

TRANSANNULAR CYCLIZATIONS OF TETRACYCLO[6.3.0.0.^{2,6}0^{5,9}]-
UNDECAN-3,11-DIONE TO 4-HETERO-9,10-SECOBIRD-CAGE SYSTEM¹

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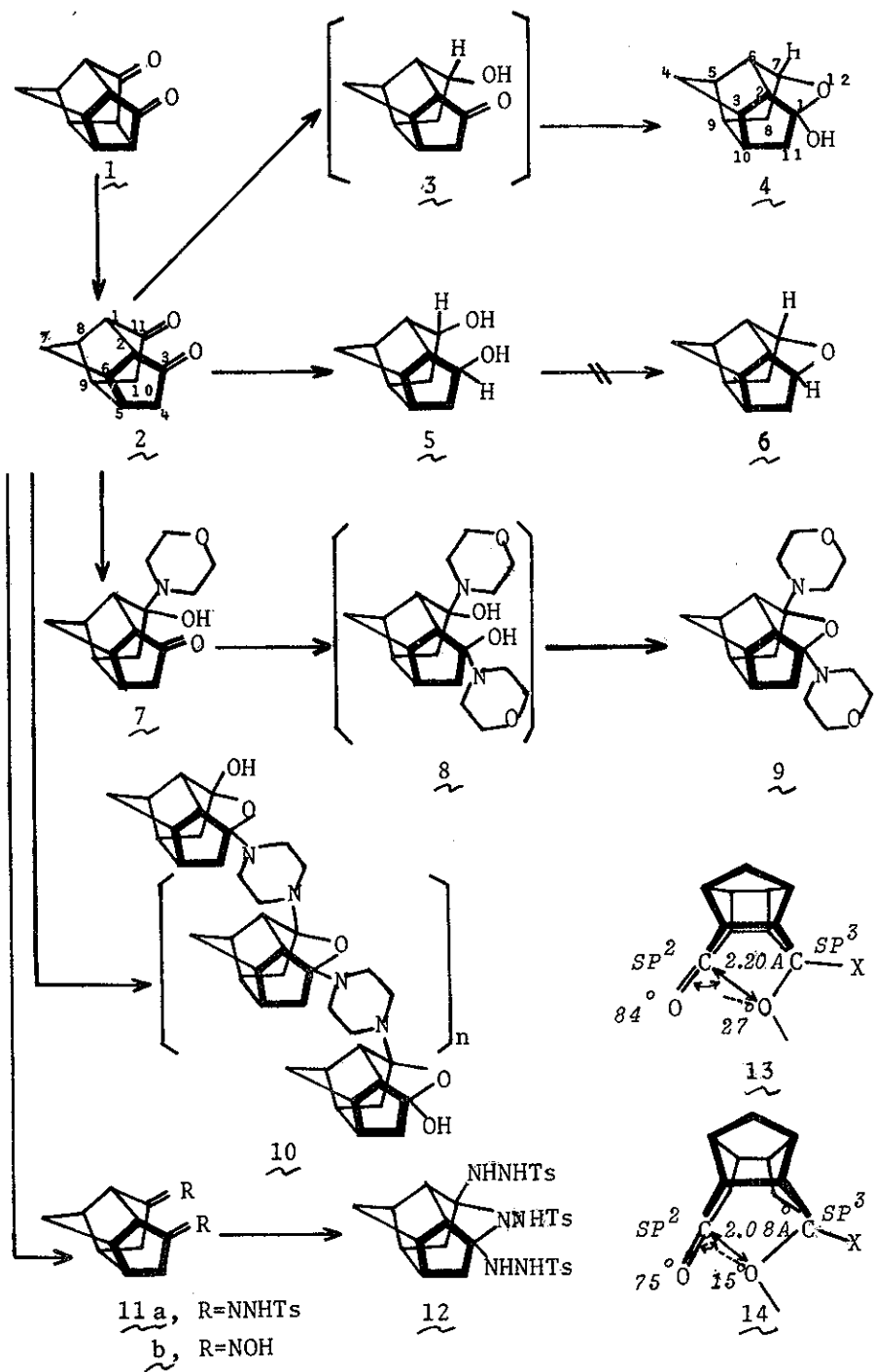
Transannular cyclizations of dione (2) in the title were observed on NaBH₄ reduction, and on additions of morpholine, piperazine, and p-toluenesulfonylhydrazine, affording the corresponding 4-oxa- and -aza-9,10-secobird-cage compounds.

We have previously reported a facile synthesis of 4-hetero-bird-cage system via the transannular cyclization of pentacyclo[6.2.1.0.^{2,7}0.^{4,10}0^{5,9}]undecan-3,6-dione (1).² In this communication we wish to report the transannular cyclizations of tetracyclo[6.3.0.0.^{2,6}0^{5,9}]undecan-3,11-dione (2)³ as a facile route to 4-hetero-9,10-secobird-cage system.

Reduction of 2 with sodium borohydride (1/4 molar equivalent) in refluxing 90% aqueous ethanol for 10 min afforded directly transannularly cyclized product 4 (1-hydroxy-12-oxapentacyclo[5.4.1.0.^{2,6}0.^{3,10}0^{5,9}]undecane) in 80% yield, mp 212-214°; $\nu_{\text{max}}^{\text{KBr}}$ 3360 cm⁻¹; $\delta(\text{CDCl}_3)$ 4.60 (1H, t, J=5.5Hz, C₇H), 4.42 (1H, s, OH), 3.0-1.8 (10H, m, other protons), and

^{†1} All mps were measured in a sealed tube and are uncorrected.

Satisfactory analyses were obtained for all new compounds reported in this communication.



1.75 (2H, AB-q, $\underline{J}=11.5\text{Hz}$, $\underline{J}/\Delta\delta=0.956$, $\text{C}_4\text{Hx2}$); $\underline{m/e}$ 178 (M^+).

Reduction of 2 with excess LiAlH_4 in ether gave diol 5 in 53% yield, mp $258-261^\circ$; $\nu_{\text{max}}^{\text{KBr}}$ 3220 cm^{-1} ; $\delta(\text{CDCl}_3)$ 5.52 (2H, s, OHx2), 4.34 (2H, broad t, $\underline{J}=\text{ca.}6\text{Hz}$, C_3H and C_{11}H), $^{+2}$ 2.5-1.9 (10H, m, other protons), and 1.52 (2H, AB-q, $\underline{J}=12\text{Hz}$, $\underline{J}/\Delta\delta=0.888$, $\text{C}_7\text{Hx2}$); $\underline{m/e}$ 180 (M^+). Even on heating at 195° for 5 min 5 did not afford transannularly dehydrated product (6) but a complex olefinic mixture in contrast to the diol from 1, which is known to give 4-oxabird-cage.²

Treatment of 2 with an equimolar amount of morpholine in tetrahydrofuran for 5 hr at room temperature afforded 7 (34%), mp 170° dec; $\nu_{\text{max}}^{\text{KBr}}$ 3300 and 1686 cm^{-1} ; $\delta(\text{CDCl}_3)$ 3.7 (5H, m, $-\text{CH}_2\text{OCH}_2-$ and OH), 3.12 (2H, broad s, C_1H and C_2H), 2.8-2.3 (12H, m, $-\text{CH}_2\text{NCH}_2-$ and protons at $\text{C}_{4-6,8-10}$), and 1.70 (2H, AB-q, $\underline{J}=12\text{Hz}$, $\underline{J}/\Delta\delta=0.522$, $\text{C}_7\text{Hx2}$); $\underline{m/e}$ 263 (M^+).

Treatment of 2 with 3 molar excess morpholine in refluxing benzene for 6 hr afforded transannularly cyclized bis-adduct 9 (34%), mp $204-205^\circ$ dec; $\nu_{\text{max}}^{\text{KBr}}$ 1152 and 1107 cm^{-1} ; $\delta(\text{CDCl}_3)$ 3.67 (8H, t, $\underline{J}=4.5\text{Hz}$, $-\text{CH}_2\text{OCH}_2-\text{x2}$), 2.85 (2H, s, C_2H and C_6H), 2.78 (8H, t, $\underline{J}=4.5\text{Hz}$, $-\text{CH}_2\text{NCH}_2-\text{x2}$), 2.5-2.2 (4H, m, protons at C_3 , C_5 , C_9 and C_{10}), 1.92 (4H, s, C_8H and C_{11}H), and 1.70 (AB-q, $\underline{J}=12\text{Hz}$, $\underline{J}/\Delta\delta=0.750$, $\text{C}_4\text{Hx2}$).

On refluxing with an equimolar amount of piperazine hexahydrate in ethanol for 5 hr, 2 afforded an oligomer 10 (33%), mp $>300^\circ$; $\nu_{\text{max}}^{\text{KBr}}$ 3420 and 1625 (broad and weak) cm^{-1} . From analytical data (Found: C, 72.20; H, 8.23; N, 9.79. Calcd for $\text{C}_{86}\text{H}_{114}\text{N}_{10}\text{O}_8 \cdot \text{C}_2\text{H}_5\text{OH}$: C, 72.30; H, 8.27; N, 9.58) 10 had $n=4$, tentatively.

$^{+2}$ The diol may be a mixture of stereoisomers.

Treatment of 2 with 2 molar equivalent p-tosylhydrazine in refluxing ethanol for 6 hr gave bistosylhydrazone 11a (40%), mp 275° dec; $\nu_{\text{max}}^{\text{KBr}}$ 3042 and 1647 cm^{-1} . However, on the same treatment of 2 with 4 molar excess tosylhydrazine, an aza-bridged product 12 was obtained (60%), mp 165-166°; $\nu_{\text{max}}^{\text{KBr}}$ 3275 cm^{-1} ; δ (CDCl_3 - CF_3COOH) 7.6 (12H, AB-q, $J=8.4\text{Hz}$, $J/\Delta\delta=0.350$, phenyl protons), 3.50 (2H, s, C_2H and C_6H), 3.2-2.6 (8H, m, other protons), 2.50 (9H, s, $\text{CH}_3 \times 3$), and 2.03 (2H, AB-q, $J=12\text{Hz}$, $J/\Delta\delta=0.800$, $\text{C}_4\text{H} \times 2$).

Similar treatment of 2 with hydroxylamine (4 times equivalent) in 70% aqueous ethanol gave only bisoxime 11b (95%), mp 240-242°; $\nu_{\text{max}}^{\text{KBr}}$ 3220 and 1668 cm^{-1} ; δ (CDCl_3 - CF_3COOH) 4.0-3.46 (2H, m, C_1H and C_2H), 3.42-2.88 (8H, m, other protons), and 3.08 (2H, AB-q, $J=12\text{Hz}$, $J/\Delta\delta=0.885$, $\text{C}_7\text{H} \times 2$); m/e 206 (M^+).

These results indicate that the transannular cyclization reactivity of 2 is larger than that of 1 where ketol is isolable.⁴ Studies on the Dreiding stereomodel indicate also that the distance between the carbonyl carbon and the alcoholic oxygen in 3 is 0.12 Å closer than that in the corresponding ketol from 1 (see 13 and 14).

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