

RAMAN EFFECT AND CHEMICAL CONSTITUTION

Influence of Constitutive and other Factors on the Double Bonds in Organic Compounds

Part IV. The Frequency of the Ethylenic Double Bond in Unsaturated Carbonyl Compounds

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IN a recent communication¹ it has been shown by us that a phenyl group attached directly to the carbon of the C = O lowers its frequency and this was attributed to the existence of resonance. This view has further been strengthened by the results obtained by us in the investigation of the C = O frequencies of the esters of phenyl acetic acid.²

A similar effect of an ethylenic double bond on the carbonyl frequency has been noted by many workers. When these groups are in conjugation the C = O frequency is markedly lowered as will be clear from the typical examples given in Table I.

In this respect the phenyl ring and the ethylenic double bond behave alike and the same mechanism should hold good for both. The lowering of the carbonyl frequency by the ethylenic link is also then due to the existence of resonance as expressed below :



As a result of conjugation both the double bonds should be weakened simultaneously and hence the C = C frequency should undergo reduction at the same time as the C = O. It has sometimes been stated that under these circumstances there is a slight increase in the frequency of the ethylenic double bond.³ When carefully examined and when comparisons are effected between closely related groups of compounds we find that there is no such discrepancy and that the ethylenic double bond exhibits invariably a lowered frequency. The ideal cases for comparison are isomeric esters such as ethyl cinnamate and cinnamyl acetate, ethyl acrylate⁴ and allyl acetate.⁵ They are pairs having the same molecular weight, the same number and kind of

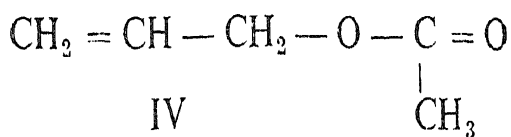
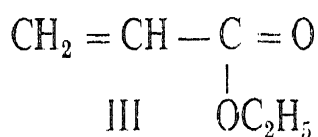
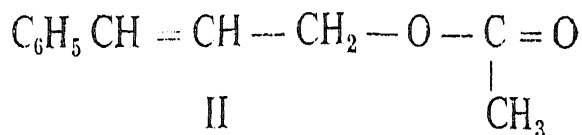
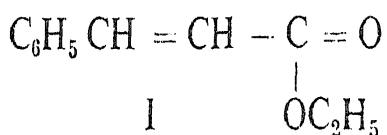
TABLE I

Formula of the Compound	C = O freq. in cm.^{-1}	Formula of the Compound	C = O freq. in cm.^{-1}	Formula of the Compound	C = O freq. in cm.^{-1}
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$	1712	$\text{CH}_3 \cdot \text{CHO}$	1716	$\text{CH}_3 \cdot \text{COOC}_2\text{H}_5$	1739
$(\text{CH}_3)_2 \cdot \text{C} : \text{CH} \cdot \text{CO} \cdot \text{CH}_3$	1685	$\text{CH}_2 : \text{CH} \cdot \text{CHO}$	1692	$\text{CH}_2 : \text{CH} \cdot \text{COOC}_2\text{H}_5$	1718
$(\text{CH}_3)_2 \cdot \text{C} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{C} \cdot (\text{CH}_3)_2$	1666	$\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$	1685	$\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{COOC}_2\text{H}_5$	1713
$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH}_3$	1666	$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$	1670	$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{COOC}_2\text{H}_5$	1712
$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$	1668

TABLE II

	C = C	C = O		C = C	C = O		C = C
Ethyl cinnamate	1634	1712	Cinnamyl acetate	1650	1673	Cinnamyl alcohol	1660
Ethyl acrylate	1635	1718	Allyl acetate	1649	1742	Allyl alcohol	1645
Ethyl crotonate (<i>trans</i>)	1653	1713	Crotonyl acetate (<i>trans</i>)	1679	1742	Crotonyl alcohol (<i>trans</i>)	1677
Ethyl isocrotonate (<i>cis</i>)	1644	1713	Isocrotonyl acetate (<i>cis</i>)	1664	1742	Isocrotonyl alcohol (<i>cis</i>)	1658

groups with the only difference that in one there exists conjugation between C = C and C = O groups and not in the other.



Their spectra should be very similar in all respects except for the values of the C = C and C = O frequencies and they are found to be so. These frequencies are markedly lower for compounds I and III (Table II). It is remarkable that the ethylenic frequencies of II and IV are practically the same as those of cinnamyl and allyl alcohols from which the esters are derived, thus again showing that the electromeric effect arising from the carbonyl is the important factor responsible for lowering the ethylenic frequencies and that it is not transmitted when there is a CH₂ group in the way. Other examples derived from the crotonyl series are also given in Table II. It should be noted that in some cases the mutual lowering of the C = C and C = O frequencies is almost to the same extent.

The Raman spectra of cinnamyl acetate and cinnamyl alcohol were studied by Gredy⁶ in 1936 but since they were obviously incomplete especially for effecting close comparison with related compounds they have now been reinvestigated. The liquids employed were pure samples from Kahlbaum which were subjected to repeated distillations under vacuum. The other experimental details are the same as those described in Part II of this series.

The results presented in Table III clearly indicate that cinnamyl alcohol and cinnamyl acetate excite many more lines than were observed by the previous investigator and that the spectra of cinnamyl alcohol and cinnamyl acetate bear a very satisfactory general agreement with those of the cinnamates studied already.

TABLE III

Cinnamyl acetate. (Murty and Seshadri.)	Cinnamyl acetate. (Gredy.)	Ethyl cinnamate. (Murty and Seshadri.)	Cinnamyl alcohol. (Murty and Seshadri)	Cinnamyl alcohol. (Gredy.)
275 (1)	..	270 (1)	272 (0)	..
359 (1)	..	357 (1)	355 (1)	..
578 (1)	..	582 (1)	580 (1)	..
620 (2)	621	619 (2)	619 (2)	621
713 (2)	..	713 (2)	713 (2)	..
..	..	836 (1)	830 (0)	..
940 (2)	..	943 (2)	940 (1)	..
972 (2)	..	972 (2)	970 (1)	..
1000 (6)	1000	999 (7)	1000 (6)	1000
1030 (2)	1031	1030 (2)	1030 (1)	1031
1157 (1)	1158	1160 (2)	1160 (1)	1158
1180 (5)	..	1182 (5)	1180 (5)	..
1204 (6)	1208	1204 (6)	1202 (6)	..
1254 (1)	1281	1250 (2)	1250 (2)	1274
..	..	1305 (1)
1450 (1)	..	1450 (2)	1450 (1)	..
1512 (1)	..	1516 (1)	1516 (1)	..
1540 (2)	..	1540 (2)	1538 (1)	..
1578 (2)	..	1578 (2)	1576 (2)	..
1597 (2)	1600	1598 (7)	1598 (7)	1600
1660 (10)	1659	1634 (10)	1660 (10)	1657
1738 (5)	1740	1712 (5b)
..	..	2940 (1)
3064 (1)	* 3062	3066 (1)	3066 (1)	3062

Summary

The Raman spectra of cinnamyl alcohol and cinnamyl acetate are re-investigated and their frequencies compared with those of ethyl cinnamate. A great similarity between the spectra of all these substances is observed. The higher C = C and C = O frequencies in cinnamyl acetate and allyl acetate as compared with ethyl cinnamate and ethyl acrylate is explained as due to the existence of resonance in the latter. It is pointed out that when comparisons are effected carefully the C = C and C = O bonds mutually weaken each other when they exist in conjugation.

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