AN INVESTIGATION OF THE STRUCTURE OF CHEMICAL COMPOUNDS
BY MEANS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

2. THE DETERMINATION OF THE STRUCTURE AND CONFIRMATION
OF A NUMBER OF SUBSTITUTED CYCLOPENTENONES*

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In [1, 2] it was shown that the main reaction products of condensation of 3,5-dimethyl-\(\Delta^2\)-cyclopentenone with vinyl acetate are erythro- and threo-isomers of 3,5-dimethyl-5-(\(\alpha\)-acetoxyethyl)-\(\Delta^2\)-cyclopentenone (IA) and (IB) respectively. It was also shown that the reaction mixture contains erythro- and threo-isomers of 3,5-dimethyl-5-(\(\alpha\)-acetoxyethyl)-\(\Delta^3\)-cyclopentenone (IIA, B), and 2-ethylidene-3,5-dimethyl-\(\Delta^4\)-cyclopentenone (III) was separated and identified.

![Chemical Structures](Image)

The use of high-resolution proton magnetic resonance (PMR) for the investigation of the reaction products made it possible to determine their structure and put forward a theory of the nature of the isomers. The PMR spectra for reaction products (IA) and (IB) are given in Fig. 1a and b. We will examine the spectrum of isomer (IA) (Fig. 1a). The chemical shift of the quadruplet (with resolution J = 5.9 cps) with a center at 4.86 millionths of the applied field (m.d.) in Fig. 1 is characteristic of protons in the CH-COOR group [3]. The multiplet structure of this signal indicates the presence of an adjoining methyl group, whose signal must be a doublet with the same resolution and located in the area of the strong field. A doublet with a center at 0.96 m.d. corresponds to these features. Judging by the chemical shift and intensity, the signal at 1.90 m.d. belongs to the methyl group in OCOCH₃. Judging by its intensity, singlet character and position in the area of the strong field, the 1.04 m.d. signal must be attributed to the methyl group at the quaternary carbon. In the area of the weakest field there is a signal (at 5.73 m.d.) which must be attributed to the proton at the C=C double bond, forming part of the conjugated chain [3]. To determine the site of this proton (in the middle or at the end of the conjugated chain) we determined the spectra of 3,5-dimethyl-\(\Delta^2\)-cyclopentenone (IV) and 3,5-dimethyl-\(\Delta^4\)-cyclopentenone (V) (Fig. 2a, b).

From the PMR spectra it may be seen that the signal from the proton in the center of the conjugated chain is located in a stronger field (at 5.71 m.d.) than the proton at the end of the conjugated chain (at 7.14 m.d.). A similar picture is observed for signals from the methyl groups: 1.60 m.d. for the methyl group at the carbon in the center.

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of the chain, and 2.01 m.d. for the methyl group at the end of the conjugated chain. From these data, the 5.73 m.d. signal in the spectrum of isomer (IA) may be attributed to the proton in the center of the conjugated chain, and the 2.09 m.d. to the methyl group at the carbon at the end of the conjugated chain. Finally, the 2.43 m.d. signal is located in the region characteristic of methylene groups at the C=C double bond (m. Fig. 2a).

Thus, the analysis of the PMR spectrum of isomer (IA) indicates the presence of the following groups in the molecule

\[
\begin{align*}
R \quad \text{CH} \quad & \quad \text{OCOCH}_3, \\
\text{CH}_3 \\
\end{align*}
\]

A comparison of this result with the structural formulas of the possible reaction products made it possible to attribute structure (IA) to this compound. Chemical data obtained in [2] confirmed that this conclusion was correct [2].

Fig. 1. PMR spectra at 20.529 Mc of isomers of 3,5-dimethyl-5-(α-acetoxyethyl)-Δ²-cyclopentenone (I): a) isomer A; b) isomer B.

The PMR spectrum of the second isomeric reaction product (IB) (see Fig. 1b) has signals which also correspond to these groups and differs from the corresponding signals in the spectrum of the first isomer only as regards small changes of the chemical shifts. Therefore, it was concluded that, in this case, isomerism involves a change to some extent in the spatial orientation of the groups, not a change in molecular structure. This conclusion was then confirmed by chemical conversions of (IA) and (IB) to 3,5-dimethyl-5-vinyl-Δ²-cyclopentenone (VI). The structure of the latter