Absorption Spectra of Ketones. Part III. The Long-wavelength Band of αβ-Unsaturated Ketones.*

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The absorption spectra of some αβ-unsaturated ketones have been measured in *n*-hexane solution from 280 to 400 mμ. The wavelength of the maximum of the weak band occurring in this region is mainly determined by the degree of alkylation of the double bond, substitution shifting it to shorter wavelengths. No simple relation was found between the structure of the ketone and the degree of vibrational fine structure of the absorption band.

ALKYL substitution on the α- and the β-carbon atom of an αβ-unsaturated aldehyde or ketone causes a predictable shift in the wavelength of the maximum of intense ultraviolet absorption (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76; Evans and Gillam, *J.*, 1941, 815; 1943, 565; Fieser and Fieser, " Natural Products Related to Phenanthrene," Reinhold, New York, 3rd Edn., p. 190) but little is known about the effect of structure on the position or intensity of the weak band that occurs at longer wavelengths in these spectra. The absorption of a variety of αβ-unsaturated ketones, mostly *cyclo*hexenones, has therefore been measured in the region 280—400 mμ.

The weak band has been characterised as due to an *n* → π transition, both by calculation of the expected intensity of the transition (McMurray, *J. Chem. Phys.*, 1941, **9**, 231) and by consideration of the solvent effect (McConnell, *ibid.*, 1952, **20**, 700). Since change of solvent from hydrocarbon to ethanol shifts the intense band to longer but the weak one to shorter wavelengths, the latter often appears, in ethanol, only as an inflection superimposed on the end-absorption of the main band. Although most published information on the absorption spectra of αβ-unsaturated ketones refers to ethanol solutions and records the intense band only, there are ample data to show that the maximum of the weak band of most open-chain αβ-unsaturated ketones, *cyclo*hexenones and 2-alkylidene*cyclo*hexanones in ethanol occurs between about 300 and 330 mμ. *cyclo*Pentenones seem to absorb near the lower end of this range, whereas 2-alkylidene*cyclo*pentanones form a class characterised by the exceptionally long wavelength and rather greater intensity of the weak band (Table 1). The

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* Part II, *J.*, 1955, 352.

TABLE 1. *Derivatives of 2-methylene*cyclo*pentanone in ethanol.*

No.	Substance	$\lambda_{max.}$	ε	Ref.
1	4-Methyl-2-*iso*propylidene*cyclo*pentanone	340 [a, b]	60	1
2	3β-Acetoxy-16-*iso*propylideneandrost-5-en-17-one	338	100	2
3	16-*iso*Propylideneandrosta-3 : 5-dien-17-one	338 [b]	60	2
4	3β-Acetoxycholest-8(14)-en-15-one	339	109	3
5	Anhydro-oxoelemadienyl acetate-I	342—345	86	4
6	3β-Hydroxy-22*a* : 5α-C-nor : D-homospirost-13(17*a*)-en-11-one	350	76 *	5
7	Diacetyljervine	360	80	6
8	3β : 17 : 23-Trihydroxy-22 : 26-iminojerva-5 : 13(17*a*)-dien-11-one 3 : 23 : *N*-triacetate	355	85	7

* Dr. R. F. Hirschmann has kindly informed us that log ε 2·88 quoted for this band (*J. Amer. Chem. Soc.*, 1954, **76**, 4013) should read log ε 1·88.

[a] Inflection. [b] Approx. wavelength read from small-scale graph.

position of the band in the anhydro-ketone derived from acetoxyelemadienic acid (No. 5) can therefore be taken as indicating the 2-*iso*propylidene*cyclo*pentanone chromophore, a conclusion already reached from other spectroscopic evidence (Halsall, Meakins, and Swayne, *J.*, 1953, 4139). (Substitution by hetero-atoms in certain conformations α′ or γ to the carbonyl group of the other classes of αβ-unsaturated ketones may shift the weak band into the same region : examples will be discussed in a later paper.)

In order to secure greater separation of the two absorption bands and thus better resolution of the weak one, and also to investigate the vibrational fine structure of the latter, our measurements have been made in *n*-hexane. Amongst saturated ketones, open-chain ketones and most *cyclo*hexanones show no fine structure even in paraffinic solvents, but *cyclo*pentanone (Benson and Kistiakowsky, *J. Amer. Chem. Soc.*, 1942, **64**, 80; Biquard, *Bull. Soc. chim. France*, 1941, **8**, 55, 725) and *cyclo*butanone (Benson and Kistiakowsky, *loc. cit.*) do show fine structure in *n*-hexane. Few accurate measurements are available of the $n \rightarrow \pi$ band of αβ-unsaturated ketones; those that are have been included in the Tables. (Unless otherwise indicated, the following discussion refers only to this band in *n*-hexane.)

In drawing up the Tables we have followed Mohler (*Helv. Chim. Acta*, 1937, **20**, 289) in designating successive bands by Roman letters, starting with the band of longest wavelength. Although either C or D may be the most intense band (ε shown in parentheses) the general shapes of the various absorption curves showing resolved fine structure are so similar that corresponding bands can be picked out with confidence. Band A is usually about a third to a quarter as intense as C and D, and the difference in frequency between A and B is usually rather greater than that between other pairs of successive bands. In fact band A of the ketones seems to correspond with the two longest wavelength bands of acraldehyde (No. 9). Bands of ketones not showing a complete progression, owing to poorly developed vibrational structure, have been lettered with fair confidence by careful comparison with examples showing well-developed vibrational structure. For ketones showing little or no fine structure assignment of maxima to particular vibrational bands is unjustified. These maxima are printed in italics.

Consideration of the wavelengths of corresponding maxima in the spectra of *cyclo*hexenones (Tables 3—6) clearly shows that the most important factor in determining the position of a particular band is the degree of alkyl substitution on the double bond : Amongst the monocyclic *cyclo*hexenones and the polycyclic ones having the chromophore in a terminal ring, one α- or β-alkyl substituent causes a shift of about 6 mμ to shorter wavelengths, and two alkyl substituents cause a shift of about 20 mμ in the same direction. Whether or not the β-alkyl group is exocyclic to another six-membered ring appears immaterial (compare Nos. 18 & 19) (cf. the intense band; Woodward, *loc. cit.*, 1942), and the only effect of methylation of the α-carbon atom is to increase the extinction and reduce the resolution of the vibrational structure somewhat without effecting the wavelengths of the component bands (compare Nos. 13 & 14). Amongst the *cyclo*hexenones having the chromophore in a central ring of a polycyclic system the wavelengths of corresponding bands still seem usually to be determined by the degree of alkylation of the double bond, but there are several notable deviations (Nos. 23, 24, 26—28, 33) that presumably indicate the operation of more subtle influences, perhaps of steric origin.

TABLE 2. αβ-*Unsaturated aldehydes.*

No.	Substance	A	B	C	D	E	F	Ref.
9	Acraldehyde	385·2(6·5) 378·5(6·2)	366·5(10·7)	349·2(11·5)	334·8(11·6)	—	—	8
10	α-Methylacraldehyde	370[a] (6)	360[a] (16)	—	330(26)	—	—	9
11	β-Methylacraldehyde	370[a] (7)	360[a] (16)	—	330(25)	—	—	9

TABLE 3. *Unsubstituted* cyclo*hex-2-enones.*

No.	Substance	A	B	C	D	E	F	Ref.
12	*trans*-$\Delta^{3:6}$-Hexahydro-10-methyl-2-oxonaphthalene	373[a] (8)	355(20)	342(26)	332(25)	322[a] (23)	313[a] (21)	3
13	Cholest-1-en-3-one	374(9·5)	357(21)	344(27·5)	333(26)	322·5[a] (23)	—	3
14	β-Amyra-1 : 12-dien-3-one	—	359[a] (48)	344(63)	332(66)	321[a] (59)	—	3
15	Cholest-2-en-1-one	—	350(50)	342(54)	331(49)	318·5[a] (37)	—	3

TABLE 4. 2-*Substituted* cyclo*hex-2-enones.*

No.	Substance	A	B	C	D	E	F	Ref.
16	2-Methyl*cyclo*hex-1-en-3-one	369(3·5)	351(9·5)	337(14)	327(18)	315(18)	—	3
17	Carvone	370	356	340	327	313	—	10

TABLE 5. 3-*Substituted* cyclo*hex-2-enones.*

No.	Substance	A	B	C	D	E	F	Ref.
18	*iso*Phorone	368(9)	349(22·5)	337(30)	325(29)	—	—	3
19	Cholest-4-en-3-one	367[a] (22)	349(41)	336(54)	323·5(56)	314(52)	—	3
		—	354	338	324	313	—	10
20	D-Homoandrosta-4 : 9 (11) : 16-trien-3-one	368[a] (17)	350(33)	338(43)	326(42)	314[a] (35)	—	3
21	Cholest-5-en-7-one	—	345[a] (29)	334(32)	322[a] (28)	—	—	3
22	3β-Acetoxycholest-5-en-7-one	—	350[a] (13)	337(17)	325[a] (13)	—	—	3
23	3β-Acetoxylanost-5-en-7-one	380[a] (19)	364(38)	350(47)	339(44)	—	—	3
24	3β-Acetoxyergosta-7 : 22-dien-6-one	360(24)	345(53)	332(68)	320(67)	310·5(59)	—	3
25	3β-Acetoxy-23-bromo-5α : 22*a*-spirost-9(11)-en-12-one	369(7)	350(18)	337·5(24)	327(23)	—	—	3
26	11-Oxo-β-amyrin acetate	374(9)	355(18·5)	345(22)	335(22)	—	—	3
27	11-Oxo-18-*iso*-β-amyrin acetate	*ca.* 370[a] (29)	*ca.* 351[a] (64)	340(80)	329(82)	—	—	3
28	11-Oxo-α-amyrin acetate	374[a] (11)	357(26)	345(34·5)	335(34)	—	—	3

TABLE 6. 2 : 3-*Disubstituted* cyclo*hex-2-enones.*

No.	Substance	A	B	C	D	E	F	Ref.
29	1 : 14-Dimethyl-2 : 8-dioxo-$\Delta^{1(11)}$-dodecahydrophanthrene	351(26)	336(41)	322(50)	308(54)	297(53)	—	3
30	$\Delta^{1(11)}$-Dodecahydro-1 : 14-dimethyl-6β : 7β-*iso*-propylidenedioxyphenanthrene	349(41)	336(55)	324(57)	—	—	—	3
31	3β-Acetoxyergosta-8(9) : 22-dien-7-one	—	—	*332(36)*	—	*304(33)*	—	3
32	3β-Acetoxyergosta-8(9) : 22-dien-11-one	—	—	*327(51)*	—	*306(48)*	—	3
33	Methyl 3β-acetoxy-4 : 4 : 14α-trimethyl-11-oxochol-8(9)-enoate	—	353(29)	342·5(31)	—	322[a] (24)	—	3

TABLE 7. *Derivatives of 2-methylene*cyclo*hexanone.*

No.	Substance	A	B	C	D	E	F	Ref.
34	Pulegone	—	—	*329*	—	—	—	10
35	3β-Acetoxycholest-8(14)-en-7-one	—	—	*329(63)*	—	—	—	3
36	Methyl 3β-acetoxy-19-oxo-olean-13(18)-en-28-oate	—	—	*324(104)*	—	—	—	3

Turning now to the degree of fine structure exhibited by the various ketones, we can observe in the examples tabulated the complete range from a smooth curve with no detectable fine structure through intermediate degrees to a complex band showing up to eight well-resolved subsidiary maxima. Acraldehyde (No. 9), the simplest substance, shows well-defined vibrational structure; α-methylacraldehyde (No. 10) shows less and β-methylacraldehyde (No. 11) almost none; acylic unsaturated ketones and derivatives of 2-methylene*cyclo*hexanone show no detectable fine structure. There is a striking and rather unexpected contrast between the 5-en-7-ones of the cholestane (Nos. 21 and 22) and lanostane (No. 23) series, the former showing only a trace of fine structure, the latter having bands A to D well developed and shifted to abnormally long wavelengths. The spectra of the 12-en-11-ones of the α- and β-amyrin series are very similar, consisting of a rather weak band with sub-maxima A to D well resolved: the spectrum of the 18α-epimer of the β-amyrin series is quite different, consisting of a more intense band with only faint indications of fine structure.

The approximately constant separation between successive vibrational bands of about 1000—1200 cm.$^{-1}$ probably corresponds roughly with the strongest band progression of 1260 cm.$^{-1}$ in the vapour spectrum of acraldehyde (Lüthy, *Z. phys. Chem.*, 1923, **107**, 285). Since this is probably the CO stretching frequency in the excited state of the ketones, analysis of the fine structure of the spectra offers, in principle, a means of investigating the influence of ring size and molecular structure on the excited-state frequencies to match the detailed knowledge of the ground-state frequencies recently gained from infrared and Raman spectra. It may be significant that the most highly developed fine structure is shown by the most rigid molecules, the 2-alkylidene*cyclo*pentanones (cf. Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 318; Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127).

TABLE 8. *Derivatives of 2-methylene*cyclo*pentanone.*

No.	A	B	C	D	E	F	G	H	Ref.
37	3β-Acetoxycholest-8(14)-en-15-one								
	389(22)	369(54)	356(69)	342·5(61·5)	328• (45)	—	303• (57)	291(66)	3
38	3β-Hydroxy-22*a* : 5α-C-nor : D-homospirost-13(17*a*)-en-11-one								
	385(36)	368(59)	354(69)	340(61)	324(45)	313(37)	—	288• (34)	3

Refs.: 1, French and Wiley, *J. Amer. Chem. Soc.*, 1949, **71**, 3702. 2, Ross, *J.*, 1945, **25**. 3, This paper. 4, Halsall, Meakins, and Swayne, *J.*, 1953, 4139. 5, Hirschmann, Snoddy, Hiskey, and Wendler, *J. Amer. Chem. Soc.*, 1954, **76**, 4013. 6, Fried and Klingsberg, *ibid.*, 1953, **75**, 4929. 7, Wintersteiner and Moore, *ibid.*, p. 4938. 8, Lüthy, *Z. phys. Chem.*, 1923, **107**, 285. 9, Saksena and Kagarise, *J. Chem. Phys.*, 1951, **19**, 994. 10, Mohler, *Helv. Chim. Acta*, 1937, **20**, 289.

EXPERIMENTAL

Absorption spectra were measured at room temperature as described previously (*J.*, **1954**, 282) in 1-cm. or 4-cm. silica cells, according to the solubility of the ketone in *n*-hexane, which was B.D.H. " Special for Spectroscopy."

Liquids were fractionally distilled just before use and had b. p.s and refractive indices very close to the recorded values. Solids were purified by recrystallisation, preceded when necessary by chromatography. Their purity was checked by m. p. and/or rotation. The intense absorption bands of all the ketones had the expected wavelengths and intensities. In most cases, including all that showed poorly resolved fine structure, the spectrum was remeasured after further purification, with very similar results.

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