

144. *The Effect of Molecular Environment on the Absorption Spectra of Organic Compounds in Solution. Part II. $\alpha\beta$ -Unsaturated Ketones.*

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The absorption spectra of a number of $\alpha\beta$ -unsaturated ketones have been examined, and the new data discussed as a test of Woodward's recent generalisation (*J. Amer. Chem. Soc.*, 1941, **63**, 1123) that the nature of the substitution of the chromophoric group in these compounds can be predicted from the location of the main absorption band. It has been found that, with very few exceptions, Woodward's main thesis holds well, and the generalisation thus extends the usefulness of absorption spectra to the structural organic chemist.

The effect on the absorption spectra produced by substituting simple $\alpha\beta$ -unsaturated ketones with methyl groups stepwise has also been studied. It has been found that substitution on the β -carbon atom produces a larger bathochromic effect than does substitution on the α -carbon atom.

The structural implications to be drawn from the observed absorption spectra of certain ketophenanthrene derivatives have also been discussed.

IN Part I (J., 1940, 1453) new and old absorption-spectra data on conjugated dienes were systematised in order to facilitate their use in the interpretation of the chemical structure of unknown dienes. Similar new and already published data on compounds containing the related conjugated system $C=C-C=O$ have been collected and considered by us, but since we started this work the existing data on compounds containing this chromophore have been discussed by Woodward (*loc. cit.*). New absorption-spectra data on $\alpha\beta$ -unsaturated ketones are now brought forward and discussed with the older data and in the light of Woodward's generalisations.

The characteristic absorption spectra of individual $\alpha\beta$ -unsaturated carbonyl compounds have been known for a considerable time, *e.g.*, citral and mesityl oxide (Bielecki and Henri, *Ber.*, 1914, **47**, 1690; Henri, "Photochimie," 1919, Paris), but it was Menschick, Page, and Bossert (*Annalen*, 1932, **495**, 225) who first clearly suggested that the presence of a highly intense absorption band ($\log \epsilon = ca. 4.0$) between 2200 and 2500 \AA . in the absorption spectrum of an unsaturated ketone was reasonable evidence of conjugation of the ethylene linkage with the carbonyl group. Since then, this test for the chromophoric group $C=C-C=O$ has been successfully applied to many compounds of various types. It should be remembered, however, that if the substituents on the chromophore are other than hydrogen atoms or saturated hydrocarbon residues the absorption band may be displaced outside the above limits. It is proposed to review this aspect of the subject in a later paper.

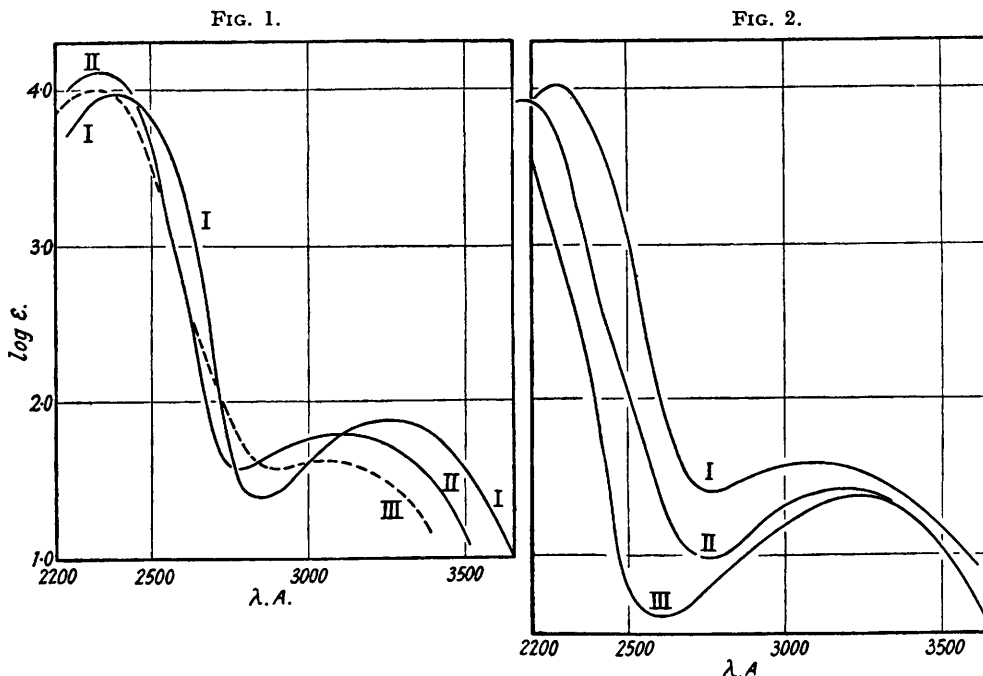
The absorption spectra of saturated ketones are notable for a band of low intensity (ϵ of the order of 10—100) situated close to that of acetone near 2750 \AA ., but the location of the band is very much influenced by the molecular environment (cf. Ramart-Lucas, *Bull. Soc. chim.*, 1932, **51**, 289; Gillam, *J. Roy. Coll. Sci.*, 1940, **10**, 21; Part I, *loc. cit.*). Ethylene, on the other hand, exhibits an absorption band of high intensity (ϵ of the order of 10,000) near 1950 \AA . When, however, an ethylenic and a carbonyl group are conjugated in the same molecule the effect is apparently to displace both bands towards longer wave-lengths. Hence, we get the characteristic absorption spectrum of an $\alpha\beta$ -unsaturated ketone (cf. Fig. 1) with its highly intense *K*-band and its low-intensity *R*-band due to the carbonyl group.* Although the ethylene band is characteristic, the carbonyl band is absent in certain special cases (*e.g.*, ascorbic acid).

Woodward (*loc. cit.*) tabulated the wave-lengths of the absorption maxima of some fifty compounds of this type, and his analysis of the data shows that these compounds fall into three classes, as follows:

Substitution of the $C=C-C=O$ group.	Location of intense absorption band, \AA .
Monosubstitution (α or β)	2250 \pm 50
Disubstitution ($\alpha\beta$ or $\beta\beta$)	2390 \pm 50
Trisubstitution ($\alpha\beta\beta$)	2540 \pm 50

* For definitions of *K*-bands and *R*-bands, see Burawoy, J., 1939, 1177.

In the course of the present work we have prepared and investigated the absorption spectra of further compounds of this type, a number of them specially designed to test the effect of substituents (particularly methyl groups) on the light absorption (cf. Table I).



Absorption spectra of ethyl-alcoholic solutions of:—
I. Cedrone. II. 1-Methylcyclohexen-3-one.
III (broken line). Tetrahydroacetophenone.

Absorption spectra of ethyl-alcoholic solutions of:—
I. Butylideneacetone. II. Methyl isopropenyl ketone.
III. Methyl vinyl ketone.

TABLE I.

Absorption spectra of $\alpha\beta$ -unsaturated ketones in alcohol.

Compound.	K-Band.		R-Band.		Substitution of C=C=O group.*
	$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\max.}$	$\epsilon_{\max.}$	
Methyl vinyl ketone	< 2190	> 3,600	3240	24	H only
2-Ethyl- Δ^1 -hexen-3-one	2210	6,460	3200	26	mono, α
2-Methyl- Δ^1 -penten-3-one	2200	7,880	3195	26.7	mono, α
Methyl isopropenyl ketone (I)	2180	8,300	3190	26.5	mono, α
"2-Methyl-6-methylenecyclohexanone" †	2365	6,840	3230	40	mono, α ?
Ethylideneacetone (II)	2240	9,730	3135	37.5	mono, β
Butylideneacetone (III)	2280	10,600	3100	39	mono, β
Irone ¹	2280	11,400	3080	100	mono, β
α -Ionone ¹	{ 2280	{ 13,300	{ (3050)	{ —	{ mono, β
Mesityl oxide ² (IV)	2350	14,000	3135	58	di, $\beta\beta$
1-Methylcyclohexen-3-one	2350	12,930	3100	48	di, $\beta\beta$
Cedrone	2400	9,330	3260	27	di, $\beta\beta$
2:3:4:5-Tetrahydroacetophenone	2335	9,660	3050	44	di, $\alpha\beta$
3-Methyl- Δ^2 -penten-2-one (V)	2295	11,090	3100	42	di, $\alpha\beta$
Carvotanacetone ³	2330	9,150	—	—	di, $\alpha\beta$
isoThujone ³	2375	12,000	3100	80	tri-?
cycloHexylidene-cyclohexanone	2575	> 800	—	—	tri-
3:4-Dimethyl- Δ^2 -penten-2-one (VI)	2490	> 4,000	—	—	tri-
1:2:3-Dimethyl-4-isopropyl- Δ^2 -cyclopentenone ³	2310	6,180	3100	35	tri-?
(I.) $\text{CH}_2:\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$	(II.) $\text{CH}_2:\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	(III.) $\text{CH}_2:\text{CH}_2:\text{CH}_2:\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$			
(IV.) $\text{CMe}_2:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	(V.) $\text{CHMe}\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$	(VI.) $\text{CMe}_2:\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$			

¹ Gillam and West, *Nature*, 1941, 148, 114. ² Morton, J., 1926, 719. ³ Gillam and West, preceding paper. ⁴ Burawoy, this vol., p. 20.

* For significance of α and β , see formula (I) in preceding paper.

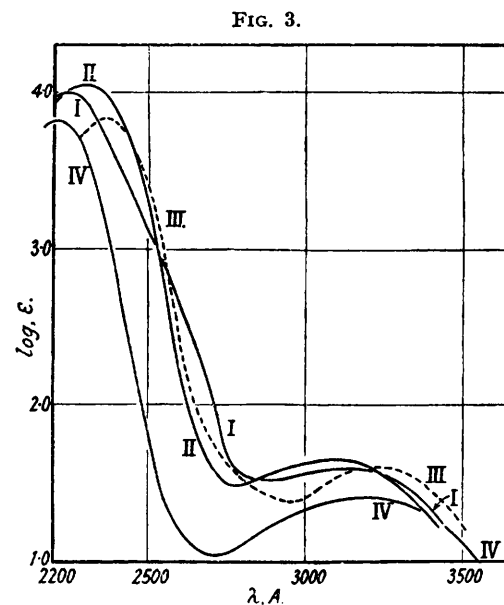
† See p. 818.

It was intended that this survey of the absorption data of α - β -unsaturated carbonyl compounds should include both aldehydes and ketones, but it has been found that the aldehydes present certain anomalies which are being investigated further, and in view of this and the scarcity of published light-absorption data on these compounds more data are being obtained before attempting a generalisation.

Examination of the data in Table I shows that Woodward's generalisation holds in the majority of cases; *isothujone* is apparently exceptional, but there is some doubt about its formula (see preceding paper).

When considering the chromophoric group in an organic compound with a view to predicting the probable location of the absorption band the presence of methyl groups is relevant since, although normally regarded as transparent groups, these and similar saturated radicals exert an environmental effect on the absorption due to conjugated systems. This effect is almost invariably bathochromic, and in the case of the conjugated dienes (see Part I, *loc. cit.*) the increment for a methyl group is 50–100 Å., a value comparable with that observed by Kuhn and Grundmann (*Ber.*, 1937, 70, 1318) for the carotenoid series, where it is found that a methyl group exerts a bathochromic effect equivalent to about one quarter of that produced by a conjugated ethylenic linkage.

Woodward's data show that the replacement of one hydrogen atom by a single alkyl or substituted-alkyl group results in a bathochromic displacement of the absorption band which *on the average* amounts to 150 Å. Data on the following set of simple unsaturated ketones demonstrate the effect of introducing methyl groups stepwise, and it is clear that in individual cases there are wide variations from the average increment; *e.g.*, for one methyl group in this set of compounds the increment ranges from 50 to 195 Å. One generalisation stands out clearly within this rather limited series, *viz.*, that replacement of hydrogen by methyl on the β -carbon atom produces a greater displacement of the absorption band than does substitution on the α -carbon atom, and further, that the difference between α - and β -substitution is approximately constant at 55 Å. in each of the three pairs of compounds considered (cf. Table II).



Absorption spectra of ethyl-alcoholic solutions of:—
I. Ethylideneacetone. II. 3-Methyl- Δ^3 -penten-2-one.
III. "2-Methyl-6-methylenecyclohexanone" (broken line). IV. 2-Ethyl- Δ^1 -hexen-3-one.

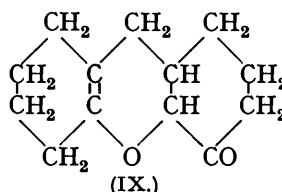
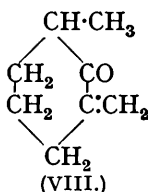
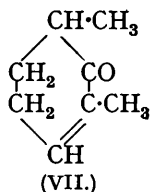
TABLE II.

Compound.	λ_{max} of K-band, Å.		λ_{max} of K-band, Å.
$\text{CH}_2\text{:CH}\cdot\text{CO}\cdot\text{CH}_3$	A. <2190	$\text{CHMe}\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$	D. 2295
$\text{CH}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$	B. 2180	$\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	E. 2350
$\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$	C. 2240	$\text{CMe}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}_3$	F. 2490
α -Substitution.	β -Substitution.	Greater displacement due to β -substitution.	
A to B = x Å.	A to C = $x + 50$ Å.	50 Å.	
C to D = 55 Å.	B to D = 115 Å.	60 Å.	
E to F = 140 Å.	D to F = 195 Å.	55 Å.	

In order to confirm the first generalisation, it was decided to prepare and examine one or more further α -substituted compounds, 2-ethyl- Δ^1 -hexen-3-one and 2-methyl- Δ^1 -penten-3-one being chosen as representative examples. The absorption-spectra results are shown

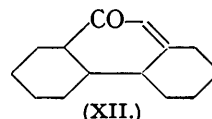
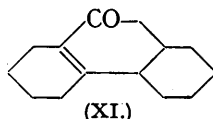
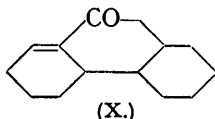
in Table I and it will be seen that, as expected, these compounds have their main absorption band situated at shorter wave-lengths than is usual with similar β -substituted derivatives.

A further compound of this type which has also been examined is "2-methyl-6-methylencyclohexanone," which, according to du Feu, McQuillin, and Robinson (J., 1937, 53), is obtained when the Mannich reaction is carried out with 2-methylcyclohexanone and diethylamine hydrochloride. The final product (see p. 820) was found to exhibit an absorption maximum at 2365 A. ($\epsilon = 6840$), which would be more consistent with a disubstituted $\alpha\beta$ -unsaturated ketone (2390 ± 50 A.) than with the β -substituted compound believed to be present by du Feu *et al.* (*loc. cit.*). It seems probable in the light of this spectroscopic evidence that the exocyclic ethylene linkage has moved into the ring to give (VII)—containing a disubstituted C=C-C=O group—instead of (VIII), and thus that we are not dealing with the $\alpha\beta$ -unsaturated ketone that was expected.



According to Dimroth, Resin, and Zetsch (*Ber.*, 1940, 73, 1399; from *Chem. Abs.*, 1941, 35, 2866), the product obtained by Mannich from cyclohexanone is not the expected methylenecyclohexanone but the saturated *o*-methylcyclohexanone, whilst other methods give the dimeric ketone (IX). It is clear that the ketone prepared by us is not analogous with either of these two compounds, both of which should show only the low-intensity absorption band due to the isolated carbonyl group.

In the course of work on the stereoisomerism of the perhydrophenanthrenes, Linstead and Walpole (J., 1939, 842) prepared two isomeric unsaturated ketones of m. p.'s 39° and 94° severally. Absorption-spectra data showed that the compounds were in fact



$\alpha\beta$ -unsaturated ketones, and from the chemical evidence their structures could be represented by (X) and (XI). These authors incline to the view, on evidence which is, as they point out, by no means conclusive, that the compound of m. p. 94° is (X) and that of m. p. 39° is (XI). This is a case in which Woodward's rule can be applied, since (X) is a disubstituted $\alpha\beta$ -unsaturated ketone, whereas (XI) has a trisubstituted C=C-C=O group and should therefore have its absorption maximum situated at longer wave-lengths than (X). In fact, Linstead and Walpole record that the absorption maxima of the two compounds are situated at 2410 A. for the compound of m. p. 39° and at 2470 A. for that of m. p. 94°. The solvent in which the absorption measurements were made is not recorded, but if it be assumed to be ethyl alcohol, the two compounds fall into line approximately as di- and tri-substituted $\alpha\beta$ -unsaturated ketones. Whatever the solvent, the absorption-spectra evidence indicates that the high-melting compound (which absorbs at longer wave-lengths) is represented by (XI) and the low-melting one by (X), a finding contrary to the other, admittedly inconclusive, evidence.

A third isomeric ketododecahydrophenanthrene, of m. p. 89°, had been prepared by Rapson and Robinson (J., 1935, 1285) who, on chemical grounds, assigned to it the formula (XII), which contains a disubstituted C=C-C=O chromophore. The absorption spectrum (λ_{\max} . 2380 A., $\log \epsilon_{\max}$. 4.14) was recorded by Linstead and Walpole, who conclude from this that the compound contains an $\alpha\beta$ -unsaturated ketone group. The location of the absorption band shows by Woodward's rule that the compound is a disubstituted $\alpha\beta$ -unsaturated ketone and thus lends support to the formulation (XII).

One other question arises in connection with the absorption spectra of $\alpha\beta$ -unsaturated ketones, *viz.*, whether the regular relation which Woodward has shown to exist between molecular structure in these compounds and the location of the short-wave absorption band also affects the location of the band due to the carbonyl group. Examination of the data in Table I, however, shows that such a regularity is entirely lacking.

EXPERIMENTAL.

Ethylideneacetone (II) was prepared by condensation of acetone and acetaldehyde in the presence of sodium hydroxide (Grignard and Fluchaire, *Ann. Chim.*, 1928, **9**, 5); dehydration was completed by distilling the solvent-free material over solid oxalic acid, a product of b. p. 110—140° being obtained. Two further fractionations through a short column gave a constant-boiling fraction, b. p. 122°.

Methyl vinyl ketone. A commercial sample was twice distilled in nitrogen under atmospheric pressure, a column being used; the main product boiled at 79—80°.

3-Methyl- Δ^3 -penten-2-one (V) was prepared by the method of Hinkel *et al.* (J., 1931, 817). The crude product (b. p. <160°) on fractionation gave the main bulk, b. p. 130—145°, and on redistillation a main fraction, b. p. 138°. Semicarbazone, m. p. *ca.* 200° (decomp.).

Butylideneacetone (III) was prepared by condensation of butaldehyde (obtained by oxidation of *n*-butyl alcohol) and acetone in the presence of sodium hydroxide (cf. Weizmann and Garrard, J., 1920, **117**, 334). The main product boiled at 140—180°, and after two fractionations had b. p. 157°. Semicarbazone, m. p. 116—117°.

2 : 3 : 4 : 5-Tetrahydroacetophenone (Darzens, *Compt. rend.*, 1910, **150**, 707). Acetyl chloride and cyclohexene were condensed together in carbon disulphide solution, stannic chloride being the agent. After treatment with water, the solvent was removed, the residue refluxed with dimethylaniline, and the product distilled. The crude product had b. p. 190—210°, and after three fractionations the main bulk boiled at 200—202° and was finally distilled in a vacuum. Semicarbazone, m. p. 220—221°.

3 : 4-Dimethyl- Δ^3 -penten-2-one (VI). Trimethylethylene was prepared by dehydrating amylene hydrate with 30% sulphuric acid (cf. Norris and Reuter, *J. Amer. Chem. Soc.*, 1927, **49**, 2630). The product (b. p. 37°) was condensed with acetyl chloride by means of stannic chloride, the mixture being meanwhile cooled in ice (cf. Colonge and Mostafi, *Bull. Soc. chim.*, 1939, **6**, 335). The mixture was hydrolysed with hydrochloric acid (15%), and, after being washed with water and sodium bicarbonate, was dried and vacuum distilled. The fraction, b. p. <40°/30 mm., was refluxed with dimethylaniline and fractionated, giving a main fraction, b. p. 140—150°/760 mm. The ketone was converted into the semicarbazone (m. p. 140—160°), which after six recrystallisations had m. p. >170°; 22 recrystallisations raised the m. p. to 190—193° (lit., 199°). The ketone was regenerated from the semicarbazone, m. p. >170°, with oxalic acid (20%), followed by ether extraction, but the best fraction (b. p. 140—150°) when examined spectroscopically gave a value for ϵ_{\max} of only 4000 at λ_{\max} 2490 Å. No more intensely absorbing fractions were obtained, although the low value of ϵ suggests that the material was far from pure.

Methyl isopropenyl ketone (I). This compound was prepared by Decombe's method (*Compt. rend.*, 1936, **202**, 1685). Condensation of methyl ethyl ketone with formaldehyde was effected by shaking for 14 days with potassium carbonate in the cold (D.R.P. 223,207). The pure ketone had b. p. 93° and was submitted to a final distillation under reduced pressure in an atmosphere of nitrogen immediately before being examined spectroscopically. Semicarbazone, m. p. 174—176°.

cycloHexylidenecyclohexan-2-one was prepared by passing dry hydrogen chloride through cooled cyclohexanone for 24 hours (Zelinski, Shuiken, and Fataev, *J. Gen. Chem., U.S.S.R.*, 1932, **2**, 671). After treatment of the brown oil with water, the resulting semi-solid hydrochloride was filtered off and treated with excess of sodium carbonate solution, followed by ether extraction. The purified product had b. p. 147° and an ϵ value of only 800. This low intensity of absorption suggests the predominance of an unconjugated isomer.

1-Methylcyclohexen-3-one. Methylene diacetoacetic ester was prepared by condensation of acetoacetic ester with formaldehyde in the presence of a trace of piperidine (cf. Knoevenagel and Klages, *Annalen*, 1894, **281**, 94). The crude product was decarboxylated and ring-closed by boiling with sulphuric acid (10%). The purified ketone had b. p. 195—197°, and immediately before spectroscopic examination was redistilled under reduced pressure in nitrogen (b. p. 97—98°/27 mm.).

Cedrone. The sample, for which we are indebted to Dr. T. F. West, had the following constants: m. p. 30—31°, b. p. 130—131°/2 mm., $[\alpha]_D - 69.4^\circ$, $n_D^{21} 1.5118$ (Found: C, 82.5; H, 10.1. Calc. for $C_{15}H_{22}O$: C, 82.6; H, 10.1%). The absorption spectrum (Fig. 1 and Table I) is typical of a disubstituted $\alpha\beta$ -unsaturated ketone and supports the structure $C_{11}H_{18} \begin{matrix} \text{CO} \\ \diagdown \quad \diagup \\ \text{CMe} \end{matrix} \text{CH}$ established on chemical grounds by Ruzicka and van Melsen (*Annalen*, 1929, 471, 54).

α -Ionone. The absorption spectrum of this compound has recently been reported by Burawoy (this vol., p. 20) but only the *K*-band was recorded. The ketone band is also present, but only as an inflexion of negligible persistence. On account of this lack of persistence and the marked overlap of the intense *K*-band it is not possible to give even an approximate value of ϵ for the *R*-band.

2-Methyl-6-methylenecyclohexanone was prepared by du Feu, McQuillin, and Robinson's method (J., 1937, 53) from 2-methylcyclohexanone. This compound (40 g.) was mixed with diethylamine hydrochloride (19.6 g.), paraformaldehyde (6.5 g.), and cyclohexanol (100 g.), and the mixture heated at 110° for 2 hours. After addition of water and ether to the cooled product, the aqueous layer was separated and concentrated, leaving a thick oil, some of which later crystallised. The oil was heated under reduced pressure and distilled, the aqueous distillate being dried before being again distilled in a vacuum. Most of it boiled over a narrow range (yield 6 c.c., ϵ of the order of 6000). After a further fractionation, the main product had b. p. 85—87°/30 mm. and gave an absorption band, $\lambda_{\max} 2365 \text{ \AA.}$, $\epsilon = 6840$.

2-Ethyl- Δ^1 -hexen-3-one, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CEt \cdot CH_2$. Butyrene, prepared by the method of Senderens (*Ann. Chim. Phys.*, 1913, 28, 243), was dried, distilled (b. p. 144°), and treated with 30% formalin, acetic acid, and dry hydrogen chloride and allowed to stand (Colonge, *Bull. Soc. chim.*, 1936, 3, 2116). The separated ketone was dried, and distilled in a vacuum, the fraction, b. p. <90°/14 mm., being re-treated with formalin and hydrogen chloride. The main product, consisting largely of 1-chloro-2-ethylhexanone, had b. p. 95—105°/16 mm., and this was heated with diethylaniline and fractionated, the product being washed with dilute acid to remove any diethylaniline and again fractionated (b. p. 155°/760 mm.).

2-Methyl- Δ^1 -penten-3-one, $CH_3 \cdot CH_2 \cdot CO \cdot CMe \cdot CH_2$. Diethyl ketone was prepared by passing propionic acid over thoria-pumice at 400—420° (cf. Senderens, *loc. cit.*) (yield ca. 80%, b. p. 104—106°). The chloro-ketone was obtained as above by Colonge's method (*loc. cit.*) and had b. p. 63—64°/12 mm. After treatment with diethylaniline as above, the purified product had b. p. 120—122°/760 mm.

Absorption Spectra.—These were determined with a Hilger E3 quartz spectrograph and a Spekker photometer by standard methods. Specially purified ethyl alcohol was used as solvent in all cases.

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