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Abstract

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CHEMISTRY

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DETERMINATION OF THE STRUCTURE OF CERTAIN DIHYDROFURAN DERIVATIVES BY THE METHOD OF RAMAN SCATTERING OF LIGHT

(Presented by Academician A. N. Terenin, May 23, 1960)

The interaction of β-bromo-β-nitrostyrene with substances containing active methylene groups (acetyl- and benzoylacetone, dimedone, acetoacetic and malonic esters), in the presence of triethylamine, led to the formation of products (I–V), to which in each case three different isomeric structural formulas could be assigned:

$$\begin{array}{l} O_2N \\ \backslash \\ C=CH \end{array} + H_2C \begin{array}{l} O \\ \| \\ C-R \\ \backslash \\ C-R' \\ \| \\ O \end{array} \xrightarrow[-HBr]{(C_2H_5)_3N} \left\{ \begin{array}{ll} O_2NCH_2-C=C \begin{array}{l} C(=O)-R \\ C(=O)-R' \end{array} & (2) \\ O_2NCH=C-CH \begin{array}{l} C(=O)-R \\ C(=O)-R' \end{array} & (1) \\ H_5C_6-CH-C-C(=O)-R \quad \begin{array}{c} O_2N-CH \quad C-R' \\ \backslash \quad / \\ O \end{array} & (3) \end{array} \right.$$

	(I)	(II)	(III)	(IV)	(V)
R	CH_3	CH_3	$CH_2\backslash C(CH_3)_2$	OC_2H_5	OCH_3
R′	CH_3	C_6H_5	$CH_2/C(CH_3)_2$	CH_3	OCH_3

Products of type (1) could arise as the result of addition of the methylene component to β-bromo-β-nitrostyrene and subsequent dehydrohalogenation; products of type (2) should be regarded as the result of isomerization of (1), in which the hydrogen atom of the methine group of the acti-

stabilized by two carbonyl residues; the formation of (3) was explained by enolization of the addition products and subsequent elimination of hydrobromic acid. The possibility of isomerization of the double bond in the dihydrofuran ring to the 3-4 position was not excluded. The available chemical methods proved insufficient for the final choice of one of the possible formulas.

Investigation of the intensities of the bands in the Raman spectra made it possible to establish unambiguously the structure of the reaction products.

We have previously shown that the intensity values of the bands in the Raman spectra of the nitro group, the double bond, and the benzene ring change, respectively, depending on the nature of their conjugation by up to three orders of magnitude ([1]).

Formulas of type (1) contained the conjugated system of nitrostyrene, those of type (2) the system of cinnamic acid or benzylidene ketones and an unconjugated nitro group; in the dihydrofuran derivatives (3) there was an acrylic acid or vinyl ketone residue and an unconjugated benzene ring and nitro group.

In the spectra of products I-V, frequencies of the nitro group, benzene ring, and double bond were found whose intensities coincided with, or were close to, the intensities of the unconjugated nitro group and benzene ring and of the double bond conjugated with carboxyl or carbonyl groups, which were precisely those contained in the proposed formula (3) (Table 1). Thus, the dihydrofuran structure of the reaction products of β-bromo-β-nitrostyrene with the named active methylene components was beyond doubt.

Table 1

Substances	Intensities* – C_6H_5	Intensities* – CH=CH–	Intensities* –NO_2
C_6H_5–CH=CH–NO_2	2.4	4.3	9
C_6H_5–CH=CH–COOH	0.7-1.0	1.2	–
CH_2=CH–COOH	–	0.04	–
C_6H_5–CH_3	0.02	–	–
CH_3NO_2	–	–	0.02
I	0.01-0.02	0.1-0.2	0.01-0.02
II	1.0	0.5-1.0	0.01-0.02
III	0.06	0.15-0.3	0.01-0.02
IV	0.035	0.08-0.15	<0.01-0.02
V	–	0.1	<0.01-0.02

* On a single arbitrary scale.

The increased intensity values of the bands of the benzene ring and of the double bond in product II, close to the corresponding values in cinnamic acid, made it possible to conclude that it was formed as a result of enolization of the carbonyl group adjacent to the benzene ring, and not to the methyl group. Some increase in the intensities of the double-bond bands in products I–V, in comparison with acrylic acid, is evidently explained by conjugation of this bond with the unshared electron pair of the oxygen atom of the furan ring.

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1. Ya. S. Bobovich, V. V. Perekalin, DAN, **121**, 1028 (1958); **127**, 1239 (1959).

Note: Figure translations are in progress. See original paper for figures.