INVESTIGATION OF THE CONFORMATION OF EPOXYCHALCONES BY IR SPECTROSCOPY

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Molecules of ketone oxides in the solid phase exist exclusively in the gauche form, whereas compounds of the open type form a mixture of cis and gauche conformers in solution. The effect of temperature on the conformational equilibrium was investigated.

In our preceding communications [1, 2], we examined some problems of the conformational structure of epoxychalcones. In developing these concepts we studied the IR spectra of some ketone oxides (Table 1) in the solid phase and in solution.

The selection of the objects of the investigation was determined by the peculiarities of the structure of their molecules: I-V, as shown in [1, 2], can exist in the form of several conformers, whereas VI-VIII have a fixed position of the carbonyl group and the epoxide ring. An analysis of Briegleb-Stuart models shows that because of the noncoplanarity of the cyclohexane ring, the geometry of the molecules is close to gauche (Fig. 1) [2].

The IR spectra of all of the investigated compounds in the solid phase contain one absorption band in the region of the stretching vibrations of the carbonyl group. In solution, I-V are characterized by two intense absorption bands in this region, and both of them experience a regular low-frequency shift on passing from CCl_4 to $CHCl_3$, which, in conformity with [3], make it possible to assign them to $\nu_{C=O}$ whereas epoxy ketones VI-VIII in solutions have one carbonyl absorption band.

In our opinion, these results constitute persuasive evidence that ketone oxides of the open type (I-V) form mixtures of conformers when they are dissolved.

An analysis of the $\nu_{C=O}$ values (Table 1) makes it possible to conclude that epoxychalcones in the solid phase exist exclusively in the form of gauche conformers. This conclusion becomes understandable if one takes into account the fact that precisely this form corresponds to the least steric hindrance [1] and that factors that promote the most compact packing of the molecules play the decisive role during the formation of the crystal lattice [4]. This is in good agreement with the fact that the frequency of the stretching vibrations of the carbonyl group of the investigated 4'-R-epoxychalcones in the solid phase is extremely close to the frequency observed for o-substituted acetophenones [5], i.e., the effect of the strained epoxy ring on the distribution of the electron density in the benzoyl portion of the molecule of these compounds is insignificant; as we previously noted in [1], this is peculiar to molecules existing in the gauche conformation.

In CCl_4 solutions the gauche conformation is partially converted to the cisoid form, for which an electron-donor interaction of the strained σ bonds of the oxide ring with the π electrons of the benzoyl group is characteristic [2]. This interaction is responsible for the decrease in the $\nu_{C=O}$ value of this form as compared with that observed for the gauche conformer.

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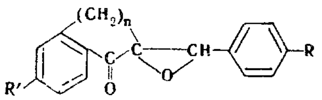
TABLE 1. Frequencies of the Stretching Vibrations of the Carbonyl Group (cm^{-1}) of Epoxychalcones



Compound	R, R′	n*	KBr Pellet	CCl_4		$CHCl_3$		μ
				gauche	cis	gauche	cis	
I	H, H	—	1690	1702	1685	1696	1674	3,43†
II	H, CH_3O	—	1685	1696	1677	1692	1672	
III	CH_3O, H	—	1690	1700	1681	1694	1675	4,00†
IV	H, Cl	—	1692	1701	1683	1694	1675	—
V	Cl, H	—	1690	1696	1677	1692	1672	3,47†
VI	H, H	2	1698	1700	—	1692	—	4,50
VII	CH_3O, H	2	1695	1700	—	1692	—	—
VIII	Cl, H	2	1695	1700	—	1692	—	4,16

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*The $-CH_2-$ bridge is absent in I-V.

†The μ values were taken from [2].

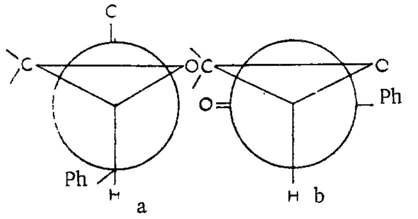

Fig. 1

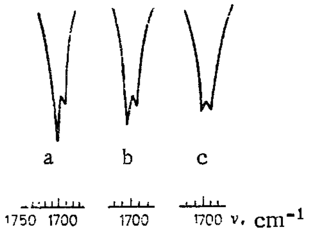

Fig. 2

Fig. 1. Conformations of the epoxy-chalcone molecule: a) cisoid; b) gauche form.

Fig. 2. Change in the intensities of the bands of the carbonyl absorption of epoxychalcone in tetrachloroethylene solution as the temperature rises: a) 20°; b) 50°; 3) 80°.

It has been shown [2] that in benzene solutions at 25° the gauche conformer is the predominant one. The observed increased intensity of the high-frequency absorption as compared with the intensity of the low-frequency band may be determined by this fact (Fig. 2).

The predominance of the gauche conformer is due, in our opinion, to the fact that it is thermodynamically more favorable at room temperature than the cisoid form. This is confirmed by an analysis of the IR spectra measured at 25-80° (Fig. 2). Despite the relatively low temperature range, it can be ascertained that the differences in the spectra of the investigated compounds, regardless of the nature of the aryl group, follow a definite principle — the ratio of the intensities of the carbonyl bands ($\varepsilon_g/\varepsilon_{cis}$) decreases as the temperature rises, i.e., the conformational equilibrium is shifted to favor the cisoid form.

These conclusions are in good agreement with the results of measurements of the dipole moments (Table 1). The gauche form has a higher μ value than the cis form [2] and is the only form possible for VI-VIII, and this also explains the high μ values of the latter as compared with the μ values of I, III, and V, the molecules of which form mixtures of conformers in solution.

EXPERIMENTAL

The IR spectra of KBr pellets of the solid compounds (2 mg of the compound per 100 mg of potassium bromide) and chloroform and CCl_4 solutions of the compounds (0.02 M) were measured with a UR-20 spectrometer at 700-3600 cm^{-1}. The dipole moments were measured by the method in [2].

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