

Letter to the Editor

Nitronic Ester Formation in the Reaction of a 3-Trinitromethylcyclohexene with Nitrogen Dioxide: A Nitro–Denitro Cyclization Reaction

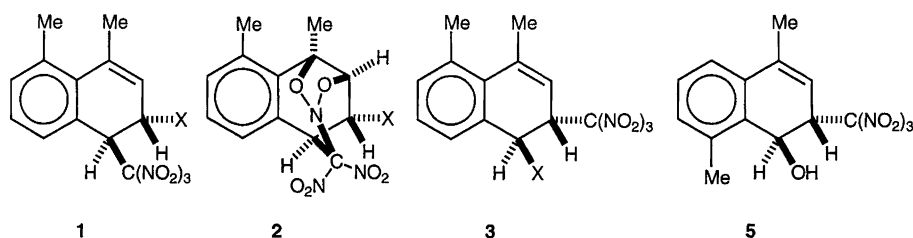
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Although nitroalkene cycloadditions of *r*-1-trinitromethyl-*t*-2-*X*-1,2-dihydronaphthalenes, e.g. **1** (*X* = NO₂, OH) to give the corresponding cage structures **2** have been dem-

Essentially quantitative yields of this nitronic ester **4** were formed on reaction of 4,8-dimethyl-*t*-2-trinitromethyl-1,2-dihydronaphthalen-*r*-1-ol **5** with a dilute solution of



onstrated to occur readily in the dark,¹ analogous cycloadditions are not found for *r*-2-trinitromethyl-*t*-1-*X*-1,2-dihydronaphthalenes **3**, presumably because of the additional strain which would characterize the corresponding cage structures.

During the course of an investigation of the photolysis of the charge transfer complex of 1,5-dimethylnaphthalene with tetranitromethane the nitronic ester **4** (Fig. 1), m.p. 157°C (decomp.), was isolated in low yield and its structure determined by single-crystal X-ray analysis.*

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* Crystal data: C₁₃H₁₃N₃O₇, *M* = 323.26, orthorhombic, space group *Pbca*, *a* = 13.119(2), *b* = 9.269(4), *c* = 21.86(1) Å, *V* = 2658(2) Å³, *Z* = 8, μ (Mo *K*α) 1.34 cm⁻¹, Mo *K*α radiation (λ = 0.71073 Å). Data were collected at 130(2) K using a Siemens P4 four-circle diffractometer for a colourless crystal of dimensions 0.55 × 0.50 × 0.12 mm. All 1730 reflections were used in all calculations with SHELXS-86 for solution by direct methods and SHELXL-93 for refinements using intensities [*w**R*² = 0.1122 for all data; *R* 1(*I*) > 2σ(*I*) 0.037]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

nitrogen dioxide in dichloromethane in a darkened flask (1 h, 20°C). The latter reaction is seen as being initiated

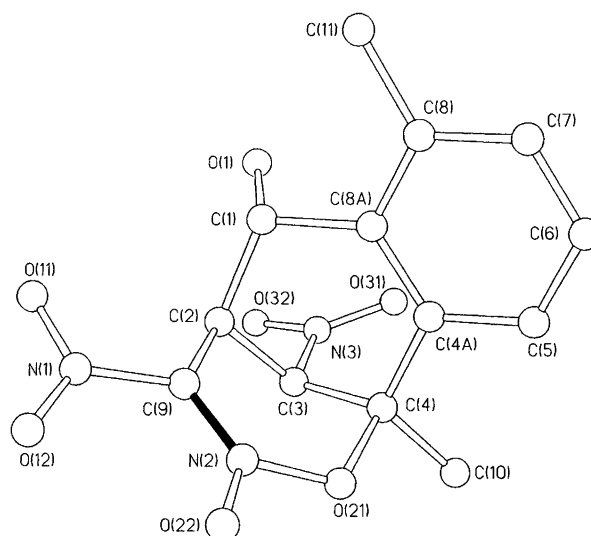


Fig. 1. Perspective drawing of nitronic ester **4**. Double bond shown in black.

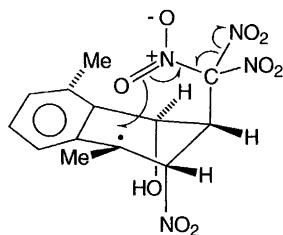


Fig. 2. Cyclization mechanism for radical **6**.

by attack of nitrogen dioxide at C3 in **5**, *anti* to the bulky trinitromethyl group, to give the tertiary benzylic radical **6**. Cyclization, with loss of nitrogen dioxide from the trinitromethyl group (Fig. 2), would yield the observed nitronic ester **4**.

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References

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