*Tetrahedron*. Vol. 30, pp. 2707 to 2712. Pergamon Press 1974. Printed in Great Britain

# STUDIES ON HETERO-CAGE COMPOUNDS—VI[1]

## TRANSANNULAR CYCLIZATIONS IN PENTACYCLO[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]UNDECAN-3,6-DIONE SYSTEM[2]

T. SASAKI,* S. EGUCHI, T. KIRIYAMA and O. HIROAKI

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464, Japan

(*Received in Japan* 30 *March* 1974; *Received in the UK for publication* 23 *April* 1974)

**Abstract**—Several 4-oxa- and -aza-bird-cage compounds were prepared by transannular cyclizations of pentacyclo[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]undecan-3,6-dione (3). Diol derivatives of 3 cyclized to afford the corresponding 4-oxa-bird-cage derivatives such as **9**, **16a** and **16b**. The corresponding 3-keto-6-ol derivatives (**6**, **10a** and **10b**) did not cyclize transannularly, while 3-imino-6-ol, 3-keto-6-amino, and 3-imino-6-amino type derivatives cyclized to afford 3-substituted 4-oxa- and -aza-bidr-cage compounds such as **12**, **14** and **18**. The transannular cyclization reactivity in the **3** system has been compared with that in the bicyclo[3.3.1]nona-3,7-dione system (**1**).

Transannular cyclizations provide often a convenient method for preparation of polycyclic caged molecules. For example, facile conversion of bicyclo[3.3.1]nona-3,7-dione (**1**) to 1-substituted 2-heteroadamantane (**2**) is well-known.[3] From our interest in the synthesis of hetero-cage compounds we investigated the transannular cyclizations in pentacyclo[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]undecan-3,6-dione (**3**)[3] as a facile route to 4-hetero-bird-cage (4 - heterohexacyclo[5.4.1.0.$^{2,6}$0$^{3,10}$0.$^{5,9}$0$^{8,11}$]dodecane) system.[5]

**1**→**2** **3**→**4**

### RESULTS AND DISCUSSION

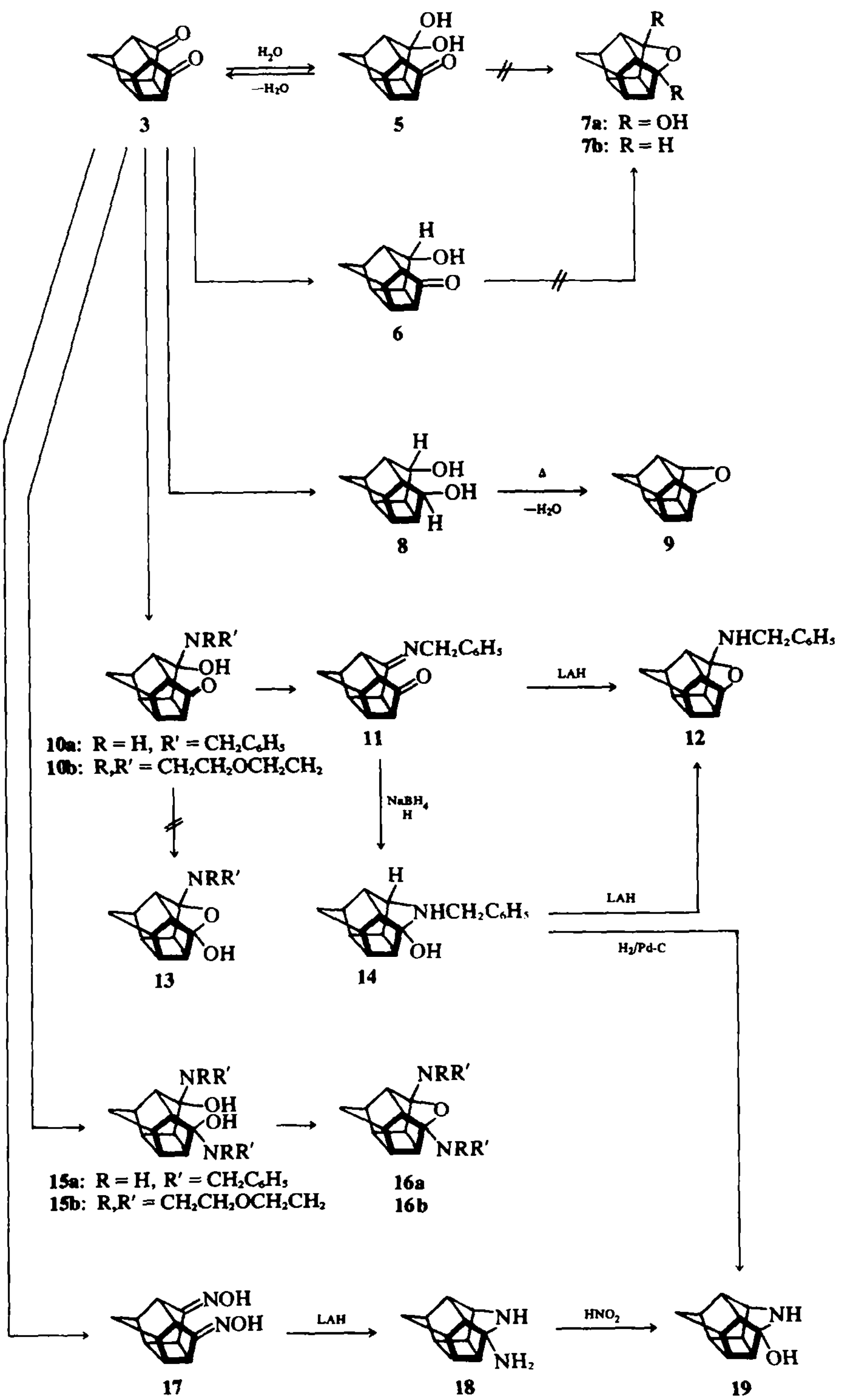
*Synthesis of 4-oxa-bird-cage compounds.* When diketone **3** was heated in aqueous ethyl acetate at 60° for 3 days, an hydrate **5** was obtained. The presence of a CO group and an OH group in **5** was demonstrated by characteristic IR absorptions at 3300 and 1715 cm$^{-1}$. On heating at 180° **5** was reconverted to **3** with loss of water but no trace of transannularly cyclized hydrate **7a** was produced. The known ketol **6**[4] did not cyclize to **7b** even on heating at 270°. These facts indicate that the system **3** has a lower transannular cyclization reactivity compared with the system **1** which is known to afford directly 1-hydroxy-2-oxa-adamantane on sodium borohydride reduction.[3] Reduction of **3** with excess sodium borohydride[4] or better with LAH gave diol **8** which on heating at 280° for several minutes without solvent afforded 4-oxa-bird-cage (4-oxahexacyclo-[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$] dodecane) (**9**) in 60% yield.[6]

Treatment of **3** with an equimolar amount of benzylamine and morpholine in THF afforded the corresponding 1:1 adduct **10a** and **10b** in 80 and 56% yields, respectively. Both **10a** and **10b** exhibited strong CO and OH absorptions in IR spectra and hence, the possibility of transannular cyclization leading to **13b** was excluded. **10a** was very unstable and was converted to the corresponding Schiff base **11** on standing at room temperature in chloroform, which was characterized as its trifluoroacetate. Morpholine adduct **10b** dissociated rapidly to **3** and morpholine in chloroform at room temperature.

Treatment of **3** with two molar equivalent benzylamine under ice-cooling and then at room temperature gave 3,5-dibenzylamino-4-oxa-bird-cage **16a** in 72% yield. Similarly, 3,5-dimorpholino derivative **16b** was obtained in 85% yield. These 3,5-disubstituted oxa-bird-cage compounds are considered to be produced by transannular dehydration of the corresponding bis-adducts **15a** and **15b**, because no transannular cyclizations of the mono-adducts **10a** and **10b** were observed. In fact, an OH absorption at 3400 cm$^{-1}$ observed for crude 1:2 adduct **15b** disappeared gradually during the course of its recrystallization from n-hexane-methanol and pure **16b** was obtained.

On the other hand, treatment of **3** with hydroxylamine afforded exclusively bisoxime **17** in 85% yield contrary to the previous report[4] that 3,5-dihydroxylamino derivative is produced instead of **17**. These results are summarized in Scheme 1.

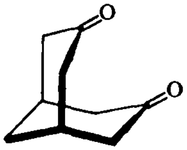
*Synthesis of 4-aza-bird-cage compounds.* Reduction of oxime **17** with LAH afforded 3-amino-4-aza-bird-cage **18** in 40% yield. The aza-bridged structure of **18** was supported by analytical and


3
H₂O
–H₂O
5
OH
OH
O
R
O
R
7a: R = OH
7b: R = H
6
H
OH
O
8
H
OH
OH
H
Δ
–H₂O
9
NRR'
OH
O
10a: R = H, R' = CH₂C₆H₅
10b: R,R' = CH₂CH₂OCH₂CH₂
NCH₂C₆H₅
O
11
LAH
NHCH₂C₆H₅
O
12
NaBH₄
H
13
NRR'
O
OH
14
H
NHCH₂C₆H₅
OH
LAH
H₂/Pd-C
15a: R = H, R' = CH₂C₆H₅
15b: R,R' = CH₂CH₂OCH₂CH₂
NRR'
OH
OH
NRR'
16a
16b
NRR'
O
NRR'
17
NOH
NOH
LAH
18
NH
NH₂
HNO₂
19
NH
OH

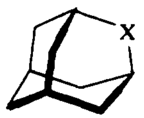
SCHEME 1.

spectral data ($M^+$ at m/e 174). Deamination of **18** with $NaNO_2$ in 75% HCOOH-AcOH at 5° afforded **19** in 80% yield. In the NMR spectra of **18** and **19**, a characteristic triplet due to $C_5H$ appeared at $\delta$ 3·68 ($J$ = 4·5 Hz, 1H) and 4·59 ($J$ = 5·2 Hz, 1H) respectively. LAH reduction of **11** gave rise to oxa-bridged **12** in 30% yield, while sodium borohydride reduction of **11** afforded aza-bridged **14** in 36·5% yield. Both **12** and **14** had the same formula $C_{18}H_{19}NO$ on the basis of analytical and mass spectral data. In IR spectra, **12** has a characteristic NH stretching absorption at 3200 $cm^{-1}$, and **14** exhibited an OH stretching abosption at 3290 $cm^{-1}$. In the NMR spectra, **14** had a characteristic triplet signal at $\delta$ 4·50 ($J$ = 4·5 Hz, 1H) due to $C_5H$ supporting an aza-bridged structure, while **12** had a singlet signal at $\delta$ 3·65 (1H) indicating an oxa-bridged structure. A decisive evidence for the above assignment was obtained by conversion of **14** to **19** derived from oxime **17** (Scheme 1). It is also noticeable that **14** was converted to **12** in 81% yield on refluxing in THF in the presence of excess LAH.

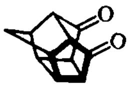
***Transannular cyclization reactivity of* 3 *in comparison with* 1.** Above results on the transannular cyclizations in pentacyclo[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$-undecan-3,6-dione (**3**) system are summarized in Scheme 2. The transannular cyclization reactivity of 3-OH group or its metal complex against 6-CO group (Case 1) is very small in the system **3** as demonstrated by isolation of ketol **6**, and monohydrate **5**, and monoamine adducts **10a**, and **10b**. On the other hand, very facile transannular cyclization in the same case is well known for bicyclo-[3.3.1]nonan-3,7-dione system.[3] The transannular cyclization reactivity in case 2–4, i.e., imino-hydroxyl, carbonyl-amino, and imino-amino combinations are large enough to afford the corresponding bridged products as exemplified by the forma-



1

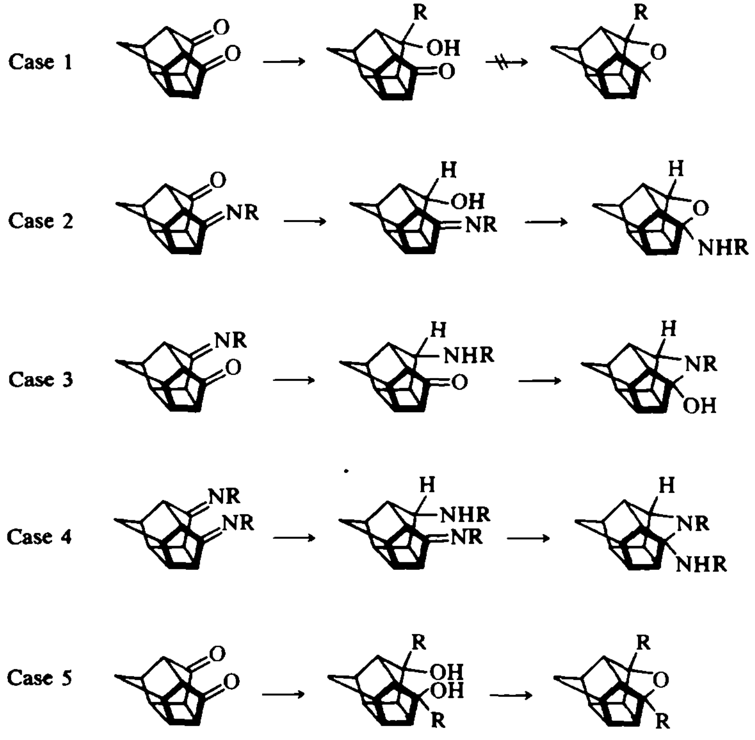


2



3

4



Scheme 2.

tion of **12**, **14**, and **18** respectively. The selectivity of the transannular cyclizations observed in case 2 and 3 with the metal hydride reagents might be useful in synthesis. The similar selectivity is also reported for the system **1**.[3a] The fact that **14** is converted to **12** with LAH indicates the presence of an equilibrium between metal coordinated **12** and **14**, in which aluminum may coordinate predominantly with N atom and boron with O atom. Finally, the facile dehydration of glycol type derivatives such as **8**, **15a** and **15b** to the corresponding oxa-bridged-cages shown as case 5 could be rationalized by considering a relief of steric crowdedness of two OH groups at $C_3$ and $C_5$.

Studies on the Dreiding stereomodel show that the system **3** is conspicuously strained in contrast to the strainless **1** system; the C–C bonds adjacent to the CO groups ($C_2$–$C_3$, $C_3$–$C_4$, $C_5$–$C_6$, $C_6$–$C_7$) are extremely stretched out as depicted in Fig I. An introduction of a $sp^3$ carbon instead of one of the carbonyl $sp^2$ carbons releases the strain somewhat in accordance with the facile formation of monohydrate **5** and amine adducts **10a** and **10b**. A comparison of the transannular distance and transannular angle between **1** (on assuming a chair-chair conformation) and **3** systems on the stereomodel reveals clearly a preference of the former to the latter for the transannular cyclization as depicted in Fig 1. For example, the distance between the $sp^2$ CO carbon und the alkoxy oxygen attached to the $sp^3$ carbon in **3** is 0·52 Å longer than that in **1**. Furthermore, the transannular angular deformation in the system **3** is *ca* 27°, while that in the system **1** is *ca* 5° (Fig 1). As for the angular direction of the nucleophilic attack of the oxygen lone pair to the CO group, an orthagonal direction may be stereoelectronically favorable as in pi-route cyclization.[7] Inspection of these angles (58° for **1** and 84° for **3** system) predicts somewhat unfavorable **1** system compared to **3** system for the nucleophilic cyclization. However, conformatinally mobile **1** system might take more preferable conformation such as partially flattened double chair form. Furthermore, on assuming $sp^3$-$sp^3$ carbons at $C_3$ and $C_7$ for **1** and at $C_3$ and $C_6$ for **3**, the system **1** is obviously more reactive in transannular cyclization from both transannular distance and angle deformation.

## EXPERIMENTAL

M.ps were measured in a sealed tube with a Yanagimoto micro-melting point apparatus (a hot-stage type) and are uncorrected. The NMR spectra were determined with a JEOL C-60HL spectrometer at 60 MHz, using TMS as the internal standard and the chemical shifts are expressed as δ-values. Mass spectra were taken with a JEOL-01SG spectrometer at 70 eV, and the IR with a JASCO IRA-1 grating spectrophotometer. Microanalyses were performed with a Perkin-Elmer 240 Elemental Analyzer.

*Preparation of monohydrate* **5**. Compound **3**[4] (160 mg, 0·92 mmol) was dissolved in EtOAc (10 ml) and water (0·4 ml), and the soln was heated at 60° for 3 days. Precipitated crystals were filtered off and washed with EtOAc to give monohydrate **5** (50 mg, 27%), m.p. 178–180

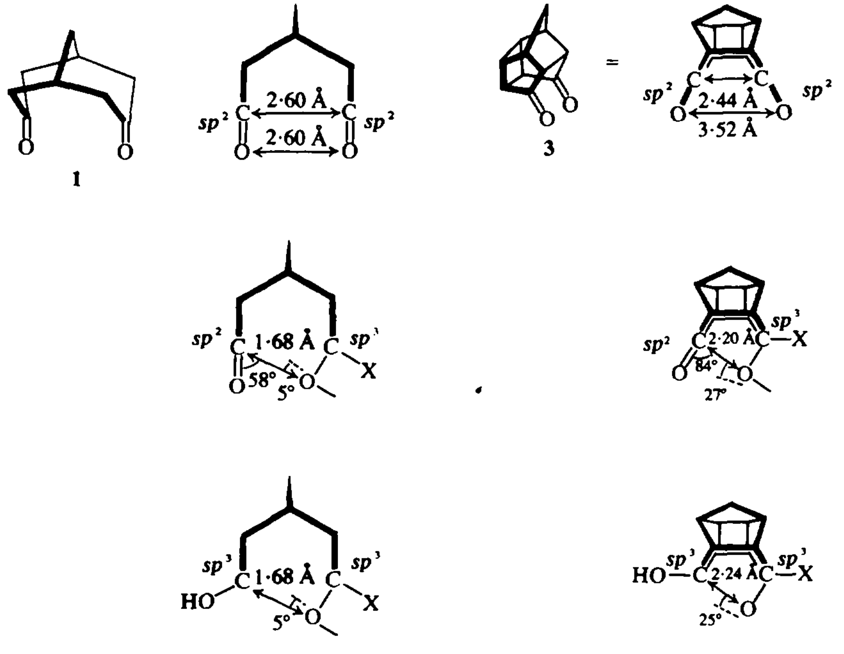


Fig. 1. Transannular distances in 1 and 3 on the Dreiding model.

(dec); $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3300 and 1715 cm$^{-1}$; *m/e* (rel. int.) 174 (M$^+$–$H_2O$, 72%), 146 (35·5), 145 (22), 118 (47), 117 (100), 115 (22), 91 (41), 66 (50), 51 (23), and 39 (40). (Found: C, 68·58; H, 6·19. $C_{11}H_{12}O_3$ requires: C, 68·73; H, 6·29%).

### *Pentacyclo*[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]*undecan*-3,6-*diol* (8)

*A. With* $NaBH_4$. Diketone **3** (0·82 g, 5·0 mmol) was reduced with $NaBH_4$ (0·76 g, 20 mmol) in 95% aqueous EtOH according to Cookson's procedure[4] to afford **8** (0·39 g, 45%), m.p. 273–276° (lit,[4] 276–276·5°) and an isomer of **8** (probably 3α, 6β isomer, 32 mg, 0·9%), m.p. 251–254° (lit,[4] 273–273·5°). Since $NaBH_4$ reduction affords an isomeric mixture of the diol, LAH reduction was performed, which gave better results for preparation of **8**.

*B. With* LAH. To a stirred suspension of **3** (8·28 g, 47·6 mmol) in anhyd ether (40 ml) was added dropwise a suspension of LAH (3·80 g, 0·10 mol) in anhyd ether (200 ml) under ice-cooling. After stirring for 12 h at room temp and then 1 h at refluxing temp, the cooling mixture was treated with water in order to decompose the excess reagent. The aqueous layer was treated with 7% HCl aq (50 ml) and was extracted with chloroform (50 ml × 6). The combined extracts and organic layer was dried ($Na_2SO_4$) and evaporated to afford **8** as colorless solids (7·87 g, 95%) which were practically pure enough for further experiments.

### 4-*Oxahexacyclo*[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$]*dodecane* (9)

Diol **8** (0·50 g, 2·8 mmol) was heated at 280° for several min in a sublimation flask. Products were purified by repeated sublimations at 80° under pressure at 25 mmHg to afford **9** as colorless solids (0·35 g, 60%), m.p. 190–191° (lit.,[6] 190–191°); $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 2963, 2862, 1323, 1025, 963, 927, 910 and 863 cm$^{-1}$; δ ($CDCl_3$) 4·73 (s, 2H), 3·0–2·2 (m, 8H), and 1·71 (AB-q, *J* = 11 Hz, *J*/Δδ = 0·416, 2H); *m/e* (rel. int.) 160 (40·5), 132 (74·5), 117 (74), and 91 (100). (Found: C, 82·47; H, 7·54. $C_{11}H_{12}O$ requires: C, 82·46; H, 7·55%).

### 3-*Benzylamino* - 3 - *hydroxypentacyclo*[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]-*undecan* - 6 - *one* (10a)

To a stirred soln of **3** (348 mg, 2·00 mmol) in THF (5 ml) benzylamine (214 mg, 2·00 mmol) was added under ice-cooling and the stirring was continued for 0·5 h. The resulting ppt was filtered off and washed with THF to give **10a** as colorless crystals (0·45 g, 80%), m.p. 95–97° (dec.); $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3355, 3000–2400 and 1745 cm$^{-1}$; *m/e* (rel. int.) 281 (3·4), 263 (99), 174 (92) and 117 (110). (Found: C, 76·62; H, 6·78; N, 4·99. $C_{18}H_{19}NO_2$ requires: C, 76·84; H, 6·81; N, 4·98%).

### 3 - (1 - *Morpholino*) - 3 - *hydroxylpentacyclo*-[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]*undecan* - 6 - *one* (10b)

To a stirred and ice-cooled soln of **3** (0·87 g, 5·0 mmol) in THF (20 ml) morpholine (0·44 g, 5·0 mmol) was added. After stirring for 24 h at room temp, the ppt was filtered off and washed with THF to give **10b** as colorless crystals (0·735 g, 56%), m.p. 186–189° (dec); $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3250 and 1690 cm$^{-1}$; $\nu^{\mathrm{CHCl_3}}_{\mathrm{max}}$ 3 1735 cm$^{-1}$; *m/e* (rel. int.) 174 (28), 118 (40), 117 (95), 91 (60), 66 (70), 57 (100) and 39 (95). (Found: C, 68·72; H, 7·22; N, 5·13. $C_{15}H_{19}NO_3$ requires: C, 68·94; H, 7·33; N, 5·32%).

### 3,5 - *Bis*(*N* - *benzylamino*) - 4 - *oxahexacyclo*-[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$]*dodecane* (16a)

To a stirred and ice-cooled soln of benzylamine (1·1 g, 10 mmol) in THF (10 ml) **3** (0·45 g, 2·6 mmol) was added and the stirring was continued for 12 h at room temp. After removal fo the solvent, crystallization of the residue from n-hexane-methylene chloride afforded crude **16a** as colorless crystals which showed strong IR absorption at 3310 cm$^{-1}$. Repeated recrystallizations from n-hexane-methylene chloride gave analytically pure **16a** as colorless needles (0·63 g, 72%), m.p. 94–95°; $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3280, 1600, 1490, 1340, 820 and 730 cm$^{-1}$; δ ($CDCl_3$) 7·45–7·0 (m, 10H), 3·95 (s, 4H), 2·62 (broad s, 8H), 2·25 (s, 2H, NH × 2), and 1·65 (AB-q, *J* = 11 Hz, *J*/Δδ = 0·517, 2H); *m/e* (rel. int.) 370 (0·1), 352 (90), 351 (100), 263 (50), 262 (70), 261 (75), 260 (85), 247 (60), 246 (70), 182 (90) and 180 (95). (Found: C, 80·85; H, 6·92; N, 7·40. $C_{25}H_{26}N_2O$ requires: C, 81·04; H, 7·07; N, 7·56%).

### 3,5 - *Bis*(1 - *morpholino*) - 4 - *oxahexacyclo* - [5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$]*dodecane* (16b)

*A. From* **3**. A mixture of **3** (1·74 g, 10·0 mmol) and morpholine (1·74 g, 20·0 mmol) in benzene (50 ml) was refluxed for 1 h by using a Dean-Stark trap. Concentration of the soln afforded **16b** as colorless crystals (2·80 g, 85%), m.p. 232–234° (dec); $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3306, 2931, 2816, 1460 and 1366 cm$^{-1}$; δ ($CDCl_3$) 3·95–3·55 (m, 8H), 3·14–2·30 (m, 8H), and 1·70 (AB-q, *J* = 10 Hz, *J*/Δδ = 0·429, 2H); *m/e* (rel. int.) 330 (0·1), 174 (14), 117 (31), 87 (32), and 57 (100). (Found: C, 68·93; H, 7·89; N, 8·44. $C_{19}H_{26}N_2O_3$ requires: C, 69·06; H, 7·93; N, 8·48%).

*B. From* **10b**. A mixture of **10b** (0·30 g, 1·2 mmol) and morpholine (0·30 g, 3·5 mmol) in chloroform (10 ml) was refluxed for 27 h. Removal of the solvent afforded a solid residue which was recrystallized from n-hexane-methylene chloride to afford crude **15b** as colorless crystals (0·32 g, 76·6%), m.p. 218–225°; $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3400 cm$^{-1}$. Repeated recrystallizations from $CH_2Cl_2$–MeOH gave **16b** as colorless prisms (0·26 g, 68%).

### 3 - *Benzyliminopentacyclo*[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]*undecan* - 6 - *one* (11)

Monobenzylamine adduct **10a** (281 mg, 1·0 mmol) was refluxed in dry benzene (20 ml) for 1 h and the solvent was removed to afford **11** as an oil (264 mg, 100%), $\nu^{\mathrm{CHCl_3}}_{\mathrm{max}}$ 1755, 1685 and 1603 cm$^{-1}$. Treatment of **11** in chloroform with trifluoroacetic acid and crystallization from n-hexane gave trifluoroacetate of **11** as colorless prisms, m.p. 123–125°; $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3300–2400, 1700–1600, 1340, 1190, and 1140 cm$^{-1}$; δ ($CF_3COOH$–$CDCl_3$) 7·4–7·0 (m, 5H), 4·59 (d, *J* = 4·5 Hz, 2H), 3·9–2·2 (m, 8H), and 1·85 (AB-q, *J* = 12 Hz, *J*/Δδ = 0·667, 2H). (Found: C, 61·99; H, 5·25; N, 3·53. $C_{20}H_{18}NO_3F_3 \cdot \frac{1}{2}H_2O$ requires: C, 62·20; H, 5·01; N, 3·62%).

### 3 - *Benzylamino* - 4 - *oxahexacyclo*[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$]-*dodecane* (12)

A soln of **3** (1·74 g, 10·0 mmol), benzylamine (1·07 g, 10·0 mmol) in benzene (50 ml) was refluxed for 3 h. Removal of the solvent gave the Schiff base **11** as an oil which was reduced with LAH (0·8 g, 21 mmol) in ether (30 ml) under refluxing for 2 h. Work-up as usual and purification on a silica gel column eluting with $CH_2Cl_2$–MeOH afforded **12** as colorless crystals (0·75 g, 30%), m.p. 116–116°; $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ 3200, 2900, 1600, 755 and 699 cm$^{-1}$; δ ($CDCl_3$) 7·22 (s, 5H), 5·58 (s, 1H, NH), 3·71 (s, 2H), 3·65 (s, 1H), 2·9–2·1 (m, 8H), and 1·33 (AB-q, *J* = 10·5 Hz, *J*/Δδ = 0·300, 2H); *m/e* (rel. int.) 265 (15), 264 (13), 175 (36), 105 (100), 90 (95), and 64 (33). (Found: C, 81·61; H, 7·32; N, 5·03. $C_{18}H_{19}NO$ requires: C, 81·47; H, 7·74; N, 5·28%).

### 3 - *Hydroxy* - 4 - *benzyl* - 4 - *azahexacyclo*-[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$]*dodecane* (**14**)

The Schiff base (**11**) prepared from **3** (3·48 g, 20·0 mmol) and benzylamine (2·14 g, 20·0 mmol) as above was reduced with $NaBH_4$ (1·0 g, 26 mmol) in THF (50 ml) and EtOH (10 ml) under refluxing for 4 h. After removal fo the solvent, water (50 ml) was added to the residue and the mixture was extracted with $CH_2Cl_2$ (20 ml × 5). The combined extracts were dried ($Na_2SO_4$) and evaporated to afford an oil which was purified on an alumina column eluting with n-hexane-benzene to give **14** as colorless needles (1·86 g, 35·5%), m.p. 77–78°; $\nu_{max}^{KBr}$ 3290, 1603, 1490, 1000, and 735 cm$^{-1}$; $\delta$ ($CCl_4$) 7·5–7·0 (m, 5H), 4·50 (t, $J = 4{\cdot}5$ Hz, 1H), 3·87 (s, 2H), 3·0–2·2 (m, 8H), 1·95 (s, 1H, OH), and 1·67 (AB-q, $J = 10{\cdot}5$ Hz, $J/\Delta\delta = 0{\cdot}467$, 2H); *m/e* (rel. int.) 265 (19), 141 (16), 91 (51), and 40 (100). (Found: C, 81·77; H, 7·24; N, 5·34. $C_{18}H_{19}NO$ requires: C, 81·47; H, 7·22; N, 5·28%).

*Conversion of* **14** *to* **12**. A mixture of **14** (0·53 g, 2·0 mmol) and LAH (0·40 g, 1·1 mmol) in THF (20 ml) was refluxed for 48 hr. Usual work-up and extraction with benzene followed by recrystallization from n-hexane-benzene afforded **12** as colorless plates (0·46 g, 86%) which were identical with a sample of **12** prepared from **11** and LAH by mixed m.p. and spectral comaprisons.

### 3 - *Hydroxy* - 4 - *azahexacyclo*[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$]-[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$] *dodecane* (**19**) *from* **14**

Compound **14** (1·0 g, 3·8 mmol) was hydrogenated with 5% Pd-C (0·3 g) in EtOH (30 ml) for 12 h under atmospheric pressure and at room temp. After filtration of the catalyst, the solvent was removed to give **19** as colorless plates after recrystallization from n-hexane-methylene chloride (0·465 g, 70%), m.p. 138–140°; $\nu_{max}^{KBr}$ 3320, 3060, 1370, 1000, and 750 cm$^{-1}$; $\delta$ ($CDCl_3$) 4·59 (t, $J = 5{\cdot}2$ Hz, 1H), 3·1–2·1 (m, 8H), 2·20 (s, 2H, OH and NH), and 1·70 (AB-q, $J = 10{\cdot}5$ Hz, $J/\Delta\delta = 0{\cdot}439$, 2H); *m/e* (rel. int.) 175 (46), 130 (100), 116 (36), 115 (34), 95 (60), 90 (68), 82 (40), and 79 (39). (Found: C, 75·45; H, 7·51; N, 7·91. $C_{11}H_{13}NO$ requires: C, 75·40; H, 7·48; N, 7·99%).

### *Pentacyclo*[6.2.1.0.$^{2,7}$0.$^{4,10}$0$^{5,9}$]*undecan*-3,6-*dione dioxime* (**17**)

A mixture of **3** (1·74 g, 10·0 mmol), hydroxylamine hydrochloride (2·80 g, 40·0 mmol), and $K_2CO_3$ (2·76 g, 20·0 mmol) in EtOH (70 ml) and water (40 ml) was refluxed for 3 h. After the mixture was condensed to *ca* 50 ml, addition of water afforded a colorless ppt which was collected by filtration (1·40 g). Neutralization of the mother liquor with 5% HCl aq gave the second crop of **17** (0·33 g, total yield 85%). An analytical sample was obtained after recrystallization from EtOH aq, m.p. 302° (dec); $\nu_{max}^{KBr}$ 3240, 3150, 1690, 925 and 859 cm$^{-1}$; $\delta$ ($CF_3COOH$–$CDCl_3$) 4·2–3·2 (m, 4H), 2·91 (m, 4H), and 1·85 (AB-q, $J = 11{\cdot}5$ Hz, $J/\Delta\delta = 0{\cdot}500$, 2H). (Found: C, 64·50; H, 5·92; N, 13·58 $C_{11}H_{12}N_2O_2$ requires: C, 64·69 H, 5·92; N, 13·71%).

### 3 - *Amino* - 4 - *azahexacyclo*[5.4.1.0.$^{2,6}$0.$^{3,10}$0.$^{5,9}$0$^{8,10}$] - *dodecane* (**18**)

To an ice-cooled and stirred suspension of **17** (0·50 g, 2·4 mmol) in THF (5 ml) was added LAH (0·50 g, 13 mmol) in THF (5 ml). After stirring was continued for 1 h at room temp, the mixture was refluxed for 2 h. The cooled mixture was treated with water as usual and extracted with benzene (20 ml × 5). The combined extracts were dried (KOH) and the solvent was removed to give **18** as colorless crystals (0·22 g, 40%), m.p. 192–195°; $\nu_{max}^{KBr}$ 3240, 3120, 1600 (broad and weak), and 1350 cm$^{-1}$; $\delta$ ($CDCl_3$) 4·42 (s, 3H, NH and $NH_2$), 3·68 (t, $J = 4{\cdot}5$ Hz, 1H), 3·5–2·1 (m, 8H), and 1·59 (AB-q, $J = 12$ Hz, $J/\Delta\delta = 0{\cdot}615$ ,2H); *m/e* (rel. int.) 174 (95), 157 (30), 111 (40), 107 (39), 95 (80), 91 (75), 82 (98), 80 (90), and 39 (100). (Found: C, 76·07; H, 8·10; N, 15·83. $C_{11}H_{14}N_2$ requires: C, 75·82; H, 8·10; N, 16·08%).

**18** gave dipicrate as yellowish crystals from EtOH, m.p. 220–222° (dec). (Found: C, 43·42; H, 3·25; N, 17·41. $C_{23}H_{20}N_8O_{14}$ requires: C, 43·68; H, 3·19; N, 17·71%).

*Deamination of* **18** *to* **19**. To an ice-cooled and stirred mixture of **18** (0·51 g, 2·9 mmol) and AcOH (2·5 ml) in formic acid (7·5 ml) was added $NaNO_2$ (0·28 g, 4·0 mmol). After stirring was continued for 0·5 h at 5° and 0·5 h at room temp, the mixture was diluted with water (30 ml) and extracted with $CH_2Cl_2$ (20 ml × 5). The aqueous layer was neutralized with 20% NaOH aq and extracted with $CH_2Cl_2$ (20 ml × 5). The combined extracts were dried ($Na_2SO_4$) and evaporated to afford crude products which were purified on an alumina column eluting with benzene-$CH_2Cl_2$ to give **19** (0·40 g, 80%). This sample was identical with a specimen prepared from **14** by mixed m.p. and spectral comparisons.

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