

# The Reactions of Some Dienes with Tetranitromethane

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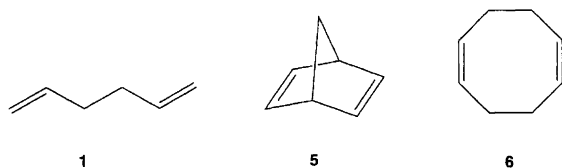
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Reaction of 1,5-hexadiene (**1**) with tetranitromethane in diethyl ether gives a crystalline product, previously assigned the 1-aza-2-oxa-3-nitromethyl-8,8-dinitro-1,6-epoxycyclooctane structure (**2**), is now identified as 1-aza-2-oxa-7,9,9-trinitro-1,4-epoxycyclononane (**4**) from its NMR spectra. Compound **4** is seen as arising by thermal intramolecular nitroalkene cycloaddition of the nitro-trinitromethyl adduct (**7**).

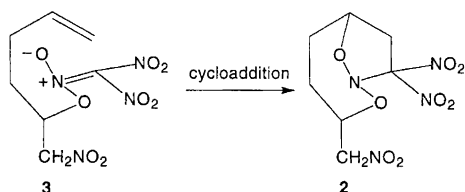
Attempts to study the additions of tetranitromethane to norbornadiene (**5**) and cycloocta-1,5-diene (**6**) are reported.

In 1972 Andreava *et al.*<sup>1</sup> reported the formation of a crystalline product (11%), m.p. 138 °C and molecular formula C<sub>7</sub>H<sub>10</sub>N<sub>4</sub>O<sub>8</sub> on treatment of 1,5-hexadiene (**1**) with tetranitromethane in diethyl ether solution.



This product was assigned the 1-aza-2-oxa-3-nitromethyl-8,8-dinitro-1,6-epoxycyclooctane structure (**2**) essentially on the basis of its infrared spectrum, and was seen as being formed by the intramolecular cycloaddition of the nitronic ester function to the remaining olefinic function in the intermediate (**3**) (Scheme 1).<sup>1</sup>

As part of a continuing study of the reactivity of tetranitromethane with unsaturated systems,<sup>2</sup> we have re-examined the reaction of 1,5-hexadiene (**1**) with tetranitromethane in diethyl ether solution. On the basis of a consideration of the NMR spectra the structure of the crystalline material isolated by Andreava *et al.*<sup>1</sup> is now



Scheme 1.

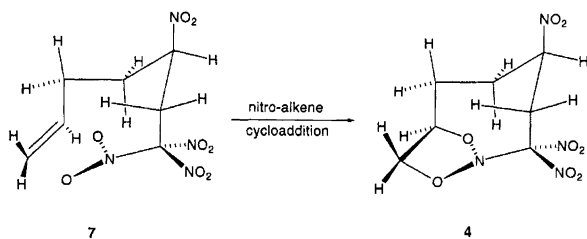
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assigned as the nitro cycloadduct (**4**), a type of structure which is known to arise by the thermal cycloaddition of the trinitromethyl group of a nitro-trinitromethyl adduct to an adjacent alkene function.<sup>3</sup> We now report the results of this study and attempts to extend the study of the additions of tetranitromethane to norbornadiene (**5**) and cycloocta-1,5-diene (**6**).

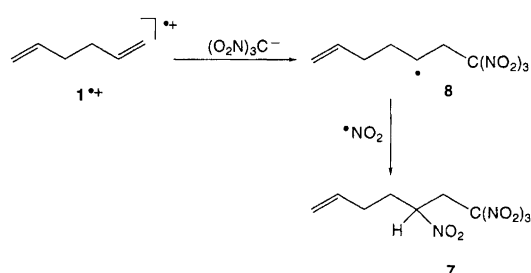
## Results and discussion

Reaction of 1,5-hexadiene (**1**) with tetranitromethane in diethyl ether solution gave a crystalline deposit from solution which was apparently identical with the material reported earlier by Andreava *et al.*<sup>1</sup> Unfortunately all crystals examined were twinned, and it was not possible to determine the structure of the product by single-crystal X-ray analysis. In the event, the structure of this product was assigned as 1-aza-2-oxa-7,9,9-trinitro-1,4-epoxycyclononane (**4**) on the basis of a consideration of its NMR spectra, and the likely molecular conformation of the unsaturated nitro-trinitromethyl precursor (**7**), which on cycloaddition yields the nitro cycloadduct (**4**).

The connectivity in nitro cycloadduct (**4**) was deduced from the multiplicities of the <sup>1</sup>H NMR signals and the associated coupling constants, together with the <sup>13</sup>C NMR spectrum and the results of heteronuclear correlation (HETCOR) experiments. Crucially these data placed the H–C–NO<sub>2</sub> function (<sup>13</sup>C resonance, δ 89.77) between the methylene groups at C6 and C8, the latter carbon atom having a <sup>13</sup>C resonance (δ 33.48) compatible with its location adjacent to the O<sub>2</sub>N–C(9)–NO<sub>2</sub> function. The <sup>13</sup>C NMR resonances for C(3) (δ 76.92) and C(4) (δ 73.07) pointed to the presence of carbon–oxygen bonding at those carbon atoms. The observed coupling



Scheme 2.



Scheme 3.

constants in the  $^1\text{H}$  NMR spectrum of nitro cycloadduct (**4**) are consistent with the molecular conformation illustrated in Scheme 2, including a close to staggered relationship of the adjacent methylene functions at C(5) and C(6). Perhaps coincidentally, the likely conformation for the unsaturated nitro-trinitromethyl precursor (**7**), with the C(7)– $\text{NO}_2$  bond *anti* to the C(8)–C(9) bond, would lead smoothly to this conformation for the nitro cycloadduct (**4**) (Scheme 2). Although the thermal cycloaddition of the 5-nitro-6-trinitromethylhex-1-ene (**7**) to give the nitro cycloadduct (**4**) has extensive precedents,<sup>3</sup> the precise mode of formation of the 5-nitro-6-trinitromethyl compound (**7**) remains somewhat uncertain. However, it appears likely that compound **7** is formed by initial attack of trinitromethanide ion at a terminal carbon atom of the 1,5-hexadiene radical cation ( $1^{+\bullet}$ ), followed by coupling of nitrogen dioxide with the carbon radical (**8**) so formed (Scheme 3).

In attempts to extend the above study of the additions of tetranitromethane to cyclic non-conjugated dienes, we examined the analogous reactions of norbornadiene (**5**) and cycloocta-1,5-diene (**6**). In the event, the product from norbornadiene (**5**) proved to be inadequately stable for further study, and the reaction mixture with cycloocta-1,5-diene reacted spontaneously and violently after 2 h in the dark at 20 °C.

## Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer;  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 spectrometer. Mass spectrometry was performed on a JEOL JMS SX-102 instrument. Tetranitromethane, cycloocta-1,5-diene and norbornadiene were from Aldrich, and 1,5-hexadiene was from Acros Organics.

**WARNING.** It should be noted that mixtures of tetranitromethane with hydrocarbons are detonative within certain concentration limits.<sup>4</sup> In the present study a solution of cycloocta-1,5-diene and tetranitromethane in diethyl ether solution reacted spontaneously and violently, and the product of reaction of norbornadiene with tetranitromethane decomposed violently during the workup procedure (for the experimental details, see below).

*Reaction of 1,5-hexadiene (1) with tetranitromethane in diethyl ether solution and the identification of a nitro cycloadduct (4).* A cold (0 °C) solution of tetranitromethane (3.92 g) in diethyl ether (5 ml) was added to a cold (0 °C) solution of 1,5-hexadiene (1.64 g) in diethyl ether (5 ml) and, after storage at 0 °C for 1 h under conditions of normal laboratory light, the solution was stored in the dark at 20 °C for 3 days. During this time 1-aza-2-oxa-7,9,9-trinitro-1,4-epoxycyclononane (**4**) (714 mg; 13%), m.p. 139–140 °C [lit.<sup>1</sup> m.p. 138 °C assigned to structure (**2**) earlier] crystallized from the reaction mixture and was identified from its spectroscopic data (Found:  $M\text{H}^+$  279.0580.  $\text{C}_7\text{H}_{11}\text{N}_4\text{O}_8$  requires 279.0576. Found:  $M\text{H}^+ - \text{NO}_2$  232.0570.  $\text{C}_7\text{H}_{10}\text{N}_3\text{O}_6$  requires 232.0569).  $\nu_{\text{max}}$  (KBr) 1590, 1578, 1558, 1550  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $[\text{D}_2\text{O}]_2$  acetone)  $\delta$  5.39 (dddd,  $J_{\text{H}7,\text{H}8\text{A}}$  8.0 Hz,  $J_{\text{H}7,\text{H}8\text{B}}$  6.3 Hz,  $J_{\text{H}7,\text{H}6\text{A}}$  ca. 4 Hz,  $J_{\text{H}7,\text{H}6\text{B}}$  ca. 2 Hz, H7), 4.93 (dddd,  $J_{\text{H}4,\text{H}3\text{A}}$  9.7 Hz,  $J_{\text{H}4,\text{H}3\text{B}}$  3.5 Hz,  $J_{\text{H}4,\text{H}5\text{A}}$  ca. 10 Hz,  $J_{\text{H}4,\text{H}5\text{B}}$  ca. 1 Hz, H4), 4.62 (dd,  $J_{\text{H}3\text{B},\text{H}3\text{A}}$  13.8 Hz,  $J_{\text{H}3\text{B},\text{H}4}$  3.5 Hz, H3B), 4.51 (dd,  $J_{\text{H}3\text{A},\text{H}3\text{B}}$  13.8 Hz,  $J_{\text{H}3\text{A},\text{H}4}$  9.7 Hz, H3A), ca. 3.42 (m, H8A, H8B), ca. 2.20 (m, H6A), ca. 1.91 (m, H5B), ca. 1.85 (m, H6B), ca. 1.75 (m, H5A).  $^{13}\text{C}$  NMR ( $[\text{D}_2\text{O}]_2$  acetone)  $\delta$  89.77 (C7), 76.92 (C3), 73.07 (C4), 33.48 (C8), 28.08 (C5, C6); a resonance for C9 was not observed. The above assignments were confirmed by double irradiation experiments and HETCOR experiments.

Removal of the solvent and excess tetranitromethane under reduced pressure gave an oil (2.33 g) which was a complex mixture containing further nitro cycloadduct (**4**) (ca. 10%).

*Reaction of norbornadiene (5) with tetranitromethane in ether solution.* A cold (0 °C) solution of tetranitromethane (1.065 g) in diethyl ether (2.5 ml) was added to a cold (0 °C) solution of norbornadiene (**5**) (500 mg) in diethyl ether (2.5 ml) and, after storage at 0 °C for 1 h under conditions of normal laboratory light, the solvent and excess tetranitromethane were removed at 0 °C under reduced pressure. The resulting solid product decomposed spontaneously and violently before any spectroscopic examination of it could be carried out.

*Reaction of cycloocta-1,5-diene (6) with tetranitromethane in diethyl ether solution.* A cold (0 °C) solution of tetranitromethane (1.96 g) in diethyl ether (2.5 ml) was added to a cold (0 °C) solution of cycloocta-1,5-diene (**6**) (1.08 g) in diethyl ether (2.5 ml) and, after storage at

0 °C for 1 h under conditions of normal laboratory light, the reaction mixture was stored in the dark for 2 h, at which time it reacted spontaneously and violently.

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