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1962

SovietRxiv

Abstract

Full Text

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KETO-CIS-TRANS-ENOL EQUILIBRIUM OF 3-ALKYLACETYLACETONES

For 3-alkylacetylacetones, three tautomeric forms are possible: ketonic, cis-enolic, and trans-enolic.

As in the case of α-alkylacetoacetic esters ([1], [2]), the introduction of branched substituents into position 3 creates steric hindrance to cis-enolization and leads to the appearance of a trans-enolic form. Qualitatively, these relationships can be followed from the action of copper acetate on an alcoholic solution of the keto-enol. This reaction is in principle analogous to the well-known Henecka test ([3]) with ferric chloride for cis-enolization of α-alkylacetoacetic esters. 3-Alkylacetylacetones with primary alkyl groups form blue precipitates with copper acetate. By contrast, with secondary radicals ($R = iso\text{-}C_3H_7$, sec.-C_4H_9) this reaction is negative, which indicates the absence of cis-enol. At the same time, according to bromometric data, these substances are strongly enolized. Consequently, their enolic forms have the trans configuration. We have shown earlier ([1], [2]) that trans-enolization of α-alkylacetoacetic esters does not depend on the nature of the solvent, whereas cis-enolization obeys the well-known Meyer equation ([4]).

$$K_{\mathrm{t\,(trans)}} = (\text{trans-enol}) : (\text{ketone}) = \text{const} = E_1, \tag{1}$$

$$K_{\mathrm{t\,(cis)}} = (\text{cis-enol}) : (\text{ketone}) = EL. \tag{2}$$

The overall constant of tautomeric equilibrium is equal to the sum of the partial constants:

$$K_{\mathrm{t}} = K_{\mathrm{t\,(cis)}} + K_{\mathrm{t\,(trans)}} = [(\text{cis-enol}) + (\text{trans-enol})] : (\text{ketone}) = EL + E_1. \tag{3}$$

3-Alkylacetylacetones with the following substituents were investigated: I. $R = CH_3$, II. $R = C_2H_5$, III. $R = C_3H_7$, IV. $R = C_4H_9$, V. $R = iso\text{-}C_4H_9$, VI. $R = C_6H_5CH_2$, VII. $R = iso\text{-}C_3H_7$, VIII. $R =$ sec.-C_4H_9, IX. $R =$ cyclo-C_5H_9, in a series of solvents.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The method of direct bromometric titration (5) showed that the enolization of 3-isopropyl- and 3-sec.-butylacetylacetones (VII and VIII) is practically independent of the nature of the solvent (enol content 30 and 20%, respectively). Since solutions of these substances form only trans-enols, it follows, therefore, that their trans-enolization does not depend on the nature of the solvent. 3-Cyclopentylacetylacetone (IX) is not enolized at all in any solvent. For the remaining substances (I—VI), containing cis-enolic forms, only approximate observance of Meyer’ s rule was observed.

The reason for these deviations is that 1% solutions of these keto-enols are still insufficiently dilute for independence of the equilibrium constant from concentration to be observed (dilution by factors of 10 and 50 substantially changed the relative content of the enolic form (6)). However, the use of more dilute solutions (0.02%) sharply lowers the accuracy and reproducibility of the determinations. Therefore, the results of the bromometric method give only a qualitative picture of the influence of the solvent on enolization.

The vibrational spectra of acetylacetone and its 3-substituted derivatives have been studied previously (7-9). In the infrared spectra of the substances studied by us, bands at 1700-1725 cm^{-1} are observed, which in intensity and position coincide with the bands of symmetric and antisymmetric vibrations of the $C = O$ groups of 3,3-dimethylacetylacetone (X) and acetylacetone and characterize the presence of the ketone form. In addition, in the region 1585 and 1615 cm^{-1}, compounds I—V have absorption bands that are present in keto-enols with “cis-fixed” enol forms (10,11) and are undoubtedly associated with vibrations of the molecules of the cis-enols. In the spectra of 3-isopropyl- and 3-tert.-butylacetylacetones (VII and VIII), the bands of the cis-enol form are absent, while bands at $\sim$ 1580 and 1680 cm^{-1}, characteristic of trans-enol forms (12), are observed. Absorption bands of the ketone form are also present. In the spectrum of 3-cyclopentylacetylacetone, only absorption bands of the $C = O$ groups of the ketone form, 1700 and 1725 cm^{-1}, are observed. The IR spectral data confirm the conclusions drawn from the bromometric determinations. However, like the latter, they have only qualitative significance, since

Fig. 1. UV spectrum of 3-isobutylacetylacetone (V). 1 –hexane, 2 –ether, 3 –ethanol, 4 –dioxane, 5 –67% methanol

Fig. 2. UV spectrum of 3-isopropylacetylacetone (VII). Designations (1-5) as in Fig. 1; 6 –abs. methanol, 7 –85% methanol; 8 –75% methanol

they were obtained in the study of insufficiently dilute solutions (1%).

UV spectra make it possible to study dilute solutions ($5 \cdot 10^{-4}$ mole/liter); thus the limitations inherent in the preceding methods are removed. The electronic spectra of 3-alkylacetylacetones with primary substituents differ from the spectra of compounds with secondary radicals; the former have an absorption band with a maximum at ~ 290 mμ, the latter at ~ 260 mμ (Figs. 1–2).

Since absorption by the molecules of the ketone form, according to the electronic spectrum of 3,3-dimethylacetylacetone, is negligible in this region, the absorption bands observed in the spectra of 3-alkylacetylacetones should be assigned to electronic transitions of the enol forms, namely, the 290 mμ band to the cis form, and the 260 mμ band to the trans form. In the spectra of 3-alkylacetylacetones with primary substituents (Fig. 1), the 290 mμ band has a sharply pronounced asymmetry of contour, and in the spectra of solutions of some of them (III–V) in 67% aqueous methanol a second absorption maximum is observed in the same region in which molecules of the trans-enol forms absorb (260 mμ). In the spectra of other solutions, the absorption band of the cis form at 290 mμ has a high intensity, and the band in the region of 260 mμ merely distorts the contour of the 290 mμ band or appears as a shoulder of this band. When the complex contour of the doublet is resolved into individual components, under the assumption that the component bands are symmetrical, the wavelength values of the bands in the region of 260 mμ in the spectra of solutions in different solvents practically coincide with the corresponding wavelength values of the absorption bands of the trans forms of isopropyl- and tert.-butylacetylacetones (VII and VIII). From the UV and IR spectral data it follows that solutions of 3-alkylacetylacetones with primary radicals contain three forms: ketone, cis- and trans-enol, whereas solutions of compounds with secondary radicals contain only two forms: ketone and trans-enol. The integral intensities of the absorption bands can serve as a measure of the concentration of the tautomeric forms. Since in the spectral region studied there is no appreciable absorption by the ketone form, it is impossible from the integral intensities

Table 1

Integral intensities of the electronic absorption bands of enol forms ($I \cdot 10^6$ l/cm$^2 \cdot$ mole) of 3-alkylacetylacetones

Compound $CH_3COCHRCOCH_3$	Cis-enol 67% aq. methanol	Cis-enol ethanol	Cis-enol dioxane	Cis-enol ether	Cis-enol hexane	Trans-enol 67% aq. methanol	Trans-enol ethanol	Trans-enol dioxane	Trans-enol ether	Trans-enol hexane
$R = CH_3$*	6.7	23.0	22.9	40.9	44.8	–	–	–	–	–
$R = C_2H_5$**	5.0	14.6	13.8	21.6	24.8	4.0	5.7	3.9	4.2	5.9

Compound $CH_3COCHRCOCH_3$	Cis-enol 67% aq. methanol	Cis-enol ethanol	Cis-enol dioxane	Cis-enol ether	Cis-enol hexane	Trans-enol 67% aq. methanol	Trans-enol ethanol	Trans-enol dioxane	Trans-enol ether	Trans-enol hexane
$R = C_3H_7$	4.0	14.5	14.0	18.8	21.3	9.9	9.9	9.4	8.9	9.4
$R = C_4H_9$	3.1	15.3	13.7	23.9	24.1	10.1	10.1	8.7	8.4	8.9
$R =$ iso-C_4H_9	6.0	14.7	12.6	21.4	25.1	9.9	10.2	8.6	7.7	8.0
$R =$ iso-C_3H_7	–	–	–	–	–	27.8	28.8	23.8	23.4	22.3
$R =$ tert.-C_4H_9	–	–	–	–	–	17.6	16.6	14.7	16.0	13.5

* For $R = CH_3$: cis-enol in 75% CH_3OH, 8.6; in 85% CH_3OH, 10.1; in abs. CH_3OH, 14.4.

** For $R = C_2H_5$: cis-enol in 75% CH_3OH, 6.1; in 85% CH_3OH, 7.4; in abs. CH_3OH, 9.3.

obtain the constants of tautomeric equilibrium. However, a definite conclusion can be drawn about the form of the equation describing the tautomeric equilibrium of ketoenols. Table 1 gives the values of the integral intensities of the cis and trans absorption bands for 3-alkylacetylacetones in different solvents. Analysis of the data makes it possible to conclude that trans-enolization of 3-alkylacetylacetones, as also of a number of other open-chain ketoenols investigated by us earlier [1,2], is practically independent of the nature of the solvent. As for cis-enolization, in analyzing the data of Table 1 it is necessary to bear the following in mind. If C_c and C_t denote the concentrations of the cis- and trans-enol forms, respectively, I_c, I_t the integral intensities, and ε_c, ε_t the molar absorption coefficients, then the constant $K_{\mathrm{t(cis)}}$ of the keto–cis-enol equilibrium is expressed as follows:

$$K_{\mathrm{t(cis)}} = C_\mathrm{c}/C_\mathrm{k} = [I_\mathrm{c}/\varepsilon_\mathrm{c}] : [C - (I_\mathrm{c}/\varepsilon_\mathrm{c} + I_\mathrm{t}/\varepsilon_\mathrm{t})], \tag{4}$$

where C is the total concentration of the ketoenol.

It can be shown that if Meyer' s rule $K_\mathrm{t} = EL$ is applicable to the cis-enols under consideration, with acetoacetic ester as the standard substance, and trans-enolization is independent of the solvent, then at constant total concentration C, there should be a linear dependence between the quantities $(1/I_\mathrm{c})$ and $(1/L)$:

Fig. 3

Figure 3: Fig. 3

$$I_{\mathrm{c}}^{-1} = A + BL^{-1}, \tag{5}$$

where:

$$A = \varepsilon_{\mathrm{t}}(\varepsilon_{\mathrm{t}}\varepsilon_{\mathrm{c}}C - I_{\mathrm{t}}\varepsilon_{\mathrm{c}})^{-1} \quad \text{and} \quad B = \varepsilon_{\mathrm{t}}E^{-1}(\varepsilon_{\mathrm{t}}\varepsilon_{\mathrm{c}}C - I_{\mathrm{t}}\varepsilon_{\mathrm{c}})^{-1}.$$

It may be assumed that ε_{c}, ε_{t} do not depend on the solvent; the constancy of I_{t} follows from the experimental data; hence it follows that for each of the substances studied (at constant total concentrations C) the quantities A and B are constant.

Fig. 3. Dependence of the reciprocal integral intensities ($10^{-5}/I$) of 3-methylacetylacetone (I) and 3-ethylacetylacetone (II) on $1/L$.

Figure 3 gives a plot of $10^{-5}/I_{\mathrm{c}}$ versus $1/L$ for 3-methyl- and 3-ethylacetylacetones (I and II). From this plot it is evident that cis-enolization of 3-alkylacetylacetones satisfies Meyer' s formula and, consequently, the overall enolization of these substances is expressed by equation (3).

Thus, it may be asserted that the cis-enol forms of esters of β-keto acids and β-diketones belong to one chemical type in the sense of the Brønsted–Izmailov theory [13,14]. Trans-enolization of this type of substances is, to a first approximation, independent of the nature of the solvent, which, apparently, is the result of identical changes in the solvation energies of the ketone and trans-enol forms upon changing the solvent.

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Received
23 February 1962

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