The Base-catalyzed Condensation of Nitrophenylpyruvates. II. The Absorption Spectra of α-Oxo-β-aryl(or alkyl)-γ-arylmethyl(or alkyl)-γ-ethoxycarbonyl-γ-butyrolactones

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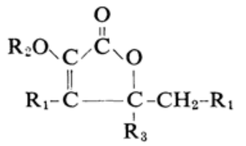
In the preceding paper,[1] the base-catalyzed condensation of ethyl *o*-nitrophenylpyruvate (in situ) was reported to give a dimeric condensate, the structure of which was confirmed by chemical means to be α-oxo-β-(*o*-nitrophenyl)-γ-(*o*-nitrobenzyl)-γ-ethoxycarbonyl-γ-butyrolactone (I). However, the infrared spectra of this compound and its derivatives do not agree, in some respects, with their structures. In order to make a correct interpretation of the spectra, those compounds in which the two *o*-nitrophenyl groups in compound I had been substituted with two methyl or two phenyl groups were prepared and their absorption spectra were comparatively examined. Table I lists the compounds used in this study and the references for their preparation.[2,3]

TABLE I. LIST OF COMPOUNDS



Compd. No.	R_1	R_2	R_3	Ref.
I	*o*-$NO_2C_6H_4$	H	CO_2Et	1
II	Me	H	CO_2Et	2
III	Me	Me	CO_2Et	*
IV	Me	Ac	CO_2Et	2
V	Me	H	H	2
VI	Me	Ac	H	2
VIII	*o*-$NO_2C_6H_4$	Me	CO_2Et	1
IX	*o*-$NO_2C_6H_4$	Ac	CO_2Et	1
X	*o*-$NO_2C_6H_4$	H	H	1
XI	Ph	H	CO_2Et	3
XII	Ph	Me	CO_2Et	3
XIII	Ph	Ac	CO_2Et	*
XIV	Ph	H	H	3

* New compounds.

Infrared Absorption Spectra

The spectral data[4] are listed in Table II. The ester $\nu_{C=O}$ of compounds II, III, and IV appeared in the normal position for esters[5] (1740~1742 cm^{-1}), and there is no such effect of an α-alkoxyl group on carbonyl as that observed by Jones and his co-workers[6] in ketones and by Singh[7] in a lactone. This is probably due to the presence of a double bond in the α, β-position of the lactone. On the other hand, the absorption spectra of II and V, and of IV and VI[8] showed that the $\nu_{C=O}$ due to lactone had shifted by 8~15 cm^{-1} to a higher wave number region in II and IV, apparently due to the presence of an ethoxycarbonyl group. The $\nu_{C=O}$ and ν_{OH} of lactone carbonyl and enol in II and V are split in two, even in a dilute solution; this is considered to show that these compounds are present as a mixture of enols with and without hydrogen bonding,[9] because the intramolecular hydrogen bond of VII-type is a labile five-membered ring.[10] A dicarbonyl type is possible but, since compounds of this type exist completely in the enol type[11] in an aqueous solution (dielectric constant of the solvent: 81[12])[13] and since a

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[1] T. Sakan, M. Kato, T. Miwa and N. Nakamura, This Bulletin, **37**, 1161 (1964).

[2] J. Monnin, *Helv. Chim. Acta*, **40**, 1983 (1957).

[3] R. Hemmerlé, *Compt. rend.*, **162**, 758 (1915); *Ann. chim.*, [9] **7**, 226 (1917).

[4] Infrared absorption spectra were measured with a Hitachi model EPI-2 infrared spectrophotometer. We are indebted to Miss Hiromi Tokuda for the measurements.

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., London; John Wiley & Sons, New York (1954), p. 152.

[6] R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, *J. Am. Chem. Soc.*, **70**, 2030 (1948).

[7] G. Singh, ibid., **78**, 6109 (1956).

[8] In IV and VI, the $\nu_{C=O}$'s of lactone and acetate completely overlap to form one peak.

[9] The absorptions on the lower wave number side in these peaks are those due to the intramolecular hydrogen bonding.

[10] W. Klyne, "Progress in Stereochemistry," Vol. I, Butterworths Publications, London (1954), p. 224.

[11] G. S. Hammond, in M. S. Newman, "Steric Effects in Organic Chemisty," John Wiley & Sons, New York (1956), p. 449.

[12] A. E. Remick, "Electronic Interpretation of Organic Chemistry," John Wiley & Sons, New York (1949), p. 256.

[13] In general, keto-enol tautomers are more likely to exist in the keto form in an aqueous solution than in other solvents. See A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London (1954), p. 227.

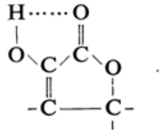
TABLE II. INFRARED ABSORPTION SPECTRA*

Compd. No.	ν_{max} cm^{-1}					
I	3550^{s}	3350^{bw}	1785^{vs}	1739^{s}	1528	1352
II	3580	3395^{b}	1785^{vs}	1768^{sh}		
			1742^{s}			
III			1783^{vs}	1740^{s}		
			1690^{ms}			
IV			1798^{s}	1739		
			1703^{vw}			
V	3570^{m}	3365	1770	1753		
			1728	1717^{sh}		
VI			1790	1705		
VIII			1787^{vs}	1738^{s}	1528	1350
IX			1798^{vs}	1739^{s}	1528	1355
X	3500		1764^{s}		1526	1350
XI	3540	3340^{b}	1778^{s}	1747^{s}		
XII			1778^{vs}	1748^{s}		
XIII			1800^{vs}	1750		
XIV	3550	3325^{b}	1770^{s}	$1748^{sh,w}$		

* Spectra of compounds with R_1=Me and Ph were measured in CCl_4 solution, and those of compounds with R_1=o-$NO_2C_6H_4$ were taken in $CHCl_3$ solution.

TABLE III. ULTRAVIOLET ABSORPTION SPECTRA

Compd. No.	λ_{max}^{EtOH} mμ	(log ε)
I	248	(4.28)
II	242	(3.92)
III	235	(3.91)
IV	212	(4.04)
V	234.5	(3.95)
VI	213.5	(4.09)
VIII	244	(4.02)
IX	266	(3.79)
X	253	(4.28)
XI	288	(4.28)
XII	283	(4.28)
XIII	276	(4.14)
XIV	288	(4.30)

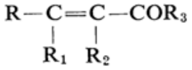


VII

ν_{OH} of a very strong intensity appears in their infrared absorption spectra in carbon tetrachloride (dielectric constant of the solvent: 2.24[12]), it is apparent that they are mainly present in the enol type in these solution.[14] When the hydroxyl is methylated (III), ν_{OH} disappears and the lactone $\nu_{C=O}$ alone remains, at 1783 cm^{-1}. When this is derived to an acetate, IV, there is no change in the $\nu_{C=O}$ of ethoxycarbonyl, but the lactone $\nu_{C=O}$ shifts further to a higher wave number region as a result of the interaction of the lactone with the newly-introduced acetate group.

In the compounds with a phenyl ring, XI and XII, the $\nu_{C=O}$ due to lactone is shifted by 5~7 cm^{-1} to a lower wave number side than that of the corresponding compounds with a

TABLE IV. ULTRAVIOLET ABSORPTION SPECTRA OF



$$R-\underset{R_1}{\underset{|}{C}}=\underset{R_2}{\underset{|}{C}}-COR_3$$

			K-Band λ_{max} mμ (log ε)				$\Delta\lambda_{max}$ mμ
R_1	R_2	R_3	R=Me		R=Ph		
H	H	OH	204	(4.07)[*1]	273	(4.32)[*1]	69
OH	H	Me	ca. 270	(4.08)[*1]	ca. 310	(4.18)[*1]	ca. 40
H	Me	OH	216	(3.98)[*2]	259~263	(4.22)[*3]	ca. 45

[*1] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London (1954).

[*2] W. E. Parham, W. N. Moulton and A. Zuckerbraun, *J. Org. Chem.*, **21**, 72 (1956).

[*3] A. Mangini and F. Montanari, *Gazz. chim. ital.*, **88**, 1081 (1958).

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[14] As will be stated later, these compounds are present almost in an enolized form even in ethanol, and completely their ultraviolet absorption spectra can be interpreted on the same structural basis.

TABLE V. ANALYTICAL VALUES AND PHYSICAL CONSTANTS OF α-OXO-β-METHYL-γ-ETHYLBUTYROLACTONES

Compd. No.	C, % Found	C, % Calcd.	H, % Found	H, % Calcd.	B. p., °C (mmHg.) Found	B. p., °C (mmHg.) Lit.*1	n_D (°C) Found	n_D (°C) Lit.*1
II	56.40	56.07	7.06	6.59	86 (0.04)	112～115 (0.1)	1.4779 (25)	1.4785 (20)
III	57.69	57.88	7.09	7.07	70～74 (0.02)	—	1.4652 (22)	—
IV	56.30	56.24	6.54	6.29	100～104 (0.02)	100～102 (0.01)	1.4630 (22)	1.4636 (21)
V	57.51	57.34*2	7.51	7.22*2	90～94 (0.2)	78～79 (0.05)	1.4868 (22)	—
VI	58.41	58.69	6.72	6.57	110～141*3 (0.01)	90～92 (0.05)	1.4685 (16)	1.4660 (23)

*1 Ref. 2.

*2 +1/4 H_2O. Due to hygroscopicity.

*3 Bath temperature due to small amount available.

TABLE VI. MELTING POINTS OF α-OXO-β-PHENYL-γ-BENZYLBUTYROLACTONES

Compd. No.	M. p. °C	Lit. m. p. °C
XI	141～141.3	140³⁾
XII	80.0～80.5	80³⁾
XIII*	93～94	—
XIV	171.2～172.2	171³⁾

* Found: C, 69.76; H, 5.48. Calcd.: C, 69.46; H, 5.30%.

methyl group (II and III) as a result of conjugation with the phenyl ring,15) while the ester $\nu_{C=O}$ is shifted by 9～10 cm^{-1} to a higher wave number region, now being present at 1747～1750 cm^{-1}. The reason for the latter shift is still not clear.16) The splitting of the ν_{OH} of compounds XI and XIV in two, without the splitting of the carbonyl $\nu_{C=O}$, is probably due to hydrogen bonding with the π-electron of the phenyl ring.17)

In the infrared absorption spectra of I and X with an enol structure, there are only one $\nu_{C=O}$ due to lactone carbonyl and one ν_{OH} in the higher wave number region, and practically no evidence of an intramolecular hydrogen bonding. In the methyl ether compound VIII and the acetate IX, absorptions in the $\nu_{C=O}$ region are similar to that of the corresponding III and IV with a methyl group in place of the phenyl. This indicates that the o-nitrophenyl ring is not conjugated with the lactone ring.

Ultraviolet Absorption Spectra

The results18) are shown in Table III. As has already been stated, α-oxo-γ-butyrolactone is completely enolized in an aqueous solution and is expected to be present chiefly in the enolized form in the ethanol solution (dielectric constant of the solvent: 25.712)) in which its ultraviolet absorption spectrum was measured. Actually, the absorptions of the enols, II and XI, are shifted by 7 and 5 mμ respectively to a longer wavelength region than those of the methyl ethers, III and XII,19) without any change in their intensity; this is evidence for the above assumption.20)

Compared to the spectrum of II, that of the acetate IV shows a hypsochromic shift of 31 mμ; this is in good agreement with the generally accepted value of 34 mμ.21) The absorption maximum of V seems to have shifted slightly to a shorter wavelength side; the reason for this is not clear.

In general, α,β-unsaturated carbonyl compounds with a phenyl group in the β-position show the so-called K-band in a region of wavelengths longer by 40～65 mμ than those with a methyl group in the same position, as is illustrated in Table IV. Consequently, in compounds with a phenyl group such as R_1, the absorptions of XI and XII show a bathochromic shift of 46～48 mμ compared to the corresponding methyl compounds, II and III,

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15) In $CH_3=CHCO_2CH_3$ (*trans*) and $C_6H_5CH=CHCO_2C_2H_5$ (*trans*), the difference is -11 cm^{-1}, not greatly different from the above shift. See J. L. H. Allan, G. D. Menkins and M. C. Whiting, *J. Chem. Soc.*, **1955**, 1874.

16) The change in absorption wave numbers may be due to interaction with π-electrons of the phenyl ring.

17) There is no splitting of the $\nu_{C=O}$ and a close proximity of the hydroxyl and phenyl ring is possible. Such an example has been observed in the β-phenylethyl alcohol derivatives. See G. Büchi, L. Crombie, P. J. Godin, J. S. Kaltenbornn, K. S. Siddalingiah and D. A. Whiting, *J. Chem. Soc.*, **1961**, 2843.

18) The ultraviolet apsorption spectra were measured with a Hitachi model EPS-2 recording spectrophotometer.

19) P. Grossmann, *Z. physik. Chem.*, **109**, 327 (1924). The difference between the enol form of ethyl acetoacetate (245 mμ) and ethyl β-ethoxycrotonate (232 mμ) is 13 mμ.

20) H. Schinz and M. Hinder (*Helv. Chim. Acta*, **30**, 1349 (1947)) have reported that α-oxobutyrolactones have an absorption maximum at 232 mμ (log ε 4.1); but the direct bonding of a methyl group with the chromophore group should cause a shift of about 10 mμ to the longer wavelength region and 242 mμ in II seems to be a normal value.

21) K. Hirayama, "Zikken Kagaku Kōza," I/1, Maruzen, Tokyo (1957), p. 104.

indicating that the phenyl group is in conjugation with the enol in the α-oxobutyrolactone ring. The presence of the absorption of the acetate XIII on a longer wavelength side than is to be expected is inexplicable.[22] The absorption maximum of XIV is in a normal position and is not different from that of XI.

In compounds with an *o*-nitrophenyl group, absorptions in the enol I and the enol methyl ether VIII are in a shorter wavelength region than those of the corresponding compounds with a phenyl group. In these cases, the introduction of an *o*-nitrophenyl group probably prevents the conjugation of the phenyl group with the α, β-unsaturated lactone ring and the *o*-nitrotoluene-type absorption (λ_{max} 260 mμ) of a weak intensity overlaps the absorption of II or III to show the absorption in a somewhat longer wavelength region. In the deethoxycarbonylated compound X this steric hindrance is diminished slightly and a weak conjugation appears,[25] which probably results in the presence of absorption in a longer wavelength region and with an increased intensity. Since there is no absorption absorption around 235 mμ in the acetate IX the of the *o*-nitrotoluene system alone must have appeared in a weak intensity.

Conclusion

To summarize the above results, we may say that all compounds in which R_1 is methyl show absorptions in the position to be expected for an enol and its ether and ester. Compounds in which R_1 is phenyl have the lactone ring and phenyl ring in the same plane and a complete conjugation is established. The compounds in which R_1 is an *o*-nitrophenyl group, however, do not have the *o*-nitrophenyl ring and lactone ring in the same plane; they are present as separate and individual chromophores. However, a slight conjugation phenomenon is observed in X in which the ethoxycarbonyl group has been liberated.

Experimental

The α-oxo-β-methyl-γ-ethyl-γ-butyrolactones (II, IV, V, and VI) were synthesized according to the procedure reported by Monnin.[2] Compound III, a new compound, was prepared by the addition of an ether solution of diazomethane to a solution of II in methanol-ether (1 : 1 v/v); after the mixture had stood overnight, it was distilled. These were all oily substances and were confirmed through elemental analysis and a comparison of their physical constants (Table V).

The α-oxo-β-phenyl-γ-benzylbutyrolactone derivatives (XI, XII, XIV) were synthesized according to the method of Hemmerlé.[3] Compound XII was obtained by heating XI with acetic anhydride on a water bath for one hour. The melting points of these compounds are compared in Table VI.

The synthesis of α-oxo-β-(*o*-nitrophenyl)-γ-(*o*-nitrobenzyl)-butyrolactone derivatives (I, VIII, IX, X) has been reported in a previous paper.[1]

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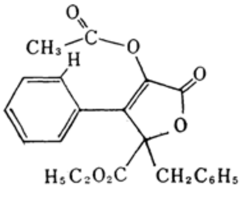
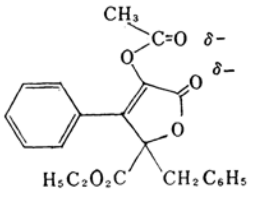
[22] It appears that conformation i is impossible because of steric interference, and that conformation ii, with two oxygen atoms in close proximity, will result. Consequetly, the unshared electron pair of ether oxygen in the ester takes part in the conjugation system; this probably causes the shift of the absorption to a longer wavelength region. Such a consideration has been used by Jones and his co-workers,[23] and by others[24] in explaining infrared absorption spectra.



(i)



(ii)

In comparing the infrared absorption spectra of IV and XIII, the $\nu_{C=O}$ of XIII is found to be shifted to a little higher wave number side by the same cause.

[23] R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2820 (1952).

[24] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, **1957**, 861.

[25] The conjugation phenomenon is manifested as the function of $\cos^2\theta$, where θ is the angle formed by the two rings. E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, New York (1955), p. 174.