## XCVII.—*Absorption Spectra and Tautomerism. Part I. Keto-enol Tautomerism. Ethyl Acetoacetate, Acetylacetone, and α-Benzoylcamphor.*

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ALTHOUGH the absorption spectra of ethyl acetoacetate and its derivatives have been studied repeatedly (Baly and Desch, J., 1904, **85**, 1029; Stewart and Baly, J., 1906, **89**, 489; Hantzsch, *Ber.*, 1911, **44**, 1771; Hantzsch and Voigt, *Ber.*, 1912, **45**, 85; Baly and Rice, J., 1913, **103**, 91; Morgan and Reilly, J., 1913, **103**, 1494; Bielecki and Henri, *Compt. rend.*, 1913, **156**, 1332; 1914, **158**, 866; *Ber.*, 1913, **46**, 3627; Hantzsch, *Ber.*, 1912, **43**, 3029), a reconsideration of the problem of the origin of their absorption bands is called for in view of the improved experimental methods which are now available (compare Grossmann, *Z. physikal. Chem.*, 1914, **109**, 305).

The vapour from ethyl acetoacetate, cooled to $-80°$ in order to reduce the vapour pressure, shows an absorption band, without fine structure, at $\lambda_{(max.)} = 2381$ Å., $e_{(max.)} = 1000$ (approx.). Thin layers of the liquid ester show a band at $\lambda_{(max.)} = 2430$, $e_{(max.)} = 367$, and the same band appears in solutions in ether, alcohol ($e = 2000$), and hexane ($e = 9100$). Since the ratio $e_{alcohol}$ to e_{hexane} agrees excellently with the relative content of enol in the solutions as measured by the addition of bromine, the band at 2430 Å. may be ascribed to the enol. This band is shifted to 2550 Å. in ethyl ethylacetoacetate, $CH_3 \cdot C(OH){:}CEt \cdot CO_2Et$, and to 2348 Å. in ethyl β-ethoxycrotonate, $CH_3 \cdot C(OEt){:}CH \cdot CO_2Et$.

Aqueous solutions of ethyl acetoacetate, which appear to be mainly ketonic since they do not absorb bromine appreciably, give a band at 2550 Å., which is nearer to the enolic band than to the undoubtedly ketonic band of acetone at 2747 Å. Its absorptive power, $e = 81$, is intermediate between those of acetone (17·2) and liquid ethyl acetoacetate (367). Since a displacement of 100 Å. is often produced by a change of solvent, there is as much

FIG. 1.
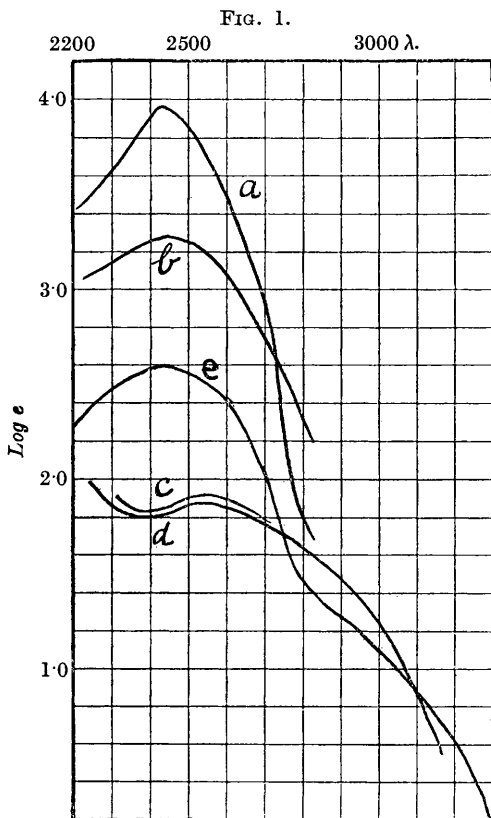
Ethyl acetoacetate (a) in hexane, (b) in alcohol, (c) in dilute hydrochloric acid, (d) in water, (e) liquid.

reason to ascribe the band at 2550 Å. to a trace of enol as to a large amount of ketone. There is, however, an inflexion in the curves for the liquid ester and for its solution in hexane, which may be due to an incipient ketonic band at 2700—2800 Å. This conclusion is confirmed by the fact that the liquid dialkylaceto-acetic esters exhibit well-defined bands near 2900 Å., which are weakened on the addition of alcohol, but reappear when alkali is

added.   Moreover, analogy with other ketones would lead us to predict a band in ethyl acetoacetate at about 2750 Å. and $e_{(max.)}$ about 100.   Since in hexane, where 80% of the ester is enolic, $e_{(max.)}$ is 9100, the value for the pure enol must then be about 100 times greater than for the pure ketone.   We therefore conclude that the band at 2430 Å. can be attributed to the enolic form and

Fig. 2.
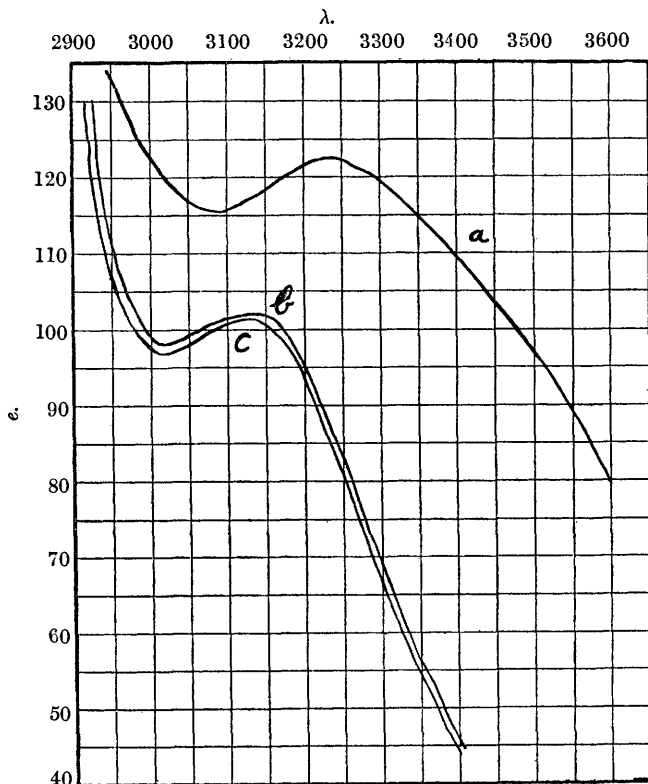
Ketonic α-benzoylcamphor in (a) *piperidine,* (b) *chloroform, and* (c) *alcohol.*

that the ketonic form possesses a weak band near 2700 Å., which is usually masked by the stronger absorption of the enol.

Acetylacetone, which is too absorbent to be examined in the liquid state, gives a strong band at 2750 Å. in aqueous and alcoholic solutions.   The ratio of the molecular extinction coefficients, $8920/2200 = 4.05$, agrees with the ratio 4.2 of the enol content of these solutions as measured by K. H. Meyer.   The band appears, therefore, to be due to the enol, although its wave-length corresponds with that of the acetone band at 2747 Å.   Since hexa-

methylacetone shows the usual ketonic band, even when very carefully purified (Rice, *Proc. Roy. Soc.*, 1914, *A*, **91**, 76), and the weak bands of the dimethyl- and diethyl-acetoacetic esters could not have been detected in presence of strongly absorbing enolic impurities, it is clear that the ketonic band cannot be attributed to the presence of a trace of enol in all ketones. It is therefore necessary to conclude that the enolic form of acetylacetone gives a band at the same wave-length as the ketonic form. This con-clusion is confirmed by the facts that addition of alkali to acetone (which presumably gives rise to a trace of an enolic salt) increases the intensity of the band but does not produce a new band, and

Fig. 3.

(a) *Dibenzoylcamphene in alcohol.   Enolic a-benzoylcamphor in*
(b) *piperidine*, (c) *alcohol.*
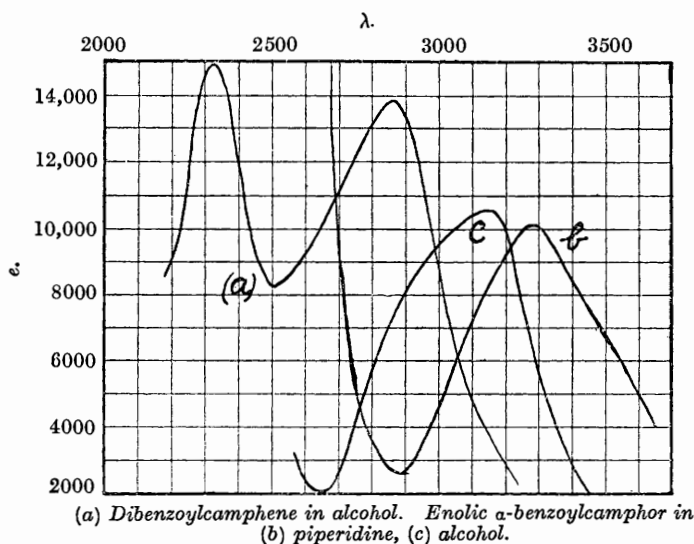
that the two isomeric forms of benzoylcamphor give bands at the same wave-length but of unequal intensity.

Formation of a new compound from acetone by addition of alkali must result in a redistribution of selective absorption. If the compound exhibits a new absorption band, the number of acetone molecules absorbing at 2747 Å., and therefore $e_{(max.)}$, should decrease. The reverse is observed, so that whatever the nature of the new absorbing entity its position of maximum absorp-tion must coincide with that of acetone itself. The data on acetone are thus in agreement with the view that enolic and ketonic modi-fications possess the same wave-length of maximum absorption. Since the enolic sodium salt can be present only in minute amount,

the enolic form must have a high molecular extinction, as otherwise no increase would have been observed.

The effect of alkali on ethyl acetoacetate and acetylacetone is more complicated, new bands being developed, with high extinction coefficients varying directly as the ratio of alkali to ester up to a molecular ratio of 100 : 1.

Alkaline solutions of ethyl acetoacetate were rapidly neutralised and the bromine addition was measured immediately. Although the nature of the experiments precluded reproducible quantitative data, the concurrent increases of the alkali/ester ratio and of $e_{(max.)}$ were accompanied by an increased capacity for bromine addition. Hence the bands at 2430 and 2725 Å. for ethyl acetoacetate, and the bands at 2750 and 2913 Å. for acetylacetone, all correspond with enolic substances.

The substitution of potassium, lithium or other metals for sodium causes a small shift in the position of maximum absorption which is roughly proportional to the atomic weight of the substituent. We can therefore infer $\lambda_{(max.)}$ when hydrogen replaces sodium. The position of such a band for ethyl acetoacetate would be nearer 2700 Å. in alcoholic solution, i.e., the enolic ester corresponding with the enolic sodium salt would display the same position of maximum absorption as the ketonic tautomeride. In acetyl-acetone, the normal ketonic substance has already been shown to absorb at the same wave-length as the ordinary enolic form. The hypothetical enolic form of acetylacetone would, however, show a band different from that of the ketonic form.

Much valuable work has been done in recent years leading to a ringed, chelate, co-ordinated or polar structure for the metallic derivatives of acetylacetone. From the present work, it is evident that the free enolic tautomerides are different from the metallic derivatives in a very distinct way. The free enol does not give the same band as the metallic salts. It therefore seems erroneous to picture the free enol as co-ordinated or ringed in structure (compare Lowry, *Trans. Faraday Soc.*, 1924, **18**, 495, 537).

The views advanced may be subjected to a fairly rigorous test by the isolation and examination of pure ketonic and enolic tauto-merides. The isolation of such forms of ethyl acetoacetate can be accomplished by aseptic distillation from evacuated quartz vessels. Unfortunately, it proved quite impossible to retain the purity of thin films of the liquids between quartz plates for the period of time necessary to secure absorption spectra photographs.

The tautomeric forms of benzoylcamphor exhibit the same frequency of maximum absorption, but differ widely in absorptive power. The molecular extinction coefficients of the ketonic form

and of camphor are of the same order (34—100), and the extinctions of the enolic modification and of dibenzoylcamphene are of the order 10,000—14,000. Addition of alkali causes the appearance of a new band, which confirms the view advanced by Lowry that the metallic salts of α-benzoylcamphor are co-ordinated compounds.

Summary of Results.

Substance.	λ (max.).	e (max.).	Remarks.
Ethyl acetoacetate, vapour .	2381	*ca.* 1000	No fine structure.
,, ,, liquid ...	2430	367	
,, ,, in ether .	2430	High.	
,, ,, in alcohol	2430	2000	Confirming Henri.
,, ,, in hexane	2430	9100	,, ,,
,, ,, in water	2550	81·3	,, ,,
,, ,, in dil. HCl	2550	80	
,, ,, in NaOH	2725	11,500	Extinction varies as recorded.
Ethyl acetoacetate in alc. NaOEt	2725	29,500	Extinction varies with alkali/ester ratio.
Ethyl acetoacetate in alc. HCl	2430	2,000	
,, ,, in dil. aq. KOH	2743	High.	Max. varies with alkali/ester ratio.
Ethyl acetoacetate in LiOH	2707	High.	Max. varies with alkali/ester ratio,
,, ,, in piperidine (anhydrous)	2735	150	Low extinction in ketonising solvent.
Cu derivative of ethyl aceto-acetate	2736	10,000	
Al derivative in heptane	2684	High.	Extinction of the order 10,000.
,, ,, in alcohol	2687	High.	
Mg cmpd. in alcohol	2687	High.	
Ethyl ethylacetoacetate, pure liquid	2550	400	
Ethyl ethylacetoacetate in alcohol	2550	680	Henri records max. at 2341.
Ethyl ethylacetoacetate in water	2700	Low.	
Ethyl ethylacetoacetate in dil. NaOH	2740	10,000	
Ethyl ethylacetoacetate in alc. NaOEt	2810	20,000	
Ethyl ethylacetoacetate in piperidine	2695	Uncertain.	
Ethyl ethylacetoacetate, vapour	*ca.* 2380		No fine structure.
Ethyl methylacetoacetate in alcohol	2520		Hantzsch's data (*loc. cit.*) measured from published curves.
Ethyl methylacetoacetate in water	2680		
Ethyl methylacetoacetate in alkali	2825		
Ethyl β-ethoxycrotonate, vapour	2275	Uncertain.	

Substance.	λ (max.).	e (max.).	Remarks.
Ethyl β-ethoxycrotonate, liquid	Indications of band near 2050.		
Ethyl β-ethoxycrotonate in alcohol	2348	2880	
Ethyl β-ethoxycrotonate in alc. NaOEt	2348	1820	
Ethyl dimethylacetoacetate, liquid	2837	Low.	Film too thin to allow of reproducible values of e.
Ethyl dimethylacetoacetate in alcohol	Inflexion only.		
Ethyl dimethylacetoacetate in alc. NaOEt	2840		
Ethyl dimethylacetoacetate in water	Inflexion only.		
Ethyl dimethylacetoacetate in aq. NaOH	2760		
Ethyl dimethylacetoacetate in piperidine	Inflexion only.		
Ethyl diethylacetoacetate, liquid	2848	Low.	
Ethyl diethylacetoacetate in alcohol, water, or piperidine	Inflexions only.		
Ethyl diethylacetoacetate in aq. NaOH	2762		
Ethyl diethylacetoacetate in alc. NaOEt	2850		
Acetylacetone, liquid	Continuous end absorption.		
,, in water	2750	2200	
,, in alcohol ...	2748	9000	
,, in dil. HCl ...	2750	2000	
,, in aq. LiOH	2917		
,, in aq. NaOH	2926	Order 20,000	Extinction varies with alkali/ester ratio.
,, in aq. KOH	2935		
,, in aq. RbOH	2967		
,, in piperidine (anhydrous)	2955	Not measured owing to difficulties of manipulation.	
,, in alc. NaOEt	2927	19,500	
Camphor in alcohol	2840	34	
Dibenzoylcamphene in alcohol	2860	13,700	
	2365	15,100	
a-Benzoylcamphor, ketonic modification in alcohol ...	3130–3145	103	
a-Benzoylcamphor, ketonic modification in chloroform	3125	104	
a-Benzoylcamphor, ketonic modification in piperidine	3240	123	
a-Benzoylcamphor, enolic modification in alcohol ...	3150	10,600	
a-Benzoylcamphor, enolic modification in piperidine	3280	10,300	
a-Benzoylcamphor, enolic modification in alc. NaOEt	3275	15,250	
Benzoylcamphor, ketonic modification freshly dissolved in alc. NaOEt	3072 2750	1380 1040	
Same solution after standing	3275	4000	
Same solution after some days...............................	3270	12,300	

The following maxima have been measured for metallic derivatives of acetylacetone :

Metal.	Solvent.	λ (max.).			Metal.	Solvent.	λ (max.).
Cu	Alcohol	2435 and 2965			Th	Alcohol	2840
,,	Heptane	2445	2970		,,	Heptane	2735
Be	Alcohol	2930			,,	Ammonia +	2960
Fe^{III}	Alcohol	2730	3525	4350		alcohol	2960
,,	Heptane	2720	3527	4340	Al	Alcohol	2893
Mg	Alcohol	2837			,,	Heptane	2875

Some of the results are recorded as supplementing the work of Lowry and Desch (J., 1909, **95**, 807), Morgan and Moss (J., 1914, **105**, 189), and French (*Proc. Roy. Soc.*, 1924, *A*, **106**, 489).

The present investigation was completed before the appearance of Grossmann's work (*loc. cit*). Whilst our experimental data are on the whole in excellent agreement with those of this investigator, some important differences may be noted. Grossmann does not record the fact that thin films of ethyl acetoacetate exhibit a band at 2430 Å., and the existence of a band in the dialkylacetoacetic esters appears to have escaped his notice.

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