Preparation and X-Ray Crystal Structure Analysis of 1,6-Dinitrocycloheptatriene

Ian J. Burnett, Gráinne Conole, Gerard J. O'Donovan and Michael K. Shepherd*

School of Applied Chemistry, University of North London, London, UK N7 8DB

Nitration of cycloheptatriene by copper nitrate in acetic anhydride gives 1-nitrocycloheptatriene and subsequent nitration by nitric acid gives 1,6-dinitrocycloheptatriene; the crystal structure of the dinitro-derivative is described.

Few substitution reactions of cycloheptatriene and its derivatives have been discovered. The parent compound can be acylated if sufficiently mild conditions are used, *via* 1,6-addition of an acyl halide followed by elimination of hydrogen halide, to give 1-substitution products.[1] Similarly, cycloheptatriene-1-carbaldehyde has been obtained in moderate yield by the Vilsmeier reaction.[2] The sole reported example of further substitution is that of diacetylation, giving the 1,6-disubstitution product.[3] Other reagents lead to formation of oxidation or rearrangement products; thus attempted nitration of the system, under conditions applied to the preparation of other nitroalkenes, resulted in formation of the tropylium ion by hydride abstraction.[4,5]

We have found that nitration of cycloheptatriene with a mixture of acetic anhydride and copper(II) nitrate in dichloromethane at 25 °C gave 1-nitrocycloheptatriene in 15–20% yield, after purification by column chromatography. While the role of the salt is primarily as a source of acetyl nitrate, the presence of copper(II) may be important as an inhibitor of autoxidation of cycloheptatriene;[6] little or no products were obtained using other transition-metal nitrates. Substitution, which presumably occurs *via* an addition–elimination mechanism,[1] was very slow below 20 °C and, in the absence of dichloromethane, became uncontrollably exothermic if allowed to rise above 30 °C. 1-Nitrocycloheptatriene† is a bright yellow oil, stable indefinitely at −15 °C,‡ with a strong odour similar to that of nitrobenzene. Further nitration of this product with a mixture of nitric acid, sulfuric acid and acetic anhydride at 0 °C gave the 1,6-dinitro derivative in up to 60% yield.

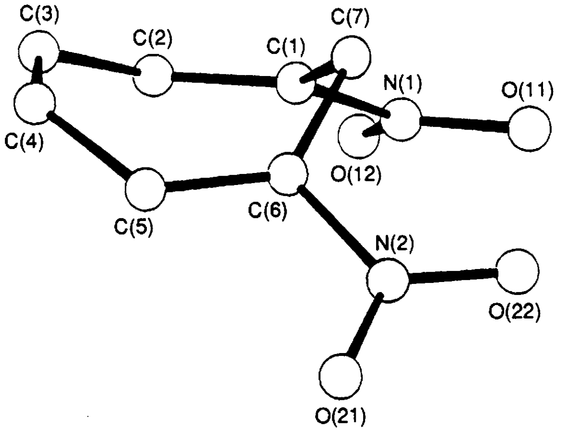

Fig. 1 The structure of 1,6-dinitrocycloheptatriene. Selected bond distances (Å) and angles (°): N(1)–O(11) 1.220(10), N(2)–O(22) 1.217(10), N(1)–O(12) 1.227(10), N(2)–O(21) 1.222(9), C(1)–N(1) 1.491(10), C(6)–N(2) 1.487(9), C(1)–C(7) 1.487(9), C(6)–C(7) 1.477(9), C(1)–C(2) 1.336(11), C(5)–C(6) 1.320(11), C(2)–C(3) 1.421(11), C(4)–C(5) 1.425(10), C(3)–C(4) 1.339(9).

C(7)–C(1)–C(2) 124.4(7), C(7)–C(6)–C(5) 124.9(6), C(3)–C(2)–C(1) 123.6(7), C(6)–C(5)–C(4) 123.9(7), C(4)–C(3)–C(2) 126.0(7), C(5)–C(4)–C(3) 126.0(7), O(12)–N(1)–O(11) 124.1(8), O(22)–N(2)–O(21) 122.8(7), O(11)–N(1)–C(1) 116.6(6), O(22)–N(2)–C(6) 118.0(6), N(1)–C(1)–C(7) 117.7(6), N(2)–C(6)–C(7) 116.8(6), C(6)–C(7)–C(1) 107.4(5).

An X-ray structural§ analysis was carried out on 1,6-dinitrocycloheptatriene (Fig. 1). The cycloheptatriene ring adopts the expected boat conformation, similar to that found in the related derivative 2,5-dimethyl-3,4-diphenylcycloheptatriene.[7] The C–C bond distances within the main ring alternate, whilst the C–N bond lengths support minimal conjugation of the nitro substituents with the ring system. This may provide an explanation for the observation that both derivatives are inert towards dienes in the Diels–Alder reaction, either as 2π- or 6π-components, in contrast to the potent dienophilic reactivity associated with other nitroalkenes.

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Footnotes

† New compounds gave satisfactory microanalytical and mass spectroscopic data. 1-Nitrocycloheptatriene: mp 3–5 °C, δ_H (250 MHz) 3.05 (2H, d, $-CH_2$), 5.67 (1H, m, 6-H, $J_{6,7}$ 7.08 Hz), 6.38 (1H, dd, 5-H, $J_{5,6}$ 9.50 Hz), 6.62 (1H, m, 3-H, $J_{3,4}$ 11.20 Hz), 6.97 (1H, dd, 4-H, $J_{4,5}$ 5.81 Hz), 7.55 (1H, d, 2-H, $J_{2,3}$ 6.45 Hz); δ_C (62.89 MHz) 26.1 (C-7), 124.3 (C-6), 125.9 (C-3), 126.6 (C-2), 128.5 (C-5), 137.4 (C-1), 137.7 (C-4). 1,6-Dinitrocycloheptatriene: mp 120–122 °C, δ_H 3.93 (2H, s, $-CH_2$), 7.02 (2H, m, 3-, 4-H), 7.72 (2H, m, 2-, 5-H); δ_C 24.6 (C-7), 127.7 (C-2, -5), 132.1 (C-3, -4), 139.7 (C-1, -6).

‡ Pure 1-nitrocycloheptatriene deteriorates and can decompose explosively if stored at room temp.

§ *Crystal data* for $C_7H_6N_2O_4$, $M = 182.07$, monoclinic, space group *Cc*, $a = 4.998(1)$, $b = 11.5393(3)$, $c = 10.7114(2)$ Å, $\beta = 98.45(2)°$, $U = 815.32$ Å^3, $F(000) = 376$, μ(Mo-Kα) = 0.81 cm^{-1}, $Z = 4$, $D_c = 1.48$ g cm^{-3}. Data were collected on a Philips PW 1100 diffractometer in the θ-range 3–26° with a scan width of 0.90°. Equivalent reflections were merged to give 527 absorption corrected data with $I/\sigma(I) > 3.0$. $R = 0.0495$ and $R_w = 0.0537$ with weights of $w = 1/\sigma 2F_o$ assigned to the individual reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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