

**TAUTOMERY OF 5,5-DIMETHYL-2,4-DIOXOHEXANE ACID METHYL ESTER
ACTYHYDRAZONES**

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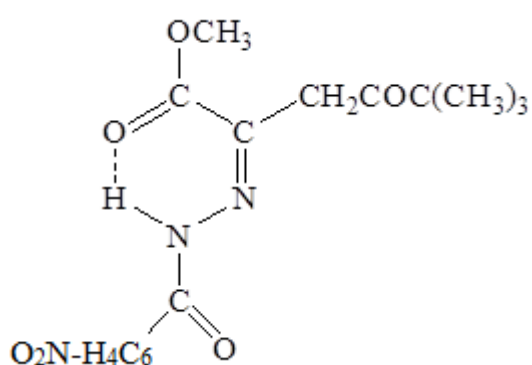
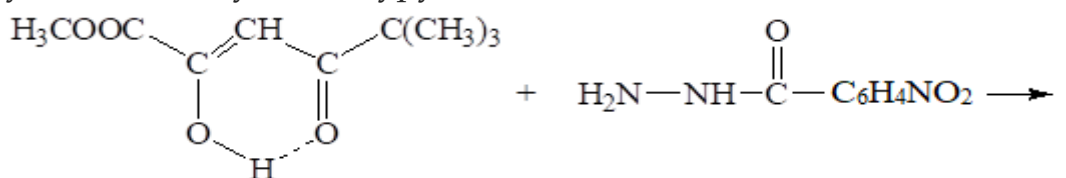
Abstract.

The structure of condensation products of 5,5-dimethyl-2,4-dioxohexanoic acid methyl ether with aromatic acid hydrazide was studied, and their YAMR structure was studied.

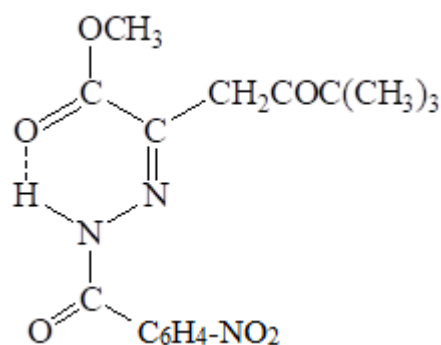
Key words.

hydrazine, enehydrazine, tautomer, spectrum.

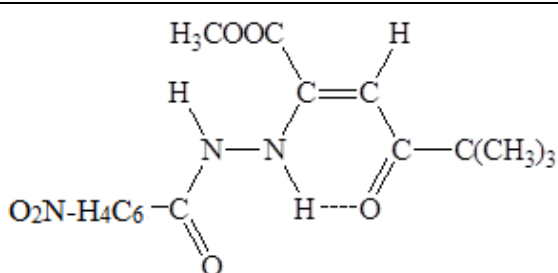
We have studied the structure of the condensation product of 5,5-dimethyl-2,4-dioxohexanoic acid methyl ester with aromatic acid hydrazide. H_2L^2 compound in the solution state is in the form of a tautomeric mixture of hydrazone, enehydrazine and cyclic 5-oxypyrazoline forms.



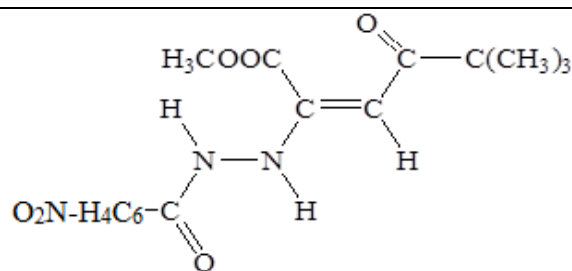
A_Z



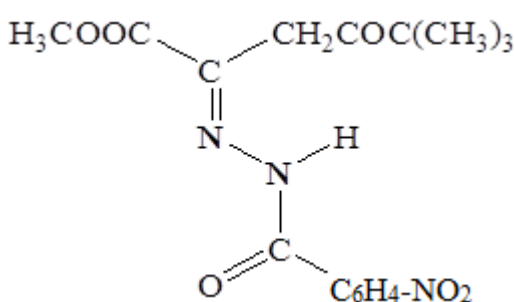
$A_{Z'}$



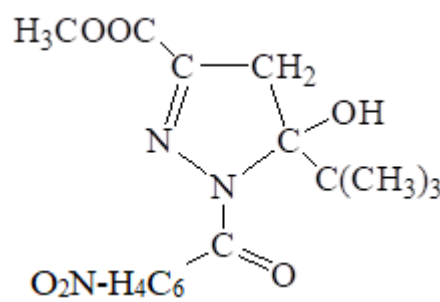
B'



B



A_E



V

The compound H_2L^2 has been obtained by reacting an alcoholic solution of ketoethers with an alcoholic solution of benzoylhydrazine in an equimolar amount. The reaction of 1,3-dicarbonyl compound with acetylhydrazine takes place in a regiospecific way. It can be said with confidence that the obtained compound is a condensation product of the carbonyl group. The attack on the alternative carbonyl group is spatially hindered by the large size of the adjacent tertiary-butyl radical. The YMR spectra of this compound in $SDCl_3$ have resonance signals of the 1st line related to one of the stereoisomers of the hydrazone form (A). In the spectra obtained after several 10 seconds, it is observed that the 2nd signal corresponding to ring 5-hydroxy-2-pyrazolone form (V) is formed. Such rapid formation of the ring form (V) indicates that the products have an E-hydrazone (A_E) structure in the crystalline state. The subsequent temporal change of NMR spectra confirms this conclusion. Another part of the resonance signals related to the 2-stereoisomer of the hydrazone form appears in the spectra obtained a few hours after the prepared samples. It shows that the proton signal of the NH-bond of the diastereoisomer of the hydrazone form is shifted to a relatively weaker area than that of the original stereoisomer (A_E) of this form. A strong intramolecular chelate hydrogen bond can be formed in the Z-configuration. Accordingly, the stereoisomer of the initial hydrazone form has the E-configuration (A_E).

According to the spectra of compounds, ring 5-hydroxy-2-pyrazoline form (V) and linear hydrazone form Z(AZ) and E(AE) stereoisomers are present for several days. In any case, the formation of signals related to nyhydrazine (B) is not observed. The ring-chain equilibrium is shifted towards the hydrazone (A) form. Its share changes very little when an electron-accepting substituent is introduced into the N-aryl radical aromatic nucleus. One would expect ring-chain equilibrium to depend very little on the nature of the substituent on the aromatic nucleus. The hydrazone (A) and ring (V) forms should have a similar interstitial system and the indicated substituents should affect the change of electronic properties in a similar way. The predominance of Z-diastereomer (AZ) between hydrazone forms, chelate is explained by the formation of an intramolecular hydrogen bond. The configurational equilibrium in the selection series is kept constant.

Table 1

NMR spectrum parameters of H₂L² δ, m.h.

Linear hydrazone form (A)								Ring 5-hydroxy-2-pyrazoline form (B)			
A _Z				A _E							
(CH ₃) ₃ C	CH ₂	OC H ₃	NH	(CH ₃) ₃ C	CH 2	OC H ₃	NH	(CH ₃) ₃ C	CH ₂ ^a	OC H ₃	NH
1,18	3,93	3,83	13,33	1,20	4,0 6	3,90	11,5 4	1,06	3,10; 3,42	3,84	6,14
Explanation. ^a AV s, J _{AB} = system19-20 Gst.											

In the NMR spectra of the proton signal of the NH-bond of E-hydrazone form (AE), N-aryl radical shifts to a relatively weak region when an electron-withdrawing substituent is inserted into the aromatic nucleus. Particularly interesting is the shift of the proton signal in the NH-bond of the Z-hydrazone form (AZ) with chelate intramolecular hydrogen bonding (IMVB) to a significant partially weak region. For compounds of this type, internal molecular hydrogen is explained by the strength of the bond.

The strength of the internal molecular hydrogen bond in the Z-hydrazone form (AZ) is determined by the electron density of the oxygen atom in the S=O bond in the complex ether group and the acidity of the proton in the NH bond. The exchange of an electron-donating substituent in an aromatic nucleus with an electron-accepting substituent, on the one hand, and the S=O bond of a complex ether radical, on the other hand, reduces the intensity of the system between the non-generalized electron pairs of the nitrogen atom, and the basic property of the oxygen atom in this bond decreases. With the introduction of an electron-accepting substituent, the signal shifts to a relatively weak field. The strength of IMVB in the

Z-hydrazone form of the H_2L^2 compound is primarily determined by the acid nature of the NH-bond.

The Z-conformer (BZ) is more polar than the E1-conformer (BE); Therefore, the use of polar solvents shifts the conformational equilibrium to the side of the Z1-conformational isomer. When switching from $CDCl_3$ to $DMSO-d_6$, the intensity of the signals of the first set decreases (the ratio of stereoisomers is 69:31). Thus, the polarity of the first set of signals of the preferred conformer belongs to the E¹-conformer. Finally, it should be said that for the studied compound, the tautomeric equilibrium does not change when passing from $CDCl_3$ to pyridine- d_5 (Py- d_5) and dimethylsulfoxide- d_6 (DMCO- d_6), the equilibrium is hydrazone (A) and ring 5-hydroxy-2-pyrazoline (V) forms are involved. As previously shown when studying the tautomerism of other β -dicarbonyl compounds acetylhydrazones, the formation of enhydrazine is observed when $DMSO-d_6$ is used as a solvent. Experiments have shown that it is not enough to use these solvents to form the enhydrazine form of the compound.

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