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Abstract

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SPECTROSCOPIC STUDY OF THE TAUTOMERISM OF THE METHYL AND ETHYL ESTERS OF 4-KETOTETRAHYDROTHIOPYRAN-3-CARBOXYLIC ACID

The esters of 4-ketotetrahydrothiopyran-3-carboxylic acid I should, analogously to the esters of cyclohexanone-1-carboxylic-2 acid, possess keto–enol tautomerism.

$$\text{[structural formula: keto form]} \rightleftharpoons \text{[structural formula: enol form]}$$

I

We found no data in the literature on the study of the indicated tautomerism, which prompted us to carry out the present investigation.

All attempts to select suitable conditions for determining the enolic form of esters I by chemical means, because of the presence of the sulfur atom, did not give satisfactory results. At the same time it seemed of interest to elucidate the influence of the sulfur atom on the tautomerism of these esters by comparing their spectra with the spectra of esters of cyclohexanone-1-carboxylic-2 acid.

As examples we took the ethyl and methyl esters of 4-ketotetrahydrothiopyran-3-carboxylic acid (I and II) and, for comparison, the ethyl and methyl esters of cyclohexanone-1-carboxylic-2 acid (III and IV). Ethyl ester I was obtained according to ([1]) and had the following constants: b.p. 129–130°/8, n_D^{25} 1.5282. On cooling it partially crystallizes. The crystals pressed on a porous plate had m.p. 58°. Methyl ester II, described as a liquid ([2]), crystallizes completely upon seeding. After recrystallization the crystals had m.p. 68°. Constants of the ester: b.p. 97–100°/2, n_D^{25} 1.5250. Ethyl ester III was obtained according to ([3]) and had the following constants: b.p. 115–117°/18, n_D^{25} 1.4772.

Methyl ester IV was obtained analogously to ethyl ester III. Its constants: b.p. 103–105°/17, n_D^{25} 1.4832.

The spectrum of liquid ethyl ester I is presented in Fig. 1a. As is seen, in it, along with the keto form ($C{=}O_{\text{ester}}$ 1740 cm^{-1}, $C{=}O_{\text{keto}}$ 1712 cm^{-1}), a considerable amount of the enolic form is present ($C{=}O_{\text{chelated}}$ 1657 cm^{-1}, $C{=}C$ 1614 cm^{-1}).

The spectrum of liquid methyl ester II is analogous to the spectrum of liquid ethyl ester I.

The spectrum of solid methyl ester II (m.p. 68°, KBr pellet 1:1000) is given in Fig. 1b. As is seen, it represents the pure keto form ($C{=}O_{\text{ester}}$ 1731 cm^{-1}, $C{=}O_{\text{keto}}$ 1700 cm^{-1}). The same spectrum was also obtained in Vaseline oil (Fig. 1c). The spectrum of solid ethyl ester I (m.p. 58°) is analogous to the spectrum of solid methyl ester II.

In Fig. 1g, d are given the spectra of esters III and IV. From comparison of the spectra it is seen that, in the equilibrium of esters III and IV, the enolic form predominates (74.2 and 72.4%, respectively)*. Replacement of the CH_2 group in the ring by sulfur leads to a decrease in the enol content.

* The titration was carried out by a modified method (4).

For studying the influence of solvents on the keto–enol equilibrium, solutions of the keto form of methyl ester II were prepared in isobutyl alcohol, CCl_4, and hexane (0.1 N). In the case of ethyl ester I, the solutions were prepared from the liquid phase (Fig. 3).

Fig. 3 presents the spectra of the esters in isobutyl alcohol after equilibrium had been established. As is seen from the spectra, esters I (Fig. 3a), III (Fig. 3b), and IV (Fig. 3c) contain a considerable and approximately equal amount of the enol form. Methyl ester III contains less enol (Fig. 3b).

In carbon tetrachloride, for esters III (Fig. 3d) and IV (Fig. 3e), after 12 days a considerable decrease in the content of the keto form is observed in comparison with its content in the esters before dissolution (Figs. 1c and d, respectively).

In the case of esters I and II, the conversion of the keto form into the enol form in nonpolar solvents proceeds more slowly, as is seen from the example of solutions of the keto form of methyl ester II (Fig. 2).

After standing for 15 days, the solution in CCl_4 contains only the keto form (Fig. 2c), and only after standing for 47 days at room temperature does a considerable amount of the enol form appear (Fig. 2d). Passing hydrogen chloride into the solution sharply increases the content of the enol form (Fig. 2e). The same occurs in the hexane solution (Figs. 2g, h).

An analogous picture is also observed for ethyl ester I in CCl_4.

Figure 2a gives the spectrum of ethyl ester I in CCl_4 after 10 days of standing. As can be seen, the spectrum differs substantially from the spectrum of the substance from which the solution was prepared (Fig. 1a). When hydrogen chloride is passed into the solution, a considerable increase in the content of the enol form occurs (Fig. 2b). On further standing, the character of the solution spectrum does not change.

The iodomethylate of methyl ester II was obtained (m.p. 122°, calculated in %: C 30.39; H 4.44; found %: C 30.53; H 4.40). As can be seen from the spectrum

(Fig. 2f), it is an enol.

Fig. 1

In Table 1 a comparison is made of the characteristic frequencies of the esters in the solid and liquid states and in solvents. As is seen from the comparison, replacement of the CH_2 group in the ring by sulfur does not cause changes in the characteristic frequencies of the enol form. From Table 1 it is seen that

the frequencies of the carbonyl groups in the solid esters I and II are considerably lower than in their solutions in nonpolar solvents. It is not excluded that such a lowering of the frequency of the carbonyl groups may occur as a result of intermolecular interaction of the sulfur atom with the carbonyl oxygen ($S^{\delta+} \cdots O^{\delta-} = C$), similarly to the way this is recognized by Leonard and co-workers (7) for the transannular interaction of sulfur and carbonyl oxygen in some cyclic thioketones.

Fig. 2

Fig. 3

The UV spectra of the esters were recorded (see Table 2).

To determine at least the approximate enol content in solutions of esters I and II, we made use of the fact that, in isobutanol solutions of esters I and III, approximately the same amount of enol is present according to the IR spectra. Using the literature data of bromometric

Table 1

Characteristic frequencies of the esters

	I	II	III	IV		I	II	III	IV
A. $C=O_{ef.}$	1742	1738	1746	1751	V. $C=O_{ef.}$	1747	1752	1744	1750
$C=O_{ket.}$	1714	1710	1717	1720	$C=O_{ket.}$	1719	1723	1720	1724
$C=O_{chel.}$	1657	1662	1653	1656	$C=O_{chel.}$	1664	1659	1656	1658
$C=C$	1614	1614	1620	1618	$C=C$	1614	1613	1618	1617
B. $C=O_{ef.}$	1735	1735	1738	1737	G. $C=O_{ef.}$	1728	1731		
$C=O_{ket.}$	1714	1712	1719	1717	$C=O_{ket.}$	1700	1700		
$C=O_{chel.}$	1657	1652	1650	1658					

	I	II	III	IV	I	II	III	IV
C = C	1614	1614	1620	1617				

Note. A—liquid, B—in isobutanol, V—in hexane and CCl_4, G—solid. Assignment of the frequencies according to (8, 9).

titration of ester III in methanol and ethanol, from the UV spectra we calculated the enol content in the isobutanol solution of ester III and adopted the figure obtained as the enol content in an isobutanol solu-

of ester I. We then calculated the absorption of 100% enol of esters I, II and III, IV in isobutanol solution and, with its aid, determined the enol content in the remaining solutions. It is considered that this method gives a good

Table 2

UV absorption and enol content in the esters

Solvent	I λ_{max}	I ε	I %	II λ_{max}	II ε	II %	III λ_{max}	III ε	III %	IV λ_{max}	IV ε	IV %
Methanol	254	3590	41	254	2890	34	257	4700	45(8)	257	4200	41
Ethanol	254	4700	55	254	3590	42	257	5880	57(9)	257	5890	57
Butanol	254	5590	65	254	4550	53	257	6750	65	257	7000	67

approximation when the absorption maximum is constant(10), which is fulfilled in our case.

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