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Application of IR Spectroscopy to Study of Ring-Chain Tautomerism in Some β-Aroylacrylic Acids

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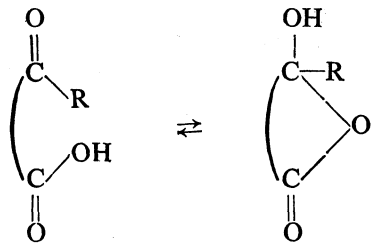
The Infrared absorption spectra of some β-aroylacrylic acids have been recorded in potassium bromide and chloroform. The characteristic features relevant to existence of open and cyclic tautomeric forms are discussed.

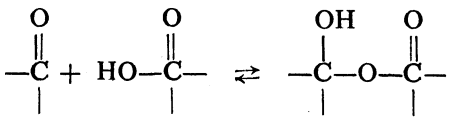
INTRODUCTION

Large number of organic compounds such as carbohydrates, alkaloids, steroids, and γ-oxoacids etc. exhibit the phenomenon of ring-chain tautomerism.[1–3] The substituted or unsubstituted γ-oxocids are capable of existing in keto-acid (chain) and lactol (ring) tautomeric forms due to characteristic features present in them.



Keto-acid form Lactol form

During the conversion of keto-acid form into lactol form, hydrogen from carboxylic function migrates to oxo group as an electrophile and therefore, tautomerism of this type was termed as electrophilic tautomerism[1]. Taking into consideration the intramolecular addition of the carboxylic group to the oxo group, the keto-lactol tautomerism can be regarded as carbonyl addition equilibrium involving a weakly nucleophilic carboxylate group[4].



This addition is a rapid and reversible phenomenon and a tautomeric equilibrium is established between the two forms[4,5].

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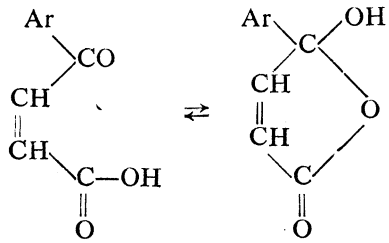
It has been observed that usually γ-oxoacids exist as lactol or as an equilibrium mixture of keto-acid and lactol tautomeric forms[6,7]. Infrared[8–12] and ultraviolet[11,13] spectroscopy have been frequently used to study the structure as well as equilibrium composition of ring-chain tautomers of *o*-acylbenzoic and *o*-aroylbenzoic acids etc. and their esters. Our general interest in the chemistry of γ-oxoacids motivated us to examine the IR spectra of some β-aroylacrylic acids (Ia–If) in an attempt to detect their keto-acid and lactol tautomeric forms.

EXPERIMENTAL

The β-aroylacrylic acids (Ia–If) examined, were prepared by the Friedel-Crafts reaction of benzene, toluene, chlorobenzene, bromobenzene, biphenyl and naphthalene respectively with maleic anhydride in presence of anhydrous aluminium chloride. For the acids Ia to Id, procedure reported by D. Papa *et al.*,[14] was followed while the acids Ie and If were prepared by the method given by H. G. Oddy[15]. IR spectra were recorded with a Perkin Elmer 577 double beam grating instrument as potassium bromide pellets. Infrared spectra of the acids Ia–Ie, were run in chloroform also but due to insufficient solubility of If, its spectrum could not be taken in chloroform. The acids used in the investigation were chromatographically pure and were first dried *in vacuo* over phosphorous pentoxide. AnalaR chloroform was dried several times by passage through a column of silica gel and used directly.

RESULTS AND DISCUSSION

Ideally the keto-acid(I) and lactol(II) tautomeric forms of β-aroylacrylic acids are expected to exhibit characteristically different IR spectra. It can be assumed that the cyclic lactol form should exhibit alcoholic hydroxy group absorption and lactonic carbonyl absorption. Similarly, the open keto-acid form is expected to display ketonic carbonyl absorption, carboxylic carbonyl absorption and a hydroxy absorption of carboxylic group.



Ia–If IIa–IIf

I-II : a, Ar = phenyl; b, Ar = 4-methylphenyl
c, Ar = 4-chlorophenyl; d, Ar = 4-bromophenyl
e, Ar = 4-biphenyl; f, Ar = 2-naphthyl

IR spectra of the β-aroylacrylic acids (Ia–If) have been measured in KBr and chloroform (ν_{max} in cm^{-1}) and the results are presented in Table 1. All the compounds investigated showed the presence of four hydroxy absorptions at 3640 to 3590, 3580 to 3510, between 3500–3300 (broad), and 3200–2300 (broad). On the basis of the results reported[16] for

TABLE 1

STRETCHING ABSORPTIONS OF β-AROYLACRYLIC ACIDS

Acid	Method	ν_{max} (cm^{-1})	
		Hydroxyl region	Carbonyl region
Ia	KBr	3640, 3560, 3440–3300, 3200–2300	1785, 1750, 1690, 1660
	$CHCl_3$	3640, 3580, 3430–3300, 3000–2300	1785, 1742, 1700, 1665
Ib	KBr	3610, 3530, 3480–3360, 3100–2300	1772, 1750, 1685, 1655
	$CHCl_3$	3590, 3530, 3430–3300, 3000–2300	1775, 1745, 1690, 1660
Ic	KBr	3600, 3540, 3480–3300, 3200–2300	1790, 1755, 1695, 1660
	$CHCl_3$	3655, 3510, 3430–3300, 3300–2300	1780, 1740, 1710, 1645
Id	KBr	3600, 3540, 3400–3300, 3200–2300	1795, 1740, 1690, 1655
	$CHCl_3$	3600, 3550, 3470–3300, 3000–2300	1725, 1740, 1700, 1660
Ie	KBr	3620, 3550, 3500–3400, 3200–2500	1785, 1747, 1685, 1655
	$CHCl_3$	3610, 3540, 3500–3300, 3000–2500	1780, 1755, 1710, 1660
If	KBr	3640, 3510, 3470–3350, 3200–2300	1795, 1765, 1710, 1640

penicillic acid and other related compounds, first two absorption bands at higher wave numbers can be assigned to free OH stretching and the broad band between 3500 and 3300 to bonded OH stretching of the lactol form(II). The broad band between 3200 and 2300 is assignable to hydroxy absorption of the carboxylic group of the keto-acid form(I).

Two feeble bands exhibited by Ia–If around 1795–1772 and 1765–1740 can be ascribed to lactonic carbonyl group of the lactol form(II). It is on

record[17] that five membered α, β-unsaturated-γ-lactones display two bands near 1790–1774 and 1765–1740 due to lactonic carbonyl stretching modes. The doubling of this carbonyl absorption has been attributed to an intramolecular vibrational effect similar to that which occur in cyclopentanone and Δ^2-cyclopentenone derivatives[17]. The keto-acid form(I) of all the acids gave two strong bands at 1710–1685 and 1665–1640 due to carboxylic C=O and ketonic C=O respectively. α, β-Ethylenic double bond in these compounds appeared as a weak band near 1630–1615.

These IR spectral studies reveal that the β-aroylacrylic acids investigated exist as a tautomeric mixture of keto-acid(I) and lactol(II) forms. On the basis of relative intensities of lactonic carbonyl band of the lactol form and carboxyl and carbonyl bands of the keto-acid form, it can be concluded that under these conditions, the amount of open keto-acid form is greater than that of cyclic lactol form.

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