690. *Stereochemistry and Infrared Spectra of αβ-Unsaturated Ketones.*

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The infrared spectra of some fixed *cisoid* and *transoid* αβ-unsaturated ketones have been examined. It is concluded that the ratio of the integrated band intensities of the C=O and C=C stretching vibrations gives the most certain indication of the geometry of the chromophore, being low in *cisoid* and high in *transoid* structures. The effect of steric hindrance to coplanarity of the chromophore on the infrared spectra is discussed.

THE infrared spectra of some polycyclic rigidly *cisoid* αβ-unsaturated ketones are characterised by absorption bands attributable to C=O and C=C stretching vibrations which are of nearly equal peak height (ε^a),[1] whereas in rigidly *transoid* systems the C=O band is much the stronger. As examples we may quote cholest-5-en-4-one, having $r = \varepsilon^a_{CO}/\varepsilon^a_{CC} = 1{\cdot}5$, and cholest-4-en-3-one, with $r = 7{\cdot}6$. The intensity relation holds for some labile *s-cis*-ketones such as mesityl oxide ($r = 1{\cdot}2$), but not for others, *e.g.*, 3,4-dimethylpent-3-en-2-one ($r = 4{\cdot}2$).[2] The C=C band of the last compound, and also of 1-acetyl-2-methylcyclohexene and the fixed *cisoid* ketone pulegone, is very broad.[2] We have prepared some other fixed *cisoid* ketones and have compared their infrared spectra with the spectra of some appropriate *transoid* ketones.

EXPERIMENTAL

Microanalyses are by Miss J. Cuckney and the staff of the Organic Microanalytical Laboratory.

Materials.—The ketones were prepared by standard methods, or suitable modifications thereof, and purified as detailed below.

2-*Methylenecyclopentanone.* A mixture of piperidine hydrochloride (29 g.), 40% aqueous formaldehyde (24 g.), cyclopentanone (20 g.), and dioxan (50 ml.) was heated on a steam-bath for 24 hr., then evaporated under reduced pressure. The residue crystallised and was boiled with acetone (100 ml.). The acetone extract gave on evaporation a pale brown solid, m. p. 90—120° (28 g.), which was rejected; the insoluble residue was again extracted with boiling acetone. Evaporation of the second extract gave a white solid (8·2 g.), m. p. 142—143° (decomp.). Mannich and Schaller [3] give m. p. 145° for pure 2-piperidinomethylcyclopentanone. Without further purification this material was heated for 2 hr. at 150—180°/0·2 mm., and the vapours were collected in a trap cooled by liquid air. The condensate was redistilled at 40°/0·2 mm. into a series of three liquid-air-cooled traps, and each fraction examined by infrared spectroscopy. The first was deemed to be pure 2-methylenecyclopentanone and had $\nu_{max.}$ (in CCl_4) 1727vs, 1644s, 1406m, 1392m, 1252m, 1169m, 1122m, 1084s, 941s cm.$^{-1}$. The ketone dimerised too rapidly for elemental analysis.

2-*Methylenecyclohexanone.* 2-Piperidinomethylcyclohexanone,[4] m. p. 160° (decomp.) (from acetone–ethanol), was heated at 150—180°/0·2 mm. for 2 hr. Piperidine hydrochloride sublimed to cool parts of the apparatus, and the more volatile products were condensed at −196°. The condensate was distilled, without release of the vacuum, into a second trap at −196°, and small portions (*ca.* 30 mg.) were injected by means of a hypodermic syringe into known weights of (*a*) carbon tetrachloride and (*b*) ethanol, contained in weighing bottles sealed by soft-rubber caps. The bottles were re-weighed and the solutions diluted as required for infrared and ultraviolet spectroscopy. The liquid ketone dimerises with extreme rapidity at room temperature [5] and it was never possible to obtain a product completely free from dimer. The light-absorption data have been corrected for the amount of dimer, as determined by the intensity of the band

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[1] Barton and Narayanan, *J.*, 1958, 963, and references therein.

[2] Waight and Erskine, "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958, p. 73.

[3] Mannich and Schaller, *Arch. Pharm.*, 1938, **276**, 575.

[4] Mannich, *Ber.*, 1920, **53**, 1874; Mannich and Hornig, *Arch. Pharm.*, 1927, **265**, 603.

[5] Mannich, *Ber.*, 1941, **74**, 557; Warnhoff and Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 496.

at 1727 cm.$^{-1}$ (pure dimer has $\varepsilon^a = 410$, in CCl_4). The monomer is considered to have $\nu_{max.}$ (in CCl_4) 1697vs, 1618s, 1439m, 1414m, 1290s, 1135s, 1069m, 993m, 940s, 884m cm.$^{-1}$.

2-*Methylenecycloheptanone.* 2-Piperidinomethylcycloheptanone (16 g.), m. p. 156°, prepared by the method used for the cyclohexanone analogue, was heated for 1·5 hr. at 170—180°/0·1 mm. The vapours were collected (liquid-air trap) and the crude product immediately redistilled in a conventional micro-distillation apparatus. The fraction, b. p. 75°/14 mm., was shown by gas–liquid chromatography to be a mixture of the required product and cycloheptanone. Chromatography on alumina (Brockmann grade 4) gave a band which was eluted with 1 : 25 ether–pentane. Evaporation of the eluate gave a residue, shown by gas–liquid chromatography to be homogeneous, which on distillation gave 2-*methylenecycloheptanone,* b. p. 80—82°/14 mm., n_D^{23} 1·4825 (Found: C, 77·2; H, 9·8. $C_8H_{12}O$ requires C, 77·4; H, 9·7%), $\nu_{max.}$ (in CCl_4) 1694vs, 1613s, 1456s, 1404m, 1333m, 1304m, 1190m, 1143m, 1105m, 942s cm.$^{-1}$.

2-*Isopropylidenecyclopentanone.*[6] Ethyl 2-oxocyclopentanecarboxylate,[7] prepared by Dr. R. Houghton, was converted into *ethyl 2-ethylenedioxycyclopentanecarboxylate* (75%), b. p. 132—136°/21 mm., n_D^{21} 1·4600 (Found: C, 59·75; H, 8·2. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·05%), which on reaction with methylmagnesium iodide yielded 2-isopropylidenecyclopentanone. Purification *via* the semicarbazone, m. p. 228° (decomp.; m. p. varies with rate of heating), undepressed on admixture with a sample supplied by Dr. M. F. Ansell,[8] gave the ketone, b. p. 88·0—88·5°/21 mm., n_D^{22} 1·4961, shown to be pure by gas–liquid chromatography and having an infrared spectrum identical with that of a specimen supplied by Dr. Ansell.[8] The intensity of the C=O band differs markedly from that reported by Horák and Munk [9] for a solution in chloroform, and the ultraviolet intensity (see Table 1) is considerably higher than the value given by French and Wiley [10] but in good agreement with Ansell and Brown's figure.

2-*Isopropylidenecycloheptanone.* This was obtained from ethyl 2-oxocycloheptanecarboxylate,[11] *via* the ethylenedioxy-derivative. Regeneration from the *semicarbazone,* m. p. 182—183° (from aqueous ethanol), $\lambda_{max.}$ 240 mμ (ε 10,600) (Found: C, 63·4; H, 9·2; N, 20·3. $C_{11}H_{19}N_3O$ requires C, 63·15; H, 9·15; N, 20·1%), gave the pure *ketone,* b. p. 120—124°/17 mm., n_D^{21} 1·4943 (Found: C, 78·7; H, 10·9. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%).

Pulegone. A commercial specimen, purified through the semicarbazone, had b. p. 69·5°/5 mm., n_D^{20} 1·4849.

2-*Benzylidenecycloalkanones.* These were prepared by condensation of benzaldehyde and the cycloalkanone in presence of alkali, followed where necessary by dehydration of the intermediate ketol. 2-Benzylidenecyclopentanone had m. p. 71° (from methanol) (Vavon and Conia [12] give m. p. 71—72°), $\lambda_{max.}$ 297, 230, 224 mμ (ε 21,600, 6300, 6600, respectively). 2-Benzylidenecyclohexanone had m. p. 52—53° (from light petroleum) (recorded m. p.s from 51—53° to 56·5° [12,13]), $\lambda_{max.}$ 288, 222 mμ (ε 19,000, 7400). 2-Benzylidenecycloheptanone had m. p. 37·5—38° (from pentane), $\lambda_{max.}$ 283, 221 mμ (ε 14,500, 6600) [lit.,[14] m. p. 37·5°, $\lambda_{max.}$ 290, 281, 270 mμ (ε 13,500, 14,500, 14,000)]. 2-Benzylidenecyclo-octanone, prepared by Dr. R. Houghton,[15] had m. p. 76—77°.

3-*Methylcyclopent-2-enone.* This was obtained by the action of boiling aqueous sodium hydroxide on acetonylacetone.[16] Regeneration from the semicarbazone, m. p. 219—221° (decomp.), gave the pure ketone, b. p. 63°/10 mm., n_D^{21} 1·4868.

Isophorone. A commercial sample was purified *via* the semicarbazone and then had b. p. 94°/16 mm., n_D^{18} 1·4778.

2,3,5,5-*Tetramethylcyclohex-2-enone.* A mixture of this ketone and isophorone, obtained by Conia's method,[17] was purified by gas–liquid chromatography. The fraction of longer retention time was shown to be homogeneous on an analytical gas–liquid chromatographic column. Conia gives b. p. 90°/8 mm., n_D^{21} 1·4798, $\lambda_{max.}$ 247 mμ (ε 9600).

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[6] Cf. Black, Buchanan, and Jarvie, *J.*, 1956, 2971.

[7] Linstead and Meade, *J.*, 1934, 935.

[8] Ansell and Brown, *J.*, 1958, 2955.

[9] Horák and Munk, *Coll. Czech. Chem. Comm.*, 1954, **24**, 3024.

[10] French and Wiley, *J. Amer. Chem. Soc.*, 1949, **71**, 3702.

[11] Prelog and Hinden, *Helv. Chim. Acta*, 1944, **27**, 1854.

[12] Vavon and Conia, *Compt. rend.*, 1952, **234**, 526.

[13] Emerson, Birum, and Longley, *J. Amer. Chem. Soc.*, 1953, **75**, 1312; Billimoria, *J.*, 1955, 1126.

[14] Braude, Forbes, and Evans, *J.*, 1953, 2204.

[15] Braude, Forbes, Gofton, Houghton, and Waight, *J.*, 1957, 4711.

[16] Acheson and Robinson, *J.*, 1952, 1127.

[17] Conia, *Bull. Soc. chim. France*, 1954, 690.

5,5-Dimethyl-3-phenylcyclohex-2-enone. The ethyl enol ether of dimedone was treated with phenylmagnesium bromide, giving the ketone, m. p. 54—55° (Woods [18] gives m. p. 54—54·5°).

Pent-3-en-2-one. A commercial specimen was fractionally distilled through a Stedman column (*ca.* 40 theoretical plates). The fraction of b. p. 120°/756 mm., $n_{\mathrm{D}}^{23\cdot5}$ 1·4338, was shown by gas–liquid chromatography to contain less than 2% of an (unidentified) impurity.

Mesityl oxide. A commercial sample was purified *via* the semicarbazone, m. p. 165°, and had b. p. 112°, n_{D}^{24} 1·4412.

3,4-Dimethylpent-3-en-2-one. This was prepared by Evans and Gillam's method.[19] Regeneration from the semicarbazone, m. p. 193°, gave the ketone, b. p. 146°, n_{D}^{19} 1·4503. Gas–liquid chromatography showed that the main impurity (*ca.* 5%) was probably ether.

Benzylideneacetone. A sample prepared by the reaction of benzaldehyde and acetone in the presence of aqueous alkali [20] had b. p. 83°/2 mm., m. p. 41—42°.

1-Acetyl-2-methylcyclopentene. The ketone was prepared by the method of Marshall and Perkin,[21] and after regeneration from the semicarbazone, m. p. 219° (decomp.), had b. p. 61°/10 mm.

1-Acetyl-2-methylcyclohexene. This was prepared by condensing acetyl chloride with 1-methylcyclohexene in carbon disulphide in the presence of stannic chloride.[22] Purification *via* the semicarbazone, m. p. 222°, $\lambda_{\text{max.}}$ 241 mμ (ε 10,500) [Braude *et al.* give m. p. 212—214°; Turner and Voitle [23] give m. p. 227—227·5°, $\lambda_{\text{max.}}$ 240 mμ (ε 10,360)], gave the ketone, b. p. 92°/15 mm., n_{D}^{20} 1·4890 [Braude *et al.* give b. p. 98—98·5°/25 mm., n_{D}^{25} 1·4852, $\lambda_{\text{max.}}$ 245 mμ (ε 6500); Turner and Voitle give $\lambda_{\text{max.}}$ 249 mμ (ε 6890)], which was shown to contain ~2% of a very volatile impurity (ether?) by gas–liquid chromatography.

1-Acetyl-2,4,4,5,5-pentamethylcyclopentene. This compound was isolated from the liquid products of the self-condensation of mesityl oxide in ether catalysed by lithium.[24] Regeneration from the semicarbazone, m. p. 170—171° (from methanol), gave the ketone, b. p. 70°/1 mm., n_{D}^{23} 1·4743 [Kolobielsky [25] gives the following physical properties for the ketone: b. p. 96°/15 mm., n_{D}^{19} 1·4750, $\lambda_{\text{max.}}$ 251 mμ (ε 6200); semicarbazone, m. p. 166—166·5°]. The infrared spectrum of our product is similar to that given by Kolobielsky except that a few weak bands in the latter's are not present.

We are indebted to Dr. M. F. Ansell for the sample of 2-ethylcyclopent-2-enone,[8] to Dr. L. M. Jackman for samples of pinocarvone, 2,2,5-trimethylhex-4-en-3-one, and cholest-5-en-4-one,[26] to Dr. L. N. Owen for a specimen of eremophilone from the collection of Sir John Simonsen, and to Dr. C. J. Timmons for the sample of isopropenyl methyl ketone.

Spectroscopic Measurements.—Infrared spectra of solutions in carbon tetrachloride were recorded under standard conditions on a Grubb–Parsons double-beam S4 spectrometer with rock-salt optics. The computed spectral slit width was 8·9 cm.$^{-1}$ at 1670 cm.$^{-1}$. Apparent molecular extinction coefficients (ε^{a}) were calculated (after graphical separation of overlapping bands) from the expression, $\varepsilon^{a} = \log_{10}(I_0/I)/cl$, where the symbols have their usual significance. $\nu^{a}_{\frac{1}{2}}$ is the apparent band width in cm.$^{-1}$ at half intensity. A is the integrated band intensity in l. mole^{-1} cm.$^{-2}$, calculated from $A = 2\cdot3 \times K \times \nu^{a}_{\frac{1}{2}} \times \varepsilon^{a}$, values of K given by Ramsay [27] being used.

Ultraviolet spectra were determined for ethanolic solutions on a Perkin–Elmer " Spectracord " 4000.

RESULTS AND DISCUSSION

The infrared and ultraviolet absorption for some αβ-unsaturated ketones are given in Tables 1, 2, and 3. In comparable systems our results agree well with the generalised data presented by Mecke and Noack.[28]

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[18] Crossley and Renouf, *J.*, 1908, **93**, 640; Woods, *J. Amer. Chem. Soc.*, 1947, **69**, 2549.

[19] Evans and Gillam, *J.*, 1941, 815.

[20] Vorländer, *Annalen*, 1896, **294**, 275.

[21] Marshall and Perkin, *J.*, 1890, **57**, 241.

[22] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890.

[23] Turner and Voitle, *J. Amer. Chem. Soc.*, 1951, **73**, 1403.

[24] Braude, Gofton, Lowe, and Waight, *J.*, 1956, 4054.

[25] Kolobielsky, *Compt. rend.*, 1953, **237**, 1717; *Ann. Chim.* (*France*), 1955, **10**, 271.

[26] Jackman, Lown, and Wusteman, unpublished work.

[27] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 73.

[28] Mecke and Noack, *Spectrochim. Acta*, 1958, **12**, 391.

The results show that *cisoid* and *transoid* αβ-unsaturated ketones can be differentiated in carbon tetrachloride solution, by measuring the ratio (r^i) of the integrated band intensities of the C=O and C=C stretching vibrations. This ratio depends also on the nature and position of substituents at the carbon–carbon double bond. For alkyl or phenyl substituents the ratio lies between 0·6 and 3·5 for *cisoid* ketones and is greater than 6 for *transoid* ketones, but more strongly electronegative groups may give very different values. Thus the ethyl enol ether (VI; R = H, R′ = OEt) of dimedone has $r^i = 1·3$. On this basis the most important contributing conformation can be determined for the ketones given in Table 3. Some of these ketones exhibit two bands in the carbonyl region, and Timmons and his co-workers[29] have suggested that in pent-3-en-2-one this is due to the presence of both *s-cis-* and *s-trans*-conformations; the same explanation possibly applies to benzylideneacetone and 1-acetyl-2-methylcyclopentene (VII; $n = 1$). The relative intensities of the two bands indicate that pent-3-en-2-one and benzylideneacetone exist mainly (~75%) in the *s-trans*-form (in carbon tetrachloride at room temperature), while in the ketone (VII; $n = 1$) the *s-cis*-form predominates, a conclusion in agreement with the nuclear magnetic resonance evidence.[26]

s-trans-: $\nu_{C=O}$ 1678 cm.$^{-1}$. *s-cis-*: $\nu_{C=O}$ 1701 cm.$^{-1}$.

The main factor influencing the intensity of the C=C band in an αβ-unsaturated ketone is likely to be the direct field effect of the carbonyl group. The resultant induced dipole in the C=C group will be greater in the planar *cisoid* than in the planar *transoid* form.* The mutual effect of the two dipoles will be to reduce the intensity of the C=O band and increase the intensity of the C=C band in the *cisoid* form as compared with the *transoid*. For conformations other than planar an intermediate effect will be observed. In such cases resonance in the chromophore will be inhibited and this will have a small effect on infrared absorption but a much larger effect on the ultraviolet absorption.

Consider the 2-methylenecyclanones (I; R = R′ = H): The intensities of infrared C=O, C=C, and ultraviolet bands all decrease with ring size. Bürer and Günthard[30] have shown that the intensity of the C=O band in saturated cyclic ketones decreases with ring size up to cyclodecanone. The decrease in both C=O and C=C intensities in 2-methylenecyclohexanone, compared with 2-methylenecyclopentanone, is very similar to the decrease in C=O intensity of cyclohexanone (A = 25,000[30]) compared with cyclopentanone (A = 28,000[30]); in 2-methylenecycloheptanone a further decrease in intensities is observed, which is rather larger than occurs in going from cyclohexanone to cycloheptanone (A = 22,300[30]). The ultraviolet intensity of 2-methylenecycloheptanone is also considerably lower than the values exhibited by the C_5- and C_6-ring analogues. The ultraviolet intensities parallel closely those of the corresponding 1,2-benzocyclanones[31] in which it has been suggested that the C=O group is twisted out of the plane of the benzene ring, the angle of twist increasing with ring size. This explanation cannot apply to the 2-methylenecyclanones since non-planarity of the chromophore should result in an *increase* in A_{CO} towards the value of the saturated ketone.

For pinocarvone (II) ε_{2410} and A_{CO} are both very low, while the carbonyl frequency is

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* By using Hampson and Weissberger's method (*J.*, 1936, 393; see also Bentley *et al.*, *J.*, 1949, 2957) it can be estimated that the dipole induced by the carbonyl group in a *cisoid* C=C group is about four times greater than that induced in a *transoid* C=C group.

[29] Timmons, Straughan, Forbes, and Shilton, paper presented at the IVth International Meeting of the European Molecular Spectroscopy Group, Bologna, 1959.

[30] Bürer and Günthard, *Helv. Chim. Acta*, 1956, **39**, 356.

[31] Huisgen and Rapp, *Chem. Ber.*, 1952, **85**, 826; Huisgen, Ugi, and Mergenthaler, *Annalen*, 1954, **586**, 1; Hedden and Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 3744.

TABLE 1. *Fixed* cisoid *ketones.*

	C=O band				C=C band					Ultraviolet	
Compound	ν (cm.$^{-1}$)	ε^a	$\Delta\nu^a_{\frac{1}{2}}$	$10^{-2}A$	ν (cm.$^{-1}$)	ε^a	$\Delta\nu^a_{\frac{1}{2}}$	$10^{-2}A$	r^i	$\lambda_{max.}$ (Å)	ε
(I; R = R′ = H; *n* = 1)	1727	420	13	175	1644	119	18	70	2·5	2310	7550
(I; R = R′ = H; *n* = 2)	1697	333	~15	160	1618	106	~18	65	2·5	2300	7400
(I; R = R′ = H; *n* = 3)	1694	280	12	105	1613	108	13	40	2·6	2300	5770
(II)	1704	250	15	125	1623	91	13	35	3·5	2410	4250
(III)	1691	346	13	145	1623	219	17	125	1·2	2410	7600
Cholest-5-en-4-one	1684	—	~11	—	1624	—	~22	—	~0·8	2410	7590 *
(I; R = R′ = Me; *n* = 1)	1706	412	11	145	1633	344	14	155	0·94	2540	11,600
(IV)	1687	260	21	190	1618	60	57	125	1·52	2520	6500
(I; R = R′ = Me; *n* = 3)	1685	288	16	155	1626	63	45	100	1·55	2480	6400
(I; R = H, R′ = Ph; *n* = 1)	1718	391	14	175	1628	298	17	170	1·0	2970	21,600
(I; R = H, R′ = Ph; *n* = 2)	1691	239	17	135	1601	137	34	165	0·82	2880	19,000
(I; R = H, R′ = Ph; *n* = 3)	1684	314	11	100	1609	166	16	85	1·2	2830	13,900
(I; R = H, R′ = Ph; *n* = 4)	1686	278	12	105	1603	139	32	155	0·68	2850	15,000

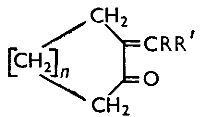
* Fieser and Fieser, " Steroids," Reinhold, New York, 1959, p. 287.

TABLE 2. *Fixed* transoid *ketones.*

Compound	ν (cm.$^{-1}$)	ε^a	$\Delta\nu^a_{\frac{1}{2}}$	$10^{-2}A$	ν (cm.$^{-1}$)	ε^a	$\Delta\nu^a_{\frac{1}{2}}$	$10^{-2}A$	r^i	$\lambda_{max.}$ (Å)	ε
(V; R = H, R′ = Me)	1711	605	20	415	1625	209	11	65	6·4	2260	13,700
(V; R = Et, R′ = H)	1706	733	13	305	1634	~35	~13	~10	~30	2270	9300
(VI; R = H, R′ = Me)	1679	510	16	280	1639	89	16	45	6·2	2340	11,300
(VI; R = R′ = Me) ...	1669	454	19	295	1639	82	14	35	8·4	2440	10,000
(VI; R = H, R′ = Ph)	1670	670	17	400	1615	124	15	60	6·7	2835	19,500

TABLE 3. *Ketones of labile* S-*conformation.*

Compound	ν (cm.$^{-1}$)	ε^a	$\Delta\nu^a_{\frac{1}{2}}$	$10^{-2}A$	ν (cm.$^{-1}$)	ε^a	$\Delta\nu^a_{\frac{1}{2}}$	$10^{-2}A$	r^i	$\lambda_{max.}$ (Å)	ε
$CH_2{:}C(Me){\cdot}COMe$	1683	275	14	135	1632	33	15	15	9·0	2180	9600
$CHMe{:}CH{\cdot}COMe$	1678 1701	413 119	10 ~9	115 ~25	1632	165	11	50	2·8	2200	10,800
$CMe_2{:}CH{\cdot}COMe$	1693	275	11	100	1619	226	21	165	0·61	2370	12,600
$CMe_2{:}CH{\cdot}COBu^t$	1678	203	21	145	1617	209	21	150	0·97	2370	10,850
$CMe_2{:}CMe{\cdot}COMe$	1692	250	16	135	1623	60	44	95	1·4	2455	6000
$CHPh{:}CH{\cdot}COMe$	1673 1697	273 105	17 10	155 25	1612 1627	218 (sh)	13 —	85 —	2·1	2870	20,900
(VII; *n* = 1)	1657 1679	125 268	17 11	70 90	1615	176	24	145	1·1	2520	8900
(VII; *n* = 2)	1690	276	15	140	1619	66	47	110	1·3	2475	6300
(VIII)	1665	311	29	300	1620	58	19	35	8·6	2520	7900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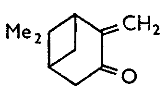
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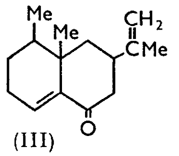
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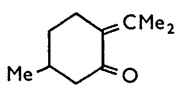
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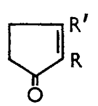
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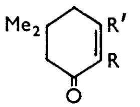
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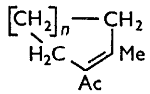
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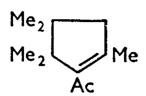
(VIII)

high. Again it seems unlikely that this is due to non-planarity in the C=C–C=O chromophore. The high C=O frequency suggests that the presence of the 1,3-fused cyclobutane ring causes a deformation in the valency angles. The wavelength of maximal ultraviolet absorption is exceptionally high for a chromophore of this degree of alkyl substitution and is consistent with the assumption that a large amount of strain in the ground state is relieved in the excited electronic state of the molecule.

Eremophilone (III) has a stronger C=C band and a weaker C=O band than 2-methylenecyclohexanone, and this is caused by the inductive effect of the ring alkyl group at the γ-carbon atom reinforcing the field effect of the carbonyl group and thus producing a larger dipole in the C=C group. The inductive effect is even more pronounced in the isopropylidenecyclanones, as can be seen by comparing 2-isopropylidenecyclopentanone with 2-methylenecyclopentanone.

For pulegone (IV) and 2-isopropylidenecycloheptanone, differing from the 2-methylene analogues, A_{CO} is larger than for 2-isopropylidenecyclopentanone, while the values of A_{CO} are much smaller than might have been expected by considering the effect of ring size alone. This is exactly what is to be expected if the C=C–C=O chromophore is non-planar in the C_6- and C_7-ring compounds. Non-planarity in the chromophore in these compounds arises because (*a*) the well-known *cis*-butane interactions tend to force alicyclic rings into non-planar conformations and (*b*) there is steric hindrance between the carbonyl-oxygen atom and a methyl group of the isopropylidene group; these effects together equal or exceed the gain in resonance energy obtained in a planar conformation. Pulegone and 2-isopropylidenecycloheptanone exhibit the very broad C=C bands also shown by 3,4-dimethylpent-3-en-2-one and 1-acetyl-2-methylcyclohexene (VII; $n = 2$), and the four compounds have rather similar ultraviolet spectra. The low ultraviolet intensities have been attributed by Mecke and Noack[32] to the hyperconjugative effect of the β-alkyl group but this could not, in our opinion, account for such a large decrease [cf. for example the data for (VI; $R = H$, $R' = Me$; and $R = R' = Me$)]. A possible explanation of the broad C=C bands is to be found in Wepster's discussion[33] of steric effects on mesomerism (resonance). Wepster suggested that van der Waals repulsion forces, which will be at a maximum in molecular conformations with the dihedral angle (θ) between the nodal planes of the C=O and C=C groups 0° and 180°, can counteract the stabilisation due to mesomerism, also greatest when $\theta = 0°$ and $180°$, to produce a molecule with a very large degree of rotational freedom of the C=C group with respect to the C=O group. The shape of the curve for variation of potential-energy with θ will be very sensitive to the exact shape of the van der Waals curve, but it can be visualised that at room temperature molecules such as 1-acetyl-2-methylcyclohexene may spend a large fraction of time in conformations other than the planar *s-cis*. Such a compound will have broader C=O and C=C bands than, for example, mesityl oxide which exists predominantly in the planar *s-cis*-form, because the frequency as well as the intensity of the vibration is dependent on θ. If the chromophore is in a rigid polycyclic system, or if the substituents are very bulky, as in 2,2,4,5-tetramethylhex-4-en-3-one,[29] rotational freedom will be destroyed and a sharp C=C band will again be observed, but as a result of non-planarity the intensity of the ultraviolet band will remain low.

Steric hindrance to coplanarity in the chromophore should be less in 1-acetyl-2-methylcyclopentene than in 1-acetyl-2-methylcyclohexene, and this is confirmed by the conclusion that, whereas the latter exists largely in hindered *s-cis*-conformations,[2] the former exists as a mixture of *s-cis*- and *s-trans*-forms under the same conditions. It is therefore surprising at first sight that 1-acetyl-2,4,4,5,5-pentamethylcyclopentene should prefer the *s-trans*-conformation. However, models indicate that steric hindrance is greater between the acetyl-methyl and the 5-methyl group in the *s-cis*-form than between the acetyl-methyl and the 2-methyl group in the *s-trans*-form. In contrast, both planar conformations in 1-acetyl-2,6,6-trimethylcyclohexene are so hindered that the ultraviolet intensity (ε) is only 1400,[34] suggesting [2] that θ must be 70—110°.

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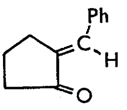
[32] Mecke and Noack, *Angew. Chem.*, 1956, **68**, 150.

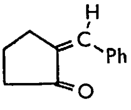
[33] Wepster, " Progress in Stereochemistry," eds. Klyne and de la Mare, Butterworths, London, 1958, Vol. II, p. 99.

[34] Henbest and Woods, *J.*, 1952, 1150.

While the general conclusion concerning the relative magnitudes of r^i for *cisoid* and *transoid* ketones holds for the benzylidene derivatives, a more detailed discussion of the spectra of the *cisoid* compounds is made difficult because a completely coplanar arrangement of the phenyl, carbonyl, and C=C groups is possible in the *anti*-form of 2-benzylidenecyclopentanone but not in the *syn*-form or in either possible form of the larger ring analogues. For the higher homologues, models show that either the phenyl group cannot be in the plane of the C=C–C=O group or the C=O group must be twisted out of the plane of the Ph–C=C group.



anti



syn

Attention must be drawn to the infrared data for the derivatives of cyclopent-2-enone. The inductive effect of alkyl groups in assisting or diminishing the field effect of the carbonyl group is particularly evident in the C=C band intensities of 3-methylcyclopent-2-enone and 2-ethylcyclopent-2-enone, and to a smaller extent in the C=O intensities. The strain produced in accommodating three trigonal centres in a five-membered ring is reflected in C=O and C=C frequencies, respectively higher and lower than might have been expected and similar, in fact, to those of the *cisoid* ketone 2-isopropylidenecyclopentanone. The latter has only two trigonal centres in the ring and is correspondingly less strained.

The nuclear magnetic resonance of αβ-unsaturated ketones, which will be discussed in a forthcoming paper by Jackman and his co-workers, gives stereochemical information complementary to that obtained in studies of electronic and vibrational spectra.

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