

AN UNUSUAL REARRANGEMENT OF A CAGE DIKETONE MONOTOSYLHYDRAZONE; A NEW FRAGMENTATION OF THE PCUD SKELETON

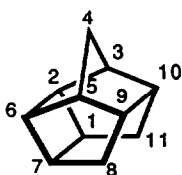
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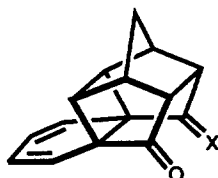
Christchurch, New Zealand

Summary: The cage diketone monotosylhydrazone **3** undergoes rearrangement with double α -cleavage of the cage skeleton to give a product, **4**, which formally corresponds to insertion of cyclopentadiene between the rings of naphthoquinone.

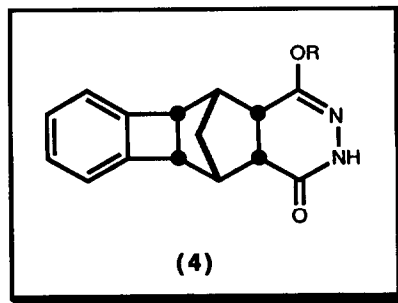
The chemistry of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCUD, **1**) derivatives has been the subject of considerable recent study¹. Synthetically important rearrangements of this carbon skeleton include C1-C7 to C1-C8 bond reorganisations to trishomocubane derivatives¹ and [2 + 2] cycloreversions to linear triquinanes (by C1-C7 and C2-C6 bond cleavage), the latter having been employed in several natural product syntheses¹⁻³. We^{4,5}, and others⁶, are currently interested in the study of π -facial selectivity in Diels Alder reactions of the PCUD-fused diene **2**. In the course of preparing functionalised derivatives of **2** we required a supply of the monotosylhydrazone **3**, which we herein report to undergo a novel rearrangement to the pentacyclic pyridazine derivatives **4**.



(1)



(2) X = O
(3) X = NNHTs



(4)

Reaction of 2 with one equivalent of *p*-tosylhydrazine in refluxing ethanol for 30 min gave the expected mono-hydrazone 3⁷ as a minor (15%) product along with a rearranged product subsequently identified as 4a (85%). The smooth conversion of 3 into 4a and 4b in refluxing ethanol and methanol respectively demonstrated that 4a was a secondary product. The structural identity of 4a was deduced from its spectroscopic properties⁷; in particular the NMR spectra indicated the presence of an *ortho*-disubstituted benzene ring and a tetra-*endo*-substituted norbornane skeleton. The structure was confirmed by a single crystal X-ray structure determination⁸ of the ethanol solvate⁹ of 4a. Figure 1 shows a perspective view of the structure of 4a. The fusion of a benzocyclobutene to the norbornane skeleton results in an elongation of the C2-C9 bond. The structure is of particular interest because of the way in which the norbornane skeleton enforces a cofacial orientation of the benzene and pyridazine rings, their meanplanes being approximately coplanar (16°) and separated by *ca.* 3 Å. As a result the molecule contains a molecular cleft which has potential to act as a host for inclusion compounds.

The conversion of 3 to 4, Scheme 1, is considered to involve a [4+2] cycloreversion of the heptacyclic intermediate 5, a process driven by aromatisation. This rearrangement represents a

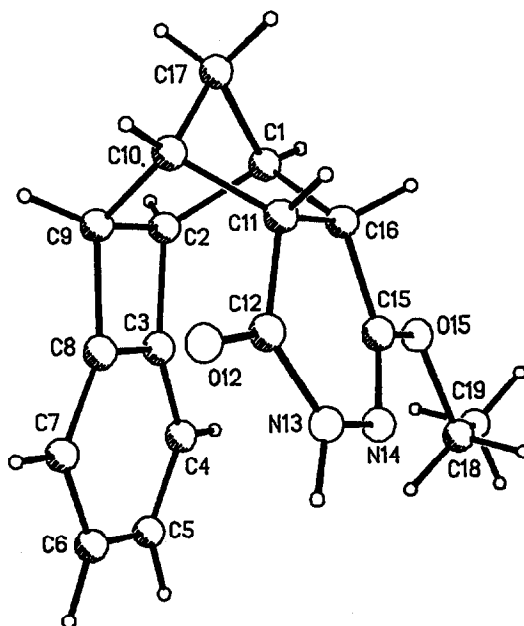
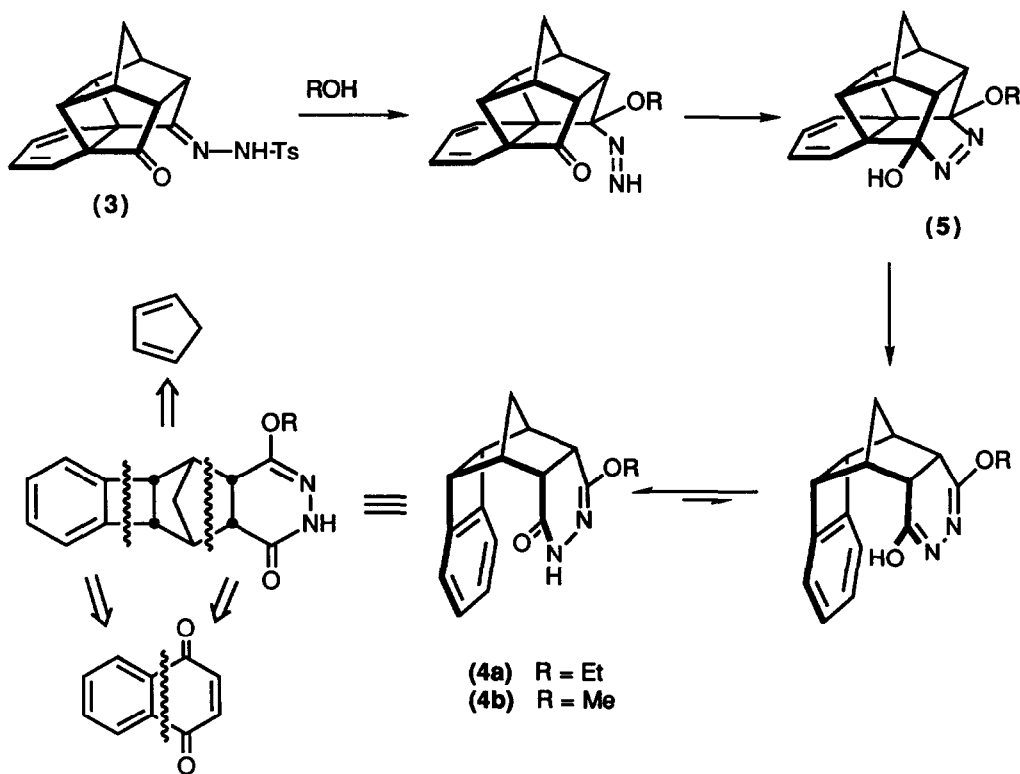


Figure 1. Perspective view of the X-ray structure of 4a. Selected bond lengths (Å) and angles (°):
 C2-C9, 1.572(3); C11-C16, 1.554(3); C3-C2-C9, 86.8(2); C2-C9-C8, 86.4(2);
 C2-C3-C4, 143.9(2); C7-C8-C9, 144.4(2); C2-C3-C8, 93.5(2); C3-C8-C9, 93.3(2).

new fragmentation pathway for the PCUD skeleton and involves double α -cleavage of the precursor. A photoinduced double β -cleavage of **2** has recently been claimed¹⁰. The structure of the carbon skeleton of **4** is of interest when one considers the origin of the component fragments; the reaction sequence leading to **4** formally corresponds to the insertion of cyclopentadiene between the rings of the naphthoquinone precursor.



Scheme 1.

References and Notes

- (1) A.P. Marchand, in 'Advances in Theoretically Interesting Molecules', Vol. 1; ed R.P. Thummel, JAI Press, Greenwich, CN, 1989, p 357.
- (2) G. Mehta, A. Srikrishna, A.V. Reddy, and M.S. Nair, *Tetrahedron*, 1981, **37**, 4543.
- (3) G. Mehta and M.S. Reddy, *Tetrahedron Lett*, 1990, **31**, 2039.
- (4) J.M. Coxon, M.J. O'Connell, and P.J. Steel, *J. Org. Chem.*, 1987, **52**, 4726.
- (5) J.M. Coxon, R.G.A.R. Maclagan, D.Q. McDonald, and P.J. Steel, *J. Org. Chem.*, submitted.
- (6) B. Pandey, U.R. Zope, and N.R. Ayyangar, *Synth. Commun.*, 1989, **19**, 585.

- (7) All new compounds gave spectral and analytical data consistent with the assigned structures. Selected data for **3**: m.p. 215-216°C; ¹H NMR (300MHz, D₆-DMSO) δ 1.59 (d, 1H), 1.89 (d, 1H), 2.48 (s, 3H), 2.70 (m, 1H), 2.78 (m, 1H), 2.91 (m, 1H), 3.12 (m, 1H), 3.25 (m, 1H), 3.71 (m, 1H), 5.40 (m, 2H), 5.98 (m, 2H), 7.47 (dd, 2H), 7.75 (dd, 2H), 10.73 (s, 1H); ¹³C NMR (75MHz, D₆-DMSO) δ 21.1, 37.4, 42.8, 45.9, 46.4, 48.5, 50.0, 50.4, 53.0, 54.0, 120.7, 122.2, 122.8, 124.1, 127.3(2C), 129.5(2C), 136.2, 143.3, 162.2, 212.1. Selected data for **4a**: m.p. 185-186°C; ¹H NMR (300MHz, CDCl₃) δ 1.30 (t, 3H), 1.80 (d, 1H), 1.86 (d, 1H), 2.92 (m, 2H), 3.03 (m, 1H), 3.21 (m, 1H), 3.70 (m, 2H), 3.76 (m, 2H), 6.71 (s, 1H), 6.96 (m, 1H), 7.12 (m, 3H); ¹³C NMR (75MHz, CDCl₃) δ 14.3, 39.2, 41.3, 43.8 (2C), 44.3, 49.1, 49.2, 61.6, 124.1, 126.5, 127.3, 127.4, 154.9, 166.8. Selected data for **4b**: m.p. 170-171°C; ¹H NMR (300MHz, CDCl₃) δ 1.82 (d, 1H), 1.89 (d, 1H), 2.93 (m, 2H), 3.03 (m, 1H), 3.22 (m, 1H), 3.50 (s, 3H), 3.72 (m, 2H), 6.64 (s, 1H), 7.01 (m, 1H), 7.15 (m, 3H); ¹³C NMR (75MHz, CDCl₃) δ 39.1, 41.3, 43.8 (2C), 44.3, 49.1, 49.2, 53.2, 124.2, 126.6, 127.3, 127.5, 155.1, 166.8.
- (8) *Crystal data*: C₁₇H₁₈N₂O₂·C₂H₅OH, M = 328.4, monoclinic, space group P2₁/n, a = 8.366(3), b = 16.209(6), c = 12.828(5) Å, β = 106.17(3)°, U = 1671(1) Å³, T = 165K, D_c = 1.31 g cm⁻³, Z = 4, colourless crystal of dimensions 0.36 x 0.24 x 0.22 mm, μ (Mo Kα) = 0.83 cm⁻¹. 3284 Unique reflections (2θ ≤ 52°) were measured with a Nicolet R3m four-circle diffractometer using graphite monochromated Mo Kα radiation (0.71069Å) and fixed speed 1.2° ω-scans. The data were corrected for Lorentz and polarization effects but no absorption correction was deemed necessary. 2070 Reflections were judged observed [|I| > 3σ(I)]. The structure was solved by direct methods and refined by blocked-cascade least-squares procedures with all non-hydrogen atoms anisotropic and hydrogens in calculated positions, except for the OH and NH hydrogens which were located from a difference map and their positions refined. The final R and R_w were 0.044 and 0.055 respectively. Atom coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Material.
- (9) The molecules are hydrogen bonded in a cyclic array about a centre of inversion wherein two molecules of **4a** are linked by ethanol hydroxyls with N13 - H ... OH_{Et} and EtOH ... O12 hydrogen bonds.
- (10) B. Pandey, U.R. Zope, and N.R. Ayyangar, *J. Chem. Soc., Chem. Commun.*, 1990, 107.