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E. S. LIPINA, V. V. PEREKALIN, Ya. S. BOBOVICH

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Abstract

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E. S. LIPINA, V. V. PEREKALIN, Ya. S. BOBOVICH

SYNTHESIS AND STRUCTURE OF 1,4-DINITROBUTADIENES-1,3

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Unsaturated nitro compounds containing a butadiene system may be of interest as starting materials in organic synthesis, for example as monomers in polymerization reactions. Meanwhile, up to the present time there have been no general methods for obtaining nitrodienes, in particular 1,4-dinitrobutadienes-1,3 ([1-4]), and their chemistry is practically unknown.

We have developed a general method for the synthesis of 1,4-dinitrobutadienes-1, consisting in the oxidation of the disodium salts of 1,4-dinitrobutene-2

$$\begin{array}{c} O_2NCH{-}C{=}C{-}CHNO_2 \\ | \quad | \quad | \quad | \\ R \quad R' \quad R' \quad R \\ \downarrow\ 2CH_3ONa \\ OON{=}C{-}C{=}C{-}C{=}NOO^{2\ominus}2Na^{\oplus} \\ | \quad | \quad | \quad | \\ R \quad R' \quad R' \quad R \\ \downarrow\ Br_2,\ I_2,\ K_3Fe(CN)_6,\ AgNO_3 \\ O_2N{-}C{=}C{-}C{=}C{-}NO_2 \\ | \quad | \quad | \quad | \\ R \quad R' \quad R' \quad R \end{array} \qquad \text{(I-IV)}$$

I. R—H, R′—H; II. R—H, R′—CH_3; III. R—C_6H_5, R′—H; IV. R—H, R′—C_6H_5.

The reaction proceeds upon addition of one mole of oxidizing agent, with cooling, to a suspension of the disodium salt of dinitrobutene in ether or to its aqueous solution (depending on the stability toward bases of the dinitrobutadiene formed). Aliphatic dinitrodienes are isolated from the ether solution in 50-55% yield, while aryldinitrobutadienes formed in aqueous medium precipitate in 70-76% yield.

By the method of band intensities of Raman spectra* it has been shown that 1,4-dinitrobutadiene-1,3 (I) is a conjugated system in which conjugation is somewhat weakened by the opposing action of the terminal nitro groups ([5]). Introduction of methyl radicals into positions 2,3 disrupts the coplanarity of the molecule, which leads to a further decrease in conjugation in it (1,4-dinitro-2,3-dimethylbutadiene-1,3 –II). The role of phenyl radicals (in positions 2,3 and 1,4) is more complex: at times they substantially alter the planar structure of the molecule (1,4-dinitro-2,3-diphenylbutadiene-1,3 –IV) and at the same time may make a significant contribution to conjugation (1,4-dinitro-1,4-diphenylbutadiene-1,3 –III).

An increase in steric hindrance in the dinitrodienes (III and IV) leads to the isolation of two series of stable geometric isome-

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* As is known, the intensity coefficients of the lines of Raman spectra change sharply depending on conjugation and can be used for its objective evaluation ([6]).

to which, on the basis of consideration of the theoretically possible configurations, comparison of their physicochemical properties, and analysis of light-scattering combination spectra, the structures of the cis–cis (III , IV) and trans–trans (III , IV) isomers were assigned (5).

cis-cis* (IIIa) $\rightleftarrows$ trans-trans (IIIb)
cis-cis** (IVa) $\longrightarrow$ trans-trans (IVb)

As a consequence of the clearly expressed electrophilicity of 1,4-dinitrobutadienes-1,3, they react successfully with nucleophilic reagents: they enter into reactions of nucleophilic bromination, diene synthesis, and Michael addition (7). Nucleophilic bromination is carried out in the presence of strong acids and leads to the addition of two moles of bromine. Dinitrobutadienes do not enter into diene synthesis as diene components because of the deactivating influence of the nitro groups; at the same time, these compounds are active dienophiles capable of adding two moles of diene.

$$O_2NCH{=}CR{-}CR{=}CHNO_2 \longrightarrow (V) \longrightarrow (VI,\ VII)$$

$$V, VI\ R{-}H; \qquad VII\ R{-}CH_3$$

Contrary to the original assertion (2) concerning inability to react with active methylene components (because of instability toward bases), 1,4-dinitrobutadiene-1,3 adds them in the 2–1 position, with subsequent isomerization of the double bond (VIII):

$$O_2NCH{=}CH{-}\overset{\downarrow}{C}H{=}CHNO_2 \xrightarrow{XH} [O_2NCH{=}CH{-}CH{-}CH_2NO_2] \longrightarrow O_2NCH_2{-}CH{=}C{-}CH_2NO_2$$
(VIII)

X | X |

In 1,4- and 2,3-diphenyl-1,4-dinitrobutadienes-1,3 (III, IV), different primary steric effects of the phenyl radicals determine the different character of addition of nucleophilic reagents to them. Cis–cis- and trans–trans-1,4-dinitro-1,4-diphenylbutadienes-1,3 (III and III) form Michael adducts at the 2–1 position, which undergo vinyl-allyl isomerization (product IX). Cis–cis- and trans–trans-1,4-dinitro-2,3-diphenylbutadienes-1,3 (IV and IV) add

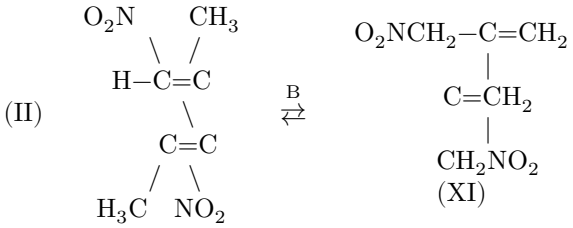
* The configuration was chosen according to the phenyl radical.
** The configuration was chosen according to the largest substituent–the nitrostyryl residue.

methylene components to the terminal carbon atoms, followed by denitration and formation of the diene system (X):

$$O_2NC{=}CH{-}\overset{\downarrow}{C}H{=}CNO_2 \qquad O_2NCH{=}C{-}\overset{\downarrow}{C}{=}CHNO_2$$
$$\begin{array}{cc} | & | \\ C_6H_5 & C_6H_5 \end{array} \qquad \begin{array}{cc} | & | \\ C_6H_5 & C_6H_5 \end{array}$$
$$\downarrow HX \qquad \downarrow HX$$
$$C_2NCH{-}CH{=}C{-}CHNO_2 \qquad O_2NCH{=}C{-}C{=}CH{-}X$$
$$\begin{array}{ccc} | & | & | \\ C_6H_5 & X & C_6H_5 \end{array} \qquad \begin{array}{cc} | & | \\ C_6H_5 & C_6H_5 \end{array}$$
(IX) (X)

Thus, 1,4-dinitrobutadienes-1,3 are characterized by the addition of nucleophilic reagents in the 2–1 position, and only as a result of the screening effect of the substituents (at the second and third carbon atoms) does the reaction begin with addition to the terminal carbon atom of the 1,4-dinitrobutadiene system.

1,4-Dinitro-2,3-dimethylbutadiene-1,3 (II), under conditions of basic catalysis (in an attempted introduction into the Michael reaction), undergoes vinyl-allylic isomerization to the unreactive 2,3-di(nitromethyl)butadiene-1,3 (XI) with non-conjugated nitro groups



In chemical properties the two isomers differ sharply from one another: for example, the nonconjugated isomer (XI) very readily forms a tetrabromide, whereas the conjugated isomer (II) adds bromine only under severe conditions, and also under nucleophilic bromination. On the basis of IR spectra it has been qualitatively shown that the isomerization II → XI is reversible, with a considerable shift of the equilibrium toward formation of the nonconjugated isomer: in the IR spectrum of the latter, in the presence of bases, a weak band of the conjugated nitro group appears (1515 cm^{-1}), along with a very intense band of the nonconjugated nitro group (1555 cm^{-1}). Usually the equilibrium in allyl-vinyl systems is shifted toward the vinyl isomers ([8,9]); however, in the present case the allylic isomer has a less sterically strained configuration, and therefore its preferential formation is energetically quite justified ([10,11]).

Leningrad State
Pedagogical Institute
named after A. I. Herzen

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