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Abstract

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ON THE STRUCTURE OF δ-KETO ACIDS

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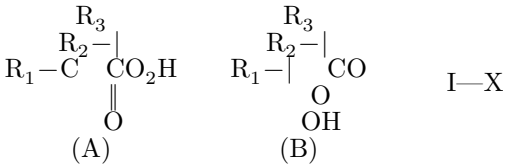
The dual reactivity of γ-keto acids has long been known ([1–3]). For some of them, cyclic oxylactone structures were demonstrated by UV and IR spectroscopy ([4–6]). In the spectra of penicillic ([4]), acetophenone-*o*-carboxylic ([5]), and other acids of the same type ([5,6]), absorption bands of the cyclic forms were found, while absorption bands of the open forms were absent. Recently, some data have also been obtained on the dual reactivity of δ-keto acids ([7,8]). The formation of cyclic derivatives of keto acids may be due either to ring–chain tautomerism or to the possibility of intramolecular cyclization of acyl cations formed in the course of the reaction from the open form ([9]).

In connection with this, it is of considerable interest to study the actual structure of δ-keto acids, which in the solid state may have the structure either of keto acids (A) or of oxylactones (B).



In the present work the IR spectra were studied of a series of solid δ-keto acids (I–VII), γ-bromo-δ-keto acids (VIII–X), and also the IR spectra of γ-*p*-tolylbutyronitrile (XI), hydrochloric acid (XII), and γ-phenylbutyric acid (XIII), as model compounds of the open form (A) of δ-keto acids.

δ-Keto acids I–III ([10]) were obtained by oxidation of the corresponding 1-alkylcyclopentanols-1. The remaining preparations were synthesized by previously developed methods and had melting points coinciding with the literature data ([11–14]).

The IR spectra of the compounds were recorded in the region 1800–600 cm^{-1} on IKS-2 and IKS-12 instruments and in the region 3600–2000 cm^{-1} on an IKS-12 instrument. The potassium bromide pellet method was used (1–3 mg of substance per 250 mg of potassium bromide). The spectra of some acids were also studied in vaseline oil, and no differences from the spectra obtained in the study of pellets were found.

Fig. 1

Figure 1: Fig. 1

Typical curves for two of the ten acids investigated are shown in Fig. 1. All the δ-keto acids studied (I–X) exhibit intense absorption in the region 3200–2600 cm^{-1}, also observed for hydrochloric acid (XII) and γ-phenylbutyric acid (XIII), and in general characteristic of acids (OH stretching vibrations). A cyclic oxylactone (B) structure of δ-keto acids should have led, in the LiF region, to the appearance of one intense absorption band in the interval 3400–3200 cm^{-1}, characteristic of lactols ([4–6]), which is not the case.

In the region 1800-600 cm^{-1}, all the characteristic absorption bands of carboxylic acids were also found, which made it possible to draw an unambiguous and convincing conclusion about the open (A) structure of the solid δ-keto acids studied. The δ-keto acids investigated in the present work absorb intensely in the regions 1700, 1400, and 1300 cm^{-1}, which is characteristic of acids in the solid and liquid states ([15]).

δ-Keto acids I–III, VI, and VIII, in which the carbonyl group is not conjugated with the aromatic ring, give in the region 1700 cm^{-1} one band associated with the stretching vibrations of the ketone and carboxyl carbonyls.

δ-Keto acids	R_1	R_2	R_3	M.p., °C	Lit. source
I	C_2H_5	H	H	47–48	[10]
II	C_3H_7	H	H	34–35	[10]
III	C_4H_9	H	H	42–43	[10]
IV	C_6H_5	H	H	127–128	[11]
V	*n*-$CH_3C_6H_4$	H	H	147–148	[12]
VI	CH_3	C_6H_5	H	47–48	[12]
VII	C_6H_5	CH_3	H	52–53	[12]
VIII	CH_3	CH_3	Br	74–75	[13]
IX	C_6H_5	H	Br	97–98	[11]
X	*n*-$CH_3C_6H_4$	H	Br	114–115	[14]

For δ-keto acids I–III and VI this band lies in the interval 1712 ± 3 cm^{-1}. γ-Bromo-γ-acetylvaleric acid absorbs at 1735 cm^{-1}. δ-Keto acids V, VII, IX, and X, in which the ketone carbonyl group is conjugated with the aromatic ring, have in the region 1700 cm^{-1} bands at 1675 ± 5 and 1705 ± 10 cm^{-1}, the first of which corresponds to stretching vibrations of the carbonyl group conjugated with the aromatic ring, and the second to stretching vibrations of $C = O$ in the carboxyl group. γ-Benzoylbutyric acid (IV) absorbs at 1690 cm^{-1}.

Fig. 1

The band at 1420±10 cm^{-1}, observed for δ-keto acids I–X, is associated not only with the carboxyl group, but also with deformation vibrations of C–H, the frequency of which changes under the influence of neighboring ketone and carboxyl $C = O$ groups. This is indicated by the greater than usual ([16]) intensity of the band and by the presence of absorption at 1421 cm^{-1} in γ-*n*-tolylbutyronitrile (XI).

In the region 1300 cm^{-1}, in the spectra of the δ-keto acids studied, as well as in the spectra of hydrocinnamic (XII) and γ-phenylbutyric (XIII) acids, an intense band was observed in the interval 1303–1280 cm^{-1}, which was absent in γ-*n*-tolylbutyronitrile (XI), proving the connection of this band with the carboxyl group.

As for the band in the region 900 cm^{-1}, despite the limited characteristic nature ([16]) of absorption in this region, the acids studied can be characterized by the following data: in the spectra of δ-keto acids I–X, from one to three bands are observed in the interval 942–914 cm^{-1}, while γ-*n*-tolylbutyronitrile (XI) does not absorb in this region; hydrocinnamic acid absorbs at 937 cm^{-1}, and γ-phenylbutyric acid at 917 cm^{-1}.

Thus, in the IR spectra of solid δ-keto acids I–X, characteristic absorption bands associated with the carboxyl group are observed, and the absorption bands of lactols are absent, which proves the open (A) structure of the δ-keto acids.

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