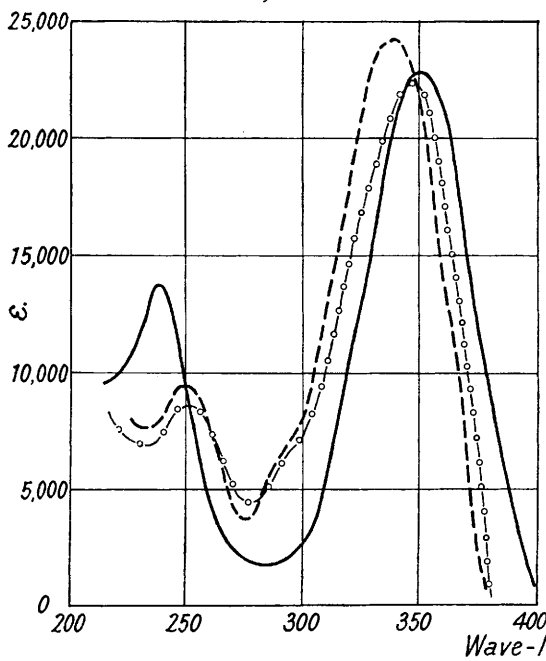
- o - o - o - *in ethyl alcohol.*   - - - - - - *in hexane.*   ——————— *Phenyl β-ethoxystyryl ketone.*
——————— *in alcoholic* NaOEt.   - - - - - - - *Phenyl β-methoxystyryl ketone.*

It is curious that phenyl styryl ketone shows only one absorption band, maximum at 310 mμ, with the very high $\varepsilon_{max.}$ of 26,100, and that a well-defined *minimum* occurs at 246 mμ, $\varepsilon_{min.}$ 6,000, in spite of the fact that the compound contains a benzoyl group. This introduces a new and important complication into the interpretation of the absorption spectra, *viz.*, that although a given maximum may be fairly consistently associated with a given chromophoric group, *e.g.*, the 247 mμ band with the benzoyl group, yet it is not possible to predict the occurrence of the band because the group is present in the absorbing molecule. The chromophoric entity may have been fused in a new chromophore of greater complexity or intensity.

The needle crystals and the prismatic crystals of " dibenzoylmethane " yield solutions which are spectrographically indistinguishable, whence the difference in crystalline form is probably merely a case of polymorphism. Although the band in the region of 250 mμ, which is usually associated with the benzoyl group, is absent in phenyl styryl ketone, it reappears in the β-hydroxy-ketone, and the 310 mμ maximum is displaced to 345 mμ

with but little change in intensity (Fig. 8). Again, in the two ethers (Fig. 9) the 250 mμ band persists as a well-marked inflexion, but the remaining band occurs at a wave-length just short of 300 mμ, and the intensity has suffered a notable diminution. This is the more remarkable since the ε values for the A-ether of benzoylacetone are very high, whilst that of the B-ether at its maximum is only about 10,000. The ether of dibenzoylmethane, therefore, resembles that ether of benzoylacetone in which the benzoyl group is no longer intact. This is a good example of the highly constitutive nature of absorption spectra, and of the way in which some chromophoric arrangements take priority over others. These data, however, do not provide the information needed for a clear-cut decision as to the structure of benzoylacetone; if the weight of evidence favours any one form, it would seem that the occurrence of the 247 mμ maximum indicates the persistence of the intact benzoyl group in the enol.

Ethyl Benzoylacetate.—The case of this compound is simpler in the sense that enolisation ·$CO_2Et \longrightarrow$:$C(OH)(OEt)$ is somewhat improbable. From the comparison of absorption intensities in various solvents (Fig. 10) with Meyer's bromine-absorption titrations it

FIG. 10.

Ethyl benzoylacetate.
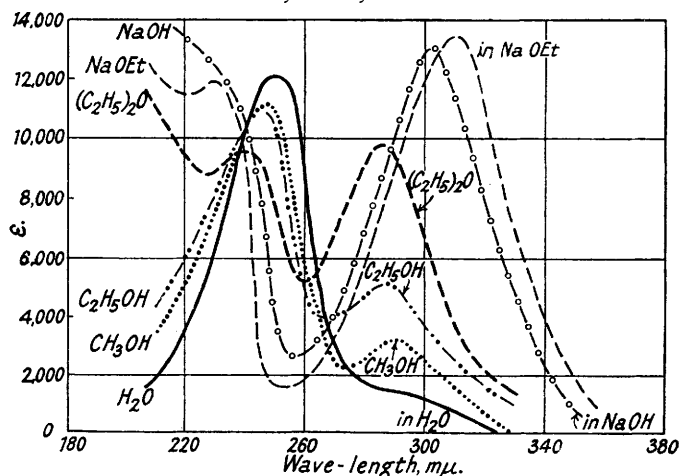
becomes clear (cf. Tables I and II) that the keto-ester shows a normal 242 mμ maximum, $\varepsilon_{max.}$ 10,600, and its close resemblance to acetophenone is indicated by the necessity for postulating a second band at 285 mμ, $\varepsilon_{max.}$ 1,200. The strong band at 285 mμ is due to $CPh(OH)$:$CH \cdot CO_2Et$ (or possibly its chelated analogue) and the absorption of the enol at 242 mμ, although non-selective, is considerable (ε, 6,000). In aqueous alkali a new band at 301 mμ appears, $\varepsilon_{max.}$ 12,950, but there is no maximum near 240 mμ, general absorption only being shown. In excess of sodium ethoxide the main maximum is at 306 mμ, $\varepsilon_{max.}$ 13,300, whilst an ill-defined band occurs near 230 mμ, $\varepsilon_{max.}$ 11,450.

In the enolic form of ethyl benzoylacetate, the carbethoxy-group appears to be chromophorically unimportant, since styrene and cinnamic acid both exhibit intense selective absorption near 280 mμ. The sodium salt may well be chelated as in (VII). From the

(VII.)

(VIII.)
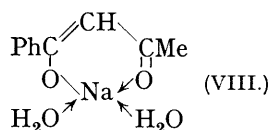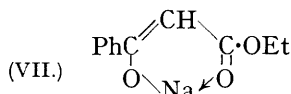
point of view of absorption spectra, a displacement in the direction of longer wave-lengths, *e.g.*, 285—306 mμ, usually accompanies an increase in the effective conjugated unsaturation. Such a displacement occurs when the hydrogen of an enol is replaced by sodium, so that

chelation may perhaps be regarded as an increase in the effective unsaturation. This conception will be amplified later when simple and complex chromophores are discussed.

Metallic Derivatives of Benzoylacetone.—Anhydrous sodium benzoylacetone is prepared by the action of dry sodium ethoxide on benzoylacetone dissolved in absolute ether and hexane. According to Sidgwick and Brewer (J., 1925, **127**, 2379), no sharp m. p. is shown, but Weygand (*J. pr. Chem.*, 1927, **116**, 293) records m. p. 225—228° in a cathode-ray vacuum. The material used in this work decomposed at 225°. Weygand also noticed a yellow form in addition to the ordinary white form. Sidgwick and Brewer recrystallised the compound from 96% alcohol and obtained a dihydrate, m. p. 110°. This material was formulated as (VIII) rather than as a simple dihydrate yielding $(Na,2H_2O)^{.}$. Weygand also obtained a trihydrate, m. p. 100°, and a tetrahydrate, m. p. 85°, and showed that solvation is fairly general in the metallic derivatives of benzoylacetone. No difficulty

FIG. 11.

Benzoylacetone in alcoholic sodium ethoxide.

------ 1 *equiv.* NaOEt.   .... 4 *equivs.* NaOEt.
- o - o - 5 *equivs.* ,,   ———— 10 ,,   ,,
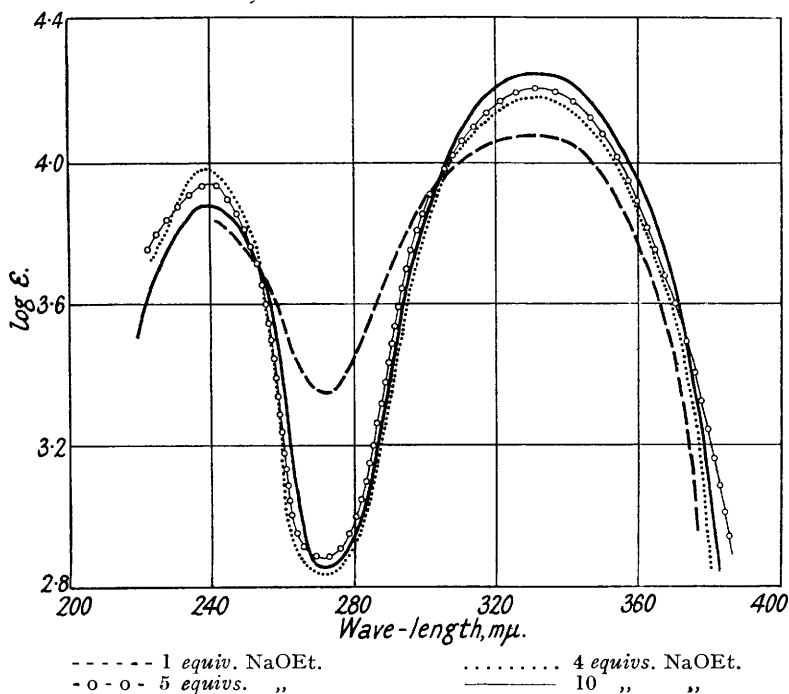
was experienced in preparing the dihydrate, m. p. 112°, but, like the anhydrous compound, it proved to be absolutely insoluble in hexane, the most suitable hydrocarbon solvent for spectrographic work. It was dissolved in absolute alcohol, but the absorption spectrum was indistinguishable from that of benzoylacetone itself, so that, at the high dilution needed, it was impossible to be sure that hydrolysis had not occurred. The dihydrate was soluble in chloroform (alcohol-free), and the absorption spectrum showed that the 247 mμ band was entirely absent, and that the 309 mμ maximum was displaced to 314 mμ ($\varepsilon_{max.}$ 14,000); $\lambda_{min.}$, 266·5 mμ ($\varepsilon_{min.}$ 2,600).

Experiments were also carried out upon solutions of benzoylacetone in absolute alcohol with 1 equiv. of sodium ethoxide. Either the normal benzoylacetone absorption spectrum was obtained (in which case the absence of moisture could not be guaranteed) or a single band at 320 mμ, $\varepsilon_{max.}$ 14,5C0, with no band in the region 230—250 mμ (see Fig. 11). In the presence of excess of alkali, the 309 mμ maximum is appreciably displaced in the direction of longer wave-lengths, and a new, very persistent band appears with a maximum near 238 mμ. It is noteworthy that with 1 equiv. of sodium ethoxide the minimum occurred

Concentrations.

Benzoylacetone.	Alkali.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
$M/10,000$	$M/2,000$ NaOH	325	17,000	239	8,500
$M/10,000$	$M/2,000$ NaOEt	325·5	17,500	236	8,900
$M/10,000$	$M/100$ NaOEt	326·5	18,250	241	8,000
$M/2,000$	$M/20$ KOH	323	20,000	236	11,000
$M/10,000$	$M/100$ NH$_4$OH	320·5	21,000	237	10,000
$M/10,000$	$M/100$ Na$_2$CO$_3$	321	17,000	240	9,000

at 266 mμ, $\epsilon_{min.}$ 2,280 ; with 5 or more equivs. the minimum at 268 mμ fell to the low value of $\epsilon_{min.}$ 790.

Various other metallic derivatives have been prepared by published methods. The potassium derivative is sufficiently soluble in ethyl alcohol for examination, although it is scarcely possible to be sure of the *complete* absence of water from the solvent used. (The alcohol had been refluxed for several hours after treatment with sodium, but with solutions at a dilution of $M/10,000$ a very small amount of water may be sufficient to alter the nature of the solute.) The near ultra-violet band occurred at 320 mμ, $\epsilon_{max.}$ 14,450, and no clear band was seen at 240 mμ. In all the other metallic derivatives listed below, two perfectly clear bands were seen in the absorption spectra of the solutions obtained by using crystalline metallic derivatives.

Metallic derivative of benzoylacetone.	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$	$\lambda_{max.}$, mμ.	$\epsilon_{max.}$
Lithium (in EtOH).	320	18,000	240	10,400
Strontium, dihydrate, in EtOH	322	15,000	235	9,750
,, ,, in H$_2$O	320	12,000	243	9,500
Aluminium and cerium	322	18,000	248	8,000

Benzoylacetone in Piperidine.—An $M/1,000$ solution (1 mm. layer) exhibits a well-defined absorption band at 333·5 mμ, $\epsilon_{max.}$ 14,000. The compensating cell of the solvent ceased to transmit at 275 mμ, so it was impossible to ascertain the presence or absence of the 247 mμ maximum. (Pure piperidine is transparent down to 220 mμ, but this is seldom attainable with the purchased liquid.) It is clear, however, that benzoylacetone is enolised in piperidine to the extent of at least 92%. The displacement from 310 to 333·5 mμ is the largest recorded with any derivative. In the somewhat analogous case of acetylacetone dissolved in pyridine, Meyer found evidence of some dienolisation. Dienolisation in acetylacetone is accompanied by an increase in $\epsilon_{max.}$, but no such increase is observed with benzoylacetone in piperidine, so little or no dienolisation can have occurred. This is supported by the fact that enolic benzoylcamphor in piperidine shows a displacement of the maximum from 315 to 328 mμ, with no appreciable change in $\epsilon_{max.}$. As this substance cannot dienolise, the close similarity with the data on benzoylacetone is in accordance with expectation.

Benzoylacetone in Sulphuric Acid.—Nef (*Annalen*, 1899, **308**, 279) has shown that when acetylphenylacetylene dissolves in concentrated sulphuric acid, benzoylacetone is formed, since it is precipitated on dilution. We found some decomposition, but benzoylacetone could easily be isolated. The mechanism of the reaction is not clear, but the scheme CPh:C·COMe + H$_2$O $\longrightarrow$ CPh(OH):CH·COMe appears to be unduly simple.

The absorption spectrum of benzoylacetone in concentrated sulphuric acid is markedly different from its spectrum in other solvents and from that of acetylphenylacetylene in neutral solvents (see Fig. 13). For instance, an extremely persistent band (ϵ 1,000—40,000) extends from 285 to 380 mμ with a maximum at 348 mμ, and two narrow bands with maxima appear at 269 and 277 mμ, with $\epsilon_{max.}$ 4,000 and 4,500 respectively. The complete absence of the acetylphenylacetylene bands indicates that an intermediate compound with the acid must be formed, but the very high extinction coefficient of 40,000 at 348 mμ shows also that a high degree of unsaturation must be attributed to the complex. The data of Scheibe (*Ber.*, 1925, **58**, 586) on the absorption spectra of benzophenone and phorone in concentrated sulphuric acid show displacements similar to those observed for benzoylacetone. Removal of the elements of water by the acid cannot account for the effects recorded, so the changes in absorption spectra must be ascribed to complex formation at the carbonyl group. Nef's observation proves that CPh(OH):CH·COMe must at the least form a connecting link

between acetylphenylacetylene and benzoylacetone, although it cannot be regarded as finally deciding the constitution of the solid.

The Possibility of Dienolisation in Benzoylacetone.—When the enolic form of methyl-benzoylacetone is studied in the presence of excess of sodium ethoxide, two maxima are seen, 319 and 239 mμ, $\varepsilon_{max.}$ 10,500 and 7,400 respectively. When these results are compared with the corresponding data on benzoylacetone, several points at once emerge : (*a*) Since dienolisation is impossible for the methyl derivative, the 239 mμ maximum cannot be ascribed to a dienol. (*b*) Since displacement of the band from 309 to 319 mμ accompanies the formation of a sodium derivative, and is associated with a *decrease* in $\varepsilon_{max.}$ for the methyl derivative and an increase in $\varepsilon_{max.}$ for the parent substance, such an increase *may* be associated with dienolisation. It is not *necessarily* so, since a similar increase occurs in the aluminium derivative of benzoylacetone. With considerable excess of alkali, the increase is, however, very definite, and is, moreover, accompanied by a larger displacement, *viz.*, from 310 to 326 mμ. These results may be compared with those of Grossmann on acetyl-acetone. The bromine-absorption method discloses as much as 130% enolisation, and the displacement from 270 to 292 mμ is reasonably large. It can easily be calculated that the extinction coefficient of the dienol must be of the order 50,000, several times larger than that of the mono-enol. On this basis, dienolisation of benzoylacetone appears to occur only in the presence of a considerable excess of alkali, and then only to the extent of a very few units % at most.
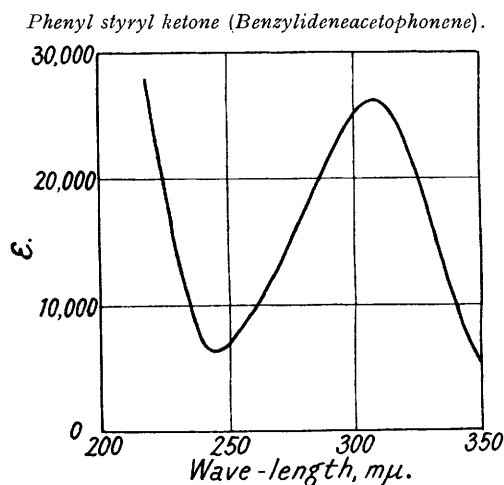
Fig. 12.

Phenyl styryl ketone (Benzylideneacetophenone).

Wave-length, mμ.

The Evidence for and against Chelation of the Enolic Forms.—(i) *Definitely unchelated compounds.* Styryl methyl ketone shows a single maximum at 285 mμ, $\varepsilon_{max.}$ 23,000, whilst phenyl styryl ketone (benzylidene-acetophenone) shows a similar band at 310 mμ, $\varepsilon_{max.}$ 26,000 (see Fig. 12). α-Hydroxy-styryl methyl ketone (benzylmethylglyoxal, enol) also shows a 310 mμ band at $\varepsilon_{max.}$ 20,000. On the other hand, β-methoxystyryl methyl ketone shows a maximum at 274 mμ with a lower $\varepsilon_{max.}$ of 10,300, and phenyl β-ethoxy- or -methoxystyryl ketone shows a band at 298 mμ, $\varepsilon_{max.}$ *ca.* 11,000, and a band at 250 mμ of nearly the same intensity, whilst α-benzoyl-β-ethoxy-β-methylethylene shows a maximum at 284 mμ, $\varepsilon_{max.}$ 33,000, with a pronounced inflexion at 250 mμ. In brief, the change

$$\text{CH:CH} \longrightarrow \text{C(OMe):CH}$$
$$285 \longrightarrow 274 \text{ m}\mu \ (\varepsilon_{max.} \text{ approximately halved})$$
$$310 \longrightarrow 298 \text{ m}\mu$$

involves Δmμ $-$ 12; and the change

$$\text{CH:CH} \longrightarrow \text{CH:C(OH)}$$
$$285 \longrightarrow 310 \text{ m}\mu$$
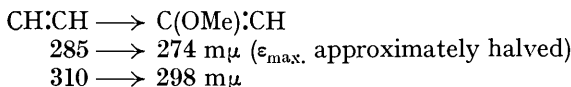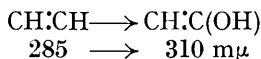
involves Δmμ $+$ 25.

(ii) *Definitely chelated compounds.* It is difficult to be sure of chelation, but the following data for maxima (mμ) are striking :

	Derivative.	Enol.	Displace-ments.
Metallic derivatives of benzoylacetone	324, 238	310, 247	+ 14, $-$ 9
Sodium dibenzoylmethane in excess NaOEt	351, 238	345, 250	+ 6, $-$ 12
Sodium methylbenzoylacetone in excess NaOEt	319, 238	310	+ 9
Sodium acetylacetone	292	275	+ 17
Ethyl sodioacetoacetate	272	243	+ 29
Ethyl sodiobenzoylacetate	306	285	+ 21
Sodium benzoylcamphor	328	312	+ 16

It is evident that the wave-length displacements when the enolic forms are compared with the chelated sodium derivatives are too large to be attributed merely to the weighting effect of the metal. This appears to indicate that, if there is chelation through hydrogen in enols, it must be different in kind from that obtaining with metallic derivatives.

(iii) *Doubtful cases.* The effect of replacing a hydrogen by a hydroxyl group may now be considered in more detail.

$$CH:CH \longrightarrow C(OH):CH.$$

Styryl methyl ketone	$285 \longrightarrow 310 \text{ m}\mu$	$\left\{\begin{array}{l}\text{Benzylmethylglyoxal enol}\\ \text{Benzoylacetone enol}\end{array}\right.$
Phenyl styryl ketone	$310 \longrightarrow 345 \text{ m}\mu$	Dibenzoylmethane enol
Mesityl oxide	$235 \longrightarrow 275 \text{ m}\mu$	Acetylacetone enol
Cinnamic ester	$260 \longrightarrow 285 \text{ m}\mu$	Ethyl benzoylacetate enol
Ethyl crotonate	*ca.* $220 \longrightarrow 243 \text{ m}\mu$	Ethyl acetoacetate enol
Benzylidenecamphor	$288 \longrightarrow 312 \text{ m}\mu$	Benzoylcamphor enol

The changes enumerated above all result in an appreciable, and roughly constant, displacement of the selective absorption. The effects are, however, not closely comparable with those appearing in the chelated metallic derivatives; yet the displacement is difficult to account for. The hydroxyl group is itself completely transparent in the region of the spectrum concerned. Its effect is of the same order and in the same sense as that caused by the introduction of an additional conjugated double bond, and this effect occurs even in such cases as $C_6H_6 \longrightarrow C_6H_5 \cdot OH$.

From the fact that the 310 mμ maximum is shown by enolic benzylmethylglyoxal as well as enolic benzoylacetone, the six-membered chelate ring, which is possible for the latter but impossible for the former, cannot be essential to the existence of the common absorbing mechanism. It may therefore be said that if chelation occurs in the enolic form of benzoylacetone it must be of a type which does not result in the displacement of bands. Similarly, the 247 mμ band of enolic benzoylacetone appears to be an undisplaced benzoyl band, which does not agree with the 238 mμ maximum of the chelated metallic derivatives.

There therefore seems no escape from one or other of the following conclusions : *either*, there is no co-ordination of hydrogen in benzoylacetone and related enols, *or*, chelation if it occurs in such enols must be qualitatively distinct and rest on a different electronic mechanism from the chelation obtaining with metallic derivatives. It is significant that the electronic energy level represented by the 310 mμ band of benzoylacetone should reappear exactly in phenyl styryl ketone. There is, in fact, very clear evidence of a discontinuous series of energy levels, as shown by the recurrence of bands at 247, 285, 310, and 345 mμ, the displacement in the direction of longer wave-lengths coinciding in most cases with an increase in unsaturation of the chromophore concerned.

This leads to the question of the sites of the different acts of absorption. Similar absorption bands to those under discussion have already been noticed in labile systems. For instance, a 243 mμ maximum characterises the enolic form of ethyl acetoacetate, and a band of high intensity at 249 mμ has been recorded for the stereoisomeric forms of ethyl diacetylsuccinate (Morton and Rogers, J., 1926, 717). The same authors, working on ethyl α-mesityloxidoxalate, $CMe_2:CH \cdot CO \cdot CH:C(OH) \cdot CO_2Et$, observed a band at 312 mμ, $\varepsilon_{max.}$ 14,000, whilst the β-isomeride, probably (IX), exhibits a clear maximum at 282 mμ, $\varepsilon_{max.}$ 12,000, with a well-defined inflexion

$$CO\underset{\underset{\text{(IX.)}}{}}{\overset{\overset{}{}}{<}}\begin{array}{c}CH_2\!-\!CMe_2\\ \!>\!O\\ CH\!=\!C\end{array}\!\!\!<\begin{array}{c}\\ \\ CO_2Et\end{array}$$

indicating a band near 250 mμ, $\varepsilon_{max.}$ 8,000. These bands, together with a third, are seen clearly when excess of sodium ethoxide is added, maxima occurring at 351, 286, and 249 mμ.

Table IV summarises the absorption maxima seen in a number of substances relevant to the present discussion. It will be seen that the bands 240—250, 280—290, and 308—320 mμ are observed in many compounds containing the C:C—C:O group but not the phenyl group. It is clear that, if a common mechanism is to be assumed, the site of the act of absorption must in each case be either a C:C group or a C:O group. From the above considerations, a simple hypothesis may be formulated. The different energy levels characteristic of the carbonyl group are the same, or very nearly the same, as those

TABLE IV.

|	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$	$\lambda_{max.}$, mμ.	$\varepsilon_{max.}$
$CH_3 \cdot CO \cdot CH_3$			275	17				
$CMe_2{:}CH \cdot CO \cdot CH_3$	235	14,000			313·5	58		
$CMe_2{:}CH \cdot CO \cdot CH{:}CMe_2$	263	20,000					357	100
$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$			ca. 275	ca. 100				
$CH_3 \cdot C(OH){:}CH \cdot CO \cdot CH_3$			ca. 275	10,000				
$CH_3 \cdot C{:}CH \cdot C \cdot CH_3$ (O O) M		(some dienolisation)			292	20,000—50,000		
$CH_3 \cdot CO \cdot CH_2 \cdot CO_2Et$			ca. 280	<100				
$CH_3 \cdot C(OH){:}CH \cdot CO_2Et$	243	10,000						
$CH_3 \cdot C{:}CH \cdot C \cdot OEt$ (O O) M			272	variable 30,000—50,000	some dienolisation			
$CH_3 \cdot C(OH){:}C \cdot CO_2Et$	249	ca. 7,000						
$CH_3 \cdot CO \cdot C \cdot CO_2Et$ / $CH_3 \cdot C{:}C \cdot CO_2Et$ (O M O) $C \cdot C \cdot CO_2Et$ CH_3			275	ca. 10,000				
$CMe_2{:}CH \cdot CO \cdot CH{:}C(OH) \cdot CO_2Et$					312	14,000		
$O{:}C{<}^{CH_2 \cdot CMe_2}_{CH{:}C \cdot CO_2Et}$ >O	inflex 250	8,000	282	12,000				
$O{:}C{<}^{CH_2{:}CMe_2}_{CH{:}C(ONa) \cdot CO_2Et}$	249·5	7,500	287	7,500			351	13,000
$C_6H_5 \cdot CO \cdot CH_3$	243	12,600	278	1,000	320	45		
$C_6H_5 \cdot CO \cdot C_6H_5$	250	ca. 20,000					ca. 343	150
$C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$	247	13,000	[280	1,000	320	50]		
$[C_6H_5 \cdot C(OH){:}CH \cdot CO \cdot CH_3]$					[310	15,000]		
$C_6H_5 \cdot CO \cdot CH{:}C(OH) \cdot CH_3$	247	5,600			310	15,000		
$C_6H_5 \cdot C{:}CH \cdot C \cdot CH_3$ (O O or) M / $C_6H_5 \cdot C \cdot CH{:}C \cdot CH_3$ (O O) M	238—243	8,900—10,000			322	18,000		
$C_6H_5 \cdot CH{:}C(OH) \cdot CO \cdot CH_3$					310	20,000		
$C_8H_{14}{<}^{CH \cdot CO \cdot C_6H_5}_{C{:}O}$	245	12,000—16,000			310	100		
$C_8H_{14}{<}^{C{:}C(OH) \cdot C_6H_5}_{CO}$					314	10,000—20,000		
$C_8H_{14}{<}^{C=C \cdot C_6H_5}_{C=O} {>}O \to M$					328	15,000		
$C_6H_5 \cdot CO \cdot CH_2 \cdot CO_2 \cdot Et$	242	10,600	[282	1,200	310	100]		
$C_6H_5 \cdot C(OH){:}CH \cdot CO_2Et$			285	13,000				
$C_6H_5 \cdot C{:}CH \cdot COEt$ (O O) M					306	12,000		
$C_6H_5 \cdot C(OH){:}CH \cdot CO \cdot C_6H_5$	250	8,500					345	23,000
$C_6H_5 \cdot CO \cdot CH \cdot CO_2Et$	249	order 20,000						
$C_6H_5 \cdot CO \cdot CH \cdot CO_2Et$ / $C_6H_5 \cdot C(OH){:}C \cdot CO_2Et$							355	high
$C_6H_5 \cdot C(OH){:}C \cdot CO_2Et$								
$C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$	243·5	13,500	295 / 286 / 282·3 }	1,083	316	406		
$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$	254	18,000					{ 395 / 370	43 / 41
$C_6H_5 \cdot (CH_2)_n \cdot CO \cdot CH_3$	260	<500	280	50				
$O=C{<}^{CH{:}CH}_{CH{:}CH}{>}C=O$	243	ca. 20,000	280	300	resolved bands reaching to visible			ca. 20
$C_6H_5 \cdot CH{:}CHMe$	246	ca. 10,000	278 / 289 }	ca. 500				
$C_6H_5 \cdot CH{:}CH \cdot CH{:}CH_2$			282	>10,000				
$C_6H_5 \cdot C_6H_5$	245	16,000						
$C_6H_5 \cdot CH{:}CH \cdot C_6H_5$	222	13,000	288	ca. 20,000	322	ca. 20,000		

(The table is presented in the above form in order to provide justification for the statement that bands near 246, 280, 312, 350 mμ *recur* both for enols and ketones and for compounds containing no oxygen, in which the levels are clearly due to activation of electrons in $C{=}C$ linkages.)

characterising the ethenoid linkage. When the site of the act of absorption is an electron under the joint control of both carbon and oxygen, the molecular extinction coefficient will be low, of the order 10—100, whereas if the electron which is raised to a higher energy level forms part of a C:C linkage, the molecular extinction coefficient will generally be high, of the order 10^3—10^5.

The absorption spectra of acetylphenylacetylene and of phenylacetylene have also been determined (Figs. 13 and 14). Detailed discussion of the data must be deferred except

FIG. 13.

Acetylphenylacetylene in hexane.

FIG. 14.

Phenylacetylene in hexane.

Wave-length, $m\mu$.

Phenylacetylene in hexane.

	$\lambda_{max.}$, $m\mu$.	log ϵ.	$1/\lambda$, cm.$^{-1}$.	Δcm.$^{-1}$.
Inflexion	294	1·56	34,010	
Very narrow and sharp	282	2·18	35,460	1450
Very sharp	278·3	2·48	35,930	470
Tiny inflexion	276·4	2·43	36,180	250
,, ,, ...	274·5	2·42	36,430	250
Very sharp ,, ...	271·6	2·53	36,820	390
Tiny inflexion	269·5	2·46	37,100	280
Very sharp	264·1	2·52	37,870	770
Very sharp	246	4·22	40,650	2780
Small band	241	4·12	41,490	840
Very sharp	235·7	4·24	42,420	930
Small band	230·8	4·16	43,340	920

Acetylphenylacetylene in hexane.

Inflexion	287·2	3·78	34,820	670
Sharp	281·8	4·02	35,490	1610
Sharp	269·5	4·10	37,100	1610
Sharp	258·3	4·03	38,710	1700
Ill-defined	247·5	3·88	40,410	1890
Ill-defined	236·4	3·79	42,300	

(In methyl-alcoholic solution the envelope of the absorption is similar, and the intensity of absorption approximately the same, but nearly all resolution into subsidiary bands has disappeared.)

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for one or two comments. The envelope of the curve for the former almost coincides with that of the methyl ether derived from it; this seems to imply that the same electronic transition is operating in the selective absorption of both compounds. It is too intense to be located in the carbonyl group, and it seems necessary to conclude that the *electronic* process occurring in the absorption of ultra-violet light is the same, in these two compounds, for the C:C and the C:C group.

The Raman spectra of a number of substances relevant to the present work have been measured, but at the present stage in the study of Raman spectra it is only necessary to record the data (see Table V).

TABLE V.

	cm.⁻¹.	Acetone.	Acetyl-acetone.	Ethyl aceto-acetate.	Benzoyl-acetone.	Ethyl benzoyl-acetate.
No. of lines		31	28	32	10*	12
$C{=}C_{ar.}$	3045	3000		2997	3018	3045
		2930	2920	2961		2961
CH_2	2930	2879		2889		
	2845	2845				
$C{=}O$		1718				
		1489	1598	1634	1601	1625
$C{=}C$ ca. 1600		1345	1364	1444		1602
		1228	1278	1345		
		1071	1238	1165	1275	
C⟨H H⟩		821	1175	1092	1002	1003
		790	1019	976		
ca. 1450		727	925			
		529	648	583	670	
			543			
			415			619
			393			

* Saturated solution in alcohol.

Conclusions.

(i) Benzoylacetone in dilute solution in hydrocarbon solvents exists almost entirely as $COPh{\cdot}CH{:}C(OH){\cdot}CH_3$, and in other solvents this is in equilibrium with appreciable quantities of diketone. The amount of the latter is small in all solvents except water.

(ii) The evidence shows that chelation through hydrogen of the mono-enol, if it occurs at all, must be different in kind from the chelation which obtains with metallic derivatives.

(iii) The absorption spectrum of the diketone is the same as that of diketonic methyl-benzoylacetone and resembles closely that of dimethylbenzoylacetone (and also aceto-phenone).

(iv) Sodium (and potassium) benzoylacetone, at the dilutions necessary for spectro-graphic examination, differ in structure from benzoylacetone enol and are probably to be formulated as $CPh(ONa){:}CH{\cdot}CO{\cdot}CH_3$.

(v) In the presence of excess of sodium ethoxide, the chelated compound is formed together with a small proportion of a dienolic derivative, probably $CPh(ONa){:}C{:}CMe(ONa)$.

(vi) The absorption spectra of metallic derivatives differ appreciably from that of the mono-enol, and on account of the approximately constant character of the absorption of the chelated derivatives, Sugden's singlet linkage is supported.

(vii) Enolic methylbenzoylacetone consists entirely of $CPh(OH){:}CMe{\cdot}COMe$ and is probably unchelated [see (ii)]. In the presence of sodium ethoxide the chelated sodium derivative is formed. Since the enol and benzoylacetone enol possess different structures, but yield spectrographically similar chelated sodium derivatives, there is strong evidence in favour of a singlet, rather than a duplet, linkage for the residual valency, since this abolishes the distinction between enolisation on the acetyl and the benzoyl group.

(viii) Dibenzoylmethane exists almost entirely as unchelated $CPh(OH){:}CH{\cdot}COPh$ [see (ii)], but in the presence of excess of sodium ethoxide the chelated sodium derivative is stable.

(ix) Ethyl benzoylacetate exists as an equilibrium mixture of $COPh{\cdot}CH_2{\cdot}CO_2Et$ and

CPh(OH)ːCH·CO$_2$Et, the enol being unchelated [see (ii)]. In the presence of excess of sodium ethoxide, the chelated derivative $\begin{smallmatrix} \text{ĊPh:CH·Ċ·OEt} \\ \text{O·Na} \leftarrow \text{O} \end{smallmatrix}$ is stable.

(x) In keto-enol tautomerides, the same wave-lengths of maximum absorption reappear frequently, but bands at 280, 310, and 345 mμ are much more intense (order 100 times) in the enols than in the ketonic forms.

(xi) The absorbing entities are chromophores which are complex, *i.e.*, made up of two or more simple chromophores such as C=C and C=O.

As a result of the operation of a complex chromophore it is often possible to distinguish two or three bands and to localise the acts of absorption in the simple constituent chromophores. For instance, of the bands associated with the benzoyl group : that near 310— 320 mμ, of low intensity, is due to the carbonyl group and may be written $\overset{*}{\text{C}}$=O, whilst that at 280 mμ is due to the carbonyl group influenced by the phenyl group and may be written C$_6$H$_5$·CO*, and that at 242 mμ is due to the phenyl group influenced by the carbonyl group $\overset{*}{\text{C}}_6$H$_5$·C=O.

(xii) The electronic energy levels associated with the carbonyl group and the ethenoid group are approximately the same. The exact specification of the energy levels is not possible from the data of organic compounds in solution, but the viewpoint adopted in the work may possibly clear the ground for more precise measurements.