# A Novel Rearrangement in a 1,3-Bishomocubyl Ring System

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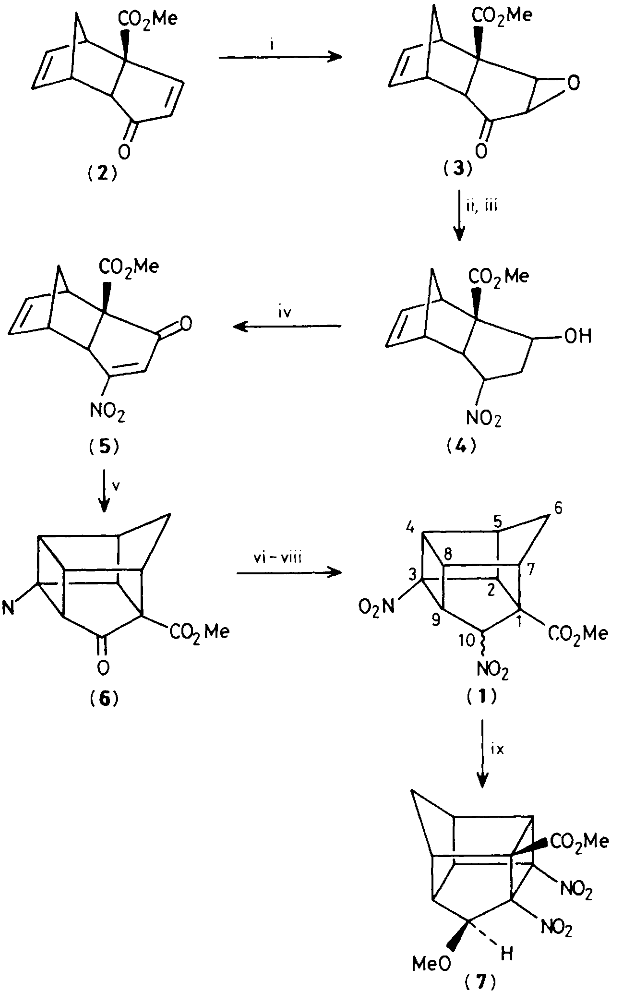
When treated with potassium ferricyanide–sodium nitrite in the presence of base, methyl 3,10-dinitropentacyclo-[5.3.0.0$^{2,5}$.0$^{3,9}$.0$^{4,8}$]decane-1-carboxylate undergoes an unusual skeletal rearrangement to afford methyl 3,9-dinitro-*exo*-10-methoxypentacyclo[5.3.0.0$^{2,5}$.0$^{3,9}$.0$^{4,8}$]decane-8-carboxylate whose structure was confirmed *via* single crystal *X*-ray crystallographic analysis.

There is considerable current interest in the synthesis and chemistry of energetic polynitropolycyclic 'cage' compounds.[1–4] In this communication we report an unusual rearrangement which occurred during an attempt to promote further nitration of methyl 3,10-dinitropentacyclo-[5.3.0.0$^{2,5}$.0$^{3,9}$.0$^{4,8}$]decane-1-carboxylate (**1**).

The synthesis of (**1**) is summarized in Scheme 1.† Compound (**2**) was prepared by using the method described by Alder and coworkers.[5] Selective epoxidation of the same carbon–carbon double bond in (**2**)[5] afforded (**3**). Subsequent conversion[6] of (**3**) into the corresponding oxime, followed by oxidation with peroxytrifluoroacetic acid[7] afforded nitro-alcohol (**4**). Oxidation of (**4**) with pyridinium chlorochromate (PCC) afforded the corresponding enone (**5**), which could be photocyclized to (**6**). The oxime derived from (**6**) upon treatment with *N*-bromosuccinimide (NBS) in aqueous dioxane followed by ozonolysis,[8] afforded (**1**).



**Scheme 1.** *Reagents:* i, $H_2O_2$, $Na_2CO_3$, 83%; ii, $NH_2OH{\cdot}HCl$, NaOAc, 82%; iii, 90% $H_2O_2$, $(CF_3CO)_2O$, 15%; iv, PCC, $CH_2Cl_2$, 84%; v, *hν*, Pyrex filter, EtOAc, 20%; vi, $NH_2OH{\cdot}HCl$, NaOAc, 80%; vii, NBS, aqueous dioxane; viii, $O_3$, $CH_2Cl_2$, 0 °C, 16% (combined yield, vii and viii); ix, $K_3Fe(CN)_6$, $NaNO_2$, NaOH, aqueous MeOH, 57%.

Further nitration of (**1**) was attempted by using an aqueous methanolic solution of potassium ferricyanide–sodium nitrite in the presence of base.[9] Instead of the anticipated product (*i.e.*, methyl 3,10,10-trinitropentacyclo[5.3.0.0$^{2,5}$.0$^{3,9}$.0$^{4,8}$]-decane-1-carboxylate), a compound, (**7**), was obtained whose $^1$H and $^{13}$C n.m.r. spectra indicated the presence of two non-equivalent methoxy groups.‡ Analysis of routine i.r.,

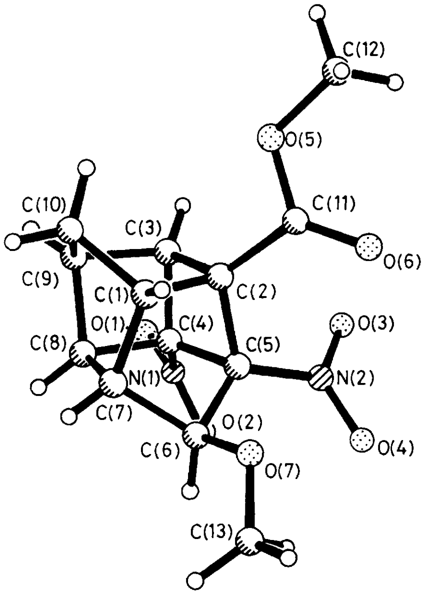


**Figure 1.** Molecular structure of (**7**). Strain in the molecule is seen in bonds and angles which lie outside normal ranges: C(2)–C(5) 1.580(5), C(2)–C(3) 1.574(5), C(4)–C(8) 1.563(5), C(5)–C(6) 1.505(5) Å, C(7)–C(1)–C(2) 99.3(3), C(5)–C(6)–C(7) 94.9(3), C(9)–C(10)–C(1) 95.8°.

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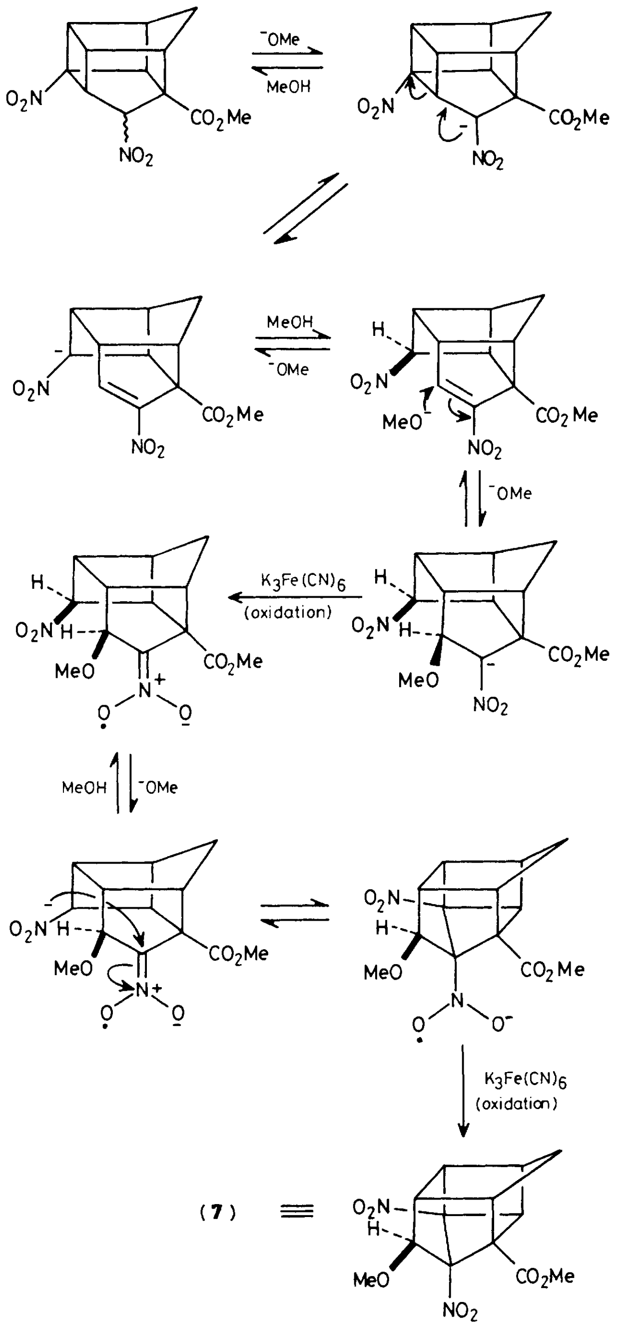
† Satisfactory analytical data (*i.e.*, elemental microanalysis and/or high-resolution mass spectra) were obtained for all new compounds.

‡ *Spectral data* for (**9**) ($C_{13}H_{14}N_2O_7$): i.r. (KBr) 2980 (m), 1680 (vs), 1550 (vs), 1350 (s), 1100 (s), 810 cm$^{-1}$ (m); $^1$H n.m.r. ($CDCl_3$) δ 1.78 [AB, *J*(AB) 9.4 Hz, 1 H], 1.96 [AB, *J*(AB) 9.4 Hz, 1 H], 2.66 (m, 1 H), 3.25 (m, 1 H), 3.42 (m, 1 H), 3.48 (m, 1 H), 3.60 (s, 3 H), 3.78 (s, 3 H), 4.12 (m, 1 H), 4.58 (m, 1 H); $^{13}$C n.m.r. ($CDCl_3$) δ 38.59 (t), 40.38 (d), 47.35 (q), 47.75 (q), 51.65 (d), 52.34 (d), 53.11 (d), 56.44 (s), 59.09 (d), 79.08 (s), 85.54 (d), 97.24 (s), 168.14 (s); mass spectrum (70 eV), *m/z* (relative intensity) (no molecular ion), 279 (*M*−31, 13.5), 115 (100).



Scheme 2

n.m.r., and mass spectra did not afford sufficient information to permit the structure of (7) to be determined unequivocally. Accordingly, we turned to single crystal $X$-ray structural analysis to establish the structure of this compound.§ The structure of (7) is shown in Figure 1.

A mechanism which accounts for the observed rearrangement of (1) to (7) is shown in Scheme 2. To our knowledge, such a rearrangement in the 1,3-bishomocubyl ring system is without precedent. Experiments designed to clarify the nature of this rearrangement and the role which substituents present in (1) might play in promoting its rearrangement to (7) are in progress.

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§ *Crystal data* for (7) (single crystal obtained *via* fractional recrystallization from methanol): $C_{13}H_{14}N_2O_7$, $M$ = 254.3, monoclinic, space group $P2_1/n$, $a$ = 7.861(1), $b$ = 17.600 (3), $c$ = 10.199(2) Å, $\beta$ = 92.52(1); $U$ = 1409.7(2) Å$^3$, $Z$ = 4, $D_c$ = 1.20 g cm$^{-3}$. Diffraction intensities were measured on a Nicolet R3M four-circle diffractometer with graphite monochromatized Mo-$K_\alpha$ ($\lambda$ = 0.71069 Å) radiation using a crystal with dimensions 0.14 × 0.16 × 0.35 mm. A total of 2576 reflections were collected at room temperature to $2\theta = 45°$, of which 1345 had $|F_o| > 3\sigma(F_o)$ and were used in the refinement. The crystal remained stable throughout data collection, and the intensity data were corrected for Lorentz and polarization effects but not for absorption, ($\mu$ = 0.08 mm$^{-1}$). The structure was solved by direct methods and refined by full-matrix least-squares (MicroVAX version of SHELXTL system).[10] All of the hydrogen atoms were located in a difference Fourier map and were allowed to ride on their covalently bonded atoms (C–H distance fixed at 0.96 Å) with thermal parameters fixed at final isotropic values of attached carbons. Non-hydrogen atoms were refined anisotropically. The weighting scheme used was $w = 1/[\sigma^2(|F_o| + 0.00025\,(F_o)^2]$. The final $R$ index was 0.057, $R_w$ was 0.050 and the goodness of fit parameter was 1.60. Final difference maps were featureless. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.