

## PMR SPECTRA OF EPOXYCHALCONES

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The PMR spectra of the epoxides of chalcone and eight of its 4- and 4'-substituted derivatives ( $\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{Cl}$ , and  $\text{NO}_2$ ) and of phenyl vinyl ketone in acetone and carbon tetrachloride were measured. It is shown that these compounds belong to the trans series and exist in hindered conformations. The transmission effects of the epoxide ring and the carbonyl group in epoxychalcone molecules are discussed.

Up to now the study of the spectra of epoxides of  $\alpha, \beta$ -unsaturated ketones has been virtually limited to an examination of their geometrical isomerism [1-5]. The problem of the conformational state of these compounds was cited only in a few papers [6,7] and also in our previous communication [8]. The physicochemical properties of epoxy ketones have not been adequately studied.

Continuing our investigation of epoxychalcones, we have measured the PMR spectra of 10 epoxides. The chemical shifts of the protons are presented in Table 1, while the PMR spectra of chalcone oxide (I) and phenyl vinyl ketone oxide (X) are given in Fig. 1. The PMR spectra of all of the epoxychalcones contain two doublets of identical intensity in the strong-field region; the  $\delta$  values are 2.62-2.94 and 3.12-3.31 ppm, respectively. The doublet at stronger field ( $\delta$  is 2.70 ppm for ketone I; see Fig. 1a) arises from the resonance of the  $\beta$  proton of the epoxy group, while the signal that is shifted to weak field ( $\delta$  is 3.17 ppm for I) is due to the resonance of the  $\alpha$  proton. This assignment is confirmed by the fact that the signal of the  $\beta$  proton is somewhat broadened as compared with the signal of the  $\alpha$  proton as a result of weak spin-spin coupling of the  $\beta$  proton with the ortho protons of the adjacent phenyl ring. If this phenyl ring is absent in the oxide molecule, for example, as in the case of phenyl vinyl ketone oxide (X), the signals of the  $\alpha$  proton experience splitting as a result of coupling with the two  $\beta$  protons to form a quartet (Fig. 1b). In this case, their chemical shift changes only slightly ( $\delta_\alpha \approx 3.00$  ppm). The signals of the  $\beta$  protons experience a considerably greater diamagnetic shift (with respect to epoxychalcone I,  $\Delta\delta_\beta$  is about 0.9 ppm); this is caused by their greater sensitivity to the shielding effect of the phenyl group.

TABLE 1. Chemical Shifts of the Protons of Molecules of the Epoxychalcone Type

| Compound | R                         | R'             | Epoxide ring |         |                | Aromatic ring |      |           |           |           |
|----------|---------------------------|----------------|--------------|---------|----------------|---------------|------|-----------|-----------|-----------|
|          |                           |                | $\alpha$     | $\beta$ | $\Delta\delta$ | <i>o</i>      | m.p. | <i>o'</i> | <i>m'</i> | <i>p'</i> |
| I        | H                         | H              | 3,17         | 2,70    | 0,47           | 6,03          |      | 6,67      | 6,22      | 6,10      |
| II       | $\text{CH}_3$             | H              | 3,16         | 2,64    | 0,52           | 5,90          |      | 6,71      | 6,25      | 6,12      |
| III      | $\text{OCH}_3$            | H              | 3,16         | 2,62    | 0,54           | 6,04          | 5,61 | 6,67      | 6,24      | 6,09      |
| IV       | Cl                        | H              | 3,21         | 2,74    | 0,47           | 6,09          |      | 6,72      | 6,24      | 6,09      |
| V        | $\text{NO}_2$             | H              | 3,31         | 2,94    | 0,37           | 6,39          | 6,97 | 6,64      | 6,23      | 6,13      |
| VI       | H                         | $\text{CH}_3$  | 3,14         | 2,67    | 0,47           | 6,01          |      | 6,62      | 5,97      | —         |
| VII      | H                         | $\text{OCH}_3$ | 3,13         | 2,66    | 0,47           | 6,03          |      | 6,76      | 5,72      | —         |
| VIII     | H                         | Cl             | 3,18         | 2,71    | 0,47           | 6,01          |      | 6,71      | 6,27      | —         |
| IX       | H                         | $\text{NO}_2$  | 3,25         | 2,78    | 0,47           | 6,05          |      | 6,97      | —         | —         |
| X        | Phenyl vinyl ketone oxide |                | 3,00         | 1,76    | 1,24           | —             |      | 6,65      | 6,26      | 6,13      |

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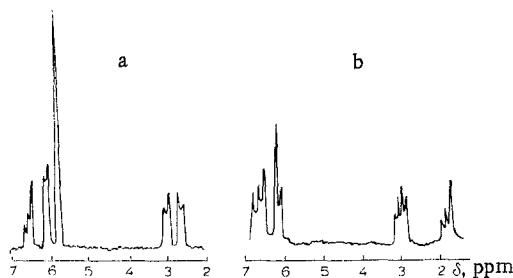


Fig. 1. PMR spectra of oxides I and X in acetone: a) chalcone oxide (I); b) phenyl vinyl ketone oxide (X).

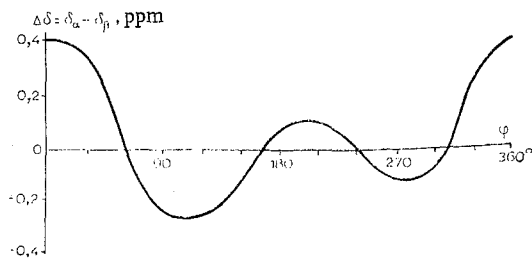


Fig. 2. Dependence of  $\Delta\delta$  on  $\varphi$  for epoxychalcone (I).

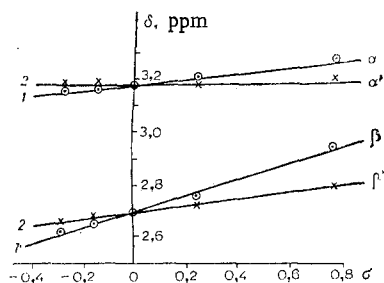


Fig. 3. Correlation of the chemical shifts of the  $\alpha$  and  $\beta$  protons of chalcone oxides with the  $\sigma$  constants of the substituents: 1) substituent in the 4 position; 2) substituent in the 4' position;  $\rho_{\alpha} = 0.15$ ,  $\rho_{\alpha'} = 0.10$ ,  $\rho_{\beta} = 0.29$ , and  $\rho_{\beta'} = 0.12$ .

An analysis of the PMR spectra of the epoxychalcones also makes it possible to draw some conclusions relative to the mutual orientation of the benzoyl and epoxy portions of the molecule. The experimentally found differences in the chemical shifts of the  $\alpha$  and  $\beta$  protons ( $\Delta\delta = \delta_{\alpha} - \delta_{\beta}$ ) are presented in Table 1. These values depend primarily on the electronic character of the groups bonded to the epoxide ring and also on their three-dimensional orientation. We calculated the differences in the chemical shifts of the  $\alpha$  and  $\beta$  protons for the epoxychalcone (I) molecule with allowance for the contributions of the anisotropy of the magnetic susceptibility of the carbonyl and phenyl groups; these differences change as the benzoyl portion of the molecule rotates. For the origin ( $\varphi = 0^{\circ}$ ) we adopted that mutually perpendicular orientation of the planes of the benzoyl group and the epoxide ring for which the carbonyl group and the oxide ring are found in the cisoid conformation; an increase in  $\varphi$  corresponds to clockwise rotation of the benzoyl group. The values of the major components of the tensor of the magnetic susceptibility were taken from [10], while those for the phenyl group were taken from [11]; the calculations were made with the MacConell dipole approximation [12]. The results are presented in Fig. 2. It is seen from Fig. 2 that

A group of signals at 6.03–6.80 ppm, which is caused by the ten protons of the aromatic rings, is observed in the spectra of chalcone oxide (Fig. 1a). The quartet centered at 6.67 ppm is related to the ortho protons of the aromatic ring of the benzoyl portion of the molecule. The considerable paramagnetic shift of the signals of these protons is due to their coupling with the electron-acceptor carbonyl group. The doublet at 6.22 ppm characterizes the resonance of the meta protons of this same ring. The signals of the 4'-proton and the protons of the second phenyl ring practically coincide to give an intense peak at 6.03 ppm. This sort of assignment is confirmed by the spectrum of phenyl vinyl ketone oxide (Fig. 1b), in which the intensity of the signal at 6.13 ppm corresponds to the resonance of only one 4'-proton.

The introduction of substituents into the aromatic rings of chalcone oxide leads to a change in the spectra pattern in the weak-field region in conformity with the electronic character of the groups introduced. Thus methyl or methoxy groups introduced into the 4 or 4' positions lead to considerable diamagnetic shifts of the signals of the 3,5- or 3',5'-protons, respectively (Table 1), while a chloro or nitro group causes a paramagnetic shift of the signals of these protons. In the case of oxide IX, the protons of the nitrobenzoyl group give one intense resonance peak in the spectrum; this is evidence for their equivalence and, consequently, for the identical shielding effect of the carbonyl and nitro groups.

The geometry of the epoxychalcone molecules can be judged from the vicinal spin-spin coupling constants of the  $\alpha$  and  $\beta$  protons of the oxide ring. These constants are practically independent of the electronic character of the substituent introduced into the benzene rings and amount to  $1.9 \pm 0.2$  Hz. It follows from the Karplus expression [9] that the dihedral angle between the planes containing the coupling protons is  $110^{\circ}$ . This angle corresponds to a trans orientation of the groups relative to the epoxide ring in the investigated compounds.

$\Delta\delta$  ranges from  $-0.25$  to  $0.4$  ppm and is close to the experimentally found value ( $\Delta\delta_{\text{exp}}$  for epoxide I is  $0.47$  ppm) only when  $\varphi = 0^\circ$ . Considering the approximate nature of the calculated  $\Delta\delta$  values, it can be assumed that conformations with  $\varphi$  ranging from  $0$  to  $45$  and  $330$  to  $360^\circ$  correspond to the epoxychalcone molecules; this is in agreement with the conclusions drawn on the basis of the dipole moments of these compounds [8]. The PMR spectra do not give any idea of the number of hindered conformers, especially since the second region of positive  $\Delta\delta$  values (Fig. 2) corresponds to the sterically hindered conformations [8]. The average  $\Delta\delta_{\text{calc}}$  value ( $0.03$  ppm) differs substantially from the experimental value ( $0.47$  ppm); this makes it possible to assume the absence of free rotation of the benzoyl group. The introduction of a substituent into the 4 or 4' position of the chalcone oxide molecule is only slightly reflected in the  $\Delta\delta_{\text{exp}}$  value. This is possibly due to the fact that substituents introduced into these positions do not create additional steric hindrance and consequently do not change the conformational structure of the epoxychalcones. It is also interesting to note that an increase in the electron-acceptor properties of an aryl group bonded to the epoxy group (ketones I-V) lowers the  $\Delta\delta$  value, while a substituent in the aroyl group (ketones VI-IX) has practically no effect on this difference.

The PMR spectra of the epoxychalcones made it possible to follow the transmission of the electronic effect in their molecules. Of greatest interest in this respect are the chemical shifts of the  $\alpha$  and  $\beta$  protons of the epoxide ring. As seen from Fig. 3, the  $\delta$  values of these protons display a linear dependence on the  $\sigma$  constants of the substituents introduced into the phenyl rings. The very fact of the existence of such correlations attests to a certain amount of conjugation of the epoxide ring with the aryl and aroyl groups. A comparison of the  $\rho_\beta$  and  $\rho_{\alpha'}$  values shows that the electronic effect of substituents introduced into the aroyl group is almost one third lower than that of substituents in the aryl ring; this is due to the considerable insulating character of the carbonyl group in epoxychalcone molecules. To a first approximation, the transmission effect of the epoxy group can be estimated by comparing  $\rho_\alpha$  and  $\rho_\beta$ ; it is about  $0.5$ .

#### EXPERIMENTAL

The PMR spectra were measured at room temperature with a YaMR-5535 spectrometer with an operating frequency of  $40$  MHz and a resolution of the order of  $1 \cdot 10^{-8}$ . The PMR spectra of acetone solutions of epoxy ketones I-X were investigated, since all of them are quite soluble in this solvent. The measurements were made with several epoxide concentrations ( $5$ - $15\%$ ), and good reproducibility of the chemical shifts was established in all cases. The PMR spectrum of X in carbon tetrachloride was also investigated, in order to identify the signals of the  $\beta$  protons [in this case the diamagnetic shift ( $\delta$ ) of the protons of the aromatic ring was  $\sim 0.1$  ppm, while that of the protons of the epoxide ring was  $\sim 0.4$  ppm]. Cyclohexane was used as the internal standard; the  $\delta$  values presented in Table 1 are the values converted to the tetramethylsilane standard.

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