

Polycyclic Rearrangements: Novel Intramolecular Hydride Shift in a Rigid Bicyclo[2.2.2]octane Framework; X-Ray Crystal Structure of One of the Products

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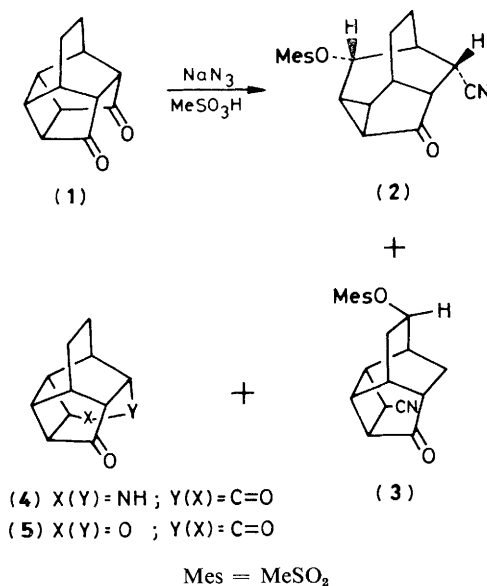
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Schmidt fragmentation of pentacyclo[6.2.2.0^{2,7}.0^{4,10}.0^{5,9}]dodecane-3,6-dione (**1**) provides a rare example of [6,2]type of intramolecular hydride shift in a conformationally constrained bicyclo[2.2.2]octane framework; the structure of one of the products (**3**) has been determined by X-ray crystallography.

While intramolecular hydride shifts ([6,2] and [3,2]) in bicyclo[2.2.1]heptane systems are well documented¹ and have proved valuable in numerous synthetic and mechanistic studies, the occurrence of corresponding shifts in the homologous bicyclo[2.2.2]octanes has not been firmly established.² We now report an authentic example of a [6,2]type of intramolecular hydride shift in a bicyclo[2.2.2]octane system, locked within a rigid molecular framework. We encountered this novel hydride shift during a study of carbonium ion rearrangements of the pentacyclic dione (**1**), initiated *via* a Schmidt fragmentation reaction.³

Reaction of the dione (**1**)⁴ with sodium azide (1 equiv.) in methanesulphonic acid-dichloromethane medium (0–5 °C; 30 min) and column chromatography of the resulting product mixture led to the isolation of (**2**), m.p. 178–179 °C (45%), and (**3**), m.p. 135–136 °C (15%), along with the structurally less significant mixture of the lactam (**4**) and the lactone (**5**). The structure of the rearranged tetracyclic cyclopropyl ketone (**2**) was firmly established on the basis of complementary spectral data;† however, the structure of the novel



† Compound (**2**): ν_{max} (KBr) 1727, 2230, 1350, and 1170 cm^{-1} ; ¹H n.m.r. (CD₃SOCD₃; 270 MHz) δ 5.42 (1H, dd, *J* 5 and 6 Hz), 3.18 (3H, s), 3.2 (1H, d), 2.83 (1H, m), 2.61 (1H, t, *J* 7 Hz), 2.53 (1H, m), 2.3 (1H, m), 2.05 (2H, m), 1.83 (1H, m), and 1.6 (3H, m); ¹³C n.m.r. (CD₃SOCD₃; 25 MHz) δ 208.7 (s), 119.1 (s), 83.0 (d), 43.4 (d), 38.0 (q), 35.7 (d), 31.4 (d), 31.3 (d), 30.0 (d), 22.3 (d), 22.1 (d), 20.3 (t), and 18.4 (t) p.p.m.; compound (**3**): ν_{max} (KBr) 1735 and 2235 cm^{-1} ; ¹H n.m.r. (CDCl₃; 100 MHz) δ 5.01 (1H, d with st), 3.79 (1H, t with st), 3.02 (3H, s), and 1.6–3.4 (10H, m); ¹³C n.m.r. (CDCl₃; 25 MHz) δ 215.2 (s), 76.7 (d), 47.7 (d), 45.0 (d), 38.7 (q), 35.9 (d), 32.4 (d), 32.0 (d), 30.3 (d), 27.6 (t), 24.9 (d), and 24.2 (t) p.p.m.

product (**3**) could not be assigned from the spectral data† alone, and its structure was consequently deduced by X-ray diffraction studies. A perspective drawing is displayed in Figure 1.

The mechanism of formation of (**2**) and (**3**) is depicted in Scheme 1; notable features are the lack of regioselectivity exhibited by the Schmidt intermediate (**6**) resulting in the formation of the carbonium ions (**7**) and (**8**), and the facile

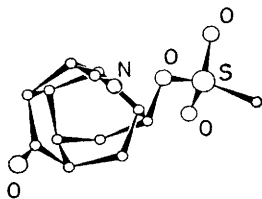
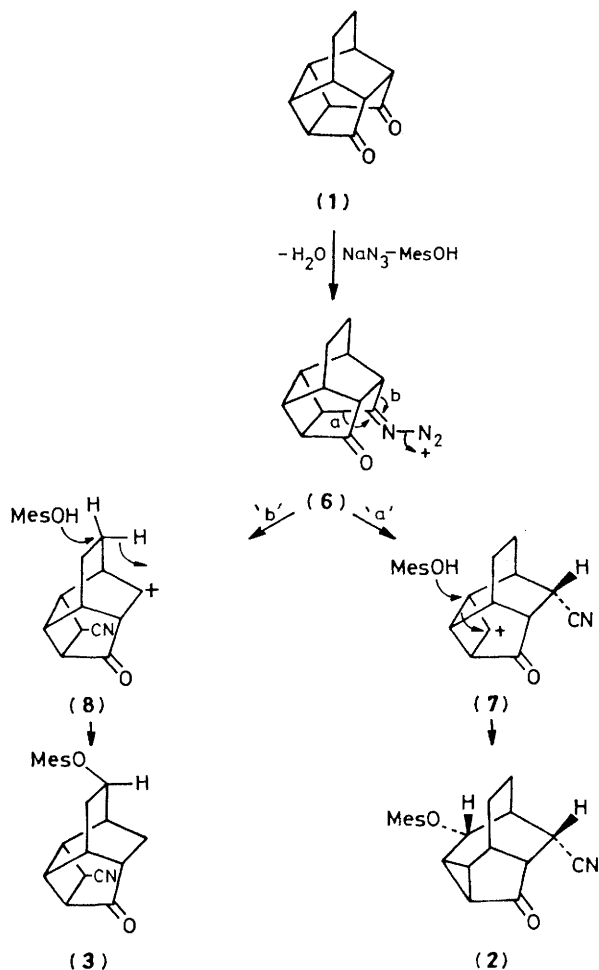


Figure 1. X-Ray structure of compound (3).



Scheme 1. Mes = MeSO₂.

intramolecular hydride shift in (8) with concomitant solvent capture to furnish (3). The unexpected formation of (3) indicates that subtle geometrical changes in the bicyclo[2.2.2]octane framework, particularly the lack of conformational flexibility, suffice to induce the [6,2]hydride shift, which is a common feature of its rigid, lower homologue, the bicyclo[2.2.1]heptane system.

Crystal data:† (3), orthorhombic, space group *Pbca*, $a = 9.057(3)$, $b = 10.254(4)$, $c = 27.08(7)$ Å, $Z = 8$, $D_c = 1.522$ g cm⁻³. Intensity data were collected on a CAD 4 four-circle diffractometer with Mo- K_α radiation and of the 1785 unique reflections, 1263 had $I > 3\sigma(I)$. The structure was solved by automatic centrosymmetric direct methods and refined by large-block least-squares. The final refinement converged at $R = 0.065$ ($R_w = 0.077$).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.