THE CARBONYL STRETCHING BANDS IN THE INFRARED SPECTRA OF UNSATURATED LACTONES[1]

R. N. JONES, C. L. ANGELL,[2] T. ITO,[2] AND R. J. D. SMITH[3]

ABSTRACT

Certain types of unsaturated lactones exhibit two bands in the region of the spectrum associated with the C=O stretching vibrational mode. This is observed both in the infrared and Raman spectra.

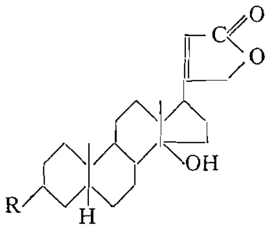
The infrared spectra of 23 simple saturated and unsaturated lactones have been examined in an attempt to determine the structural features with which this carbonyl band splitting is associated. It appears to be common to most unsaturated five- and six-membered ring lactones in which the double bond is conjugated with the carbonyl group, though one well-established exception has been observed. The relative intensities of the two bands are extremely sensitive to changes in the polarity of the solvent; they also vary reversibly with temperature but are independent of concentration.

The splitting of the C=O stretching band is attributed to an intramolecular vibrational effect similar to that which occurs in cyclopentanone and in certain Δ^2-cyclopentenone derivatives. Its possible dependence on Fermi resonance with the overtone of a lower lying fundamental vibration is discussed.

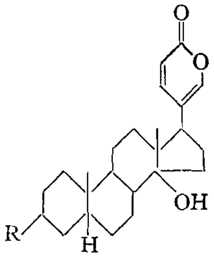
Similar effects occur in other types of carbonyl compounds, such as benzoyl chloride and cyclic five-membered ring anhydrides, and care is needed to distinguish carbonyl band splitting of this kind from that associated with equilibria between conformational isomers.

INTRODUCTION

In the course of a systematic survey of the infrared spectra of steroids, it was observed (1, 2) that compounds containing the unsaturated lactone rings of I and II show anomalous absorption in the region of the carbonyl stretching bands. The single absorption band expected for the stretching vibration of the lactone carbonyl is replaced by two bands, the relative intensities of which are extremely sensitive to the solvent polarity.



I



II

The steroids in which the effect was first observed contained hydroxy and acetoxy groups in addition to the lactone ring; this complicated study of the lactone carbonyl absorption and suggested that the bands might involve inter- or intra-molecular hydrogen bonding, or some other interaction between the lactone and the functional groups of the ring system. The spectra of a series of simple model compounds have therefore been

[1] *Manuscript received June 29, 1959.*
Contribution from the Division of Pure Chemistry, National Research Council of Canada, Ottawa, Canada. Presented, in part, at the International Conference of the European Molecular Spectroscopy Group, Freiburg-im-Breisgau, Germany, July 1957.
Issued as N.R.C. No. 5363.

[2] *National Research Council Guest Worker.*

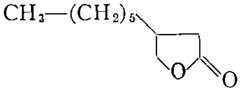
[3] *National Research Council Postdoctorate Fellow.*

Can. J. Chem. Vol. 37 (1959)

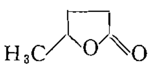
investigated. These compounds show the same anomalies as the steroid lactones, and the effects of solvent, temperature, and small structural changes on the carbonyl stretching band system have been investigated.

EXPERIMENTAL

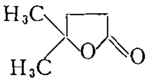
The compounds examined have the structures III–XXV; they include four saturated γ-lactones (III–VI), 13 unsaturated γ-lactones (VII–XIX), one saturated δ-lactone (XX), and five unsaturated δ-lactones (XXI–XXV). The majority of these compounds were synthesized specifically for this investigation, and the preparative details and structural characterization are noted briefly below.



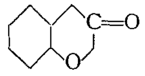
III



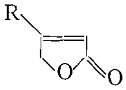
IV



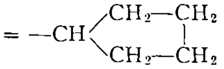
V

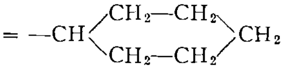


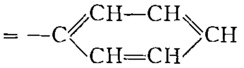
VI

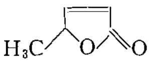


VII R = —H
VIII R = $—(CH_2)_3—CH_3$
IX R = $—(CH_2)_5—CH_3$

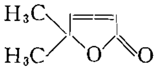
X R =


XI R =


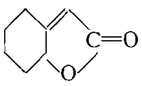
XII R =




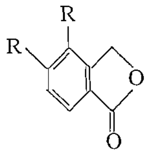
XIII



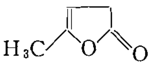
XIV



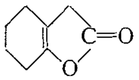
XV



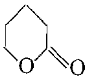
XVI R = —H
XVII R = $—OCH_3$



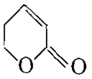
XVIII



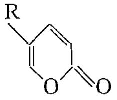
XIX



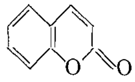
XX



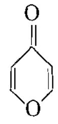
XXI



XXII R = —H
XXIII R = $—CH_3$



XXIV



XXV

Synthesis and Characterization of Compounds

III. *β-n-Hexyl-butanolide.*—Prepared by hydrogenation of VIII with 5% Pd on charcoal in methanol at 1 atm H_2.

IV. *γ-Methyl-butanolide.*—Prepared from XIII by hydrogenation under the same conditions as III, b.p. 83° (10 mm).

V. *γ,γ-Dimethyl-butanolide.*—Prepared as III from XIV, b.p. 80° (10 mm).

VI. *trans-Cyclohexanol-2-acetic acid lactone.*—Prepared as described by Newman and VanderWerf (3), b.p. 142° (20 mm).

VII. *$\Delta^{\alpha\beta}$-Butenolide.*—Prepared as described by Smith and Jones (4), b.p. 86–87° (12 mm). Found: C, 57.03%; H, 4.94%. Calc.: C, 57.14%; H, 4.80%.

VIII. *β-n-Butyl-$\Delta^{\alpha\beta}$-butenolide.*—Prepared as described by Rubin, Paist, and Elderfield (5); the product was repeatedly distilled until free from bromine, b.p. 101–101.5° (1 mm) n_D^{20} 1.4715.

IX. *β-n-Hexyl-$\Delta^{\alpha\beta}$-butenolide.*—Prepared as VIII, b.p. 120–121° (2 mm). Found: C, 70.99%; H, 9.63%. Calc.: C, 71.40%; H, 9.59%.

X. *β-Cyclopentyl-$\Delta^{\alpha\beta}$-butenolide.*—Prepared as VIII, b.p. 120–121° (2 mm). Found: C, 70.18%; H, 8.00%. Calc.: C, 71.02%; H, 7.95%.

XI. *β-Cyclohexyl-$\Delta^{\alpha\beta}$-butenolide.*—Prepared as VIII, b.p. 143–144° (5 mm). Found: C, 72.36%; H, 8.61%. Calc.: C, 72.28%; H, 8.43%. Ultraviolet spectrum: λ_{max} 2215 Å log ϵ_{max} 3.33 (*n*-heptane solution).

XII. *β-Phenyl-$\Delta^{\alpha\beta}$-butenolide.*—Prepared as VIII. Recrystallized five times from 75% aqueous methanol, m.p. 94°. Ultraviolet spectrum: λ_{max} 2020 Å log ϵ_{max} 4.34; λ_{max} 2070 Å log ϵ_{max} 4.24; λ_{max} 2530 Å (broad) log ϵ_{max} 4.37 (*n*-heptane solution).

XIII. *β-Angelica lactone.*—Prepared by isomerization of the α-isomer with triethylamine (6). Some residual α-isomer was removed by hydrolysis and redistillation (7) but the product still contained 7–10% of the α-isomer as estimated from the infrared spectrum, b.p. 83° (10 mm).

XIV. *γ,γ-Dimethyl-$\Delta^{\alpha\beta}$-butenolide.*—Prepared as described by Haynes and Jones (8) and purified by chromatography on a neutralized alumina column from petroleum ether – benzene (2:1), b.p. 80° (10 mm).

XV. *(2-Hydroxy-1-cyclohexylidine)-acetic acid lactone.*—Prepared as described by Newman and VanderWerf (3), b.p. 130° (5 mm); m.p. 30°. Ultraviolet spectrum: λ_{max} 2215 Å log ϵ_{max} 3.26 (*n*-heptane solution).

XVI. *Phthalide.*—Commercial sample recrystallized twice from water, m.p. 72°.

XVII. *5,6-Dimethoxyphthalide.*—Sample provided by Dr. O. E. Edwards. Recrystallized twice from water, m.p. 156–157°.

XVIII. *α-Angelica lactone.*—Commercial sample purified by distillation, b.p. 52° (10 mm); m.p. 18°.

XIX. *2-Hydroxy-(Δ^1-cyclohexenyl)-acetic acid lactone.*—Prepared as described by Newman and VanderWerf (3), b.p. 110° (5 mm).

XX. *δ-Valerolactone.*—Prepared by hydrogenation of XXI under the same conditions as III, b.p. 107° (7 mm).

XXI. *5,6-Dihydro-α-pyrone.*—Prepared as described by Haynes and Jones (8), b.p. 105° (7 mm). Ultraviolet spectrum: λ_{max} 2195 Å log ϵ_{max} 2.87 (*n*-heptane solution).

XXII. *α-Pyrone.*—Prepared as described by von Pechmann (9), m.p. 5°.

XXIII. *5-Methyl-α-pyrone.*—Prepared as described by Fried and Elderfield (10), m.p. 17–19°.

XXIV. *Coumarin.*—Commercial sample purified by vacuum sublimation, m.p. 70°.

XXV. *γ-Pyrone.*—Sample supplied by Dr. O. E. Edwards, m.p. 32°.

Spectroscopic Measurements

Most of the infrared spectra were measured in carbon tetrachloride, carbon disulphide, or chloroform solution on a Perkin–Elmer 112 spectrometer. A calcium fluoride prism was used above 1300 cm^{-1} and a sodium chloride prism below. After correction for background and solvent absorption the spectra were plotted as apparent molecular extinction coefficient against wave number (11). Several of the spectra were also determined as thin liquid films on a Perkin–Elmer Model 21 spectrophotometer with sodium chloride prism. The estimated precision of the carbonyl band positions reported in Tables I and II is ± 2 cm^{-1}. Only portions of selected spectra are shown here, but the complete series of spectra will be published separately (12). A standard Perkin–Elmer heated cell was used to obtain the spectra of liquid films at elevated temperatures, and the spectrum of β-phenyl-$\Delta^{\alpha\beta}$-butenolide at liquid nitrogen temperature was measured on equipment kindly made available to us by Dr. H. J. Bernstein.

TABLE I

Positions and intensities of absorption bands between 1850 and 1550 cm^{-1} in the infrared spectra of lactones exhibiting "doublet carbonyl" absorption

		Band *A*		Band *B*			
Compound	Solvent	$\nu_{\max}$ (cm^{-1})	$\epsilon_{\max}^{(a)}$ (cm^{-1})	$\nu_{\max}$ (cm^{-1})	$\epsilon_{\max}^{(a)}$ (cm^{-1})	Intensity ratio*	Other bands†
VII $\Delta^{\alpha\beta}$-Butenolide	CCl_4	1784.5	1240	1742	98	12.6	
	$CHCl_3$	1777.5	790	1745	565	1.4	1618(18); 1601(31)
VIII β-*n*-Butyl-$\Delta^{\alpha\beta}$-butenolide	CCl_4	1785	1075	1752	430	2.5	1643(96)
	$CHCl_3$	1784	335	1748	900	0.37	1638(125)
IX β-*n*-Hexyl-$\Delta^{\alpha\beta}$-butenolide	CCl_4	1787	1000	1754	405	2.45	1642(116)
	$CHCl_3$	1785	330	1750	915	0.36	1639(122)
X β-Cyclopentyl-$\Delta^{\alpha\beta}$-butenolide	CCl_4	1785	1175	1756	495	2.4	1638(117)
	$CHCl_3$	1784	335	1750	920	0.36	1636(136)
XI β-Cyclohexyl-$\Delta^{\alpha\beta}$-butenolide	CCl_4	1785	695	1764	540	1.30	1648(50); 1636(53)
	$CHCl_3$	1782	225	1748	850	0.26	1647(56); 1633(66)
XII β-Phenyl-$\Delta^{\alpha\beta}$-butenolide	CCl_4	1786	1805	1758	975	1.85	1694(25); 1628(180)
	$CHCl_3$	1789	335	1751	1400	0.24	1712(75); 1626(275)
XIII β-Angelica lactone	CCl_4	1782	900	1765	470	1.92	1735(220)
	$CHCl_3$	1783	270	1759	940	0.29	1742(490); 1634(60); 1602(138)
XIV γ,γ-Dimethyl-$\Delta^{\alpha\beta}$-butenolide	CCl_4	1776	635	1764	650	0.96	
	$CHCl_3$	1774	295	1754	975	0.30	1604(27)
XV (2-Hydroxy-cyclohexylidine)-acetic acid lactone	CCl_4	1779	855	1764	605	1.41	1653(183)
	$CHCl_3$	1755	640	1740	830	0.77	1649(205)
XXII α-Pyrone	CCl_4	1752	1480	1716	115	12.8	1780(114); 1640(60); 1622(55)
	$CHCl_3$	1739	1080	1721	920	1.17	1785(46); 1640(45); 1625(100)
XXIII 5-Methyl-α-pyrone	CCl_4	1753	1505	1731	445	3.4	1657(65); 1647(50)‡
	$CHCl_3$	1750	440	1719	990	0.45	1648(135); 1640(45);‡ 1544(190)
XXIV Coumarin	CCl_4	1757	1100	1743	1290	0.85	
	$CHCl_3$	1757	275	1731	1000	0.275	
XXV γ-Pyrone	CCl_4	1678	1270	1657	320	3.7	1730(22); 1695(180); 1619(87)
	$CHCl_3$	1674	980	1661	1210	0.81	1740(18); 1698(63); 1632(180); 1613(216)

*$\epsilon_{\max}^{(a)}$ Band *A*/$\epsilon_{\max}^{(a)}$ Band *B*.

†Band positions are reported in cm^{-1} followed by intensities ($\epsilon_{\max}^{(a)}$) in parentheses.

‡Inflection.

The Raman spectra were measured in 0.2-ml cells on a Cary Model 81 spectrophotometer using Hg 4358-Å excitation at a spectral slit width of 6 cm^{-1}. Ultraviolet spectra, determined for identification purposes only, were measured on a Cary Model 12C spectrophotometer in ethanol and *n*-heptane solution; these spectra were in good accord with those reported previously in the literature (8, 13). Most previous investigators

TABLE II

Positions and intensities of absorption bands between 1850 and 1550 cm^{-1} in the infrared spectra of lactones exhibiting "singlet carbonyl" absorption

			Carbonyl band		
	Compound	Solvent	ν_{max} (cm^{-1})	$\epsilon_{max}^{(a)}$ (cm^{-1})	Other bands*
III	β-*n*-Hexyl-butanolide	CS_2	1792	—	
		$CHCl_3$	1777	—	
IV	γ-Methyl-butanolide	CS_2	1790	—	
		$CHCl_3$	1775	—	
V	γ,γ-Dimethyl-butanolide	CS_2	1785	—	
		$CHCl_3$	1775	—	
VI	*trans*-Cyclohexanol-2-acetic acid lactone	CCl_4	1793	1050	1710(20)
		$CHCl_3$	1779	780	1716(40)
XVI	Phthalide	CCl_4	1778	—	
		$CHCl_3$	1761	—	
XVII	5,6-Dimethoxyphthalide	CCl_4	1772	—	
		$CHCl_3$	1752	—	
XVIII	α-Angelica lactone	CCl_4	1806	675	1722(27); 1686(60); 1678(45)
		$CHCl_3$	1796	435	1722(110); 1683(57)
XIX	2-Hydroxy-(Δ^1-cyclohexene-1-yl)-acetic acid lactone	CCl_4	1819†	470	1708(65)
		$CHCl_3$	1798†	450	1709(335)
XX	δ-Valerolactone	CS_2	1750	—	
		$CHCl_3$	1732	—	
XXI	5,6-Dihydro-α-pyrone	CCl_4	1743	1080	
		$CHCl_3$	1729	830	

*Band positions are reported in cm^{-1}, followed by intensities ($\epsilon_{max}^{(a)}$) in parentheses.
†Broad unsymmetrical band.

have measured the ultraviolet absorption spectra of $\Delta^{\alpha\beta}$-butenolides in ethanol solution, and under these conditions the maximum occurs near 2100 Å. The band is displaced bathochromically to 2200–2215 Å in *n*-heptane, where it is more easily observed and more precisely measured. A representative ultraviolet spectrum in *n*-heptane has been published elsewhere (4).

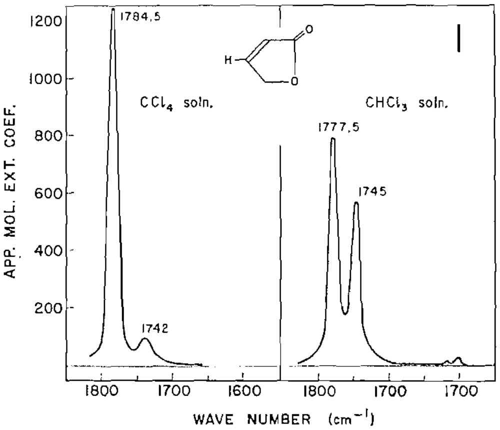
Molecular Weight Measurements

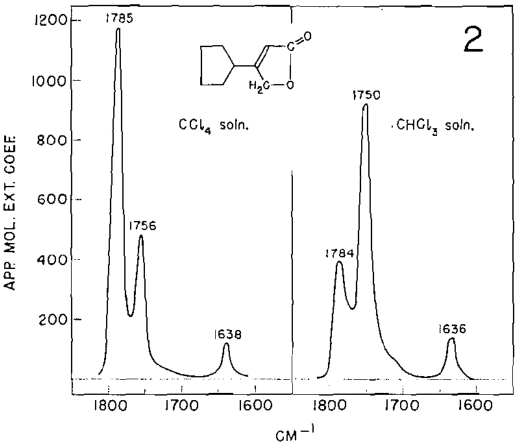
Molecular weights in solution were kindly determined for us by Dr. A. F. Sirianni of the Applied Chemistry Division of the National Research Council by measurement of the depression of the solvent vapor pressure, using the technique developed by Puddington (14).

RESULTS

The typical doublet carbonyl absorption of the conjugated unsaturated γ- and δ-lactones is illustrated by the infrared spectra of $\Delta^{\alpha\beta}$-butenolide (VII), β-cyclopentyl-$\Delta^{\alpha\beta}$-butenolide (X), and 5-methyl-α-pyrone (XXIII) in Figs. 1–3. It is characteristic of this absorption that the high frequency component (Band *A*) is more intense in carbon tetrachloride, and the relative intensities tend to reverse in chloroform solution. This is identical with the behavior of the lactone carbonyl bands of the steroids I and II. The positions and intensities of these bands for all lactones exhibiting the doublet absorption are given in Table I, while the carbonyl bands of lactones showing normal behavior are summarized in Table II.

Before discussing this absorption it will be convenient first to record some additional experiments that illustrate the effect of various environmental factors on these bands.





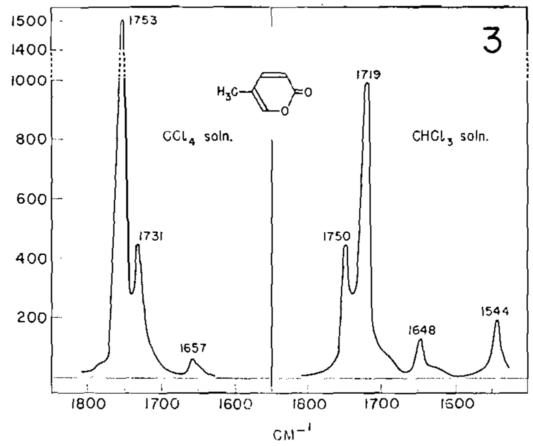


FIG. 1. Infrared spectrum of $\Delta^{\alpha\beta}$-butenolide in the region of the C=O stretching absorption.
FIG. 2. Infrared spectrum of β-cyclopentyl-$\Delta^{\alpha\beta}$-butenolide in the region of the C=O stretching absorption.
FIG. 3. Infrared spectrum of 5-methyl-γ-pyrone in the region of the C=O stretching absorption.

Most of these measurements were made with β-*n*-hexyl-$\Delta^{\alpha\beta}$-butenolide (IX), as this was the lactone in most plentiful supply. The phenyl derivative (XII) with melting point 94° was used for solid phase studies since most of the other lactones are liquids or low melting solids. We are satisfied, however, that these effects are general to all the lactones exhibiting the split carbonyl bands.

Solvent Effects

In carbon disulphide the spectrum of β-*n*-hexyl-$\Delta^{\alpha\beta}$-butenolide in the region of the carbonyl bands is similar to that in carbon tetrachloride, while the spectrum of the pure liquid is similar to that in chloroform. The spectrum in acetonitrile and methanol also resembles the spectrum of the chloroform solution, but the inversion of the band intensities is more accentuated (Table III). These band intensity changes are reversible when the same sample of lactone is examined successively in a series of different solvents.

In the last two columns of Table III are given the dipole moments and dielectric constants of the solvents. Although the relative intensity of the low frequency band (Band *B*) increases with the solvent polarity, the relationship is not a simple one. This, however,

TABLE III

Doublet carbonyl absorption of β-n-hexyl-$\Delta^{\alpha\beta}$-butenolide in various solvents

Solvent	Band A		Band B		Intensity ratio (Band A/Band B)	Dielectric constant of solvent	Dipole moment of solvent (Debye)
	ν_{max} (cm^{-1})	$\epsilon_{max}^{(a)}$ (cm^{-1})	ν_{max} (cm^{-1})	$\epsilon_{max}^{(a)}$ (cm^{-1})			
CCl_4	1787	1000	1754	405	2.5	2.238 (20° C)	0.0
CS_2	1782	1120	1750	410	2.7	2.641 (20° C)	0.0
$CHCl_3$	1785	330	1750	900	0.37	4.806 (20° C)	1.20
CH_3OH	1783	185	1741	750	0.25	32.03 (25° C)	3.01
CH_3CN	1783	325	1750	1050	0.31	37.5 (20° C)	3.4/3.5*
CCl_4 sat. HCl	1786	980	1752	460	2.1	—	—
$CHCl_3$ sat. HCl	1785	310	1749	880	0.35	—	—
$CHCl_3(20\%)/CCl_4(80\%)$†	1785	695	1751	785	0.89	—	—
$CHCl_3(50\%)/CCl_4(50\%)$	1785	470	1752	865	0.54	—	—

*Benzene solution.
†Percentage by weight.

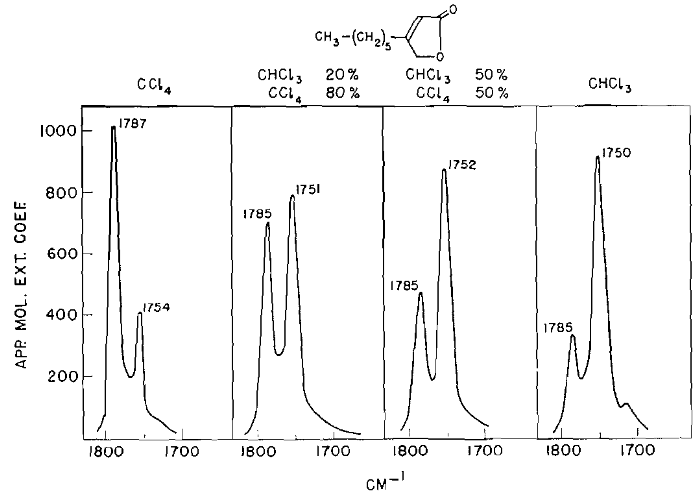


FIG. 4. Effect of solvent on the C=O stretching absorption of β-n-hexyl-$\Delta^{\alpha\beta}$-butenolide.

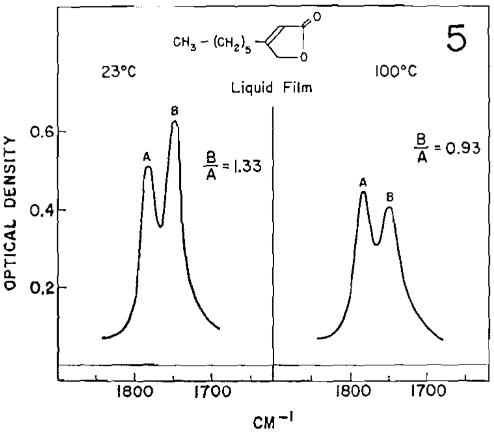
would hardly be expected in the light of recent studies of solvent effects (15). The sensitivity of the bands to the solvent polarity is illustrated by the curves for mixed carbon tetrachloride/chloroform solvents shown in Fig. 4. With increase in the chloroform concentration the relative intensities of the bands change progressively; the position of Band A remains unchanged while Band B shifts slightly from 1754 cm^{-1} to 1750 cm^{-1}. Saturation of either solvent with dry hydrogen chloride, which might catalyze a chemical bond shift, has no effect on the band positions or intensities.

Concentration Effects

The spectrum of β-n-hexyl-$\Delta^{\alpha\beta}$-butenolide in the region of the carbonyl stretching bands was measured both in carbon tetrachloride and in chloroform solution over a concentration range from 0.001 M to 0.03 M, and no significant change in the ratios of the band intensities was observed. When this is considered in conjunction with the similarity of the spectrum of the pure liquid to that of the dilute solutions in chloroform, it strongly suggests that we are not dealing with an association phenomenon; this is borne out also by the molecular weight measurements discussed below.

Temperature Effects

The effect of temperature increase on the spectra of liquid films of β-*n*-hexyl-$\Delta^{\alpha\beta}$-butenolide and 5-methyl-α-pyrone is shown in Figs. 5 and 6. In both cases there is a pronounced enhancement of the relative intensity of the high frequency component as the temperature rises. This effect is reversed on cooling. The decrease in the absolute intensity in the heated film in Fig. 5 is a secondary consequence of the decrease in the thickness of the capillary film layer.



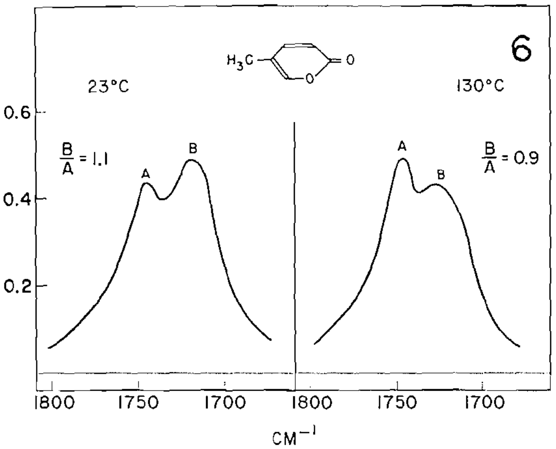


FIG. 5. Effect of temperature on the C=O stretching absorption of a liquid film of β-*n*-hexyl-$\Delta^{\alpha\beta}$-butenolide.
FIG. 6. Effect of temperature on the C=O stretching absorption of a liquid film of 5-methyl-γ-pyrone.

The spectrum of β-phenyl-$\Delta^{\alpha\beta}$-butenolide, measured as a crystalline film at room temperature and when cooled with liquid air, is shown in Fig. 7. Both spectra show the doublet carbonyl peaks. The minor bands and inflection may be due to incomplete compensation for water vapor absorption.

Raman Spectra

The Raman spectra of $\Delta^{\alpha\beta}$-butenolide and its β-*n*-butyl derivative have been determined for the pure liquids and for solutions in carbon tetrachloride and chloroform. The

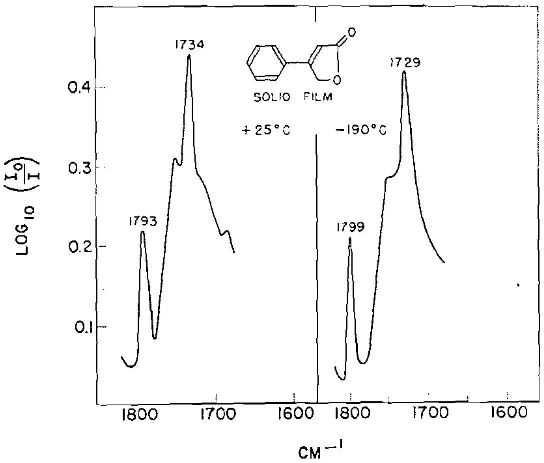


FIG. 7. Effect of temperature on the C=O stretching absorption of a solid crystalline film of β-phenyl-$\Delta^{\alpha\beta}$-butenolide.

Raman spectrum of β-phenyl-$\Delta^{\alpha\beta}$-butenolide was also measured in both solvents. These spectra show the same doublet carbonyl bands as do the infrared spectra with intensity variations in the same sense. The C=C stretching bands are relatively more intense than in the infrared spectrum, as is normally the case. A representative pair of Raman spectra is shown in Fig. 8.

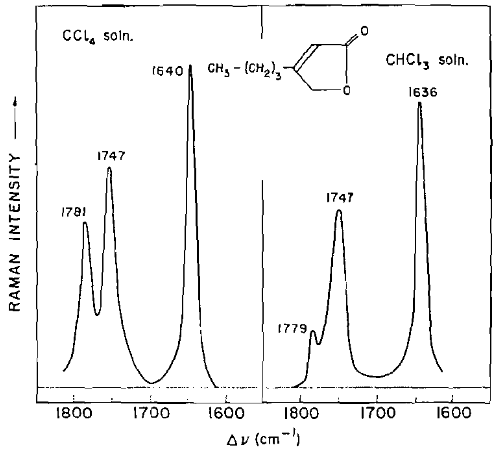


FIG. 8. Effect of solvent on the C=O stretching bands in the Raman spectrum of β-*n*-butyl-$\Delta^{\alpha\beta}$-butenolide.

TABLE IV
Molecular weights of $\Delta^{\alpha\beta}$-butenolides in solution

Solvent	Concn. (mg/100 mg of solution)	Temp. (° C)	Mol. wt.
(A) β-Phenyl-$\Delta^{\alpha\beta}$-butenolide (XII)*			
Benzene	1.360	38	169.5
	0.735	38	166.5
	0.64	38	172.2
	0.765	36	173.9
	0.735	36	175.8
	0.570	36	174.3
Ethanol	1.309	38	183.5
	1.00	38	184.6
	0.754	38	185.6
	0.756	36	167.3
	0.696	36	178.0
	0.542	36	178.5
(B) Digitoxigenin acetate (I)†			
Toluene	2.31	50	511
	1.6	50	485
	1.55	50	479
	2.15	70	470
	1.65	70	436
	1.5	70	423
	1.32	70	445
	1.13	70	447
Ethanol	3.02	50	454
	2.35	50	411
	1.67	50	422

*Mol. wt. of monomer (calc.) 160.
†Mol. wt. of monomer (calc.) 416.

Molecular Weights in Solution

Accurate molecular weight determinations on solutions of the lower melting and liquid lactones could not be obtained because of their finite vapor pressure. Measurements are reported in Table IV for β-phenyl-$\Delta^{\alpha\beta}$-butenolide (m.p. 74°) and for digitoxigenin acetate (I) (R = —OAc) (m.p. 217°). Although these data all indicate some degree of association in solution, there is no significant difference between the measurements in the more polar and less polar solvents that might reasonably be correlated with the spectral changes. The spectrum of β-phenyl-$\Delta^{\alpha\beta}$-butenolide in benzene shows the typical non-polar solvent pattern with strong reversal of the band intensity in ethanol. These molecular weight measurements therefore exclude any explanation of the carbonyl band splitting based on dimeric or polymeric association.

DISCUSSION

The infrared literature contains numerous examples of monocarbonyl compounds that exhibit two or more prominent bands between 1900 and 1650 cm^{-1}. In the absence of other acceptable explanations, both bands are usually assigned to vibrations involving the carbonyl group. In a number of cases these doublet carbonyl peaks have been attributed to equilibria between conformational isomers.

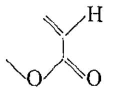
This interpretation is usually based on the demonstration that the relative intensities of the two peaks are temperature- and solvent-dependent, but are independent of the concentration. It must also be possible to write a pair of conformationally isomeric structures that are plausible on both thermodynamic and spectroscopic grounds. This requires that the energy difference between the two forms will be small enough to allow a significant concentration of the less stable form to exist in equilibrium at room temperature, while the energy barrier to interconversion must be small enough to permit rapid attainment of the equilibrium. It is also necessary that the inductive, mesomeric, and field effects on the carbonyl group must differ sufficiently in the two forms to induce a significant displacement of the two carbonyl frequencies.

The doublet carbonyl peaks of the lactones considered here do show the necessary solvent and temperature dependence and concentration independence, but for them it is not possible to write pairs of stable conformationally isomeric structures within the framework of current views of molecular structure. A similar situation occurs for cyclopentanone (16), which also exhibits a split carbonyl band, and for certain Δ^2-cyclopentenones that have been studied by Yates and his collaborators (17, 18). In both the latter cases it has been shown that the splitting of the carbonyl band must involve an intramolecular vibrational property of the molecule, since it disappears when certain of the hydrogen atoms are exchanged for deuterium. So far our attempts to introduce deuterium into the $\alpha\beta$-unsaturated-γ-lactone ring have been unsuccessful, but there can be little doubt that the nature of the carbonyl band splitting is similar to that in cyclopentanone and in the Δ^2-cyclopentenones.

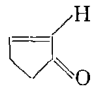
Assuming that an intramolecular vibrational effect is involved, it must depend on some form of coupling between the carbonyl stretching mode and another vibration. This would seem to require an accidental degeneracy between the C=O stretching mode and an overtone or combination band, i.e. a Fermi resonance. We have come to accept this explanation for the lactone spectra with some reluctance, since, a priori, it seemed highly unlikely that such accidental degeneracy would occur through such a wide range of different types of structure. Thus it is necessary that the overtone or combination band must be entirely uninfluenced by the nature of the substituent on the

β-carbon atom. The lack of coupling between the vibrations in the ring and in the β-side chain of the $\Delta^{\alpha\beta}$-butenolides is demonstrated in the spectrum of the β-phenyl derivative. The carbonyl bands of this compound show practically no shift from those of compounds containing β-alkyl groups (cf. VIII and XII in Table I). Models demonstrate that in β-phenyl-$\Delta^{\alpha\beta}$-butenolide there is no steric hindrance to a structure in which the aromatic and lactone rings are coplanar, but nevertheless there must be negligible π-electron flow between the rings in the ground state of the molecule.

In terms of a Fermi resonance hypothesis, it is also surprising that the perturbation effects on the five- and six-membered ring lactones should be identical (cf. Figs. 2 and 3). In looking for common structural features among the compounds in Table I we do observe that all contain the partial structure XXVI, and this closely resembles XXVII which Yates and Williams have demonstrated to be necessary for carbonyl band splitting in Δ^2-cyclopentenones (18). On the other hand it must also be noted that the $\alpha\beta$-unsaturated-δ-lactone XXI which does contain the partial structure XXVI shows the normal singlet carbonyl maximum. The possibility must be considered that an element of fortuitousness exists in the seemingly similar behavior of the γ- and δ-lactones, and this will arise again when numerical relationships with possible low-lying fundamental vibrations are considered. In γ,γ-dimethyl-$\Delta^{\alpha\beta}$-butenolide (XIV) the doublet is also rather poorly resolved.



XXVI



XXVII

In the infrared spectra of the saturated five-membered ring lactones (III–VI) the singlet carbonyl peak occurs at 1795–1785 cm^{-1} in carbon tetrachloride solution. In the absence of vibrational perturbation effects, this frequency would be expected to fall by about 20 cm^{-1} on introduction of the conjugated double bond to form the $\Delta^{\alpha\beta}$-butenolide ring. This would place the "normal" $\Delta^{\alpha\beta}$-butenolide carbonyl band in the range 1775–1765 cm^{-1}. However, the shortening of the $\alpha\beta$-bond will reduce the internal ring angles, and this will have a secondary effect, changing the hybridization to put more sp^2 character into the external bonds, and raising the carbonyl frequency slightly, perhaps to 1780–1770 cm^{-1}.

A survey of the complete spectra of the $\Delta^{\alpha\beta}$-butenolides (12) shows that there is usually a band (ν_2) in the region 900–875 cm^{-1}, the first overtone of which ($2\nu_2$) might couple with the carbonyl stretching mode to provide the postulated Fermi resonance split. These frequency relationships are summarized in Table V. In most of the compounds ν_2 is one of the strongest bands in this region of the spectrum. It might be identified with the out-of-plane deformation vibration of the hydrogen atom on the α-carbon atom, and this would be consistent with the presence of structure XXVI. In some of the compounds, however (notably XIII and XIV), the band is weak.

From Table V it will be seen that ν_2 is displaced upwards with change from carbon tetrachloride to chloroform solvent, while ν_1, the arithmetical mean of the two carbonyl frequencies, moves in the opposite direction. In the last column of Table V the difference $\nu_1-2\nu_2$ is given. In the absence of anharmonicity, the Fermi resonance coupling should depend inversely on the numerical value of this difference, irrespective of the sign. This might be changed if $2\nu_2$ is lowered below ν_1 by a strong anharmonicity term. $\Delta^{\alpha\beta}$-Butenolide itself is an exception, and for this compound stronger coupling would be expected

TABLE V

Relationships between positions of carbonyl bands and other bands that might enter into Fermi resonance

Compound	Solvent*	Mean carbonyl frequency $\nu_1 = \frac{1}{2}(\nu_A + \nu_B)$	ν_2	$2\nu_2$	$\nu_1 - 2\nu_2$
$\Delta^{\alpha\beta}$-Butenolide (VII)	CCl_4	1763 (cm^{-1})	869	1738	−25
	$CHCl_3$	1761	877	1754	− 7
β-*n*-Butyl-$\Delta^{\alpha\beta}$-butenolide (VIII)	CCl_4	1768	878	1756	+12
	$CHCl_3$	1766	891	1782	−16
β-*n*-Hexyl-$\Delta^{\alpha\beta}$-butenolide (IX)	CCl_4	1770	881	1762	+ 8
	$CHCl_3$	1767	894	1788	−21
β-Cyclopentyl-$\Delta^{\alpha\beta}$-butenolide (X)	CCl_4	1770	882	1764	+ 6
	$CHCl_3$	1767	893	1786	−19
β-Cyclohexyl-$\Delta^{\alpha\beta}$-butenolide (XI)	CCl_4	1774	878	1756	+18
	$CHCl_3$	1765	899	1798	−33
β-Phenyl-$\Delta^{\alpha\beta}$-butenolide (XII)	CCl_4	1772	886	1772	0
	$CHCl_3$	1770	895	1790	−20
β-Angelica lactone (XIII)	CCl_4	1773	878†	1756	+17
	$CHCl_3$	1771	887†	1774	− 3
γ,γ-Dimethyl-$\Delta^{\alpha\beta}$-butenolide (XIV)	CCl_4	1770	885†	1770	0
	$CHCl_3$	1764	890†	1780	−16
(2-Hydroxy-1-cyclohexylidine)-acetic acid lactone (XV)	CCl_4	1771	881	1762	+ 9
	$CHCl_3$	1747	894	1788	−41
α-Pyrone (XXII)	CCl_4	1734	833	1866	+68
	$CHCl_3$	1730	—	—	—
5-Methyl-α-pyrone (XXIII)	CCl_4	1742	822	1644	+98
	$CHCl_3$	1735	828	1656	+79
γ-Pyrone (XXV)	CCl_4	1667	846	1692	−25
	$CHCl_3$	1667	851	1702	−35

*Where the carbonyl frequency is measured in CCl_4 the value of ν_2 was taken from measurements in CS_2. For the measurements in $CHCl_3$ ν_2 was determined in the same solvent at a higher concentration in an 0.1-mm cell; these measurements were made through regions where the solvent is also absorbing, and the band positions may be displaced slightly on this account.

†These bands are weaker than those designated ν_2 in the spectra of the other compounds and their appearance suggests they are of a different origin (see reference 12).

in chloroform. The spectra in Figs. 1 and 2 give no indication of different behavior from the substituted $\Delta^{\alpha\beta}$-butenolides.

If we are indeed dealing with a Fermi resonance effect, the anharmonicity of the overtone vibration must be a major factor in connection with the sensitive solvent effects. The differential solvent displacements of the two unperturbed combining frequencies will influence the magnitude of the coupling, but in addition the resonance involves a perturbation function (designated w_{ni} by Herzberg (19)) which depends on the cubic and quartic terms of the potential energy. These terms may be considerably modified by the force fields in the solvent–solute complex, particularly in polar media. In regard to the effect of temperature on the resonance coupling, it will be noted from Figs. 4–6 that an increase in temperature alters the band intensities in the same sense as a decrease in solvent polarity. The temperature effect on the spectrum may therefore be an indirect consequence of the reduction of the polarity of the molecular environment at the higher temperature.

Additional difficulties appear when the δ-lactones are considered. Comparisons of the curves for β-cyclopentyl-$\Delta^{\alpha\beta}$-butenolide in Fig. 2 and 5-methyl-α-pyrone in Fig. 3 can leave little doubt that essentially the same phenomenon is involved in both cases. However, in the δ-lactone infrared spectra the bands that might reasonably be assigned to the out-of-plane C—H deformation of the α-hydrogen are displaced to 850–820 cm^{-1}. This would place the pure harmonic overtone at 1700–1640 cm^{-1}, and it would be necessary to invoke a large negative anharmonicity to raise this sufficiently to allow Fermi resonance with the carbonyl frequency. In the infrared spectra of the unsaturated δ-lactones there are no suitable infrared active bands nearer to the required position. It is of course possible that combination bands rather than overtone bands may be involved, or bands inactive in the infrared, as probably occurs in cyclopentanone (16). As yet we have had no opportunity to look for such bands in the Raman spectra.

Similar Effects in Other Compounds

A survey of other compounds has shown that this type of carbonyl band splitting may be much more widespread than is generally recognized.

In open chain acid anhydrides, the appearance of two carbonyl stretching bands is well known and, although probably a vibrational resonance phenomenon, it is distinct from the effect we are considering here. In five-membered ring cyclic anhydrides, however, it was noted first by Cooke (20) that the carbonyl band of lower frequency can itself be resolved into a doublet if the spectrum is measured with good dispersion. We have studied this band in maleic anhydride, phthalic anhydride, and naphthalene-1,2-dicarboxylic anhydride, and observe that the two components of the low frequency carbonyl band of these compounds show an intensity reversal with solvent change identical with that of the unsaturated lactones. This is illustrated for maleic anhydride in Fig. 9. This is not observed with the open chain anhydrides, and the cyclic structure seems to be essential.

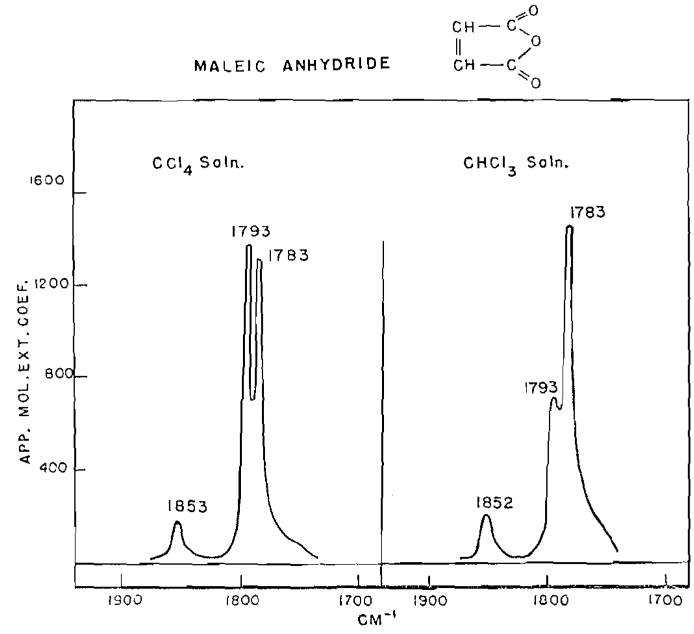


FIG. 9. Effect of solvent on the C=O stretching absorption of maleic anhydride.

The doubling of the carbonyl band in benzoyl chloride and some of its derivatives was first noted in the Raman spectrum by D. D. Thompson and J. F. Norris (21) in 1936, and subsequently by Flett in the infrared spectrum (22). We have confirmed Flett's observation, and it will be seen from Fig. 10 that with change of solvent from carbon tetrachloride to chloroform the low frequency "carbonyl" band of benzoyl chloride

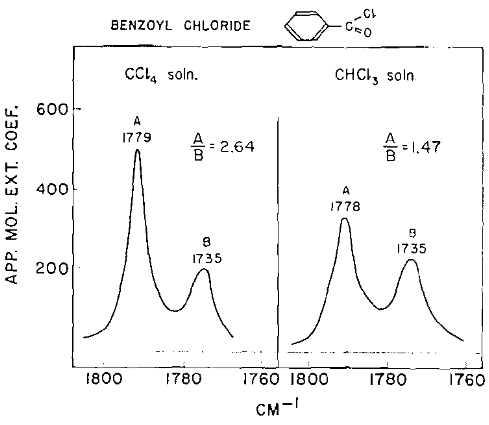


FIG. 10. Effect of solvent on the C=O stretching absorption of benzoyl chloride.

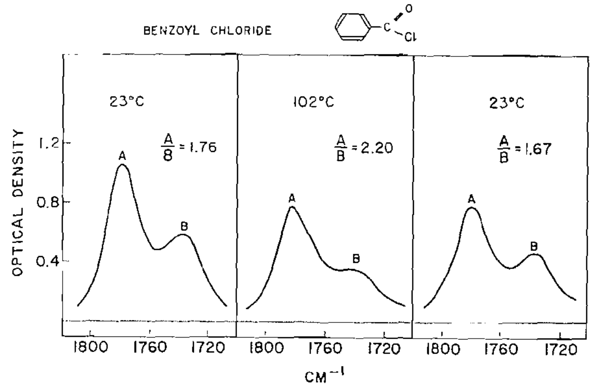


FIG. 11. Effect of temperature on the C=O stretching absorption of a liquid film of benzoyl chloride. The first spectrum at 23° C was determined before heating, and the second one after heating.

gains in intensity at the expense of the high frequency band. In both solvents the relative intensities of the "carbonyl" bands of benzoyl chloride have been shown to be independent of concentration over a 200-fold range. The two bands in the spectrum of the pure liquid show a reversible temperature effect, the high frequency band increasing relative to the low with rising temperature (Fig. 11). This also parallels the behavior of the unsaturated lactones. For benzoyl chloride one cannot write conformational equilibria involving *cis* $\rightleftharpoons$ *gauche* or *s-cis* $\rightleftharpoons$ *s-trans* forms, unless stable structures differing only in the angle between the chlorocarbonyl group and the benzene ring are considered; these are highly unlikely and here again we must resort to an interpretation based on an intramolecular vibrational phenomenon. It should be added that the possibility of the second carbonyl peak in the benzoyl chloride spectrum resulting from partial hydrolysis to benzoic acid has been disproved by the observation that on addition of small quantities of benzoic acid to liquid benzoyl chloride a third band appeared at 1695 cm^{-1}.*

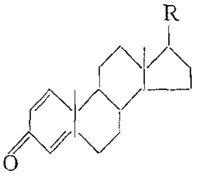
**We wish to thank Dr. K. Noack for making these measurements.*

CONCLUSIONS

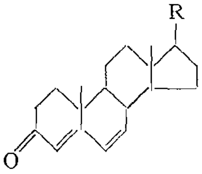
It will be apparent from the above discussion that we are not satisfied that the Fermi resonance hypothesis provides a full explanation of these effects, though there can be little doubt that some type of intramolecular vibrational effect is involved. It is to be hoped that experimental work of this kind will stimulate a more detailed theoretical study of vibrational resonance effects in complex molecules, with particular respect to the influence of solvent–solute interactions and other intermolecular force fields in the liquid phase.

The organic chemist, who is making increasing use of infrared spectra in the study of conformational isomerism and intermolecular association, must be on his guard for effects of the type discussed here. Even where it is possible to explain solvent- and temperature-dependent changes in spectra in terms of plausible conformational equilibria, such interpretations should not be accepted without further investigation. The demonstration that temperature- and concentration-dependent spectral changes can be observed in several widely separated regions of the spectrum will strongly substantiate an interpretation based on conformational isomerism. If, on the other hand, the spectral anomalies can be removed by selective deuteration, it must indicate that they have their origin in an intramolecular vibrational effect.

Finally, we must recognize that cases may arise where this type of vibrational resonance effect may be insufficient to induce a complete splitting of a band, but may broaden the band and modify its intensity and contour. This may explain the marked difference in the contours of the carbonyl bands associated with the steroid structures XXVIII and XXIX which are illustrated in Fig. 99 of reference 29.



XXVIII



XXIX

It has been shown recently (23, 24) that the various kinetic "σ-constants" of Hammett, Taft, and Roberts can be evaluated from measurements of the intensities, positions, and half-widths of infrared absorption bands associated with vibrations localized in the reactive functional group (23, 24). As work of this kind is extended, it will be particularly important to watch for small perturbation effects of vibrational resonance which would probably have little if any effects on the chemical reactivity of the group, and may cause discrepancies between σ-constants derived from spectrographic and kinetic measurements.

ACKNOWLEDGMENTS

We wish to thank Mr. R. Lauzon and Mrs. M. A. MacKenzie for technical assistance with the measurement of the spectra. We are also grateful to Dr. A. F. Sirianni and Dr. I. E. Puddington of the Applied Chemistry Division of the National Research Council for the molecular weight measurements, Dr. O. E. Edwards for samples of 5,6-dimethoxyphthalide and γ-pyrone, and Mr. H. Seguin for carbon and hydrogen analyses.

REFERENCES

1. Dobriner, K., Katzenellenbogen, E. R., and Jones, R. N. Infrared absorption spectra of steroids—an atlas. Interscience Publishers, Inc., New York—London. 1953. p. xii.
2. Jones, R. N. and Gallagher, B. S. J. Am. Chem. Soc. In press.
3. Newman, M. S. and VanderWerf, C. A. J. Am. Chem. Soc. **67**, 233 (1945).
4. Smith, R. J. D. and Jones, R. N. Can. J. Chem. This issue.
5. Rubin, M., Paist, W. D., and Elderfield, R. C. J. Org. Chem. **6**, 260 (1941).
6. Thiele, von J., Tischbein, R., and Lossow, E. Ann. **319**, 192 (1901).
7. Wolff, L. Ann. **229**, 249 (1885).
8. Haynes, L. J. and Jones, E. R. H. J. Chem. Soc. 954 (1946).
9. von Pechmann, H. Ann. **264**, 261 (1891).
10. Fried, J. and Elderfield, R. C. J. Org. Chem. **6**, 566 (1941).
11. Jones, R. N. Spectrochim. Acta, **9**, 235 (1957).
12. Angell, C. L., Ito, T., Smith, R. J. D., and Jones, R. N. National Research Council of Canada Bulletin No. 7, (1959).
13. Paist, W. D., Blout, E. R., Uhle, F. C., and Elderfield, R. C. J. Org. Chem. **6**, 273 (1941).
14. Puddington, I. E. Can. J. Research, B, **27**, 151 (1949).
15. Bellamy L. J. The infrared spectra of complex molecules. Methuen & Co., Ltd., London. 1954; 2nd ed. John Wiley & Sons, Inc., New York. 1958. pp. 380–382.
16. Angell, C. L., Krueger, P. J., Lauzon, R., Leitch, L. C., Noack, K., Smith, R. J. D., and Jones, R. N. Spectrochim. Acta. In press.
17. Yates, P., Yoda, N., Brown, W., and Mann, B. J. Am. Chem. Soc. **80**, 202 (1958).
18. Yates, P. and Williams, L. L. J. Am. Chem. Soc. **80**, 5896 (1958).
19. Herzberg, G. Infrared and Raman spectra of polyatomic molecules. D. Van Nostrand Company, Inc., New York. 1945. p. 215.
20. Cooke, R. G. Chem. & Ind. 142 (1955).
21. Thompson, D. D. and Norris, J. F. J. Am. Chem. Soc. **58**, 1953 (1936).
22. Flett, M. St. C. Trans. Faraday Soc. **44**, 767 (1948).
23. Thompson, H. W. Conference on molecular spectroscopy. *Edited by* E. Thornton and H. W. Thompson. Pergamon Press, Ltd., London. 1959. pp. 173–177.
24. Krueger, P. J. and Thompson, H. W. Proc. Roy. Soc. A, **250**, 22 (1959).