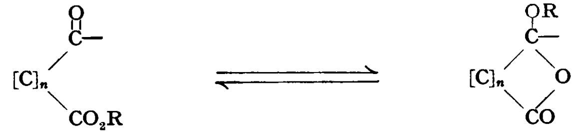
196. *Infra-red Spectroscopy and Structural Chemistry. Part I. Keto–Lactol Tautomerism.*

By John Frederick Grove and H. A. Willis.

The application of infra-red spectroscopy to the study of keto–lactol tautomerism is discussed, and a method is described whereby the lactol and the open-chain form of aldehydic and ketonic acids may be recognised. The normal and the *pseudo*-esters of γ-aldehydic and -ketonic acids are readily distinguished by the frequencies of the stretching vibrations of the $C{=}O$ groups. The methods have been tested with some simple acids and esters of known structure and applied to other molecules of unknown structural configuration.

Numerous examples of keto–lactol tautomerism have been described in the literature, and many of the substances which have been shown to exhibit this phenomenon fall into the class of γ-aldehydic and ketonic acids (I; $n = 2$).

(I.)



(II.)

Such compounds, which may be recognised by the formation of neutral monoacetyl derivatives (II; R = Ac) derived from the lactol form (II; R = H), may give rise to two series of esters, the normal carboxylic esters (I) and the hydroxy-lactonic or *pseudo*-esters (II). Keto–lactol tautomerism is shown by a number of substances possessing biological activity, such as *o*-benzoylbenzoic acid (Sexton and Templeman, *Nature*, 1948, **161**, 974) and the weakly antibacterial mould products, penicillic acid (Birkinshaw, Oxford, and Raistrick, *Biochem. J.*, 1936, **30**, 394; and Raphael, *Nature*, 1947, **160**, 261; *J.*, 1947, 805) and gladiolic acid (Brian, Curtis, Grove, Hemming, and McGowan, *Nature*, 1946, **157**, 697; Grove, unpublished results), and it was our interest in the latter compound which led us to examine the known methods of studying this phenomenon and of distinguishing between normal and *pseudo*-esters.

The normal esters of aldehydic acids retain the characteristic chemical reactions of the aldehyde group and these may be used for the purpose of identification. Newman and McCleary (*J. Amer. Chem. Soc.*, 1941, **63**, 1537) have reviewed some of the methods for the allocation of structures to the esters of keto-acids. Chemical reactions, and in particular the hydrolysis of *pseudo*-esters by concentrated sulphuric acid to give highly coloured solutions, are stated to be unreliable for the assignment of structure, as also are such physical properties as melting point and solubility. Among other physical methods which have been used, the determination of molecular refractivity has proved of value for liquid esters (Egerer and Meyer, *Monatsh.*, 1913, **34**, 69; Auwers and Heinze, *Ber.*, 1919, **52**, 584; Lutz, Merrit, and Couper, *J. Org. Chem.*, 1939, **4**, 95). The polarographic method described by Wawzonek *et al.* (*J. Amer. Chem. Soc.*, 1944, **66**, 827) does not always give a satisfactory differentiation (Schmid, Hochweber, and von Halban, *Helv. Chim. Acta*, 1948, **31**, 354).

Ultra-violet absorption spectroscopy has been used with success in the study of keto-lactol tautomerism in the aromatic acids, phthalonic acid (Buu-Hoï and Lin, *Compt. rend.*, 1939, **209**, 346), *o*-formylbenzoic acid (Buu-Hoï, *Compt. rend.*, 1939, **209**, 221), opianic acid and substitued opianic acids (Buu-Hoï, *Compt. rend.*, 1941, **212**, 242, 268), *o*-benzoylbenzoic acid (Hantzsch and Schweite, *Ber.*, 1916, **49**, 213; Schmid *et al.*, *loc. cit.*), and benzil-*o*-carboxylic acid (Schmid *et al.*, *loc. cit.*), and their esters. This method can also be applied to αβ-unsaturated γ-keto-acids such as β-acetylacrylic acid (Shaw, *J. Amer. Chem. Soc.*, 1946, **68**, 2510), although some disagreement exists in the case of penicillic acid (Shaw, *loc. cit.*; Raphael, *loc. cit.*). A disadvantage of the method is that prediction of the absorption curve for a new compound is difficult even if the structure is known, and model compounds of known structure are usually necessary for purposes of comparison. Little useful information concerning structure can be obtained from the ultra-violet absorption spectra of saturated keto-acids.

Since a reliable general method for the study of keto–lactol tautomerism was lacking, we turned our attention in 1947 to infra-red absorption spectroscopy, which at that time had not been used for this purpose. However, while this work was in progress, the application of infra-red spectroscopy to the study of tautomerism in penicillic acid was reported by Munday (*Nature*, 1949, **163**, 443).

Initially it was hoped that, providing there were no complicating factors such as the presence in the molecule of additional carbonyl groups, the normal and *pseudo*-esters could be distinguished by a simple qualitative test, the normal esters showing two absorption bands, one due to the ester and the other to the ketonic C=O group, and the *pseudo*-esters showing only one such band arising from the C=O in the lactone ring. Similarly it was hoped that acids in the open keto-form (I; R = H) could be recognised by two bands in the C=O region of the spectrum, whereas the presence of one such band together with an absorption frequency in the 3-μ. region, attributable to the alcoholic hydroxy-group, could be used to identify acids in the lactol form (II; R = H). In practice it was soon found that while the presence of a characteristic alcoholic hydroxy-group absorption was a reliable indication of the presence of an acid in the lactol form, a single band only in the C=O region could not be used for identification purposes, some open-chain acids and normal esters showing only a single broad absorption band, the characteristic frequencies of the two C=O groups being almost identical and the bands superimposed. A more detailed quantitative study of the problem was therefore attempted.

EXPERIMENTAL.

Infra-red Spectra.—The spectrometer was a modified Hilger D 209 instrument enclosed in an air-tight " Perspex " casing, the air within the case being circulated continuously over a suitable desiccant. By this means the water-vapour background in the C=O stretching region was reduced to almost negligible proportions and the determination of the positions of the C=O stretching bands greatly facilitated. All measurements were taken with a rock-salt prism. Calibration was made by interpolation between hydrocarbon bands of known frequency. In the region of 1700 cm.$^{-1}$ the calibration was considered accurate to ±3 cm.$^{-1}$, a slit width of 4 cm.$^{-1}$ being used; at 3000 cm.$^{-1}$ the calibration was considered accurate to ±10 cm.$^{-1}$, with a slit width of 20 cm.$^{-1}$.

Solid compounds were first dried *in vacuo* over phosphoric oxide, and the spectra were obtained in "Nujol" suspension between rock-salt plates. The suspensions were made by grinding the solids to fine powders in an agate mortar and then stirring the powder with " Nujol." When acids were being examined the melting points of the compounds were taken before and after grinding; no differences were noted and no effects analogous to those described by Munday (*loc. cit.*) for penicillic acid were observed. Liquids indicated in the Tables by an asterisk were examined in cells of 0·01-mm. thickness.

Materials.—With few exceptions, listed below, the organic compounds examined were prepared by literature methods and purified by crystallisation or distillation.

Normal methyl *o*-formylbenzoate, b. p. 130°/10 mm., was obtained by Rosenmund reduction of the acid chloride from methyl hydrogen phthalate although the yields claimed by Eliel and Burgstahler

(*J. Amer. Chem. Soc.*, 1949, **71**, 2251) were not realised. It formed a semicarbazone, obtained as needles, m. p. 194°, from methanol (Found : C, 54·2; H, 5·3; N, 18·8. Calc. for $C_{10}H_{11}O_3N_3$: C, 54·3; H, 5·0; N, 19·0%).

*Benzil-*o*-carboxylic acid* pseudo*acetate*. Benzil-*o*-carboxylic acid (lactol form; 0·3 g.) was suspended in acetic anhydride (2 c.c.) and one drop of concentrated sulphuric acid added. After 30 minutes the solution was poured into water, and the solid product crystallised from ethanol. It formed prisms, m. p. 138° (Found : C, 68·5; H, 4·3. Calc. for $C_{17}H_{12}O_5$: C, 68·9; H, 4·1%). Schmid, Hochweber, and von Halban (*loc. cit.*) give m. p. 137—138°.

*Methyl ω-bromoacetophenone-*o*-carboxylate*. A solution of the acid (25 g.; m. p. 113°) in dry methanol (100 c.c.) was saturated with hydrogen chloride at 0°. After 20 hours at room temperature the solvent was removed and the residual oil taken up in ether and washed with sodium hydrogen carbonate solution. The colourless oily residue solidified when kept and was crystallised from methanol; it formed plates (20·5 g.), m. p. 62° (Found : C, 46·8; H, 3·5; Br, 32·3. Calc. for $C_{10}H_9O_3Br$: C, 46·7; H, 3·5; Br, 31·1%).

*Methyl ωω-dibromoacetophenone-*o*-carboxylate* was prepared by the same method; it was obtained as plates, m. p. 122° (Found : C, 35·7; H, 2·4; Br, 46·8. $C_{10}H_8O_3Br_2$ requires C, 35·7; H, 2·4; Br, 47·6%). Gabriel (*Ber.*, 1907, **40**, 72) using essentially the same method reported the isolation of an ester, m. p. 112°, possibly identical with the above compound.

RESULTS AND DISCUSSION.

Discussion of the spectra, which are not reproduced, is limited to the OH stretching (3—4 μ.) and double-bond stretching (5—7 μ) regions.

It is well known that alcohols in very dilute solution show a characteristic sharp absorption band at about 3650 cm.$^{-1}$ associated with the " free " OH stretching vibration. If the solution is concentrated or the alcohol is examined in the solid state so that intermolecular " hydrogen bonding " can occur, the absorption band becomes broader and moves to lower frequency (about 3450 cm.$^{-1}$). Similar considerations apply to the OH stretching vibrations of carboxylic acids but the shift from the " free " vibration frequency of the monomeric form (3600 cm.$^{-1}$) to that of the solid dimeric form (2800—2500 cm.$^{-1}$) is very much greater.

In general the spectrum of an organic compound is most satisfactorily obtained in solution. Nevertheless, the interpretation of solution spectra of carboxylic acids is complicated by the persistance of the dimeric form. For example, with aliphatic acids, except in very dilute solution, bands are normally observed in the C=O stretching region both near 1760 cm.$^{-1}$ (monomer) and near 1720 cm.$^{-1}$ (bonded dimer). For the study of keto–lactol tautomerism, therefore, certain advantages were to be gained by an examination of solid samples; and in particular it appeared that the OH absorption frequencies of alcohols and carboxylic acids could be distinguished more readily. Some of the esters which it was desired to examine were in the liquid state at room temperature. However, there is some evidence that dipolar association occurs with simple esters in the liquid state (Hartwell, Richards, and Thompson, *J.*, 1948, 1436) and therefore the shifts to the carbonyl absorption bands of these compounds on passing from the solid to the liquid state would be expected to be small. It follows that valid conclusions may be drawn from comparisons between solid and liquid esters of the same general type.

The structures of the esters of *o*-formylbenzoic acid are readily established by chemical methods. The liquid normal ester, b. p. 130°/10 mm., shows reactions typical of an aromatic aldehyde including the ready formation of derivatives with carbonyl reagents—reactions which are absent in the *pseudo*-ester (3-methoxyphthalide), m. p. 46—47°. The OH and C=O absorption frequencies found for *o*-formylbenzoic acid, m. p. 98°, and its normal and *pseudo*-methyl esters are compared with phthalide, benzoic acid, and methyl benzoate in Table I. The figures for the C=O absorptions of benzoic acid and its methyl ester agree well with those previously reported (Davies and Sutherland, *Nature*, 1938, **141**, 372; Hartwell, Richards, and Thompson, *loc. cit.*). The broad absorption band with maxima at 2618 and 2538 cm.$^{-1}$ in benzoic acid is attributed to the OH stretching vibration of the carboxyl group.

TABLE I.

	Frequency (cm.$^{-1}$).			Frequency (cm.$^{-1}$).	
Compound.	C=O.	OH.	Compound.	C=O.	OH.
Phthalide	1750	—	Benzoic acid	1690	2618 2538
o-Formylbenzoic acid	1738	3250	Methyl benzoate *	1724	—
o-Formylbenzoic acid, *pseudo*-methyl ester	1768	—	Normal methyl *o*-formylbenzoate *	1725 1708	— —

The normal methyl ester of *o*-formylbenzoic acid showed a broad absorption band in the C=O region just resolvable into two peaks at 1725 and 1708 cm.$^{-1}$, attributable to aromatic ester and aromatic aldehyde C=O, respectively. The *pseudo*-ester showed only a single band, as was to be expected, at a frequency appreciably higher (1768 cm.$^{-1}$) than that of the ester C=O in the normal methyl ester. From the single C=O absorption band at 1738 cm.$^{-1}$, much closer to the five-ring lactone frequency of phthalide (1750 cm.$^{-1}$) than to the aromatic carboxylic acid (1690 cm.$^{-1}$) frequency of benzoic acid, and from the characteristic alcoholic OH absorption, it is clear that *o*-formylbenzoic acid exists in the lactol form in the solid state.

A number of simple related keto-acids, listed in Table II, were also found to be in the lactol form in the solid state. In some cases the alcoholic OH frequencies were somewhat lower than expected and this effect is discussed more fully later.

TABLE II.

Compound.	M. p.	Frequency (cm.$^{-1}$). C=O.	OH.
Phthalonic acid	144°	1765 1725	3472
Acetophenone-*o*-carboxylic acid	116—118	1732	3205
ω-Bromoacetophenone-*o*-carboxylic acid	122—123	1740	3165
ωω-Dibromoacetophenone-*o*-carboxylic acid	131—132	1740	3165

Among more complex molecules containing carbonyl groups in addition to those involved in ring-chain tautomerism, the colourless, lactol form, m. p. 125—130°, and the yellow keto-form, m. p. 142° (Graebe and Juillard, *Ber.*, 1888, **21**, 2003; Hantzsch and Schweite, *loc. cit.*), of benzil-o-carboxylic acid were examined, as was the yellow normal methyl ester, m. p. 118° (Schmid, Hochweber, and von Halban, *loc. cit.*) of this acid. Unfortunately, attempts to prepare the unknown *pseudo*-methyl ester failed. The results obtained (Table III) support the conventional structural formulation of the above compounds, the lactol form of the acid showing typical alcoholic and the keto-form typical carboxylic acid type OH absorption.

TABLE III.

Compound.	Frequency (cm.$^{-1}$). C=O.	OH.
Benzil-*o*-carboxylic acid (lactol)	1745 1692	3268
Benzil-*o*-carboxylic acid (keto)	1698 1683	2632 2513
Benzil-*o*-carboxylic acid normal methyl ester	1713 1680	— —

The bands at 1680 and 1692 cm.$^{-1}$ in benzil-*o*-carboxylic acid normal methyl ester and benzil-*o*-carboxylic acid (lactol), respectively, are attributed to aromatic ketone C=O; those at 1713 and 1745 cm.$^{-1}$ to aromatic ester and phthalide ring lactone C=O, respectively. In the keto-form of benzil-*o*-carboxylic acid the frequencies characteristic of aromatic ketone and aromatic carboxylic acid are too close together to allow definite band assignment.

As may be seen by inspection of Tables I—III, the keto- and the lactol form of carboxylic acids are readily recognised from the infra-red absorption data. With the esters of these acids, distinction is not so clear cut.

In the two examples where an α-diketone grouping occurs, the conjugation of one C=O group with a second has no effect on the absorption frequency. Since the two ketonic groups are equivalent, or very nearly so, in the normal methyl ester of benzil-*o*-carboxylic acid, the substance shows only two absorption bands. Two bands would also be expected from the *pseudo*-ester, so that in this particular case, structures could not have been allocated from the number of bands observed. Owing to the superposition of the carbonyl absorption bands, the normal ester of *o*-formylbenzoic acid is only just recognisable as such from the infra-red spectrum. At this stage of the investigation it was realised that in the case of esters of aromatic γ-keto-acids, the actual frequency of the C=O absorption always gave sufficient and reliable indication of the structure of the compound, the C=O in the phthalide ring of the *pseudo*-esters absorbing in the range 1740—1770 cm.$^{-1}$ whereas the normal esters absorbed much below these values (1710—1730 cm.$^{-1}$).

The correlation of vibrational spectra with characteristic groupings is due largely to the work of Barnes *et al.* (Barnes, Gore, Liddel, and Williams, " Infra-red Spectroscopy " Reinhold Publishing Corp., New York, 1944 : *Anal. Chem.*, 1948, **20**, 402) and of Thompson (*J.*, 1948, 328), and it has been shown that with some linkages, small alterations in the attached atoms or linkages produce small but characteristic displacements of the absorption bands. In the case of the C=O link these effects have been studied by Lecomte in a series of papers between 1941 and 1945, by Thompson and Torkington (*J.*, 1945, 640), and by Hartwell, Richards, and

Thompson (*loc. cit.*). Correlations between absorption frequency and specific types of carbonyl group in steroids have been reported by Jones, Williams, Whalen, and Dobriner (*J. Amer. Chem. Soc.*, 1948, **70**, 2024) and Jones, Humphries, and Dobriner (*ibid.*, 1949, **71**, 241); and Rasmussen, Tunnicliff, and Brattain (*ibid.*, 1949, **71**, 1068, 1073) have published much valuable data on ketones and carboxylic acid derivatives. Additional data have been obtained on esters by Hampton and Newell (*Anal. Chem.*, 1949, **21**, 914) and on lactones by Thompson and Richards (" Chemistry of Penicillin," Princeton Univ. Press, 1949, p. 386).

The characteristic frequencies of the carbonyl groups in various types of aldehydes, ketones, esters, lactones, and acids, largely taken from the recent literature mentioned above, are summarised in Table IV. With aldehydes, ketones and carboxylic acids, conjugation with C=C or the benzene nucleus produces shifts of 30—40 cm.$^{-1}$ or 20—30 cm.$^{-1}$, respectively, to lower frequencies. With lactones and esters these shifts to lower frequencies on conjugation are rather less pronounced. A shift of 25—30 cm.$^{-1}$ to higher frequencies occurs on passing from a six-membered ring to the corresponding five-membered ring compound, due to the increased strain in the ring. It cannot be emphasised too strongly that the frequencies tabulated apply only to the simplest compounds in which it is possible to vary ring size and the type of conjugation. In more complex molecules the C=O frequencies can be modified very considerably by the presence of substituents (cf. Flett, *Trans. Faraday Soc.*, 1948, **44**, 767), and either an inductive or an electromeric mechanism may be involved. Electron-attracting substituents cause shifts to higher frequencies. Interaction effects resulting in the displacement of the carbonyl absorption bands to higher frequencies have also been observed when two carbonyl groups occur in the 1 : 2-, 1 : 3-, or 1 : 4-positions relative to one another (Jones, Humphries, and Dobriner, *loc. cit.*). Still greater shifts to lower frequencies can occur in molecules containing hydroxyl groups, capable of interacting with the carbonyl groups, the magnitude of the effect depending on whether the hydrogen bonding is intermolecular or intramolecular (chelation).

TABLE IV.

Frequency–structure correlations for the C=O *stretching vibration.*

Ketones.	Frequency (cm.$^{-1}$).
Acyclic, unconjugated	1715
Acyclic, $\Delta^{\alpha\beta}$	1670
In six-membered ring, unconjugated	1720
In six-membered ring, $\Delta^{\alpha\beta}$	1680
In five-membered ring, unconjugated	1745
In five-membered ring, $\Delta^{\alpha\beta}$	1715
In five-membered ring, $\Delta^{\beta\gamma}$	1755
Aryl alkyl	1690
Diaryl	1660
Aldehydes.	
Unconjugated	1730
$\Delta^{\alpha\beta}$	1695
Aromatic	1705

Esters.	Frequency (cm.$^{-1}$).
Unconjugated	1740
$\Delta^{\alpha\beta}$	1720
Aromatic	1720
Vinyl esters	1770
Phenyl esters	1765
Lactones.	
In six-membered ring, unconjugated	1740
In five-membered ring, unconjugated	1770
In five-membered ring, $\Delta^{\alpha\beta}$	1750
In five-membered ring, $\Delta^{\beta\gamma}$	1800
Phthalide ring	1750
Acids (solid dimer).	
Unconjugated	1715
$\Delta^{\alpha\beta}$	1680
Aromatic	1690

TABLE V.

C=O *absorption frequency* (*cm.*$^{-1}$) *in esters of* γ-*aldehydic and -ketonic acids.*

Parent acid (open form).	R = H.		R = Alkyl.		R = Aryl.	
	normal.	*pseudo.*	normal.	*pseudo.*	normal.	*pseudo.*
$o\text{-}C_6H_4\langle^{COR}_{CO_2H}$	1705 1720	1750	1690 1720	1750	1660 1720	1750
$CH{\cdot}COR$ $\|$ $CH{\cdot}CO_2H$	1695 1720	1750	1670 1720	1750	1660 1720	1750
$CH_2{\cdot}COR$ $\vert$ $CH_2{\cdot}CO_2H$	1730 1740	1770	1715 1740	1770	1690 1740	1707

The C=O absorption frequencies, predicted from Table IV for the normal and *pseudo*-esters of some simple aldehydic and ketonic acids are set out in Table V. In every case the *pseudo*-

esters may be recognised by the high-frequency five-membered ring lactone C=O absorption (cf. Table I). In more complex molecules, provided something is known about the structure, due allowance may be made for the effects of substituents, where necessary by comparison with model compounds. These effects are discussed further below.

When, however, similar tables are drawn up for esters of δ-aldehydic and -keto-acids it is found that the positions of the C=O absorption bands due to normal ester and six-ring lactone are identical, and in this series therefore, the esters could only be distinguished by the number of absorption bands recorded in the C=O stretching region, assuming that the necessary degree of resolution had been achieved, and that there were no complicating factors due to the presence of additional carbonyl groups.

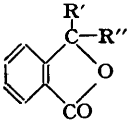
The effect of substitution in the 3-position on the absorption frequency of the phthalide (III) ring C=O is brought out in Table VI. The effect of nuclear substitution has not been studied. Electron-attracting substituents, such as carboxyl and methoxyl, give rise to shifts of 10—20 cm.$^{-1}$ to higher frequencies; the effect of the electron-repelling methyl group is negligible. Rather surprisingly, from the electronic view-point, a hydroxyl substituent in the 3-position causes an apparent shift of 10 cm.$^{-1}$ to lower frequencies, a difference of 20—30 cm.$^{-1}$ compared with the corresponding methylated compound. It is suggested that this effect is due to intermolecular hydrogen bonding, the hydroxy-group of one molecule interacting with the phthalide-ring keto-group of a second molecule and resulting in the lowering of both the C=O and OH frequencies. The OH frequencies do in fact appear close to 3200 cm.$^{-1}$ instead of at the normal bonded-hydroxyl value of 3450 cm.$^{-1}$. An interesting exception is phthalonic acid where the phthalide ring C=O and OH frequencies occur at the normal values of 1765 cm.$^{-1}$ and 3472 cm.$^{-1}$, respectively. Clearly in this case dimerisation only involves bonding between the carboxylic acid groups in the side-chain.

TABLE VI.

Absorption frequencies (*cm.*$^{-1}$) *of phthalides* (III).

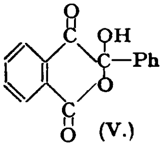
R′.	R″.	C=O in ring.	Other C=O groups present.	Alcoholic OH.	R′.	R″.	C=O in ring.	Other C=O groups present.	Alcoholic OH.
H	H	1750	—	—	OH	H	1738	—	3250
OMe	H	1768	—	—	OH	CH_3	1732	—	3205
					OH	CH_2Br	1740	—	3165
OMe	CH_2Br	1760	—	—	OH	$CHBr_2$	1742	—	3165
OMe	$CHBr_2$	1772	—	—	OH	COPh	1745	1692	3268
H	CO_2H	1775	1718	—	OAc	COPh	1745	1712	—
					3-Methylenephthalide		1780	—	—
OH	CO_2H	1765	1725	3472	Phthalidylideneacetic acid		1800	1705	—

Methyl ω-bromoacetophenone-*o*-carboxylate, m. p. 62°, probably identical with the ester, m. p. 61—62°, described by Gabriel (*Ber.*, 1907, **40**, 72) and assigned the open structure (IV), shows a single C=O absorption band at 1760 cm.$^{-1}$ and therefore should be formulated as (III; R′ = OMe, R″ = CH_2Br).



(III.)

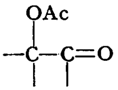
(IV.)



(V.)

Similarly, esterification of ωω-dibromoacetophenone-*o*-carboxylic acid with methanolic hydrogen chloride gave a methyl ester, m. p. 122°, with a single C=O absorption frequency at 1772 cm.$^{-1}$ and therefore clearly the *pseudo*-ester (III; R′ = OMe, R″ = $CHBr_2$). It is also apparent from a consideration of the frequency–structure correlations in Table IV that the lactol form of benzil-*o*-carboxylic acid has the structure (III; R′ = OH, R″ = COPh) and not the alternative six-ring lactol formula (V).

3-Methylenephthalide and phthalidylideneacetic acid are included in Table VI because of the high frequency of the ring C=O absorption. Both contain the —C=C—O—CO— grouping present in vinyl and phenyl esters (Table IV), and the increase in frequency has been attributed to the increase in the electron-attracting power of the oxygen atom adjacent to the double bond (Hartwell, Richards, and Thompson, *loc. cit.*; Walsh, *Trans. Faraday Soc.*, 1947, **43**, 75).



$-\overset{\overset{\textstyle OAc}{|}}{\underset{|}{C}}-\underset{|}{C}=O$

Interaction effects resulting in the displacement of one of the C=O bands to higher frequency are observed in benzil-*o*-carboxylic acid *pseudo*-acetate (III; R′ = OAc, R″ = COPh). This compound contains the grouping (inset) present in the 21-acetoxy-20-keto-steroids studied by Jones *et al.* (*loc. cit.*) and found to show similar shifts due to interaction of the C=O groups.

In the present paper only esters of aromatic acids have been investigated but it is hoped to extend the work to other types in later papers. The application of the method to gladiolic acid and its derivatives will be discussed in Part III.

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