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Abstract

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Synthesis and Structure of Nitrobutadiene Derivatives

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Polynitroalkenes and polynitrodienes are of interest because of the possibility of converting them into macromolecular products. In this connection there arises the problem of a detailed investigation of the dependence between the chemical structure of nitroalkenes and nitroalkadienes and their ability to polymerize.

With the aim of obtaining model compounds, by condensation of nitromalonaldehyde (I), 2-nitro-3-methylaminoacrolein (II), and 2-nitro-3-anilinoacrolein (III) with various compounds containing active methylene and methyl groups, we developed a general method for the synthesis of nitroaminobutadiene derivatives (V–IX), nitrobutadiene derivatives (XI–XIII), and for the first time carried out the carbocyclic condensation of nitromalonaldehyde. In contrast to methylene components with iodomethylates of picoline, quinoline, and N-methyl-methylbenzimidazole, nitromalonaldehyde reacted only through one aldehyde group (see XIV, XV, XVI). This fact could be explained by: 1) a decrease in the activity of the aldehyde group in the monoconensation products owing to its conjugation with the unshared electron pair of the heteroatom, 2) the lower reactivity of methyl components than methylene components.

If the structure of the condensation products of nitromalonaldehyde with methylene and methyl components caused no substantial doubt (linear nitrobutadiene derivatives (XI–XIII) were formed), then the structure of nitroaminoaldehydes (II, III) and nitroaminobutadienes (V–IX) required special discussion.

$$CH_3NH{-}CH{=}C(NO_2){-}CHO \quad (II) \leftarrow O{\cdot}C{-}C(NO_2){=}C{-}C{=}O \quad (I) \rightarrow C_6H_5NH{-}CH{=}C(NO_2){-}CHO \quad (II$$

$$R, R' > CH_2 \downarrow$$

$$[R(R')C{=}CH{-}C(NO_2){-}CH{=}C(R)(R')]^- \ Na^+ \quad (XI{-}XIII)$$

$$\xrightarrow{H^+}$$

$$R(R')CH{-}CH{=}C(NO_2){-}CH{=}C(R)(R') \quad (XIII)$$

$$CH_3NH{-}CH{=}C(NO_2){-}CH{=}C(R)(R') \quad (V, VI)$$

$$C_6H_5NH{-}CH{=}C(NO_2){-}CH{=}C(R)(R') \quad (VII{-}IX)$$

(XVI) (XV) (XIV)

	V	VI	VII	VIII	IX	XI	XII	XIII
R	$COOC_2H_5$	CN	$COOC_2H_5$	CN	H	CN	$COOC_2H_5$	CN
R′	CN	CN	CN	CN	NO_2	NO_2	CN	CN

The concept of ketimine-enamine tautomerism, leading to the appearance of an azomethine grouping, must be rejected, at least for the products of the Knoevenagel condensation, since their resistance to hydrolysis contradicted the easy cleavage of azomethines into aldehyde and amine. The failure of attempts at alkylation and acylation of aminobutadienes and nitroaminobutadienes indicated stabilization of the hydrogen atom of the imino group.

Thus, the data of chemical experiment proved insufficient for constructing a reliable picture of the structure of these substances. The successful application of the dipole-moment method in investigations of the spatial structure of various unsaturated nitro compounds [1,2] allowed one to hope for success in applying it to nitroaminobutadienes (Table 1).

Table 1

Compound	Dipole moment, D (benzene)	Dipole moment, D (dioxane)	Frequencies and intensities of bands of Raman spectra: symmetric vibration $-NO_2$	Frequencies and intensities of bands of Raman spectra: vibration $>C=C<$	Frequencies and intensities of bands of Raman spectra: antisymmetric vibration $-C_6H_5$
II. $CH_3NH-CH=C(NO_2)-CH=O$	–	5.82	1325-1350(1.3-0.2)	1610(0.1)	–
III. $C_6H_5NH-CH=C(NO_2)-CH=O$	5.0	5.25	1320-1390(4.0-4.8)	1640(1.6)	1585(11)
IV. $C_6H_5NH-CH=C(NO_2)-CH=NC_6H_5$	4.84	4.75	1345(140)		1555-1580(60-65)
V. $CH_3NH-CH=C(NO_2)-CH=C(CN)(COOC_2H_5)$	4.60	–	1315-1340(10-6.2)	1655(0.1-0.2)	–
VI. $CH_3NH-CH=C(NO_2)-CH=C(CN)_2$	–	–	1315-1325(12)		–
VII. $C_6H_5NH-CH=C(NO_2)-CH=C(CN)(COOC_2H_5)$	4.3	–	1310-1340(50-50)	–	1550-1595(16-17)
VIII. $C_6H_5NH-CH=C(NO_2)-CH=C(CN)_2$	3.59	3.97	1320(95)		1520-1580(12-12.5)
IX. $C_6H_5NH-CH=C(NO_2)-CH=CHNO_2$	–	7.5	1315-1350(60-90)	1615(90)	1590(80)
X. $C_6H_5NH-CH=CH-CH=NC_6H_5$	–	–	–	1655(20)	1555-1590(75-45)

It was shown that these substances have the structure:

(III) (IV)

[[chemical structural diagram visible: compound (III), an anilino nitrobutadienal structure with intramolecu

chemical structure

Figure 1: chemical structure

chemical structure

Figure 2: chemical structure

The shift of the band of the symmetric vibration of the nitro group into the long-wavelength region in products III, IV (ν = 1300 cm^{-1}) undoubtedly indicated the presence in them of an intramolecular hydrogen bond [3].

and made it possible to resolve the question in favor of a cis arrangement of the nitro and amino groups.

Compounds V–VIII had a nonplanar cis configuration with the nitro group rotated somewhat (about the C–N bond) and the vinylidene residue (about the single C–C bond of the butadiene grouping).

The weakening in them of the intramolecular hydrogen bond (the band of the antisymmetric vibration of the nitro group is shifted into the short-wavelength region, ν = 1350 cm^{-1}) confirmed the assumption of their noncoplanar structure.

The high value of the moment of IX (7.5 D) could be explained by the structure given below, with the resulting addition of the moments of both nitro groups.

The study of nitroaminobutadienes by the dipole-moment method created a picture of their spatial structure. However, the character of the π-electron interaction in them remained unexplained.

(IX)

In order to fill this gap, the method of intensities of combination Raman spectra was used; this method had given convincing results in the study of the chemical structure of unsaturated nitro compounds [4,5]*.

A characteristic feature of the Raman spectra of nitroaminobutadienes (see Table 1) was the splitting of the antisymmetric vibration of the nitro group, the cause of which could be an intramolecular hydrogen bond or Fermi resonance.

The assumption of an intermolecular hydrogen bond as the cause of the splitting was rejected because of the absence of redistribution of the intensities of the split bands in the study of concentration dependence. The sharp increase in the intensity of the nitro-group band in aromatic derivatives in comparison with aliphatic ones indicated the inclusion of the aromatic ring in conjugation through the amino group.

The very notable low intensity of the vibration of the double bond could be explained by an intramolecular hydrogen cycle, in which it largely loses its characteristic nature.

The sharp increase in the intensity of the frequency of the double bond and of the benzene ring in IX is apparently caused by the fact that conjugation involving the entire π-electron system of the molecule is energetically more favorable than conjugation involving only the hydrogen cycle, and in X by the absence of the possibility of formation of a hydrogen bond.

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* As is known, the intensities of the bands of Raman spectra, changing sharply with conjugation, can be used for its evaluation.

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