ROTATIONAL ISOMERISM OF ARYLOXY ALKYL ESTERS AND AMIDES

C. K. Tseng, J. H. Chan, D. R. Baker and F. H. Walker
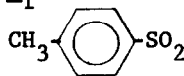
Stauffer Chemical Company, Western Research Center

Richmond, California 94804

Although the rotational isomerism in halogenated derivatives of ethanes, ketones and esters has been intensively studied by infrared spectroscopy[1,2,3], we believe that no previous report on the aryloxyl alkyl esters or amides has been presented. We have prepared various compounds with the Structure I. Their structures were confirmed by pmr and infrared spectroscopies. The synthesis and characcertization of these compounds will be reported elsewhere. In dilute solution, the infrared spectra of I_{a-e} gave rise to two carbonyl stretching frequencies. The intensities of these absorption bands were found to be solvent dependent and are shown in Table 1.

$$R_1O-\underset{\underset{H}{|}}{\overset{\overset{R_2}{|}}{C}}-\underset{\underset{O}{||}}{C}-R_3 \qquad I$$
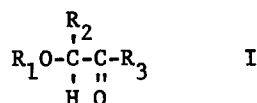
	$\underline{R_1}$	$\underline{R_2}$	$\underline{R_3}$
I_a	CH_3-⬡-SO_2	CH_3	C_2H_5O
I_b	α-naphthyl	CH_3	C_2H_5O
I_c	α-naphthyl	CH_3	$(C_2H_5)_2N$
I_d	α-naphthyl	C_2H_5	$(C_2H_5)_2N$
I_e	α-naphthyl	C_2H_5	$(CH_3)_2N$
I_f	H	CH_3	C_2H_5O

We attribute these two carbonyl absorption bands as arising from two possible isomers; the more polar <u>cis</u> form, II, and the less polar <u>gauche</u> form, III.
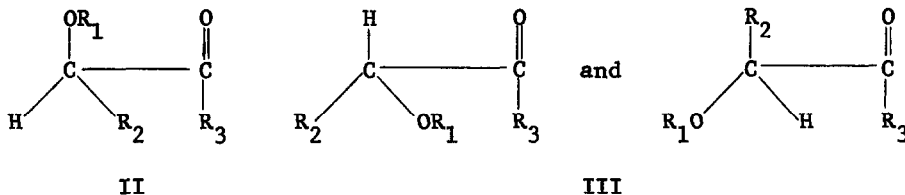
Our assignment of the higher carbonyl frequencies to the <u>cis</u> form is based on intensification of this band in acetonitrile or dimethylsulfoxide solution as compared with that in tetrachloroethylene. It is well known that the population of the more polar form of the rotamers increases in solvents of high dielectric constants.[4]

It is seen from the table that I_f (R_1=H) gave rise to only one carbonyl band in tetrachloroethylene, 1,2-dichloroethane or acetonitrile. This is believed to be due to the strong hydrogen bonding between OH and C=O groups such that the C-O and C=O groups must assume the <u>cis</u> conformation. Thus, in the α-hydroxy ester, the hydrogen bonding effect outweighs the polarity effect of the solvent.

Our results are further substantiated by the pmr studies of compounds I_b, I_c, and I_f. The proton chemical shifts of the methine proton alpha to the carbonyl group are listed in Table 2.

TABLE 1. Effect of Solvent on Carbonyl Stretching Frequencies

Compound	Solvent	$\nu_{C=O}$ $(cm^{-1})^a$		$A_{II}/A_{III}{}^b$
		cis form (II)	trans form (III)	
I_a	Tetrachloroethylene	1767	1748	0.79
	1,2-Dichloroethane	1757	1740	1.03
	Acetonitrile	1760	1747	1.06
I_b	Tetrachloroethylene	1766	1740	0.84
	1,2-Dichloroethane	1756	1738	1.70
	Acetonitrile	1755	1739	1.70
I_c	Tetrachloroethylene	1668	1647	0.55
	1,2-Dichloroethane	1658	1632	1.65
	Dimethylsulfoxide	1653	1630	1.90
I_d	Tetrachloroethylene	1668	1641	0.31
	1,2-Dichloroethane	1659	1631	1.16
	Dimethylsulfoxide	1650	1630	1.55
I_e	Tetrachloroethylene	1672	1651	0.26
	1,2-Dichloroethane	1665	1642	1.17
	Dimethylsulfoxide	1660	1642	1.87
I_f	Tetrachloroethylene	1735		
	1,2-Dichloroethane	1732		
	Acetonitrile	1739		

a. All the spectra were measured on a Beckman spectrophotometer Model IR 9.

b. Ratio of $\left[$ peak intensity of ν_{II}/peak intensity of $\nu_{III}\right]$ for carbonyl absorption.

TABLE 2. Effect of Solvent on Methine Proton Chemical Shift*

Solvent	I_b	I_c	I_f
Carbon tetrachloride	290.5	300.1	246.9
Chloroform-d_1	296.0	307.6	256.9
Acetonitrile-d_3	301.2	315.1	251.0

*The pmr spectra were measured on a Varian HA-60-IL spectrometer and
  the chemical shifts, which are expressed in Hz from tetramethylsilane,
  were obtained by extrapolating to infinite dilution.

On the basis of the anisotropic effects of the carbonyl group in the model
proposed by Karabatsos and coworkers[5], it is predicted that the methine
proton will resonate at a higher field when the proton is _cis,_ rather than
gauche, to the carbonyl group.   In a non-polar solvent, the population of
the rotamer III increases as shown in Table 1. Thus, it is expected that
the methine proton will resonate at higher field in going from a polar
solvent to a non-polar solvent. Except for I_f where intra molecular
hydrogen bonding prevents the phenomenon of rotational isomerism, this trend
is indeed observed for compounds I_b and I_c.

References

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