150. *The Effect of Molecular Environment on the Absorption Spectra of Organic Compounds in Solution. Part III. Compounds containing the Chromophore* $>C{=}\overset{|}{C}{-}\overset{|}{C}{=}N{-}$

By L. K. Evans and A. E. Gillam.

In continuation of earlier work on the absorption spectra of conjugated dienes and αβ-unsaturated ketones, the light absorption of various αβ-unsaturated aldehydes has been determined and discussed. Derivatives of carbonyl compounds containing the chromophore $>C{=}\overset{|}{C}{-}\overset{|}{C}{=}N{-}$, *i.e.*, semicarbazones, methylsemicarbazones, thiosemicarbazones, and oximes, have also been examined, and the data discussed with special reference to the detection of the $>C{=}\overset{|}{C}{-}\overset{|}{C}{=}O$ group in organic molecules. It is shown that the thiosemicarbazones of *saturated* aldehydes and ketones exhibit absorption bands near 2700 A. which are some 500 times more intense than those of the parent carbonyl compound, thus providing an additional means of spectroscopic detection of the *isolated* carbonyl group.

The primary factor determining the presence of a band in the absorption spectrum of an organic compound in solution is the occurrence of a so-called chromophoric group within the molecule. When such a group is known to be present the appearance of the corresponding absorption band can be expected. Even in the absence of definite combination between solvent and solute the precise location and intensity of this absorption band are not wholly predictable because of the effect of several variable factors such as the nature of the solvent, and, more particularly, the molecular environment of the chromophoric group. This point of view has been elaborated in Parts I and II (J., 1940, 1453; 1941, 815), in which chromophores containing two unsaturated linkages in conjugation have been considered, *i.e.*, (I) and (II). In this Part the absorption spectra of compounds containing the related chromophore (III) have been determined and discussed.

$>C{:}\overset{|}{C}{-}\overset{|}{C}{:}C<$ (I.)

$>C{:}\overset{|}{C}{-}\overset{|}{C}{:}O$ (II.)

$>C{:}\overset{|}{C}{-}\overset{|}{C}{:}N{-}$ (III.)

In Part II (*loc. cit.*) light-absorption data on αβ-unsaturated ketones were presented and discussed in the light of Woodward's suggestion (*J. Amer. Chem. Soc.*, 1941, **63**, 1143; 1942, **64**, 76) that the location of the *K*-band in the absorption spectra of such compounds is controlled by the number of substituents on the chromophore, and in fact that the degree of substitution can be inferred from the location of the band. Thus if $C\beta\beta'{:}C\alpha{\cdot}CR{:}O$ (IV) represents an αβ-unsaturated ketone where R is an alkyl group, and α, β, and β′ may be H (or any saturated hydrocarbon residue), we have Woodward's generalisation (*loc. cit.*) in its simplest form as follows :

αβ-Unsaturated ketone.	Location of *K*-band, A.	αβ-Unsaturated ketone.	Location of *K*-band, A.	αβ-Unsaturated ketone.	Location of *K*-band, A.
Monosubstitution, α or β	2250 ± 50	Disubstitution, αβ or ββ	2350 ± 50	Trisubstitution, αββ	2470 ± 50

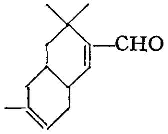
In Part II we had insufficient data on unsaturated aldehydes to justify their consideration, but there are now a sufficient number for a preliminary examination. In (IV), if we make R = H, we change from the unsaturated ketones to the unsaturated aldehydes, and since we have one alkyl group less here we might expect the substitution of H for alkyl to produce a displacement of the absorption band, due to the conjugated system, to shorter wave-lengths. In Table I are presented the absorption data on αβ-unsaturated aldehydes, and it will be seen that the maxima are, in fact, at shorter wave-lengths than for the corresponding ketones. Hence, to cover the majority of individual values in the unsaturated aldehyde series we must have a new set of empirically adjusted wave-lengths for λ max. in each of the three types of alkyl-substituted derivatives.

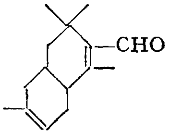
TABLE I.

Absorption spectra of αβ-unsaturated aldehydes and their semicarbazones in alcohol.

Compound.	*R*-Band. λ, max.	*R*-Band. ε, max.	*K*-Bands. Aldehydes. C=C—C=O. λ, max.	*K*-Bands. Aldehydes. C=C—C=O. ε, max.	*K*-Bands. Semicarbazones. C=C—C=N. λ, max.	*K*-Bands. Semicarbazones. C=C—C=N. ε, max.	Δλ, A.	Δε.	Substitution of aldehyde.
Acraldehyde	3278	12·6	2083 [1]	—	2645	19,000	—	—	—
Crotonaldehyde	3205	19·5	2170 [2]	15,650	2645	24,000	475	8,350	mono
Tiglinaldehyde	2900	11·3	2280	>5,000	2640	19,700	360	<10,000	di
β-Methylcrotonaldehyde [3]	—	—	2350	6,700	2730	33,460	380	26,760	di
α-Ethyl-Δ$^{\alpha}$-hexenaldehyde	3130	27	2285	10,670	2320	9,260	35	—	di
Citral [4]	3240	65	2380	13,500	2720	31,350	340	17,850	di
β-*cyclo*Citral [4]	3280	43	2445	8,300	2720	23,800	275	5,500	tri
*cyclo*Hexylideneacetaldehyde [5]	—	—	2320	17,400	2740	32,300	420	14,900	di
Phellandral:									
(*a*) *ex* water-fennel oil	—	—	2320	—	2650	24,500	307	5,730	di
(*b*) *ex* phellandrene	—	—	2325	—	2650	24,200			
(*c*) data by Cooke and Macbeth [6]	3125	417	2285	18,620	—	—			
α-Decylideneacetaldehyde [5]	—	—	2350	15,000	2730	32,400	380	17,400	di
β-Decylideneacetaldehyde [5]	—	—	2340	17,100	2740	31,000	400	13,900	di
Compound (V)	—	—	2350 [7]	14,000	2680	33,300	350	19,300	di
Compound (VI)	—	—	2400 [7]	8,000	2670	27,500	270	19,500	tri
Δ^{2}-2-Formylcholestene [8]	—	—	2350	12,600	—	—	—	—	di

(V.)





(VI.)

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[1] Luthy, *Z. physikal. Chem.*, 1923, **107**, 284.
[2] Haüsser *et al.*, *Z. physikal. Chem.*, 1935, *B*, **29**, 371.
[3] Barraclough, Thesis (Manchester University).
[4] Burawoy, J., 1941, 20 (cf. also Bielecki and Henri, *Ber.*, 1914, **47**, 1690).
[5] Dimroth, *Ber.*, 1938, **71**, 1333.
[6] Cooke and Macbeth, J., 1938, 1408.
[7] Batty, Heilbron, and Jones, J., 1939, 1556.
[8] Plattner and Jampolsky, *Helv. Chim. Acta*, 1941, **24**, 1459.

The following set of values appears to fulfil the requirements for these aldehydes and is related to the above set for unsaturated ketones by being uniformly 50 A. lower:

αβ-Unsaturated aldehyde.	Location of *K*-band, A.	αβ-Unsaturated aldehyde.	Location of *K*-band, A.	αβ-Unsaturated aldehyde.	Location of *K*-band, A.
Monosubstitution, α or β	2200 ± 50	Disubstitution, αβ or ββ	2300 ± 50	Trisubstitution, αββ	2420 ± 50

Probably the simplest type of compound containing the group (III) is to be found in the semicarbazones of αβ-unsaturated ketones and aldehydes, and several workers have recorded the absorption spectra of isolated examples of such compounds (cf. Menschick *et al.*, *Annalen*, 1932, **495**, 225; Burawoy, J., 1941, 20). Figs. 1 and 2 show the absorption spectra of typical αβ-unsaturated ketones and their semicarbazones, the displacement of the maximum to longer wave-lengths, the disappearance of the band due to the carbonyl group, and a distinct increase in intensity of absorption being usually observed in passing from the carbonyl compound to its semicarbazone. Hence, the inference of the presence of the group (II) in a molecule from the occurrence of an absorption band situated between 2200 and 2500 A. and with ε of order 10,000, is very much strengthened by the observation that this band is displaced to longer wave-lengths with an increase in intensity in the semicarbazone.

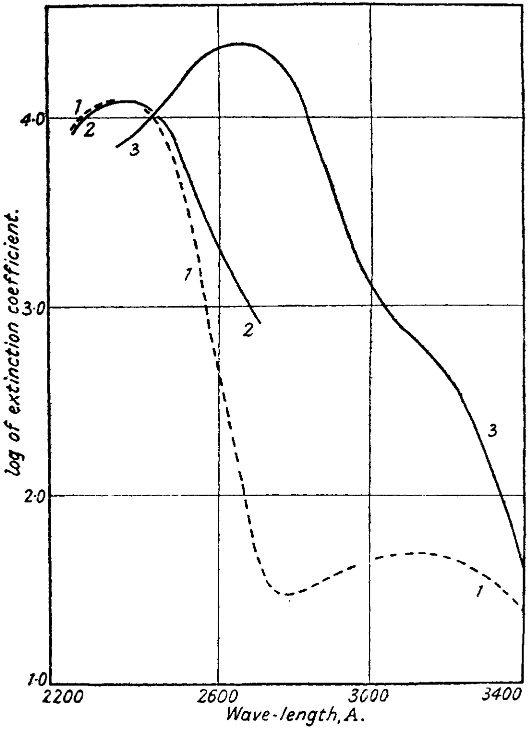
These bathochromic and hyperchromic effects are evident from the data on ketones in Table II as well as from the figures. Table I shows the corresponding data on unsaturated aldehydes and their semicarbazones, and it is clear that the results with unsaturated ketones are closely paralleled by the data on the analogous aldehydes.

Pulegone appears to be exceptional among αβ-unsaturated ketones in that the location of the absorption band of its semicarbazone is scarcely displaced from that of the ketone. Menschick *et al.* (*loc. cit.*) give λ max. 2520 and 2530 A. for the ketone and the semicarbazone respectively, and we have confirmed these observations. The anomaly is, of course, not so much in the small difference between these two values as in the low wave-length value for the location of the absorption band of the semicarbazone, since the wave-length of maximum absorption of pulegone itself is already unusually high because pulegone is a trisubstituted αβ-unsaturated ketone. On the other hand, the low wave-length value for the semicarbazone is hardly likely to be due to the presence of the unconjugated *iso*pulegonesemicarbazone, as this absorbs maximally near 2200 A. (Menschick *et al.*, *loc. cit.*).

Amongst the aldehydes, there is an almost exactly analogous case in α-ethyl-Δ$^{\alpha}$-hexenaldehyde where the semicarbazone gives an absorption band which is only slightly displaced to longer wave-lengths from that of the original carbonyl compound (35 A.) As in the case of pulegone, the intensity of absorption of the semicarbazone is much lower than usual (cf. Table II).

FIG. 1.

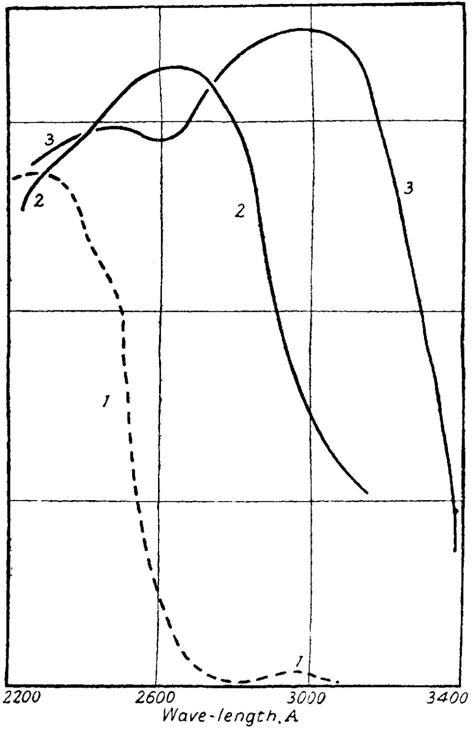
Absorption spectra in alcoholic solution.



1. 3-*Methyl*cyclo*hexen*-1-*one*.
2. ,, *oxime*.
3. ,, *semicarbazone*.

FIG. 2.

Absorption spectra in alcoholic solution.



1. *Tiglinaldehyde*.
2. ,, *semicarbazone*.
3. ,, *thiosemicarbazone*.

TABLE II.

Comparison of absorption spectra of $\alpha\beta$-*unsaturated ketones and their semicarbazones.*

K-Bands only.

	C=C—C=O.		C=C—C=N.			
Compound.	λ, max., A. †	ε, max.	λ, max., A.†	ε, max.	$\Delta\lambda$, A.	$\Delta\varepsilon$.
$CH_3\cdot CO\cdot CMe{:}CH_2$	2180 [1]	8,300	2595	21,000	415	12,700
$CH_3\cdot[CH_2]_2\cdot CH{:}CH\cdot CO\cdot CH_3$	2280 [1]	10,600	2645	25,500	365	14,900
$CH_3\cdot CH_2\cdot CO\cdot CMe{:}CH_2$	2200 [1]	7,880	2600	18,800	400	10,920
$CH_3\cdot CMe{:}CH\cdot CO\cdot CH_3$	2350 [2]	14,000	2600 [3]	12,020	250	—
$CH_3\cdot CH{:}CMe\cdot CO\cdot CH_3$	2295 [1]	11,090	2595	23,800	300	12,710
Piperitone	2355 [7]	17,780	2660	19,300	305	1,520
Carvone	2350 [9]	19,000	2660	21,200	310	2,140
1-Methyl*cyclo*hexen-3-one	2350 [1]	12,930	2655	25,700	305	12,770
2 : 3 : 4 : 5-Tetrahydroacetophenone	2335 [1]	9,660	2605	20,150	270	10,890
2 : 4-Dimethyl*cyclo*hexen-3-one	2365 [1]	6,840	2645	19,700	280	12,860
α-Ionone	2280 [4]	13,300	2635 [5]	31,600	355	18,300
Carvotanacetone [6]	2330	9,150	2680	24,900	350	15,750
*iso*Thujone [6]	2375	12,000	2670	24,800	295	12,800
Tetrahydropyrethrolone [8]	2320	12,200	2650	22,200	330	10,000
Dehydrojasmone [8]	2370	12,200	2665	20,400	295	8,200
$\Delta^{4\cdot7}$-Ergostadienone-3 [10]	2410	15,230	2670 *	36,830	320	21,600
Δ^1-Coprosten-3-one [11]	<2360	>5,840	2700 *	9,670	340	<3,830
Δ^4-Androstenedione-3 : 17 [13]	2380	16,500	2650 *	35,000	370	18,500
Δ^4-Cholesten-3-one	2400 [3]	16,220	2730	26,300	330	10,080
	2405 [17]	18,000	2705 [12]	26,000	300	8,000
Fucostadienone [12]	2400	17,000	2715	27,000	315	10,000
Stigmastadienone [12]	2410	17,000	2710	29,000	300	12,000
Sitostenone [12]	2410	17,000	2720	25,000	310	8,000

* Observed values in chloroform. † Values for ethyl-alcoholic solution.

[1] Evans and Gillam, J., 1941, 815. [2] Morton, J., 1926, 719. [3] Menschick, Page, and Bossert, *Annalen*, 1932, **495**, 225. [4] Gillam and West, *Nature*, 1941, **148**, 114. [5] Burawoy, J., 1941, 20. [6] Gillam and West, J., 1941, 811. [7] Gillam, Lynas-Gray, Penfold, and Simonsen, J., 1941, 60. [8] Gillam and West, J., 1942, 483. [9] Cooke and Macbeth, J., 1938, 1408. [10] Wetter and Dimroth, *Ber.*, 1937, **70**, 1665, 2033. [11] Inhoffen and Hueng-Minlon, *Ber.*, 1938, **71**, 1720. [12] Jones, Wilkinson, and Kerlogue, J., 1942, 391. [13] Butenandt and Peters, *Ber.*, 1938, **71**, 2690.

With these two exceptions, the absorption bands of the semicarbazones of some 33 αβ-unsaturated aldehydes and ketones all fall within the range 2670 ± 75 A., the intensities (ε) ranging from 10,000 to 35,000 with an average value near 26,000 (Tables I and II). It would therefore seem that the substituent effect observed in the unsaturated aldehydes and ketones disappears in the semicarbazones (see the similar case of the oximes, p. 570).

Although we accept as a useful fact the observation that semicarbazones have their main absorption band situated about 350 A. to longer wave-lengths than the chromophorically-similar oximes, no satisfactory explanation has yet been put forward. It would seem either that the molecular environment is sufficient to displace the absorption due to the chromophore (III) to longer wave-lengths in the semicarbazones, or that there might be an increase in the length of the conjugated system, possibly brought about by enolisation as follows:

$$CRR'{:}CH{\cdot}CR{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 \longrightarrow CRR'{:}CH{\cdot}CR{:}N{\cdot}N{:}C(OH){\cdot}NH_2$$

We proceeded to test this hypothesis by examining the methylsemicarbazones derived from 2-methylsemicarbazide, $NH_2{\cdot}NMe{\cdot}CO{\cdot}NH_2$, where no such enolisation is possible.

The methylsemicarbazones of simple αβ-unsaturated aldehydes or ketones, however, could not be prepared. On the other hand, those of some aromatic aldehydes were easily obtained, and although it was desirable to avoid complication of the issue by the introduction of a phenyl chromophore, a comparison of the absorption spectra of the methylsemicarbazones with those of the corresponding unsubstituted semicarbazones might be expected to show the effect of the methyl group without the aromatic nature of part of the molecule influencing the results. Such was found to be the case (cf. Table III). It is thus clear that the only difference in the light absorption of the two types of semicarbazones is a consistent displacement to longer wave-lengths in the case of the methyl derivatives. Both in direction and in size this displacement is typical of the normal substituent effect of a methyl group, and it is therefore evident that the chromophore responsible for the light absorption of semicarbazones in general cannot be the conjugated system of three double bonds produced by enolisation as suggested above. Burawoy's observation (J., 1939, 1177) that a hydroxy- or amino-group in conjugation with an ethylene linkage produces the equivalent of a conjugated system, provides an explanation, along the lines that the substituted amino-group in the semicarbazone in conjugation with the existing *K*-chromophore acts as though it were lengthening the conjugated system. This explanation is perfectly satisfactory in the case of the semicarbazones, but when a hydroxy-group is added to the system (III), as in the oximes, the bathochromic effect, if any, is very small (see below).

TABLE III.

Absorption spectra of semicarbazones and methylsemicarbazones (in alcohol).

	Semicarbazone.		Methylsemicarbazone.		
	λ, max., A.	ε, max.	λ, max., A.	ε, max.	Δλ, A.
Cinnamaldehyde	2295	9,580	2330	9,930	+35
	3100	40,200	3125	38,800	+25
o-Hydroxybenzaldehyde	2770	17,000	2805	16,250	+35
	3155	12,830	3215	13,200	+60
m-Hydroxybenzaldehyde	2840	20,800	2880	26,600	+40
p-Hydroxybenzaldehyde	2890	24,150	2910	24,100	+20
			Average increment = 36 A.		

When considering semicarbazide derivatives of carbonyl compounds from the point of view of chromophoric make-up, the only other related compounds of interest here are the phenyl- and the thio-semicarbazones. The absorption spectra of some of the former have been examined (Burawoy, J., 1941, 20), but since they contain the NHPh– chromophore in addition to the simple group (III), their further discussion is out of place here. The thiosemicarbazones, on the other nand, are chromophorically simple derivatives of (III), and are of interest because they differ from ordinary semicarbazones only in having a sulphur atom replacing oxygen—*i.e.*, they constitute a new molecular environment for the chromophore under discussion without the complication of an additional chromophore. The absorption spectra of thiosemicarbazones have been little studied, and we record the data (Table IV) on a selection of these derivatives of αβ-unsaturated carbonyl compounds for comparison with their oxygen analogues.

Examination of the tabulated and graphical data (Table IV and Fig. 3) shows that, unlike the true semicarbazones, the sulphur analogues all show a second absorption band which is fairly constant in location and intensity. By comparison with the absorption of thiosemicarbazide, it is clear that this band (λ max. *ca.* 2450 A., ε of the order 10,000) is due to the thiosemicarbazide part of the molecule and not to the group (III) (cf. Ruzicka, Seidel, and Fermenich, *Helv. Chim. Acta*, 1941, **24**, 1434). The data in this table further show that the thiosemicarbazones of carbonyl compounds exhibit absorption bands due to the conjugated system situated some 600—700 A. further towards the visible spectrum than in the case of the original band due to $C{=}C{-}C{=}O$. There is also an increase in intensity which is even greater than that shown by ordinary semicarbazones.

The thiosemicarbazones are therefore very valuable derivatives of unsaturated carbonyl compounds from the point of view of the identification of the $C{=}C{-}C{=}O$ group by absorption-spectra methods on account of the facts (*a*) that the absorption band is of very high intensity, (*b*) that it is displaced to a part of the spectrum which is especially suitable for accurate measurement, and, (*c*) that the band has moved so far up the spectrum

TABLE IV.

Absorption spectra of the thiosemicarbazones of αβ-unsaturated carbonyl compounds (in alcohol).

	Thiosemicarbazones.				Carbonyl compound.			
	Thiosemicarbazide band.		C=C—C=N Band.		*K*-Band.			
Carbonyl compound.	λ, max.	ε, max.	λ, max.	ε, max.	λ, max.	ε, max.	Δλ, A.	Δε.
Carvone	2450	8,400	3015	24,700	2353 [1]	19,000	662	5,700
Butylideneacetone	2460	10,150	3015	35,900	2280	10,600	735	25,300
Piperitone	2450	13,470	3020	32,200	2355	17,780	665	14,400
2 : 3 : 4 : 5-Tetrahydroacetophenone	2470	10,070	3010	37,000	2335	9,660	675	16,900
1-Methyl-Δ^1-*cyclo*hexen-3-one	2465	9,210	3025	30,350	2350	12,930	675	17,400
Irone [2]	2470	10,200	3010	32,000	2280	12,350	730	19,650
α-Ionone	2485	9,860	3025	36,500	2280	13,300	745	23,200
Tiglinaldehyde	2480	8,870	2995	29,950	2280	5,000	715	25,000
α-Ethyl-Δ^{α}-hexenaldehyde	2450	9,200	3010	33,000	2285	10,670	725	22,330
(Thiosemicarbazide) [3]	2410	13,800						

[1] Cooke and Macbeth, J., 1938, 1408. [2] Gillam and West, J., 1942, 483. [3] Ruzicka, Seidel, and Fermenich *loc. cit.*

that absorption due to many of the commoner absorbing impurities is left behind at shorter wave-lengths, thus giving a cleaner and more selective absorption band.

FIG. 3.

Absorption spectra in ethyl-alcoholic solution.

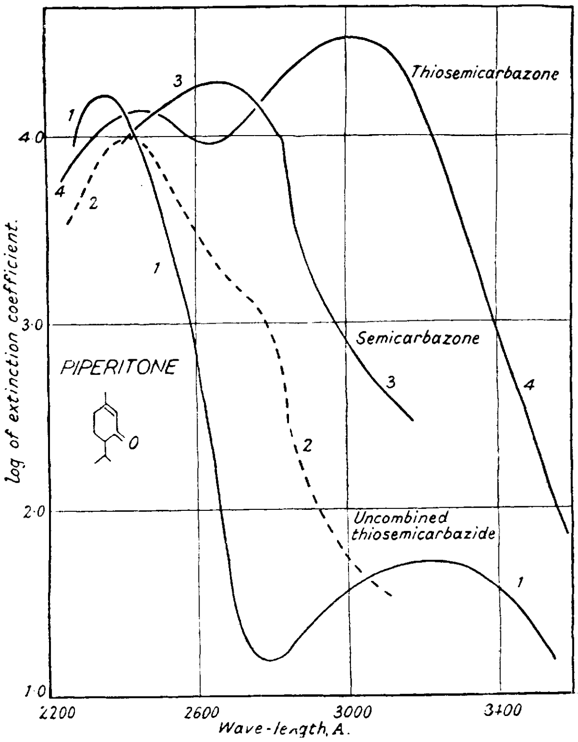
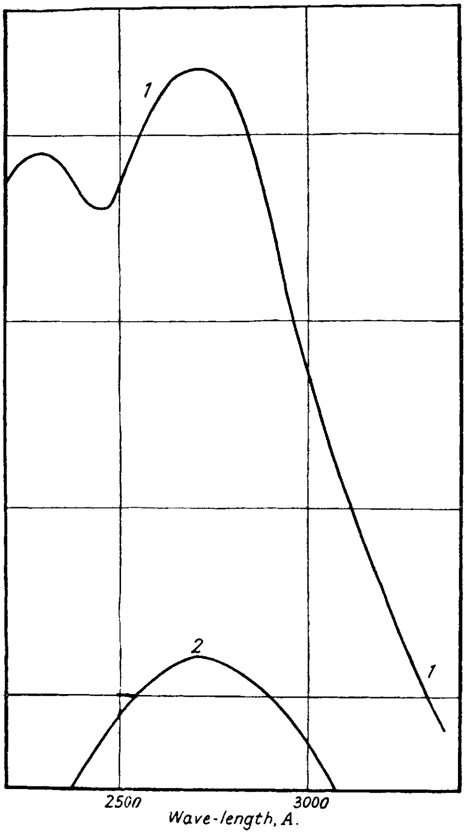


FIG. 4.

Comparison of the absorption spectrum of a saturated carbonyl compound (methyl ethyl ketone) (2) with that of its thiosemicarbazone (1).



In the thiosemicarbazones listed in Table IV the interesting point is the nearly constant location of the band at 3015 ± <20 A. It should be noted that no trisubstituted αβ-unsaturated compounds are represented, so the question whether trisubstitution would displace the band to longer wave-lengths or not must remain open.

We have seen that the simple semicarbazones of αβ-unsaturated carbonyl compounds absorb maximally near 2700 A., whilst those of the saturated analogues absorb at wave-lengths less than 2200 A., *i.e.*, almost outside the practicable range of the quartz spectrograph. In thiosemicarbazones the weighting effect of the sulphur atom apparently displaces the light absorption to longer wave-lengths. We have examined the absorption spectra of the thiosemicarbazones of a number of typical *saturated* aldehydes and ketones and find that they exhibit two distinct absorption bands near 2300 and 2700 A. severally (Table V). From their intensities, we attribute the former to the thiosemicarbazide part of the molecule displaced by about 100 A. to shorter wave-lengths by the molecular environment (contrast the opposite effect in αβ-unsaturated carbonyl thiosemicarbazones). The 2700 A. band is presumably due to the pseudo-conjugated system $-C{=}N{-}NHR$ (Burawoy, J., **1939**, **1177**) and has the intensity of a typical *K*-band. This observation gives us an additional spectroscopic method of detecting small amounts of *saturated* aldehydes or ketones *via* their thiosemicarbazones, since the absorption band of the latter is situated in an easily accessible region of the quartz ultra-violet, and, moreover, the absorption is some 500 times more intense than that of the original aldehyde or ketone (cf. Fig. 4 and Table V).

TABLE V.

Absorption spectra of thiosemicarbazones of saturated carbonyl compounds (in alcohol).

	Thiosemicarbazide band.		Thiosemicarbazone band.	
Carbonyl compound.	λ, max., A.	ε, max.	λ, max., A.	ε, max.
Acetone	2285	7080	2710	21,200
Methyl ethyl ketone	2295	8130	2710	22,000
Methyl hexyl ketone	2300	7800	2715	23,200
*cyclo*Hexanone	2295	7900	2720	23,400
3-Methyl*cyclo*hexanone	2295	8400	2730	24,300
4-Methyl*cyclo*hexanone	2280	8270	2715	24,400
Acetaldehyde	2295	6800	2700	20,400
Propaldehyde	2290	6200	2700	20,580
Butaldehyde	2285	7600	2715	22,700

Another interesting type of compound derived from (III) is that represented by the oximes of αβ-unsaturated carbonyl compounds having the chromophoric group $>C{=}\overset{|}{C}{-}\overset{|}{C}{=}N{-}OH$. Data on typical oximes of unsaturated ketones and aldehydes are shown in Table VI and in Fig. 1. The light absorption of the oximes differs from that of the original carbonyl compounds in that it is a single absorption band only, the *R*-band (due to $>C{=}O$) having disappeared. On the other hand, the absorption of the oximes differs from that of the chromophorically similar semicarbazones in being situated at much shorter wave-lengths (displacement of the order 350 A.).

TABLE VI.

Absorption spectra of oximes of αβ-unsaturated ketones and aldehydes (in alcohol).

	$C{=}C{-}C{=}O$ Band.		$C{=}C{-}C{=}N$. Band.			
Carbonyl compound.	λ, max.	ε, max.	λ, max.	ε, max.	Δλ, A.	Δε.
Crotonaldehyde	2170	15,650	2295	16,900	+125	+ 1250
Δ²-2-Formylcholestene [1]	2350	12,600	2330	20,000	− 20	+ 8000
1-Methyl*cyclo*penten-3-one [2]	—	—	2340	13,000	—	—
1-Methyl*cyclo*hexen-3-one	2350	12,930	2360	12,900	+ 10	− 30
2 : 3 : 4 : 5-Tetrahydroacetophenone	2335	9,660	2310	13,800	− 25	+ 4140
Carvone	2350	19,060	2360	16,050	+ 10	− 3010
Piperitone	2355	17,780	2360	>12,200	+ 5	−<5580
$CH_3{\cdot}CH{:}CMe{\cdot}CO{\cdot}CH_3$	2295	11,090	2305	17,800	+ 10	+ 6710
$CH_3{\cdot}CMe{:}CH{\cdot}CO{\cdot}CH_3$	2350	14,000	2365 [4]	12,600	+ 15	− 1400
Δ⁴-Cholesten-3-one	2405	18,000	2400	23,000	− 5	+ 5000
	2420	19,950	2420	17,600	± 0	− 2350
3-Acetoxy-Δ⁵-cholestene-7-one [3, 6]	2340	14,010	2380	14,090	+ 40	+ 80
Sitostenone [5]	2410	17,000	2400	20,000	− 10	+ 3000
Stigmastadienone [5]	2410	17,000	2400	22,000	− 10	+ 5000
Fucostadienone [5]	2400	17,000	2405	23,000	+ 5	+ 6000

[1] Plattner and Jampolsky, *Helv. Chim. Acta*, 1941, **24**, 1459. [2] We are indebted to Professor A. R. Todd, F.R.S., for a specimen of this oxime. [3] Eckhardt, *Ber.*, 1938, **71**, 461. [4] Value in water, not alcohol. [5] Jones, Wilkinson, and Kerlogue, J., 1942, 391. [6] Solvent not given.

The oximes of αβ-unsaturated carbonyl compounds on which absorption data are presented here all absorb within the narrow range 2360 ± 65 A. with intensities (ε) ranging from 12,000 to 23,000. Except crotonaldoxime, all the compounds are derivatives of disubstituted αβ-unsaturated carbonyl compounds, and no trisubstituted members are included. There is thus very little information on the effect of substitution, but the location of the band of the single monosubstituted αβ-unsaturated aldehyde oxime (2295 A.) is so similar to that of the disubstituted carbonyl compounds that it seems probable that—as in the semicarbazones—the location of the oxime band is independent of the substitution of the parent carbonyl compound.

EXPERIMENTAL.

Determination of Absorption Spectra.—Except in the relatively few cases where the data were available in the literature, and to which references have been made, the absorption-spectra determinations were all carried out with a Hilger E_3 medium quartz spectrograph and Spekker photometer. Purified ethyl alcohol was used as solvent. Intensities of absorption are expressed in the usual form : Molecular extinction coefficient (ε) = $(\log I_0/I)/cl$, where I_0 and I are the intensities of the incident and the transmitted light, c the molar concentration, and l the thickness of the layer (in cm.).

Preparation of Compounds.—Unless otherwise stated, the aldehydes and ketones were either freshly distilled commercial products or those described in Part II (*loc. cit.*).

Phellandral. We are indebted to Dr. T. F. West for specimens of this compound obtained from different sources. In one case *d*-phellandral was isolated from water-fennel oil, converted into the semicarbazone, and regenerated. The resulting aldehyde (b. p. 77—78°/3 mm.) had $\alpha_D^{24^\circ}$ 14·2°; $n_D^{21^\circ}$ 1·4928. The second sample was obtained by oxidation of *l*-β-phellandrene, preparation of the semicarbazone (m. p. 203—204°), and regeneration. In both cases, although the semicarbazones were good products, owing to the small amounts available, the regenerated aldehydes were not perfectly pure as judged by the low intensity of their absorption bands (λ max. 2320 A., ε = 11,700; cf. λ max. 2285, ε = 18,620, quoted by Cooke and Macbeth, J., 1938, 1408).

Tiglinaldehyde. Several attempts were made to obtain this compound spectroscopically pure. Propaldehyde (50 ml.), prepared by oxidation of propyl alcohol (*Organic Syntheses*, XII, 64), was carefully fractionated and collected over the range 47—49°; it was condensed with acetaldehyde (39 ml.) by heating with 100 ml. of 27·7% sodium acetate solution in an autoclave at 100° for 24 hours (Lieben and Zeisel, *Monatsh.*, 1886, **7**, 54), and after three fractionations through a long column, the product had b. p. 116—118° (yield, 18·8 g.). This showed an unsymmetrical curve with ε max. of only 5,000 at 2280 A., indicating it to be still very impure. Variation in the proportion of the two aldehydes in the mixture before condensation gave no better result.

α-Ethyl-Δ^α-hexenaldehyde. *n*-Butaldehyde (25 g.; prepared by oxidation of the alcohol), b. p. 73—74°, was shaken for several hours with 10% aqueous potassium hydroxide (5 ml.) in ether (15 ml.) (Weizmann and Garrard, J., 1920, **117**, 329). The product after three fractionations had b. p. 173—175° (yield, 6·5 g.).

Semicarbazones. These were prepared by the usual method from semicarbazide hydrochloride (1 mol.) and sodium acetate in aqueous alcohol, and recrystallised until the m. p.'s were constant and comparable with published values. The values obtained on our specimens were as follows: Methyl *iso*propenyl ketone, 174—176°; butylideneacetone, 116—117°; 3-methyl-Δ^3-penten-2-one, *ca.* 200° (decomp.); carvone, 152°; 2 : 3 : 4 : 5-tetrahydroacetophenone, 221·5°; piperitone, 222·5°; 1-methyl*cyclo*hexen-3-one, 197°; 2 : 4-dimethyl*cyclo*hexen-3-one, 203—205°; crotonaldehyde, 197·5°; tiglinaldehyde, 216°; α-ethyl-Δ^α-hexenaldehyde, 130—130·5°.

2-*Methylsemicarbazones.* Nitrosomethylurea (*Organic Syntheses*, XV, 48) was reduced with zinc and acetic acid to give a solution of 2-methylsemicarbazide (Young and Oates, J., 1901, **79**, 659), from which the methylsemicarbazones were prepared (as described by Young and Oates) directly without isolation of the methylsemicarbazide. M. p.'s of the derivatives were as follows: Cinnamaldehyde, 154—155°; *o*-hydroxybenzaldehydemethylsemicarbazone, 171—172°; *m*-isomer, 182—184°; *p*-isomer softens 180—190°, clears at 230—240° (decomp.).

Thiosemicarbazones. The pure ketones and aldehydes were treated with thiosemicarbazide (1 mol.), prepared from hydrazine sulphate and potassium thiocyanate (Freund and Schander, *Ber.*, 1896, **29**, 2500) in aqueous-alcoholic solution. The precipitated derivatives were purified by crystallisation. The m. p.'s of the thiosemicarbazones (most of which are new) were: 1-Methyl*cyclo*hexen-3-one, 138—140°; tiglinaldehyde, 155°; α-ethyl-Δ^α-hexenaldehyde, 160—162°; butylideneacetone, 150—151°; piperitone, 170—171°; carvone, 172—174° (decomp.); 2 : 3 : 4 : 5-tetrahydroacetophenone, 143—144°; acetone, 177°; *cyclo*hexanone, 156°; methyl ethyl ketone, 101—102°; 4-methyl*cyclo*hexanone, 161°; 3-methyl*cyclo*hexanone, 118—119°; methyl hexyl ketone, 69—70°; acetaldehyde, 140°; propaldehyde, 154—156°; *n*-butaldehyde, 108—109°.

Oximes. These were prepared from the carbonyl compound with hydroxylamine hydrochloride (1 mol.) and sodium acetate in aqueous alcohol and purified by recrystallisation. M. p.'s of the oximes of the following compounds were: Crotonaldehyde, 120·5°; 3-methyl-Δ^3-penten-2-one, 76·5°; 2 : 3 : 4 : 5-tetrahydroacetophenone, 97—98°; piperitone, 118°; carvone, 92·5°; 1-methyl*cyclo*hexen-3-one, 86—87°; Δ^4-cholesten-3-one, 152°.

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