THE SPLIT CARBONYL BAND IN THE INFRARED SPECTRA OF HALOGEN DERIVATIVES OF 4-HYDROXY-2,4-PENTADIENOIC ACID LACTONE

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Abstract—The IR spectra of a series of halogen derivatives of 4-hydroxy-2,4-pentadienoic acid lactone (protoanemonin) show, with one exception, split CO peaks commonly associated with conjugated unsaturated CO groups of small ring compounds. The intensity ratio of the two components, ε_{max} high energy: ε_{max} low energy, decreases significantly on changing from carbon tetrachloride to chloroform solvent. The components of the split CO bands show frequency shift trends on changing the nature of the halogen or its position of substitution. The 3,5-dichloro and 3,5-diiodo derivatives possess CO bands split into triplets. The origin of the split CO bands is suggested to involve symmetric-asymmetric coupling of the C—O and C—C bonds of the O=C—C group.

INTRODUCTION

SINCE 1958, when Yates *et al.*[1,2] reported on the split CO peak in the IR spectra of some phenyl-2-cyclopentenones, the nature of such splitting has been under careful scrutiny to find the true cause of this seemingly anomalous behavior. Split CO peaks are a general characteristic of conjugated unsaturated CO groups of small ring compounds, such as the cyclopentenones and conjugated unsaturated lactones,[3,4] although splitting also appears for cyclopentanone.[5] A distinguishing feature of this effect is the marked change in the relative intensities of the two bands on changing the polarity or H-bonding character of the solvent. That the two bands arise from the monomeric species and not from dimers or other associated aggregates is indicated by the independence of the relative intensities of the bands on the concentration and by their molecular weights in solution.[3]

The cause of the split CO peak has been attributed to Fermi resonance interaction between the normal CO vibration and the first overtone of a vibration occurring at about one half the CO frequency.[2] Although the Fermi resonance concept was occasionally accepted with some reluctance,[3] studies of deuterated compounds seemed to indicate that Fermi resonance was indeed responsible and that the specific interaction was a coupling of the CO stretching vibration with the out of plane bending mode of a vinyl hydrogen.[2,6] Recently, further studies of deuterated compounds have revealed that the system is even more complex than was originally thought, for the splitting also seemed to involve hydrogens other than those at the vinyl positions.[7] Furthermore, the presence of a band at one half the CO frequency does not in every case reflect its presence in a split CO.[7] Resonance involving combination bands has also been suggested as the cause of CO splitting,[3,7,8] but this

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idea has not been explored to any great extent. Hence, it is clear that more work is necessary before the underlying causes for the CO splitting in planar conjugated unsaturated lactones and cyclic ketones is really understood.

RESULTS AND DISCUSSION

The availability of halogenated 4-hydroxy-2,4-pentadienoic acid lactones (proto-anemonins) prepared in connection with some halogen exchange studies to be reported upon later, provided an unusual opportunity for studying CO splitting in an interesting and novel series of conjugated unsaturated lactones, Table 1. Note that for the most part, well defined double CO bands are a characteristic feature of this series. These bands are extremely sharp and well resolved, except where indicated, this being a result of the rigid planar structure and complete lack of conformational isomerism often associated with band broadening. The marked change in the intensity ratio of the two bands on going from carbon tetrachloride to chloroform clearly indicates that the origin of the split CO is of the same nature as that of the literature examples already cited.

Even though it has been shown that molecular association is not involved,[3] this possibility, nevertheless, should be considered in the protoanemonin series especially in view of the fact that protoanemonin itself dimerizes spontaneously in solution to give anemonin.[9,10] Molecular weight studies of 5,5-dibromoprotoanemonin (3) by freezing point depression showed that in solution the molecule exists entirely in the monomeric state. This, and the fact that the intensity ratios of the two CO bands are independent of the concentration, imply that the causes for the splitting are essentially internal.

Concerning the Fermi resonance concept of coupling between the CO vibration and the first overtone of a lower lying fundamental, all of the compounds reported in Table 1 have a medium strong band falling in the 880–950 cm^{-1} region. The difference between the mean of the two CO frequencies and twice the frequency of this lower lying fundamental (last column, Table 1) provides a measure of the effect of this difference upon the presence or absence of splitting. In one case 5,5-dichloro-protoanemonin (1), this difference is of the order of 100 cm^{-1} and no splitting was observed even at high resolution. Since the 5-bromo-5-chloro analog (2) with a frequency difference of about 70 cm^{-1} shows well developed splitting, then, if Fermi resonance is responsible, there must be a sharp cut off of the resonance at a difference value somewhere between 70 and 100 cm^{-1}, a rather stringent requirement.

Although there is no logical basis for the supposition that split CO bands of cyclic unsaturated ketones and lactones must all come from the same type of coupling, nevertheless, the close structural similarity of the various compounds which exhibit this behavior certainly suggests a common cause. Clearly coupling involving hydrogen out of plane bending modes[2,6,7] cannot be solely responsible since tetrachloro-protoanemonin (8), although having no hydrogen, exhibits a CO band which is distinctly split. With the exception of cyclopentanones, the structural feature common to all of these compounds is the O=C—C=C, and the resonance interaction may well involve various stretching modes within this group. Maleic anhydride, which also has a split CO peak (1796 and 1784 cm^{-1}), has a strong band at 889 cm^{-1}, well within the area for resonance interaction with the CO group. In an exhaustive

analysis by IR and Raman spectroscopy this 889 cm^{-1} band was assigned to a C—C stretch.[8] On this basis we suggest that the general occurrence of CO splitting in this type of structure is a result of coupled stretching vibrations of the O=C—C group, possibly through symmetric-asymmetric modes. The failure to observe splitting for the various deuterated cases reported[2,6,7] is not clear, but if on deuteration the vibrational frequencies are shifted, coupling might be altered sufficiently to prevent observation of the interaction.

Although split CO peaks have been observed only for small ring compounds, it is entirely possible that the same fundamental interaction occurs also for larger ring compounds and acyclic structures. In these cases, however, band broadening arising from various conformers would tend to obliterate any traces of CO splitting.

In an effort to determine the role of the solvent in causing the intensity changes, the intensity ratios in carbon tetrachloride, chloroform, ethylene chloride, and acetonitrile (dielectric constants 2·2, 5·0, 10, 37, respectively) were compared, Table 1.
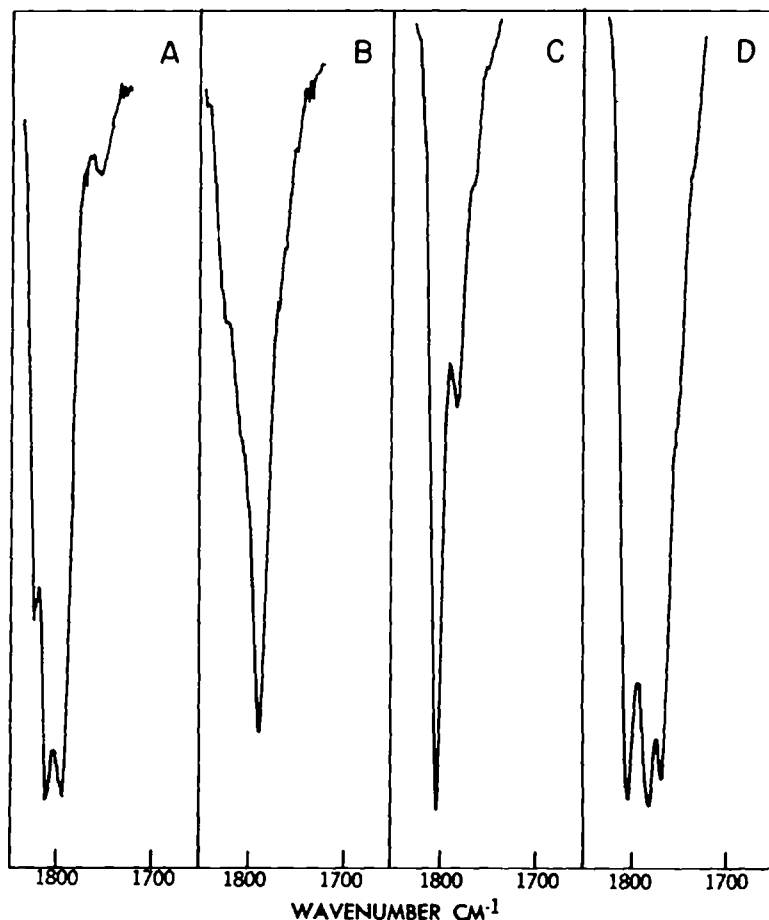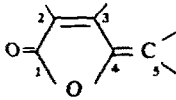

FIG 1. A. 3,5-Dichloroprotoanemonin in CCl$_4$. B. 3,5-Dichloroprotoanemonin in CHCl$_3$. C. 3,5-Diiodoprotoanemonin in CCl$_4$. D. 3,5-Diiodoprotoanemonin in CHCl$_3$.

TABLE 1. IR DATA FOR HALOPROTOANEMONINS

No.	O=[structure] C	Solvent	$\nu_{C=O}$ cm^{-1}			Intensity Ratio[*]	880–950 Region cm^{-1}	Freq. Diff.[b] cm^{-1}
			A	B	C			
				* = Shoulder				
1	5,5-Dichloro	CCl$_4$	1802	—	--	∞	948	94
		CHCl$_3$	—	--	1789	0	947	105
		C$_2$H$_4$Cl$_2$	--	—	1790	0		
		CH$_3$CN	--	—	1791	0		
2	5-Bromo-5-chloro	CCl$_4$	1800	—	1785*	4·7	928	63
		CHCl$_3$	1796	--	1781	1·0	929	69
		C$_2$H$_4$Cl$_2$	1796	—	1781	1·7		
		CH$_3$CN	1795	—	1785*	1·6		
3	5,5-Dibromo	CCl$_4$	1802	--	1779	4·6	891	8
		CHCl$_3$	1799	—	1778	1·1	894	0
		C$_2$H$_4$Cl$_2$	1797	--	1779	1·6		
		CH$_3$CN	1799	—	1780	1·6		
4	5-Bromo-5-iodo	CCl$_4$	1799	—	1760	7·7	883	4
		CHCl$_3$	1792	—	1766	2·2	888	3
5	3,5-Dichloro	CCl$_4$	1811	1823	1795	1·0[c]	904	2
		CHCl$_3$	1805*	1820*	1787	0·3[d]	910	19
		C$_2$H$_4$Cl$_2$	1810*	--	1790	0·4		
		CH$_3$CN	1810*	--	1790	0·3		
6	3,5-Dibromo	CCl$_4$	1810	—	1782	2·6	897	2
		CHCl$_3$	1809	—	1778	0·6	902	10
		C$_2$H$_4$Cl$_2$	1809	--	1780	0·8		
		CH$_3$CN	1810	—	1781	0·6		
7	3,5-Diiodo	CCl$_4$	1804	1781	1765*	8·5[e]	895	3
		CHCl$_3$	1802	1780	1768	1·1[f]	900	17
8	Tetrachloro	CCl$_4$	1815	—	1795	3·3	915	25
		CHCl$_3$	1812	—	1792	0·9	917	32
		C$_2$H$_4$Cl$_2$	1812	--	1795	1·0		
		CH$_3$CN	1809	--	1795	0·9		

[*] ε_{max} Band A/ε_{max} Band C. [b] Absolute value of the mean carbonyl frequency less 2 × the frequency of the 880–950 band. [c] Ratio B:C is 0·6. [d] Ratio of B:C is 0·3. [e] Ratio B:C is 2·1. [f] Ratio B:C is 1·2.

Although the intensity ratios for ethylene chloride and acetonitrile paralleled that of chloroform, the greatest effect was observed for chloroform, indicating that H-bonding may be somewhat more effective than polarity.

A particularly interesting feature of this series of haloprotoanemonins is that the two CO bands respond with different frequency shifts on changing the nature and the position of the halogen substituent. In the 5,5-dihalo series (1–4) decreasing the electronegativity of the halogen results in virtually no change in the frequency of the higher energy band, while the lower energy band shifts consistently to lower wavenumbers. Comparisons within the 3,5- series reveals a similar trend with the exception that there is now a slight tendency for the higher energy band to shift to lower wavenumbers. Comparison of the 5,5- series with the 3,5- series shows that switching the halogen from the C-5 to the C-3 position has a greater effect on the higher energy

band, shifting it to higher wavenumbers, while the lower energy band remains relatively unaffected. Additional chlorine atoms have little effect on either band; the CO frequencies of the 3,5-dichloro (5) and the tetrachloro (8) derivatives are almost identical.

The 3,5-dichloro (5) and the 3,5-diiodo (7) derivatives are of particular interest as these appear to be the first reported cases showing the carbonyl bands split into triplets, Fig. 1. The relative intensities of the components of the triplets are affected in the usual way by changing from carbon tetrachloride to chloroform solvent.

In the C—H stretching region of the spectrum two sharp peaks are observed in the 3,5- series as would be expected for two different vinyl protons vibrating independently. In the 5,5- series, however, the two vicinal hydrogens give rise to three sharp peaks, indicating a resonance interaction.

In the C=C stretching region two bands appear, one for each of the double bonds, the lower wavenumber band being the stronger of the two. The higher energy band is assigned to the exocyclic double bond, and the lower energy band to the endocyclic double bond, consistent with the frequency shifts observed with changing halogen.

TABLE 2. IR DATA FOR HALOPROTOANEMONINS, C—H AND C=C STRETCHING REGIONS (KBr)

No.	ν_{C-H} cm^{-1}			$\nu_{C=C}$ cm^{-1}	
1	3135	3110	3070	1635	1549
2	3135	3105	3070	1625	1549
3	3130	3105	3070	1613	1550
4	3130	3105	3065	1630*	1548
5		3140	3100	1650	1553
6		3130	3095	1645	1555
7		3125	3070	1627	1535
8		--	---	1621	1564

* Broad band

EXPERIMENTAL

Compound 1, 5,5-dichloroprotoanemonin, was prepared by the reaction of sodium trichloroacetate with succinic anhydride.[11] The 5,5-dibromo (3) and 3,5-dibromo (6) protoanemonins were prepared by treating 3,5-dibromolevulinic acid with 30% oleum and 98% H_2SO_4, respectively.[12] Tetrachloroprotoanemonin (8) was prepared through the reaction of 65% oleum with 2,2,4,5-tetrachlorocyclopentene-1,3-dione*.[13] The preparation of compounds 2, 4, 5, and 7 was affected through halogen exchange reactions with 5,5-dibromoprotoanemonin and shall constitute the subject of a separate communication. All compounds were carefully purified by crystallization or sublimation and were shown to be homogeneous by VPC. Elemental analyses, IR spectra, and NMR spectra were entirely consistent with the assigned structures. The stereochemical configurations of compounds 2, 4, 6, and 7, have not been rigorously established. The IR spectra were recorded using the Beckman Model IR-12 infrared spectrophotometer. For closely lying peaks the slit widths were adjusted to give maximum resolution.

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