## 108. The Effect of Molecular Environment on the Absorption Spectra of Organic Compounds in Solution. Part IV. Dienones and Dienals.

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In continuation of earlier work the absorption spectra of various conjugated dienones and dienals have been studied. It is found that in all the known cases the absorption band lies between 2690 and 3170 A., depending on the number and position of the alkyl substituents, for, as in the case of the $\alpha\beta$-unsaturated ketones, each successive alkyl substituent on the chromophore exerts a tendency to displace the absorption band by approximately 100 A. towards longer wave-lengths. Data on the corresponding semicarbazones and phenyl-semicarbazones are also presented.

In previous papers of this series (*e.g.*, Part III, J., 1943, 565) the light absorption of compounds containing the simple chromophores >C:C·C:C<, >C:C·C:O and >C:C·C:N– have been studied with the main object of increasing the value of absorption spectra data in the elucidation of the structure of organic compounds. The present paper extends this work by a study of conjugated dienones and dienals.

It has already been observed that the more intense band in the absorption spectrum of $\alpha\beta$-unsaturated carbonyl compounds in alcoholic solution usually lies within the range 2150—2570 A., the location being mainly dependent upon the degree of substitution of the actual chromophoric group (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72; Evans and Gillam, J., 1941, 815). For instance, in (I) when α and β = H the absorption band lies near 2150 A. and each subsequent replacement of H by R (= alkyl) results in a displacement to longer wave-lengths of about 100 A. Superimposed upon these substitutive effects is found a hypsochromic effect of 50 A. in the case of aldehydes (*i.e.*, when R also = H) and a bathochromic effect of 50 A. for each *exo*cyclic ethylene linkage.

(I.) (II.)
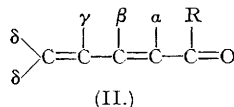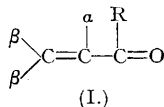
Where the absorption spectra recorded here have been obtained for the first time the values have been determined for ethyl-alcoholic solutions, but since published values have been obtained in various solvents and the location of an absorption band varies with the solvent it was necessary to establish an empirical correction that could be used to convert values in other solvents to those in ethyl alcohol. For this purpose a typical dienone—ψ-ionone—was examined in several solvents, the values and corrections being listed in Table I.

It is noteworthy that the corrections obtained with this dienone are all, with one exception, *viz.*, that in chloroform, practically identical with those collected by Woodward (*loc. cit.*) from the literature on $\alpha\beta$-unsaturated ketones. This worker gives the absorption maxima in alcohol and chloroform as identical for $\alpha\beta$-unsaturated ketones although it is common experience with other classes of compounds, like the ψ-ionone above, to have the absorption maximum in chloroform displaced slightly to longer wave-lengths.

Increasing the length of a conjugated system affects the light absorption of a compound by a movement of the K-band to longer wave-lengths; so that as we pass from an $\alpha\beta$-unsaturated ketone to a dienone we expect, and in fact obtain, such a bathochromic effect except where the dienone contains an unconjugated ethylene

TABLE I.

Absorption maxima of ψ-ionone in various solvents.

Solvent.	$\lambda_{max.}$, A.	Corrn. to give ethyl alcohol value (A).	Similar corrn., A, for C:C·C:O compounds (Woodward).
MeOH	2930	−10	−10
Et₂O	2855	+65	+60
Dioxan	2870	+50	—
Hexane	2845	+75	+70
CHCl₃	2960	+40	± 0
EtOH	2920	—	—

linkage as in methylheptenone. Here the light absorption is that of the αβ-unsaturated ketone only. Following Woodward's system (*loc. cit.*) of labelling the replacable H atoms on the chromophore in αβ-unsaturated ketones, we have the arrangement in conjugated dienones as in (II). The degree of substitution about this chromophore may vary from 0 to 5 substituents even with R = alkyl, and so for a complete analysis a considerable amount of data is necessary. Attempts to prepare suitable and relatively simple dienones by condensing available αβ-unsaturated aldehydes with various dialkyl ketones and with aldehydes have frequently produced only high-boiling polymerised products. However, it has been possible to collect sufficient data to make a preliminary classification possible.

The interesting question at once arises whether the same kind of substitutive effect applies to the dienone chromophore as has already been observed with the αβ-unsaturated ketone type. Jones and Lahey [*Univ. of Queensland Papers* (Chemistry), 1942, I, 26], in fact, considered this possibility but were limited to an examination of only three compounds.

In Table II we summarise the known data on a wider range of dienones and dienals to test this substitutive effect.

TABLE II.

Absorption Spectra of Conjugated Dienones and Dienals.

	Substituted.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
Monosubstituted.			
Tagetone [1]	β	2690	20,000
Δ³:⁵-Heptadien-2-one [2]	δ	2710	22,600
Δ²:⁴-Hexadienal [3]	δ	2700	26,500
Disubstituted.			
4-Methyl-Δ⁴:⁶-octadien-3-one	αδ	2790	—
4-Ethyl-Δ³:⁵-nonadien-2-one	βδ	2815	19,000
Δ³:⁵-Cholestadien-7-one [4]	βδ	2800	26,900
Δ⁴:⁶-Cholestadien-3-one [5]	βδ	2870 *	—
Δ⁴:⁶-Androstadiene-3 : 17-dione [6]	βδ	2850	—
Δ³:⁶-Androstadien-17-ol-7-one [7]	βδ	2760 *	—
*iso*Ergosterone	βδ	2815 *	—
*iso*Ergostatrienone [2]	βδ	2810	40,000
6-Dehydroprogesterone [9]	βδ	2820	25,120
6-Dehydrotestosterone [9]	βδ	2860	29,510
6-Dehydrodeoxycorticosterone [9]	βδ	2830	33,900
7-Keto-Δ³:⁵-aetiocholadienic acid methyl ester [10]	βδ	2790	25,120
ψ-Ionone	δδ	2920	—
Citrylideneacetaldehyde [11]	δδ	2900	21,800
Trisubstituted.			
5-Hydroxy-2-keto-αβ-di*cyclo*hexylidene-ethane [12]	αδδ	3090	23,200
Acetate of above compound [12]	αδδ	3090	23,300
6-Ethoxy-Δ⁴:⁶-cholestadien-3-one	βγδ	3015 *	—
β-Ionone [11]	γδδ	2935	8,700
β-*cyclo*Citrylideneacetaldehyde [13]	γδδ	2930	8,000
1-Keto-3-*cyclo*hexenyl-Δ²-octahydronaphthalene [14]	βγδ	2815	25,700
Tetrasubstituted.			
4 : 6-Dibromo-Δ⁴:⁶-cholestadien-3-one [15]	αβγδ	2930 *	—
4 : 6-Dibromo-Δ³:⁵-cholestadien-7-one [15]	αβγδ	3030	—
Pentasubstituted.			
4 : 6 : 7-Tribromo-Δ⁴:⁶-cholestadien-3-one [15]	αβγδδ	3130	—

* Values in other solvents corrected empirically to that in ethyl alcohol.

[1] Jones and Lahey, *loc. cit.* [2] Morton "The Application of Absorption Spectra to the Study of Vitamins, Hormones, and Coenzymes," Hilger, London, 1942. [3] Haüsser, Kuhn, Smakula, and Hoffer, *Z. physikal. Chem.*, 1935, B, **29**, 371, 378. [4] Jackson and Jones, J., 1940, 659. [5] Dane, Wang, and Schulte, *Z. physiol. Chem.*, 1937, **245**, 80. [6] Ruzicka and Bossert, *Helv. Chim. Acta*, 1937, **20**, 328. [7] Butenandt, Hausmann, and Paland, *Ber.*, 1938, **71**, 1316. [8] Wetter and Dimroth, *Ber.*, 1937, **70**, 1665, 2033. [9] Wettstein, *Helv. Chim. Acta*, 1940, **23**, 1371. [10] Reichstein and Fuchs, *ibid.*, 1939, **22**, 1160. [11] Burawoy, J., 1941, 20. [12] Aldersley, Burkhardt, Gillam, and Hindley, J., 1940, 10. [13] Barraclough, Batty, Heilbron, and Jones, J., 1939, 1549. [14] Jones and Koch, J., 1940, 10. [15] Butenandt, Schramm, and Kudzsus, *Annalen*, 1937, **531**, 176.

Examination of the data in Table II shows that all known dienones and dienals in alcoholic solution absorb light maximally between the limits 2690—3170 A., the intensity (ε) being of the order 20,000—30,000 if we exclude a number of very low values as being probably due to impure materials (cf. Table II).

The primary members of the series (CH_2:$CH\cdot CH$:$CH\cdot COR$) are not known, and attempts to prepare them have so far yielded only resinous products. The only three monosubstituted members on which data are available are very consistent in the location of λ_{max} at 2700 $\pm$ 10 A. More disubstituted members are available, mainly of the steroid type, and these absorb maximally between 2760 and 2850 A. except the two non-steroid compounds which have their absorption band displaced to longer wave-lengths, *i.e.*, 2900 and 2910 A. This gives a mean value of 2835 $\pm$ 75 A. for all the disubstituted members.

The trisubstituted compounds (with one exception) range from 2930 to 3090 A., with the average location at 3010 $\pm$ 80 A. β-Ionone and β-*cyclo*citrylideneacetaldehyde are abnormal only in their low intensity values. This cannot be explained on the grounds of impurity, since rigorously purified β-ionone has previously been noted for its low ε value as well as for its abnormally absorbing semicarbazone (Burawoy, J., 1941, 20). The location of the band of (IIA) at 2815 A. is so much outside the normal range for trisubstituted derivatives that one is inclined to doubt its structure.

(IIA.)

Values on tetra- and penta-substituted compounds are only available on bromo-substituted derivatives. On the somewhat doubtful assumption that bromine as a substituent behaves like an alkyl group we get some evidence of a normal bathochromic effect but there is too little evidence on which to generalise.

In αβ-unsaturated carbonyl compounds it was found earlier that the aldehydes usually absorbed at slightly shorter wave-lengths than the corresponding ketones (average *ca.* 50 A.). In the more unsaturated compounds which form the subject of this paper the difference between aldehydes and ketones seems to have disappeared. Thus $\Delta^{3:5}$-heptadien-2-one and $\Delta^{2:4}$-hexadienal absorb at almost the same wave-length (2705 $\pm$ 5 A.), and citrylideneacetaldehyde and ψ-ionone similarly both absorb at 2905 $\pm$ 5 A.

The absence of sufficient data on compounds containing *exo*cyclic double bonds precludes the possibility of making a sound generalisation on their effect, but it is notable that the two trisubstituted dienones that absorb at 3090 A., *i.e.*, at wave-lengths longer than the other members of their class, each contain two *exo*cyclic ethylene linkages such as have been shown by Woodward (*loc. cit.*) to exert a distinct bathochromic effect in the simpler chromophore group in αβ-unsaturated ketones.

In comparison with earlier experience on αβ-unsaturated compounds, where it was shown that substitution by alkyl groups on the carbon atom furthest removed from the carbonyl group produced a greater bathochromic effect than when the substitution was in the α-position (Evans and Gillam, J., 1941, 815), we might have expected some similar effect in dienones. Examination of the data in Table II shows in fact that a δ-substituent exerts a greater bathochromic effect than others; for instance, the δδ-substituted citrylidene-acetaldehyde ($\lambda_{max.} = 2900$ A.) and ψ-ionone ($\lambda_{max.} = 2900$ A.) absorb at longer wave-lengths than typical αδ- and βδ-substituted compounds ($\lambda_{max.} = 2790$—2860 A.).

Subject to the superimposed secondary effects of factors such as exocyclic ethylene linkages and the effect of substituents relative to the carbonyl group, the broad generalisation emerges that, as in αβ-unsaturated ketones, there is a bathochromic effect of *about* 100 A. for each successive substituent group (Table III) despite the apparent anomalies most of which are due to known disturbing factors.

TABLE III.

The effect of alkyl substituents on the location of the absorption maximum.

Dienones and dienals.	$\lambda_{max.}$, A. (order).	Dienones and dienals.	$\lambda_{max.}$, A. (order).
Unsubstituted (no known examples)	2600 ?	Trisubstituted	2900
Monosubstituted	2700	Tetrasubstituted	3000
Disubstituted	2800	Pentasubstituted	3100

In the previous discussion a small group of dienones and dienals has been deliberately omitted, *i.e.*, those having two ethylenic linkages in a single ring system, although several compounds of type (III) have been examined spectroscopically. From results given by the corresponding cyclic 1 : 3-dienes, it is to be expected that these compounds would have their absorption maxima displaced to considerably longer wave-lengths as compared with their acyclic analogues (cf. Booker, Evans, and Gillam, J., 1940, 1453; Woodward, *loc. cit.*, 1942) and this is found to be the case. Thus (IV) has $\lambda_{max.}$ 3160 A., ε = 10,900 (Barraclough *et al.*, J., 1939, 1549) and (V) has $\lambda_{max.}$ 3170 A., ε = 6,310. (Heilbron *et al.*, J., 1938, 102). Both these wave-length values are abnormally high. Safranal (VI) has $\lambda_{max.}$ 3000 A., ε = 19,000 (Kuhn and Winterstein, *Ber.*, 1934,

(III.)   (IV.)   (V.)   (VI.)   (VII.)
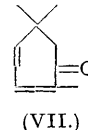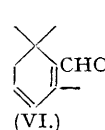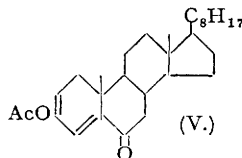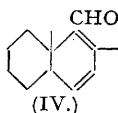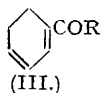
67, 344) and is thus not quite so abnormal as the compounds just mentioned. Eucarvone (VII) is not strictly comparable, since the two double bonds are situated in one ring and that a seven-atom one; it is moreover

abnormal in the very low intensity of its absorption : $\lambda_{max.}$ 3035 A., $\varepsilon = 6{,}300$ (Gillam and West, J., 1942, 483).

Derivatives of Dienones and Dienals.—The well-crystallised semicarbazones of new dienones and dienals of unknown structure are often available when the parent carbonyl compounds are not, and the characteristic absorption spectra of these semicarbazones can thus often be useful as a means of identification of the parent carbonyl compounds. Typical values are shown in Table IV and are all within the range 3090—3200 A. ($\varepsilon = 20{,}000$—$30{,}000$). The only exceptions appear to be the semicarbazones of β-ionone ($\lambda_{max.}$ 2765 A., $\varepsilon = 23{,}300$) and of eucarvone (two bands), the parent ketones of which have already been noted as abnormal. Thus the semicarbazones of dienones and dienals are with these exceptions readily distinguished from those of the αβ-unsaturated ketones by a displacement of their absorption maximum by some 500 A. (cf. Part III) to longer wave-lengths corresponding to the increased length of the conjugated system.

Of the substituted semicarbazides which are useful in the preparation of derivatives of carbonyl compounds, phenylsemicarbazide is among the simplest, although from the point of view of absorption spectra it possesses the complication of a chromophoric group (the benzene nucleus) in addition to that of the particular carbonyl condensation product. For instance, phenylsemicarbazide NHPh·CO·NH·NH$_2$ itself exhibits a single absorption band ($\lambda_{max.}$ 2475, $\varepsilon = 16{,}420$), very like that of the related acetanilide ($\lambda_{max.}$ 2385, $\varepsilon = 13{,}550$), whereas acetonephenylsemicarbazone absorbs at the same location but at a greater intensity, *i.e.*, $\lambda_{max.}$ 2470, $\varepsilon = 20{,}720$.

TABLE IV.

Absorption spectra of dienone and dienal semicarbazones.

Semicarbazone of—	$\lambda_{max.}$, A.	$\varepsilon_{max.}$.	Solvent.
$\Delta^{3:5}$-Heptadien-2-one	2900	37,000	EtOH
4-Ethyl-$\Delta^{3:5}$-nonadien-2-one	2950	38,600	—
4-Methyl-$\Delta^{4:6}$-octadien-3-one	2910	33,500	—
ψ-Ionone [1]	2995	45,400	EtOH
iso-Ergosterone [2]	3080	22,300	CHCl$_3$
2-Keto-5-acetoxy-αβ-di*cyclo*hexylidene-ethane [3]	3090	22,030	EtOH
Eucarvone [4]	{2270 / 3090	8,030} / 16,460}	EtOH
1-Keto-3-*cyclo*hexenyl-Δ^2-octahydronaphthalene [5]	3000	25,100	EtOH

[1] Burawoy, J., 1941, 20.   [2] Wetter and Dimroth, *Ber.*, 1937, **70**, 1665, 2033.   [3] Aldersley, Burkhardt, Gillam, and Hindley, J., 1940, 10.   [4] Gillam and West, J., 1942, 483.   [5] Jones and Koch, J., 1942, 393.

The phenylsemicarbazones of αβ-unsaturated carbonyl compounds, on the other hand, are all characterised by *two* intense and well-defined absorption bands near 2380 A., $\varepsilon = $ order 20,000, and near 2780 A., $\varepsilon = $ order 30,000. By comparison with acetanilide and phenylsemicarbazide itself, it would appear that the 2380 A. band is due to the NHPh·CO· chromophore, whilst the 2780 A. band of higher intensity is associated with the conjugated system originally present in the carbonyl compound, now modified from $-\overset{|}{C}\colon\overset{|}{C}\cdot\overset{|}{C}\colon O$ to $-\overset{|}{C}\colon\overset{|}{C}\cdot\overset{|}{C}\colon N-$.

When the phenylsemicarbazide is condensed with a conjugated dienone we again find two absorption maxima in the spectrum, one of which, at 2380 A., is due to the reagent, and the other, displaced to longer wave-lengths, is again due to the modified conjugated system of the dienone (now $-\overset{|}{C}\colon\overset{|}{C}\cdot\overset{|}{C}\colon\overset{|}{C}\cdot\overset{|}{C}\colon N-$) being situated at 3000—3090 A. (cf. Table V). It will be observed that once again the β-ionone derivative is abnormal in that the band is at an unusually low wave-length. Just what the explanation of this consistent discrepancy in the light absorption of β-ionone and its derivatives may be is not at present clear.

TABLE V.

Absorption spectra of carbonyl phenylsemicarbazones.

	Phenylsemicarbazide band.		Phenylsemicarbazone band.	
αβ-Unsaturated carbonyl compounds.	$\gamma_{max.}$, A.	ε.	$\gamma_{max.}$, A.	ε.
Carvone	2375	14,700	2775	28,200
Piperitone	2395	23,750	2810	30,500
1-Methyl*cyclo*hexen-3-one	2390	19,100	2780	30,800
β-*cyclo*Citral [1]	2365	19,800	2805	26,600
Compound C$_{15}$H$_{32}$O [1]	2365	21,100	2765	40,600
Dienones.				
ψ-Ionone	2375	14,400	3090	49,000
β-Ionone	2360	19,200	2890	28,600
4-Ethyl-$\Delta^{3:5}$-nonadien-2-one	2380	12,700	3025	41,000
$\Delta^{3:5}$-Heptadien-2-one	2400	16,200	3000	46,000
Acetanilide [2]	2385	13,550	—	—
Phenylsemicarbazide	2475	16,420	—	—
Acetonephenylsemicarbazone	2470	20,720	—	—

[1] Burawoy, J., 1941, 20.   [2] Klingstedt, *Z. physikal. Chem.*, 1928, B, **1**, 74.

EXPERIMENTAL.

$\Delta^{3:5}$-Heptadien-2-one was prepared by condensing freshly distilled crotonaldehyde (100 g.) with acetone (100 g.) in the presence of sodium hydroxide (10 g.) dissolved in alcohol (100 ml.), the aldehyde being added with stirring and cooling so that the temperature remained below 5°. The ethereal extract was washed with dilute sulphuric acid and water, dried, the ether removed, and the product distilled in a vacuum through a short column, giving about 10 ml. of low-boiling product. A further distillation was carried out before spectroscopic examination; b. p. 75—78°/15 mm. ψ-Ionone was prepared similarly from acetone and citral; b. p. 146—148°/14 mm.

4-Ethyl-$\Delta^{3:5}$-nonadien-2-one was prepared by condensation of 2-ethyl-Δ^{2}-hexenaldehyde (100 g.) (see Part II) with acetone (100 g.); yield 20 ml.; b. p. 116—118°/15 mm.

3-*Methyl*-$\Delta^{4:6}$-*octadien*-3-*one.* Condensation of crotonaldehyde with diethyl ketone gave only a few ml. of low-boiling liquid, much of it polymerising in the condenser; b. p. 103—105°/15 mm.

Semicarbazones were prepared in the usual manner and purified by recrystallisation from aqueous alcohol. Phenyl-semicarbazones were prepared by warming the carbonyl compound with 4-phenylsemicarbazide in aqueous alcohol, the products being finally recrystallised from 95% alcohol.

Absorption spectra were determined by standard methods using a Hilger E3 quartz spectrograph and a Spekker photometer, pure aldehyde-free ethyl alcohol being the solvent usually employed.

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