range of 0.1 to 0.5 with a 1-cm. cell. Band widths were from 2–3 mμ. The concentrations needed varied from 3×10^{-4} to 1×10^{-5} *M*. Beer's law was tested for V and was found to be nearly valid for a ten-fold change of concentration. When mixtures of acetic acid and sulfuric acid were used as the solvent, the blank cell of the spectrophotometer was filled with a mixture of the acids of the same age and composition as that used to dissolve the dye. This was done to compensate for an increase in absorption by the solvent on standing.

Acknowledgment.—We wish to thank Dr. B. M. Tolbert for the preparation of the N-dimethyl-N'-phenyl-*p*,*p*'-diaminotriphenylmethyl methyl ether and the *p*-dimethylaminophenyl-3-carbazylphenylmethyl methyl ether, and Miss E. R. Carson for the preparation of the 3,3'-dicarbazylphenylmethyl methyl ether.

Summary

N,N'-Diacetyl-N,N'-diphenyl-*p*,*p*'-diaminotriphenylmethylcarbinol, N-acetyl-N,N'-diphenyl-*p*,*p*'-diaminotriphenylmethylcarbinol, N-dimethyl-N'-acetyl-N'-phenyl-*p*,*p*'-diaminotriphenylmethylcarbinol, N-acetyl-3,3'-dicarbazylphenylmethylcarbinol, and (N-dimethyl-*p*-aminophenyl)-(N-acetyl-3-carbazyl)-phenylmethylcarbinol have been prepared and their spectra measured in acetic acid, and in some cases in other solvents.

These spectra are discussed on the basis of hypsochromic effects resulting from the lowering of the effective basicity of the amino groups by acetylation.

BERKELEY, CALIF. RECEIVED MARCH 4, 1947

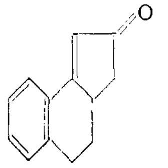
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Ultraviolet Absorption Spectra of α,β-Unsaturated Ketones Conjugated with an Aromatic Nucleus[1]

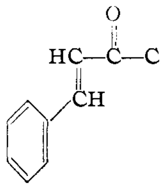
BY A. L. WILDS, LLOYD W. BECK,[2a] WARREN J. CLOSE,[2b] CARL DJERASSI,[2c] JAMES A. JOHNSON, JR., THOMAS L. JOHNSON[2d] AND CLIFFORD H. SHUNK

During the past five years we have had occasion to prepare a number of α,β-unsaturated ketones in which the double bond was in conjugation with an aromatic nucleus as well as with the carbonyl group. We are now reporting the ultraviolet absorption spectra of these compounds and of other unsaturated ketones closely related to them. The results confirm the α,β-unsaturated nature of certain of these ketones in which other locations of the double bond were possible, and lead to some interesting conclusions regarding the correlation of absorption spectrum with structure in this class of unsaturated ketones which has not been reported on very extensively before.

Ketones Related to Benzalacetone.—The spectrum of the ketone I[3] was found to be almost identical with that of benzalacetone (II), as can be seen in Fig. 1. This clearly indicates that the ketone possesses the same conjugated system present in benzalacetone as shown in formula I, rather than the alternate structure with the double bond between the five- and six-membered rings, which would be a possibility from the method of preparation. The occurrence of the main maximum at exactly the same wave length (286–287 mμ) for both ketones is coincidental, however, and the result of several compensating factors.[4]



I



II

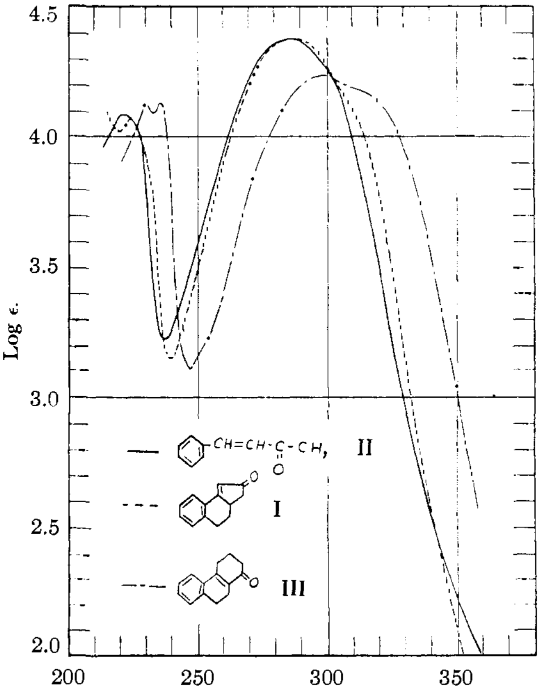


Fig. 1.

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[1] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

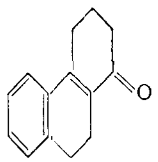
[2] Present addresses: (a) Proctor and Gamble Co., Ivorydale, Ohio; (b) The Abbott Laboratories, North Chicago, Ill.; (c) Ciba Pharmaceutical Products, Inc., Summit, N. J.; (d) Sterling-Winthrop Research Institute, Rensselaer, New York.

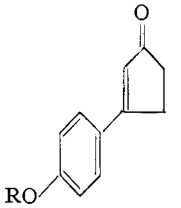
[3] Wilds and J. A. Johnson, THIS JOURNAL, **68**, 86 (1946).

[4] The effect of the additional β-substituent and the exocyclic double bond in I, tending to shift the maximum toward longer wave lengths, is offset by the opposite effect of the five-membered ring.

The presence of the benzene ring in the conjugated system of the ketones I and II has resulted in a shift of the main maximum from the region of simple α,β-unsaturated ketones (220–255 mμ)(5) to that of the doubly unsaturated dienones (approximately 275–300 mμ).(6) Thus, the effect of the benzene ring is approximately the same as that of one more double bond. This point will be considered in more detail in a later section. In addition to the main maximum at 286–287 mμ, there is a second maximum around 220–225 mμ for the aromatic unsaturated ketones.

The spectrum of 1-ketohexahydrophenanthrene (III), prepared recently by W. S. Johnson, H. C. E. Johnson and Betty Petersen,(7) also resembles that of benzalacetone, except the position of the main maximum (Fig. 1) is shifted 12 mμ to longer wave lengths because of the additional substituents on the α and β positions of the double bond.


III


IVa, R = CH_3
IVb, R = H
IVc, R = CH_3CO

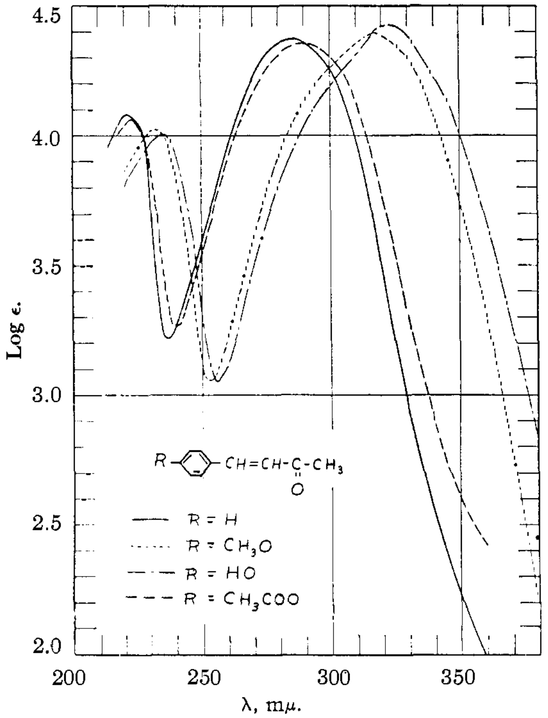
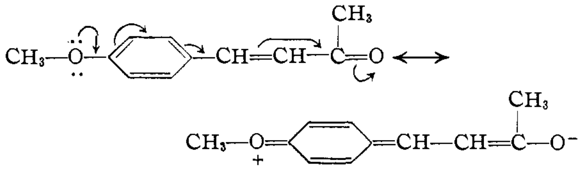


Fig. 2.

For comparison with the ketones IVa and IVb(8) we have measured the spectra of p-methoxy- and p-hydroxybenzalacetone (Fig. 2). These derivatives show a strong bathochromic shift of the main maximum of 32 and 37 mμ, respectively, compared with benzalacetone, and a somewhat smaller shift (11–13 mμ) for the subsidiary maximum.(9) This shift can be attributed to the effect of the *para* group in promoting the following electron shift



thus favoring the *para* position for the excited form and increasing the length (or effectiveness) of the conjugated system. It is of interest that this bathochromic shift due to the p-methoxyl group is almost identical with that produced by an additional double bond in the conjugated system, for the maximum (318 mμ) appears in the same position as that for cinnamalacetone (319 mμ) (Fig. 3). The slightly greater shift brought

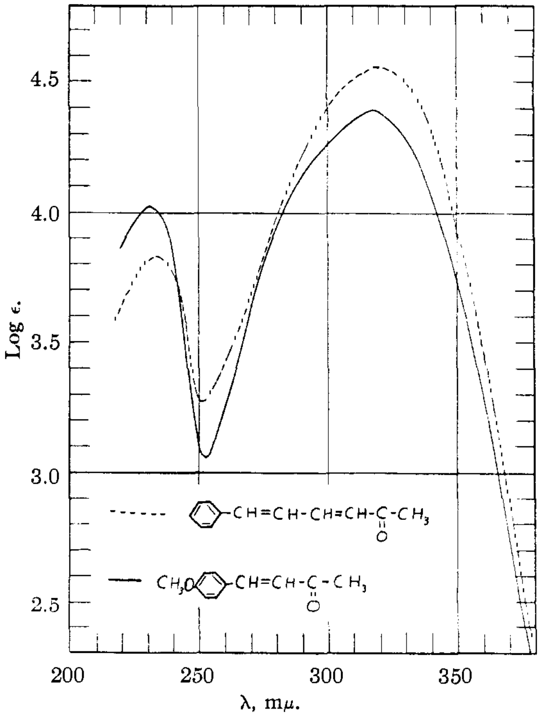


Fig. 3.

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(5) See Woodward, This Journal, **63**, 1123 (1941); **64**, 76 (1942), and Gillam and co-workers, *J. Chem. Soc.*, 815 (1941); 486 (1942), for a correlation of structure with the position of the maximum in this type of ketone.

(6) Evans and Gillam, *J. Chem. Soc.*, 432 (1945), have assembled the data available for this class of compound, and found most of the di- and tri-substituted dienones (which probably are the ones most comparable to the present examples) to be within the above limits.

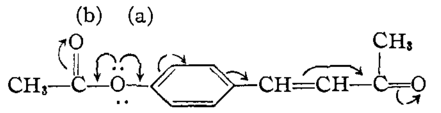
(7) Johnson, Johnson and Petersen, This Journal, **68**, 1926 (1946).

(8) Wilds and T. L. Johnson, *ibid*, **67**, 296 (1945).

(9) The values for the maxima reported for these compounds by Alexa (*Bull. soc. chim. de România*, **18A**, 83 (1936), differ from 2 to 6 mμ in wave length and are uniformly about one unit lower in log ϵ than those reported here.

about by the *p*-hydroxyl group (max. at 323 mμ) is in line with observations in other series.

On the other hand, the spectrum for *p*-acetoxybenzalacetone (max. at 290 mμ) is nearly the same as for the unsubstituted ketone (Fig. 2). This can be attributed to the electron shift (b) into the acetyl group which would tend to oppose the shift (a), and its resultant effect on the conjugated system.



$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}-C_6H_4-CH=CH-\overset{CH_3}{\overset{|}{C}}=O$

This effect probably is related to the shift toward shorter wave lengths which has been observed for the maxima of phenol acetates relative to the phenol.[10,11,12]

The curves (Fig. 4) for 3-phenyl-2-cyclopenten-1-one and its *p*-methoxy-, *p*-hydroxy- and *p*-acetoxy-derivatives IVa, b, c show shifts for the methoxy and hydroxy derivatives entirely similar to those observed in the benzalacetone series, and again this shift is nullified in the curve for the *p*-acetoxy derivative, which is nearly the same as that for the unsubstituted ketone.[13,14]

Ketones Related to 2-Naphthalacetone.—As would be expected, the spectrum of the cyclopentenophenanthrene ketone VIa[15] (Fig. 5) is considerably more complex than those for the simpler ketones related to benzalacetone. However, this spectrum is closely similar to that for the homolog VIb,[16] in which the angular methyl group fixes the position of the double bond. Thus, VIa also must contain the α,β-unsaturated ketone system as indicated in the formula, rather than the alternate possibility with the double bond between the rings. The spectra of these ketones closely resemble that of 2-naphthalacetone (V) which has the same conjugated system.[17]

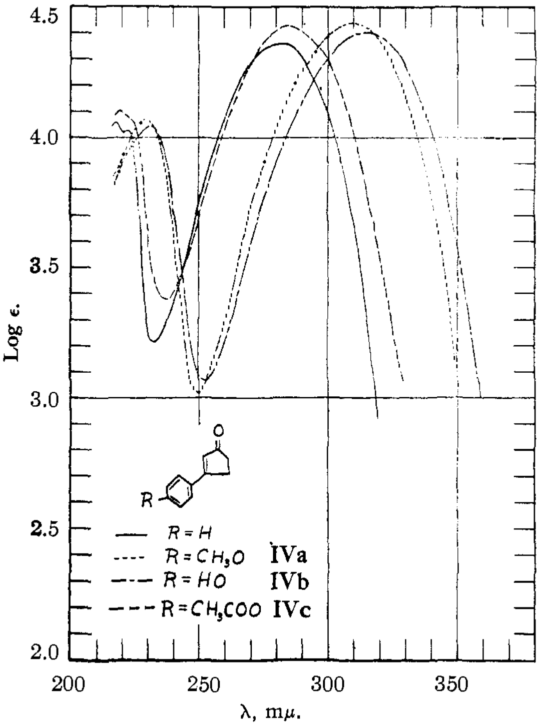


Fig. 4.

Wilds and Beck[16] reported the reduction of the unsaturated diketone VII to a hydroxyketone, to which could be assigned either the structure VIII or that in which the hydroxyl and keto groups are reversed. Experiments by Dr. R. M. Elofson[18] on the reduction of the hydroxyketone at the

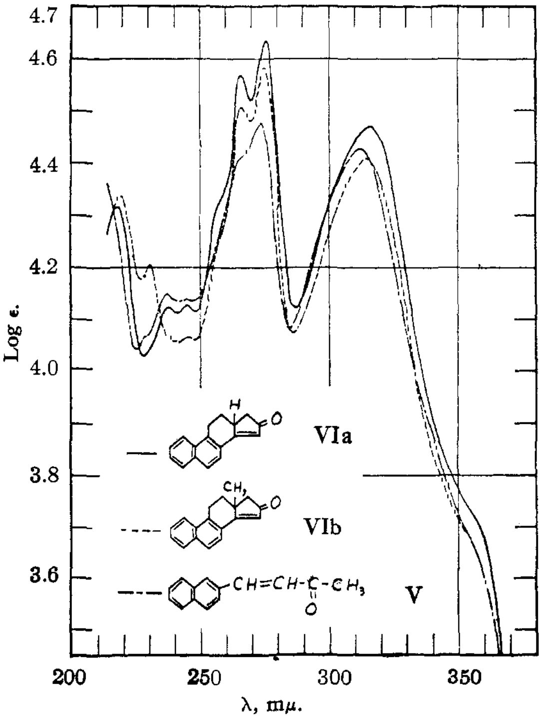


Fig. 5.

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(10) John, *Z. physiol. Chem.*, **250**, 17 (1937).

(11) Dannenberg, *Abhandl. preuss. Akad. Wiss., Math. nat. Klasse*, **No. 21** (1939).

(12) Recently Ramart-Lucas, Grumez and Martynoff [*Bull. soc. chim.*, [5] **12**, 814 (1945)] have observed that the spectra of esters of hydroxy azo compounds are essentially the same as the compounds with the RCOO-group replaced by hydrogen.

(13) It is interesting to note, in comparing the members of the two series, that in all cases the main maximum is 5–9 mμ lower for the five-membered ring ketones than for the open-chain compounds, in spite of the fact that the former have an additional β-substituent. Gillam and West [*J. Chem. Soc.*, 486 (1942)] have observed a hypsochromic shift of 10–15 mμ due to a five-membered ring in simple α,β-unsaturated ketones.

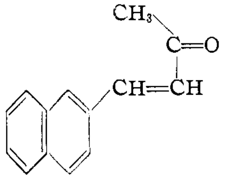
(14) Incidentally, a comparison of 3-phenyl-2-cyclopenten-1-one with 1 (main max. 281 and 287 mμ, respectively) indicates a shift of 6 mμ toward longer wave lengths as a result of the exocyclic double bond of I.

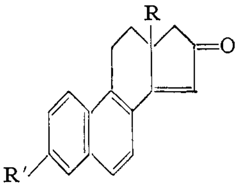
(15) Wilds, THIS JOURNAL, **64**, 1421 (1942).

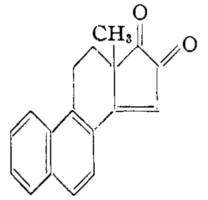
(16) Wilds and Beck, *ibid.*, **66**, 1688 (1944).

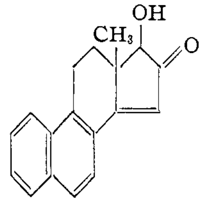
(17) The question of *cis–trans* isomerism at the double bond does not complicate the comparison of these unsaturated ketones, since all of the cyclic ketones are equivalent to a *trans* configuration, which is probably that of the crystalline forms of benzalacetone and 2-naphthalacetone.

(18) Reference 16, footnote 7.


V


VIa, R = R' = H
VIb, R = CH_3; R' = H
VIc, R = CH_3; R' = CH_3O
VId, R = CH_3; R' = HO
VIe, R = CH_3; R' = CH_3COO


VII


VIII

dropping mercury electrode led him to the conclusion that the compound was the α,β-unsaturated ketone (VIII). The close agreement between the absorption curve for the compound (Fig. 6) and those for the related ketones V, VIa and VIb, completely confirms this conclusion.[19]

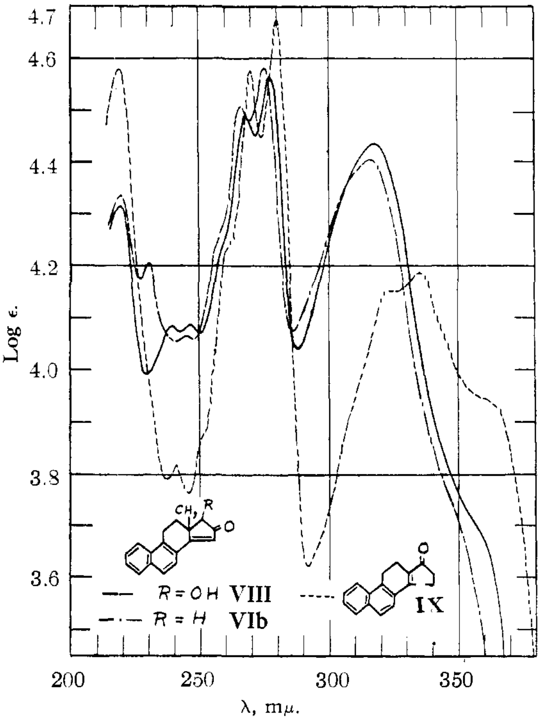
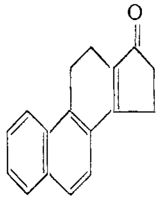
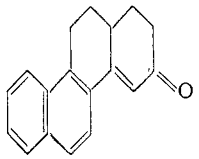
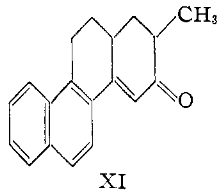
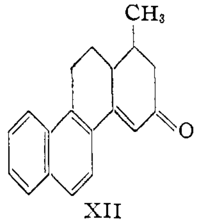


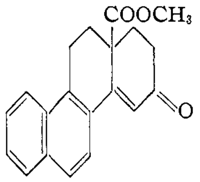
Fig. 6.


IX


X


XI


XII


XIII

For these α,β-unsaturated ketones having the double bond in conjugation with the 2-position of the naphthalene nucleus, we consider the most characteristic portion of the spectrum to be the split peak in the region 265–280 mμ, with the higher maximum at 273–280 mμ (that is, in approximately the same general region as for benzalacetone). The presence of this characteristic split peak in the spectrum of the ketone IX (Fig. 6), for which a new synthesis recently was reported by W. S. Johnson and J. W. Petersen,[20] indicates

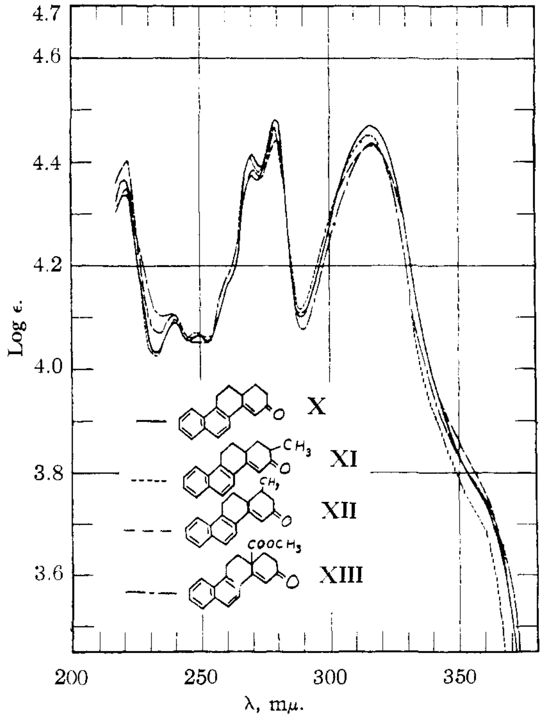


Fig. 7.

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[19] Accordingly the aldehydo acid obtained by periodic acid oxidation of VIII (Reference 16) is 2-methyl-2-formyl-1,2,3,4-tetrahydro-1-phenanthrylideneacetic acid or, more probably, the corresponding hydroxy lactone.

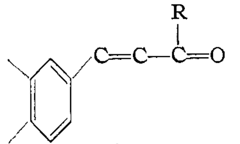
[20] W. S. Johnson and Petersen, THIS JOURNAL, 67, 1366 (1945).

that the double bond in this compound is conjugated both with the carbonyl group and the naphthalene ring, as shown in IX.

The curves for the chrysene ketones X,[21] XI[21] and XII[22] shown in Fig. 7 are very similar to those for the related cyclopentenophenanthrene ketones and 2-naphthalacetone. This similarity and the close agreement with the curve for the keto-ester XIII,[21,23] in which the angular carbomethoxyl group fixes the position of the double bond unequivocally, confirms the α,β-unsaturated structures for the other ketones.

The spectra of 2-naphthalacetone and these eight ketones related to it are all of the same general type and have three major bands: (1) a maximum around 220 mμ; (2) a split peak in the region 265–280 mμ with the main maximum at 275–280 mμ; and (3) a prominent maximum around 310–315 mμ. It seems probable that the maximum around 220 mμ corresponds to the one in the same region for benzalacetone and its derivatives.

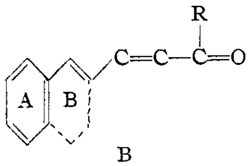
The split peak in the region 265–280 mμ we consider to be characteristic of the conjugated system



A

appearing as it does in the same general region as the main maximum of benzalacetone (286 mμ). The exact position of the main peak is influenced to a small extent by the degree of substitution on the double bond (compare V, VIa and IX), and by the size of the ring (compare VIa and X). The position of the lower maximum of this band shows small shifts similar to those of the higher. This lower peak is not completely resolved in the case of 2-naphthalacetone, but appears as a marked inflection. The resolution is sharpest in the case of IX.

The maximum in the region 310–320 mμ also seems to be characteristic for this type of compound. From its location, it seems possible that this is due to the longer conjugated system



B

for it occurs in the same region as the main maximum for cinnamalacetone (319 mμ).[24] The effect of the degree of substitution at the double bond on the location of this maximum is greater than in the case of the lower peak. The size of the ring apparently has no effect. The maximum occurs at 310 mμ for 2-naphthalacetone and at 315–317.5 mμ for those ketones having an additional β-substituent on the double bond. For the ketone IX having an additional α- as well as β-substituent, the maximum is shifted markedly toward the visible and shows separation into two peaks; the inflection around 360 mμ is particularly pronounced with this compound.

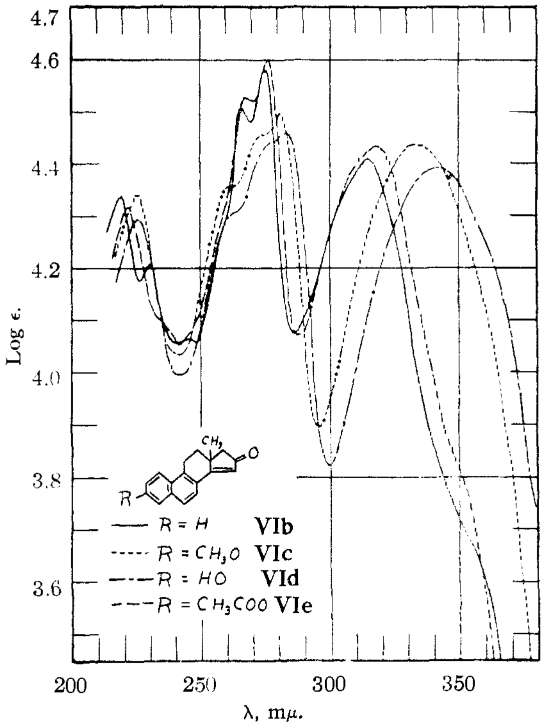


Fig. 8.

It should be possible to test these hypotheses as to the origin of the maxima around 275 and 315 mμ by measurements on methoxyl substituted 2-naphthalacetones in which the methoxyl group is in conjugation with one or the other (or neither) of the conjugated systems. The methoxy ketone VIc and the related hydroxy and acetoxy derivatives VId and VIe, which were prepared by one of us (W. J. C.) for another purpose, provide one such test. In these compounds the oxygen-containing group is so located as to enhance the conjugated system indicated in formula B, but it cannot participate directly in that shown in formula A. In the spectra (Fig. 8) the maximum at 316 mμ for the ketone VIb is shifted markedly toward the visible to 333 mμ for the methoxy derivative VIc[25] and to 342 mμ for the hydroxy ketone VId. However, the maximum at 276 mμ is shifted to a much

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[21] Wilds and Shunk, *ibid.*, **65**, 469 (1943).

[22] Wilds and Djerassi, *ibid.*, **68**, 1715 (1946).

[23] Since the carbomethoxyl group in XIII is not conjugated with the double bond or aromatic ring it has little or no effect on the absorption spectrum in this region of the ultraviolet.

[24] The participation of this double bond of Ring B in the resonance of the naphthalene nucleus may well explain the slightly shorter wave length of this maximum in 2-naphthalacetone, compared with cinnamalacetone, and also the smaller extinction coefficient.

[25] As might be expected (*cf.* footnote 24) this maximum occurs at a still higher wave length (360 mμ) in the methoxy derivative (prepared by T. L. J.) corresponding to VIc except with the 9,10-double bond reduced (phenanthrene numbering system).

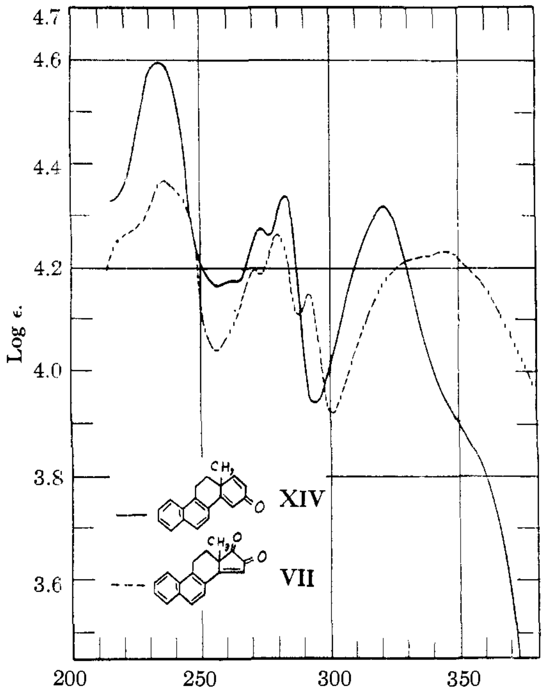


Fig. 9.

smaller extent (to 281–283 mμ),[26] in agreement with the above hypotheses. As in the case of the benzalacetone and 3-phenylcyclopentenone series, the acetoxy derivative VIe has these maxima at approximately the same location as the unsubstituted ketone (318 and 276.5 mμ).

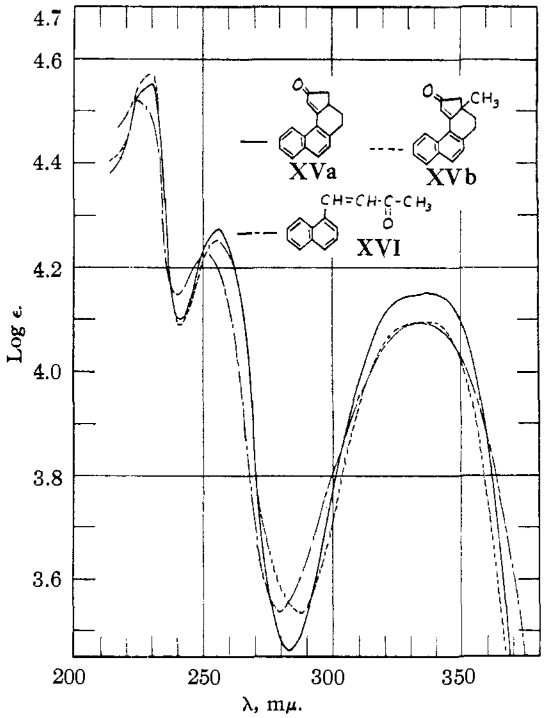
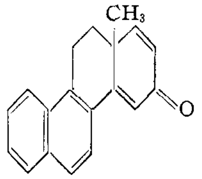
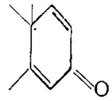


Fig. 10.



XIV

A comparison of the spectra of the dienone XIV[22] and the diketone VII (Fig. 9) reveals interesting similarities to each other and to the ketones previously considered. The curve for the doubly unsaturated ketone XIV is quite similar to that for the related mono unsaturated ketone X in the region of longer wave lengths. The major difference is the peak at 233 mμ, which is the highest of the spectrum. This could be due to the simple α,β-unsaturated ketone grouping resulting from the second double bond, although according to the rule of Woodward[5] this might be expected to occur around 225 mμ, but in our opinion it more probably results from the crossed conjugated system[27]



The spectrum of the diketone VII at shorter wave lengths shows a marked resemblance to that of the dienone XIV, with a high maximum at 236 mμ (possibly due to the analogous cross-conjugated system including the =C—C=O grouping of the diketone structure). The band in the center of the spectrum shows three maxima (as the result of a new subsidiary peak at 292 mμ) while the maximum at longer wave lengths, a broad band characteristic of 1,2-diketones, trails off slowly into the visible and is responsible for the orange-yellow color of the diketone.

Ketones Related to 1-Naphthalacetone.—Recently the synthesis of the ketone XVa was reported[28] by a process similar to that used to prepare the ketones I and VIa. As in the case of the other examples for which alternative locations of the double bond were possible, the double bond has now been shown to be conjugated with the

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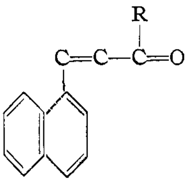
(26) This smaller shift might be ascribed to the effect of the methoxyl group on the resonance of the naphthalene nucleus and thus indirectly upon the participation of ring B in the conjugated system shown in A.

(27) To be sure, the maximum for this type of system occurs at essentially the same position as that for the more highly substituted of the two corresponding mono-unsaturated ketones in several of the cases investigated, for example, 1,4-cholestadienone-3 (245 mμ) and 4-cholestenone-3 (241 mμ); 1,4-androstadien-17-ol-3-one (244 mμ) and testosterone (241 mμ, all data for absolute alcohol solutions). However, this may be coincidental, for the maximum for santonin is reported [Ruzicka, Cohen, Furter and van der Sluys-Veer, *Helv. Chim. Acta*, **21**, 1737 (1938)] as 242 mμ while that to be expected for the related mono-unsaturated ketones would be 252 and 225 mμ, and that for 2,4-dimethyl-2,5-cyclohexadien-4-ol-1-one (*m*-xyloquinol) is reported as 230 mμ compared with the values of 235 and 225 mμ to be expected for the related mono-unsaturated ketones; and of course, the maximum for the analogous linear cross-congugated system occurs at a much higher wave length (*e. g.*, phorone at 265 mμ).

(28) Wilds and Close, THIS JOURNAL, **68**, 83 (1946).

carbonyl group. The absorption curve (Fig. 10) for the ketone XVa, although markedly different from those for the ketones considered previously, shows a close similarity to that for 1-naphthalacetone (XVI) in the general shape of the curve and in the location of the three maxima. Further evidence is afforded by the close agreement with the spectrum of the related ketone XVb in which the double bond must be conjugated with the ketone group. The marked difference in the effect of a 1- and 2-substituted naphthalene nucleus on absorption spectra has been observed in other cases.[29]

The three maxima of 1-naphthalacetone (224, 251 and 334 mμ) are displaced slightly toward higher wave lengths in the cyclic ketones (230, 255–256 and 337–338 mμ), probably due to the additional β-substituent on the double bond (now exocyclic). As to the origin of these bands, it seems possible that the broad maximum at 334–338 mμ may be due to the conjugated system



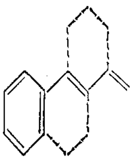
In agreement with the longer length of this conjugated system in the 1-naphthalacetone series, this band is some 23–24 mμ higher than the corresponding one in the 2-naphthalacetone series. Our conjectures as to the origin of the other two maxima will be reserved until further examples of these 1-naphthalacetone derivatives are available.

Simpler Aromatic Ketones.—The generalizations proposed above to correlate the structure and spectra of unsaturated ketones containing an aromatic nucleus in the conjugated system can also be applied to the simpler aromatic ketones having the carbonyl group adjacent to the aromatic ring. For example, the main maximum for acetophenone (243 mμ)[30] comes in the region of simple α,β-unsaturated ketones, as would be expected if the benzene ring had approximately the same effect as a double bond.[31]

For aromatic aldehydes such as benzaldehyde (main max. 243 mμ)[32] the shift toward shorter wave lengths of about 5 mμ, which has been observed for simple unsaturated aldehydes compared with ketones,[33] is not found. This shift also is not observed for dienals.[6] With the aromatic aldehydes and ketones, as was noted for the benzalacetone derivatives, etc., a *para* methoxyl group results in a shift toward longer wave lengths roughly equivalent to that produced by another double bond, although the correspondence is not as close as in the case of *p*-methoxybenzalacetone. Thus the main maximum of *p*-anisaldehyde occurs at 277 mμ[32] and of *p*-methoxyacetophenone at about 270 mμ[33a] compared to 286 mμ for benzalacetone.[34]

It may also be pointed out that the similarity in location of the maxima for dienes to that for α,β-unsaturated ketones carries over to the benzenoid counterparts. Thus styrene (245 mμ)[35] and propenylbenzene (246 mμ)[35a] have their maxima near that for acetophenone (243 mμ), and 1-phenyl-1,3-butadiene (280 mμ)[36] near that of benzalacetone (286 mμ).

The absorption spectra of the acetylnaphthalenes apparently have not been reported. However, the spectra for 1- and 4-ketotetrahydrophenanthrene included here serve as examples of 2- and 1-substituted naphthalenic ketones, respectively. The spectrum of 1-ketotetrahydrophenanthrene (XVII), shown in Fig. 11, has three distinct bands, two of which show fine structure. The highest maximum at 251.5 mμ comes in the approximate region for the carbonyl group in conjugation with the adjacent aromatic nucleus. The maximum at 284.5 mμ can be attributed to the benzalacetone type structure as follows



The very close agreement in position is no doubt a coincidence resulting from the opposing effects of the additional α and β-substituents on the double bond, which would tend to shift the maximum toward the visible, and the participation of this double bond in the resonance of the naphthalene nucleus, which might be expected to result in a shift away from the visible. The location of this maximum at 298 mμ for the ketone III, which has a true double bond, supports this view.

A methoxyl group in the 7-position (*para* to the

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(29) For some recent examples see R. N. Jones, THIS JOURNAL, **67**, 2021, 2127 (1945), and Blout, Eager and Gofstein, *ibid.*, **68**, 1983 (1946).

(30) See, for example, Morton and Sawires, *J. Chem. Soc.*, 1054 (1940).

(31) The exact degree of substitution on the double bond that one should choose in making this comparison is not unequivocal, but the location of the maximum would probably be in the range 235–245 mμ. It is interesting to apply the empirical equation of Ferguson and Branch [THIS JOURNAL, **66**, 1471 (1944)] to the vinylogous series acetophenone, benzalacetone and cinnamalacetone. Using $\lambda^2_{\text{max.}} = 2.65 \times 10^6 + 2.3 \times 10^6 (n + \beta + \gamma)$, where λ is given in ångström units, n is the number of vinylene groups and γ and β are the effects of the groups at the carbonyl group and at the other end of the vinylene chain, respectively, and taking $\gamma_{CH_3} = 0$, the effect of the phenyl group (β) for acetophenone can be calculated to be about 1.4 double bonds. A similar calculation for benzalacetone gives 1.4 and for cinnamalacetone 1.27. For comparison, the effect of an α-furyl group was reported to be equivalent to that of about two double bonds [see also Hausser, Kuhn, Smakula and Deutsch, *Z. physik. Chem.*, **B29**, 378 (1935)].

(32) Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

(33) Evans and Gillam, *ibid.*, 565 (1943).

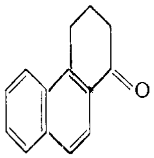
(33a) Ramart-Lucas and Segal, *Bull. soc. chim.*, [5] 1, 1049 (1934).

(34) Morton and Stubbs (ref. 32) have also determined the effect of an ortho or meta hydroxyl group on the spectra of benzaldehyde and acetophenone.

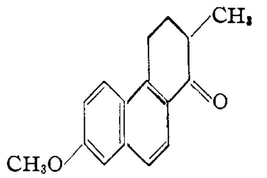
(35) Ley and Dirking, *Ber.*, **67**, 1334 (1934).

(35a) Ramart-Lucas and Amagat, *Bull. soc. chim.*, **51**, 118 (1932).

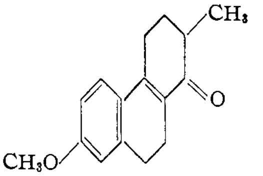
(36) Smakula, *Angew. Chem.*, **47**, 662 (1934).



XVII



XVIII



XIX

conjugated double bond) has a similar effect in this series as in those previously considered. Thus, in the spectrum for XVIII the maximum at 251.5 mμ for XVII is shifted only slightly (to 256 mμ), due to secondary effects, while the maximum at 284.5 mμ is markedly shifted to 309 mμ as a result of the conjugation with the methoxyl group.[36a]

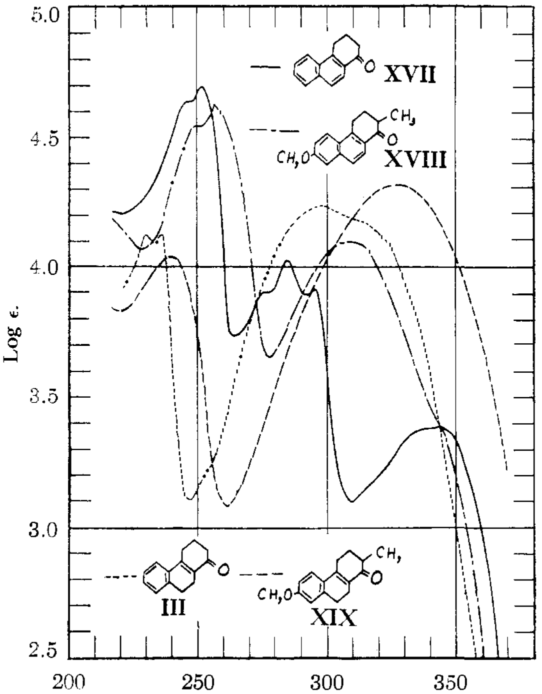
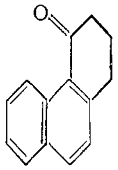


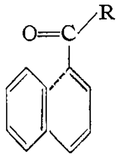
Fig. 11.

The spectrum for 4-ketotetrahydrophenanthrene (XX), shown in Fig. 12, bears a rather close resemblance to that of 1-naphthalacetone and related ketones, with the difference that the three maxima occur at shorter wave lengths.



XX

The location of the maximum at 311 mμ is approximately where it would be expected to occur if it were due to the unsaturated system



and thus falls in line with the suggestion regarding the origin of the corresponding maximum in XVa.

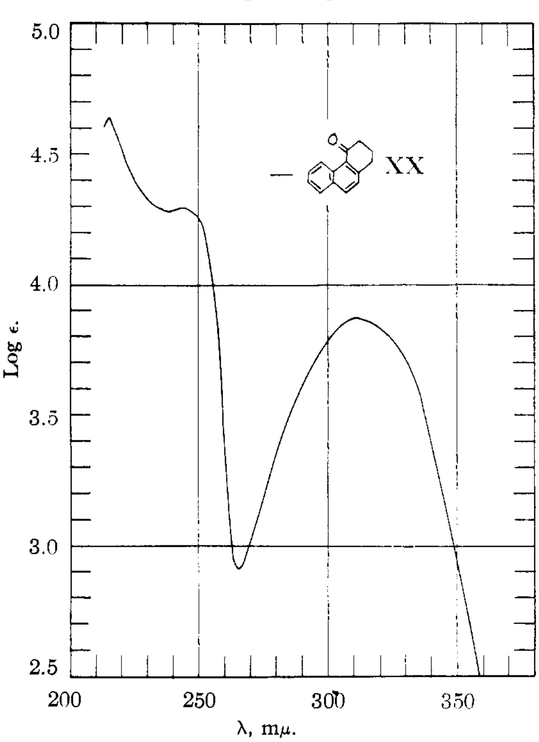


Fig. 12.

Further work is under way to test more fully the generalizations outlined above and to extend them to other derivatives.

Experimental[37]

Preparation of Compounds.—The following compounds were prepared by procedures described in the literature and were recrystallized to constant melting point from the solvents indicated: benzalacetone,[38] m. p. 41–42° (petroleum ether); *p*-methoxybenzalacetone,[39] m. p. 71.5–72.5° (methanol); *p*-hydroxybenzalacetone,[40] m. p. 110.5–111.5° (dilute acetone), a second polymorphic form,

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[36a] This shift of 24.5 mμ is not quite so large as that observed in the benzalacetone and 3-phenylcyclopentenone series (28–32 mμ). Possibly this is due to partial dissipation of the effect of the methoxyl group in the resonance of the nucleus, for a larger shift is observed with the unsaturated ketone XIX (29 mμ, relative to III).

[37] All melting points are corrected.

[38] "Organic Syntheses," Coll. Vol. 1, 77 (1941).

[39] Baeyer and Villiger, *Ber.*, **35**, 1191 (1902).

[40] Buck and Heilbron, *J. Chem. Soc.*, **121**, 1100 (1922).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA IN ABSOLUTE ALCOHOL

Compound	Maxima[a] λ(mμ)	Maxima[a] log ϵ_m	Minima λ(mμ)	Minima log ϵ_m
A. Ketones Related to Benzalacetone				
Benzalacetone (II)	220.5	4.08	237	3.22
	286	4.37		
p-Methoxybenzalacetone	232	4.02	253	3.05
	318	4.39		
p-Hydroxybenzalacetone	234	4.01	256	3.05
	323	4.37		
p-Acetoxybenzalacetone	223	4.06	240.5	3.27
	290	4.36		
Cinnamalacetone	234	3.83	252	3.27
	319	4.56		
$\Delta^{1,1'}$-2'-Keto-3,4-dihydro-1,2-cyclopentenonaphthalene (I)	223.5	4.07	220	4.02
	287	4.38	239	3.15
1-Keto-1,2,3,4,9,10-hexahydrophenanthrene (III)[b]	230	4.13	233.5	4.09
	236	4.12	247	3.11
	298	4.24		
3-Phenylcyclopenten-2-one-1	217.5	4.06	220.5	4.02
	222	4.03	233	3.21
	281	4.36		
3-(*p*-Methoxyphenyl)-cyclopenten-2-one-1 (IVa)	229.5	4.07	250	3.01
	309.5	4.44		
3-(*p*-Hydroxyphenyl)-cyclopenten-2-one-1 (IVb)	231	4.05	252.5	3.06
	314.5	4.40		
3-(*p*-Acetoxyphenyl)-cyclopenten-2-one-1 (IVc)	219	4.11	237.5	3.37
	284	4.43		
B. Ketones Related to 2-Naphthalacetone				
2-Naphthalacetone (V)	<214	>4.36	226	4.04
	(228)	(4.13)		
	237	4.15	242	4.130
	245	4.135	247.5	4.130
	(265)	(4.42)		
	273	4.48	284	4.07
	310	4.43		
$\Delta^{1,1'}$-2'-Keto-3,4-dihydro-1,2-cyclopentenophenanthrene (VIa)	218.5	4.32	228	4.03
	238	4.120	241	4.11
	245	4.125	249	4.11
	(255)	(4.27)		
	266	4.56	270	4.52
	276	4.63	287	4.12
	316	4.47		
	(360)	(3.69)		
$\Delta^{1,1'}$-2'-Keto-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene (VIb)	219.5	4.34	227	4.18
	230.5	4.21	241.5	4.053
	245.5	4.063	248	4.057
	(257)	(4.22)		
	266	4.51	269.5	4.48
	275	4.58	287	4.08
	315	4.41		
	(360)	(3.61)		
$\Delta^{1,1'}$-2'-Keto-2-methyl-7-methoxy-3,4-dihydro-1,2-cyclopentenophenanthrene (VIc)	225.5	4.34	242.5	4.03
	(260–264)	(4.35)		
	(272.5)	(4.45)		
	281	4.50	296	3.89
	333	4.44		
$\Delta^{1,1'}$-2'-Keto-2-methyl-7-hydroxy-3,4-dihydro-1,2-cyclopentenophenanthrene (VId)	226	4.29	243	3.99
	(263)	(4.30)		
	(278)	(4.44)		
	283	4.46	300	3.82
	342	4.39		
$\Delta^{1,1'}$-2'-Keto-2-methyl-7-acetoxy-3,4-dihydro-1,2-cyclopentenophenanthrene (VIe)	222	4.32		
	(235)	(4.11)	242	4.05
	(258)	(4.28)		
	267.5	4.53	271	4.52
	276.5	4.60	288	4.07
	318	4.43		
	(353)	(3.78)		
$\Delta^{1,1'}$-2'-Keto-3'-hydroxy-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene (VIII)	219	4.32	230	3.99
	239	4.080	242.5	4.070
	246.5	4.085	250.5	4.068
	(260)	(4.25)		
	268	4.49	272	4.45
	277	4.56	288	4.04
	317.5	4.44		
	(360)	(3.68)		
3'-Keto-3,4-dihydro-1,2-cyclopentenophenanthrene (IX)	219	4.58	237	3.79
	241	3.82	245.5	3.76
	(250)	(3.86)		
	(260)	(4.23)		
	270	4.58	274	4.45
	280	4.67	292	3.62
	324	4.153	326	4.150
	335	4.19		
	(360)	(3.95)		
3-Keto-1,2,3,11,12,12a-hexahydrochrysene (X)	220.5	4.36	233	4.03
	240	4.09	246	4.055
	249.5	4.065	253	4.055
	(262)	(4.17)		
	270.5	4.42	274	4.39
	279.5	4.48	289.5	4.10
	316	4.47		
	(360)	(3.75)		
3-Keto-2-methyl-1,2,3,11,12,12a-hexahydrochrysene (XI)	220.5	4.34	233	4.02
	240	4.10	245.5	4.06
	248.5	4.07	252.5	4.05
	(260)	(4.17)		
	270	4.41	273	4.38
	279	4.48	289	4.12
	315	4.45		
	(360)	(3.70)		
3-Keto-1-methyl-1,2,3,11,12,12a-hexahydrochrysene (XII)	221	4.33	234	4.07
	240	4.11	248	4.060
	250	4.065	253	4.060
	(260)	(4.16)		
	271	4.39	274	4.37
	280	4.44	290	4.10
	316.5	4.43		
	(360)	(3.76)		
3-Keto-12a-carbomethoxy-1,2,3,11,12,12a-hexahydrochrysene (XIII)	221	4.35	235.5	4.10
	239	4.11	246–250	4.05
	(260)	(4.17)		
	270.5	4.37	272.5	4.36
	279	4.46	290	4.08
	317	4.43		
	(360)	(3.75)		
3-Keto-12a-methyl-3,11,12,12a-tetrahydrochrysene (XIV)	233.5	4.59	256	4.16
	262–264	4.17		
	273	4.28	276	4.26
	282.5	4.34	294	3.94
	320	4.32		
	(358)	(3.83)		
$\Delta^{1,1'}$-2',3'-Diketo-2-methyl-3,4-dihydro-1,2-cyclopentenophenanthrene (VII)	(220)	(4.26)		
	236	4.37	256	4.04
	270.5	4.20	273	4.19
	279.5	4.26	287.5	4.11
	291	4.15	301	3.92
	(332–334)	(4.22)		
	345	4.23		
C. Ketones Related to 1-Naphthalacetone				
1-Naphthalacetone (XVI)	224	4.53	240	4.14
	251	4.22	279	3.53
	334	4.09		
$\Delta^{4,3'}$-2'-Keto-1,2-dihydro-3,4-cyclopentenophenanthrene (XVa)	230	4.56	241	4.10
	256	4.28	283	3.46
	337	4.15		
$\Delta^{4,3'}$-2'-Keto-3-methyl-1,2-dihydro-3,4-cyclopentenophenanthrene (XVb)	230	4.57	241	4.09
	255	4.25	287.5	3.53
	338	4.10		

TABLE I (*Concluded*)

Compound	Maxima[a] λ(mμ)	Maxima[a] log ϵ_m	Minima λ(mμ)	Minima log ϵ_m
D. Other Compounds				
1-Keto-1,2,3,4-tetrahydrophenanthrene (XVII)	(245–247)	(4.63)	220.5	4.21
	251.5	4.70	264	3.74
	(275.5–278)	(3.91)		
	284.5	4.03	292	3.89
	295	3.92	309	3.10
	(337–340)	(3.37)		
	342	3.38		
1-Keto-2-methyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene (XVIII)	(248.5–251)	(4.54)	228	4.07
	256	4.62	277.5	3.65
	309	4.10		
	(345)	(3.36)		
1-Keto-2-methyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XIX)	239	4.04	220	3.83
	327	4.32	261	3.08
4-Keto-1,2,3,4-tetrahydrophenanthrene (XX)	215	4.64	237	4.28
	244	4.30	265.5	2.91
	311	3.87		

[a] Values under maxima that are given in parentheses refer to inflections or in a few cases plateaus. [b] Measurements for this compound were carried out by Mr. Eugene L. Woroch.

m. p. 105–106° (petroleum ether–acetone) also was encountered; *p*-acetoxybenzalacetone,[41] m. p. 80–81° (petroleum ether); cinnamalacetone,[42] m. p. 67.5–68° (ether); 3-phenylcyclopenten-2-one-1,[43] m. p. 81.5–82.5° (petroleum ether).

The **acetate of 3-(*p*-hydroxyphenyl)-cyclopenten-2-one-1** was prepared by heating the phenol[3] with acetic anhydride and pyridine at reflux for three hours under nitrogen. The product was recrystallized from methanol to give colorless leaflets, m. p. 122–123°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 72.1; H, 5.8.

2-Naphthalacetone—A mixture of 1 g. of 2-naphthaldehyde, 6.5 cc. of acetone, 30 cc. of water and 0.2 cc. of a 20% sodium hydroxide solution was stirred and heated in an oil-bath at 40–45° for thirteen hours. The crude product (m. p. 95–98°) was obtained in 88% yield by cooling and filtering. By evaporative distillation at 160–190° (0.2 mm.) and recrystallization from methanol, colorless crystals melting at 104–104.5° were obtained (69%). Gibson, *et al.*,[44] obtained the compound as yellow crystals, m. p. 102° with sintering at 95°.

1-Naphthalacetone.—A mixture of 20.2 g. of redistilled 1-naphthaldehyde,[44] 130 cc. of acetone, 600 cc. of water and 4 cc. of 20% sodium hydroxide solution was stirred vigorously at 40–45° for twenty-two hours. The mixture was saturated with salt, extracted with ether and benzene and washed with dilute alkali and water. The product was distilled at 172–183° (1 mm.) giving 22.5 g. (90%) of a pale, greenish-yellow oil. The liquid had a pronounced vesicant action.

Fractionation of this material gave 19.1 g. (75%) of pure material, b. p. 167–173° (0.9 mm.), $n^{25}\mathrm{D}$ 1.6665, d^{25}_4 1.1035, M_D (found) 60.33, M_D (calcd.) 59.67. The ketone could not be crystallized even after regeneration from the picrate (m. p. 72–75°). Gibson, *et al.*,[44] reported the compound to be a yellow oil boiling at 200–201° (10 mm.).

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.7; H, 6.2. Found: C, 85.3; H, 6.2.

$\Delta^{4,3'}$-2'-Keto-3-methyl-1,2-dihydro-3,4-cyclopentenophenanthrene (XVb) was prepared from 4-keto-3-methyl-1,2,3,4-tetrahydrophenanthrene[45] by the method described by Wilds and Beck[16] for the related compound (VIb). This will be described in detail in a future communication. The melting point, 114–117° with previous sintering, indicated that the compound was not completely pure, although the agreement of the absorption spectrum with that of XVa showed that the amount of the impurity was small.

All of the other compounds were the analytically pure samples previously reported.

Ultraviolet Absorption Measurements.—All determinations were made using absolute alcohol as the solvent. This was purified by distilling commercial absolute alcohol and discarding the first 50–60% until the transmission curve no longer showed a hump at 254 mμ due to benzene.

Measurements were made using a Beckman quartz spectrophotometer. The spectrum was examined from 215 to 400 mμ at 2.5 mμ intervals except near maxima and minima and then at 0.5 mμ intervals. The results are given in Figs. 1–12 and Table I. The molecular extinction coefficient was calculated from the equation

$$\log \epsilon_m = \frac{1}{cd} \log \frac{I_0}{I}$$

where c is the concentration in moles per liter.

We are indebted to Prof. K. M. Watson of the Department of Chemical Engineering for making available to us the Beckman instrument on which some of the preliminary results were obtained.

Summary

The ultraviolet absorption spectra are reported for a number of α,β-unsaturated ketones related to benzalacetone and the naphthalacetones, including a number of polycyclic unsaturated ketones. The results confirm the α,β-unsaturated nature of certain of these ketones for which other locations of the double bond were possible.

The attempt has been made to correlate the major bands of the spectrum with structure in these compounds. In the benzalacetone series examples are given to illustrate the effect of five- and six-membered rings, substitution on the double bond, an exocyclic double bond, and a *p*-methoxyl, hydroxyl or acetoxyl group. The bathochromic shift produced by a *p*-hydroxyl (or methoxyl) group is nullified in the *p*-acetoxyl compound, for which the spectrum is like that of the unsubstituted benzalacetone.

In the case of 2-naphthalacetone and a number of related polycyclic analogs, it appears possible to correlate the two bands of longest wave length with specific portions of the molecule. Some evidence in support of this is cited, and a similar approach is applied to the spectra of simple aromatic ketones of the benzene and naphthalene series.

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(41) Zincke and Muehlhausen, *Ber.*, **36**, 134 (1903).

(42) Diehl and Einhorn, *ibid.*, **18**, 2320 (1885); Stobbe, Hensel and Simon, *J. prakt. Chem.*, **110**, 148 (1925).

(43) Borsche and Menz, *Ber.*, **41**, 194 (1908).

(44) Gibson, Hariharan, Menon and Simonsen, *J. Chem. Soc.*, **129**, 2247 (1926).

(45) Bachmann and Cortes, THIS JOURNAL, **65**, 1331 (1943).