68475-17-2; **29**, 68475-18-3; **30**, 68475-19-4; **32**, 68475-20-7; **33**, 68475-33-2; ethyl chloroformate, 541-41-3; dihydropyran, 25512-65-6; acrylonitrile, 107-13-1; benzyl bromide, 100-39-0.

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(2) National Institutes of Health Predoctoral Trainee.
(3) Deceased July 14, 1974.
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Transannular Cyclization Reactions of Pentacyclo[6.2.1.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]undecane-3,6-diones. Formation of Aza- and Oxa-Birdcage Compounds

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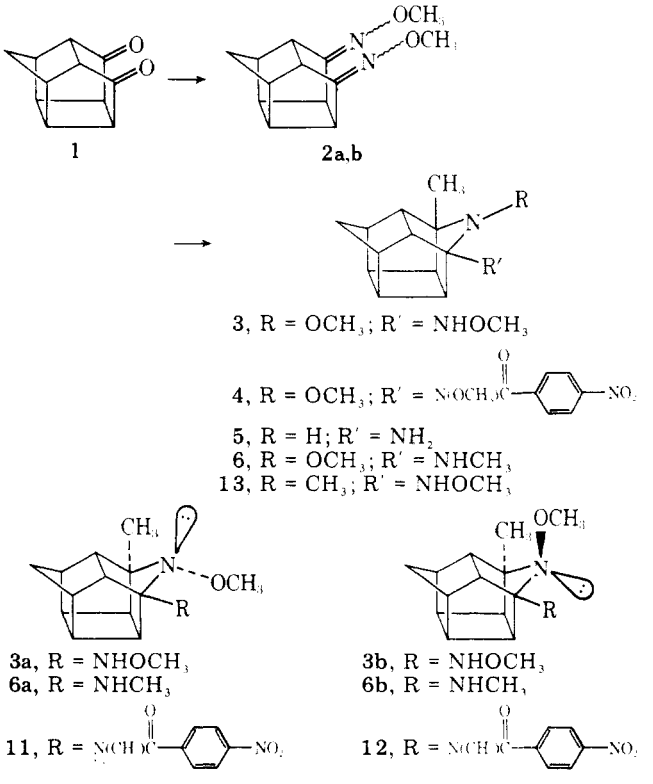
Methoxyamine reacts with cage diketone **1** to afford in excellent yield a mixture of two stereoisomeric di-*O*-methyloximes **2a** and **2b**, methylation of which gives quantitatively dimethoxy aza-birdcage amine **3**. Further reaction with lithium dimethylcuprate results in displacement of one of the methoxy groups in **3** with a methyl group to give yet another aza-bird compound **6**, and its reduction with sodium in liquid ammonia affords cage diamine **5**. NMR data of **3** and **6** suggest that both exist as isomeric pairs differing by stereoisomerism at their apical nitrogen atoms, and the hypothesis is supported by isolation of a pair of stereoisomeric *p*-nitrobenzoates **11** and **12**, prepared by reacting **6** with *p*-nitrobenzoyl chloride. Whereas the diketone **1** reacts with hydroxylamine and *tert*-butylamine to give bis(hydroxylamine) **14** and a mono-*tert*-butylimine **15**, the tetrachloro cage diketone **16** exhibits only the transannular reactions with nucleophiles. Thus, the oxa-birdcage compounds **17–19** are obtained in near quantitative yields by treating **16** with water, ethanol, and hydroxylamine, respectively.

Transannular cyclizations of appropriately functionalized molecules often provide a convenient method for preparation of heterocage compounds which are otherwise difficult to obtain.[1,3] Such transannular cyclization reactions of pentacyclo[6.2.1.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]undecane-3,6-dione (**1**) have been reported by different laboratories.[2,3] We have now extended these studies further with a hope of transforming the cage diketone **1** and its tetrachloro derivative **16** into heterobirdcage compounds and would like to report our findings below.

Treatment of diketone **3** with methoxyamine hydrochloride in pyridine afforded quantitatively a mixture of stereoisomeric di-*O*-methyloximes **2a** and **2b** in an ca. 1:1 ratio, which could be separated on silica TLC plates. Both of the oximes analyzed for $C_{13}H_{16}N_2O_2$, showed characteristic C=N stretching vibration in their IR spectra, and exhibited the expected methoxy singlets and nonequivalent apical protons as AB quartets in their NMR spectra. No attempt was, however, made to assign individual stereochemistry to these compounds believed to differ at the C=N bonds.[4] When the mixture of di-*O*-methyloximes was treated with methyllithium, aza-birdcage compound **3** was obtained as a colorless, volatile liquid in quantitative yield. Its structure is in agreement with its combustion analysis, spectral data, and mode of formation. The presence of a secondary amino group in the molecule was substantiated by its transformation to mono-*p*-nitrobenzoate **4** and to a short-lived nitroxide radical (three-line ESR spectrum, A_N 21.5 G)[5] upon oxidation. The NMR spectrum of **3** showed, in addition to other expected signals, its methyl group as a pair of singlets at δ 1.27 and 1.33 in a relative ratio



of ca. 1:4. This observation, as well as the appearance of a pair of singlets for one methyl group in its *p*-nitrobenzoate **4** and

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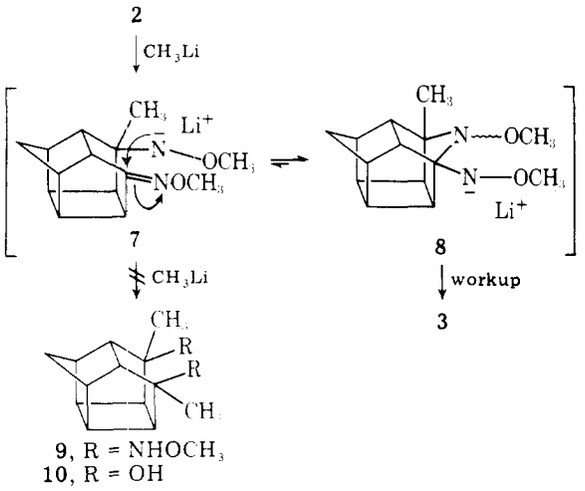
Scheme I



the products derived from it (see below), is interesting and suggests the presence of a pair of stereoisomers due to asymmetry around one of the nitrogen atoms. The stereoisomers are considered to be **3a** and **3b**, and their observation is attributed to slow pyramidal inversion at the apical (bridge) nitrogen on the NMR time scale due to rigidity of the cage structure. Similar arguments of hindered rotation in *N*-alkylaziridines in terms of ring strain during inversion have been made to explain the existence of stereoisomers of their 2,2′-dialkylated derivatives.[6] The cage diamine **5**, prepared in high yield by reduction of **3** with sodium in liquid ammonia, as expected exhibited its methyl group as a sharp singlet in its NMR spectrum at δ 1.3.[7] Neither the mixtures of aza-birdcage compounds **3** nor their *p*-nitrobenzoates could be resolved, presumably due to a low energy barrier between the isomers. The structure **3a**, having repulsion between the methoxy group on the ring and the strained cyclobutyl bond, is tentatively assigned to the minor isomer while the major isomer is considered to be **3b**.

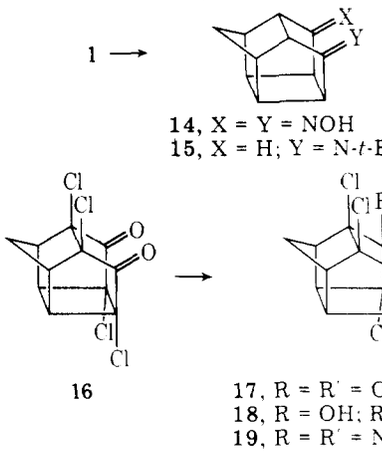
Reaction of methyllithium with **2** gave none of dimethylated product **9**; monomethylated cage **3** was the only isolable product under a variety of conditions. This observation contrasts with the reaction of parent diketone **1**, which affords dimethylated product **10** with excess methyllithium.[3] The addition of methyllithium to **2** is considered to proceed through a short-lived imine **7** which rapidly cyclizes to **8** on its way to the product **3** (Scheme I). A concerted addition of the organometallic reagent to both imines, however, is not ruled out.

Although stable to excess methyllithium, the dimethoxy compound **3** reacted rapidly with lithium dimethylcuprate to afford a monomethoxy aza-birdcage **6** in 50% yield. It was analyzed as its *p*-nitrobenzoate derivative, and the structure is in accord with its spectral data. Like the parent compound **3**, it also exhibits its methyl as a pair of singlets at δ 1.27 (minor) and 1.32 (major) in its NMR spectrum, thereby indicating the existence of stereoisomers, **6a** and **6b**, due to inversion at the ring nitrogen. The mixture reacted quantitatively with *p*-nitrobenzoyl chloride to afford a pair of stereoisomeric mono-*p*-nitrobenzoates **11** and **12** in an ca. 1:4 ratio. These isomers were resolved by careful silica TLC and characterized independently by spectral data. In addition to the expected cage protons, the major isomer **12** showed its bridgehead *C*-methyl, *N*-methyl, and methoxy protons as sharp singlets as δ 1.32, 3.1, and 3.7, respectively, in its NMR spectrum. The minor product **11** had NMR data very similar to that of the major isomer, but had its *C*-methyl singlet shifted upfield to δ 1.23. On standing at room temperature in chloroform for 4 days, the minor benzoate had isomerized to an 80:20 mixture of the major and minor isomers. Isolation of isomeric *p*-nitrobenzoates **11** and **12** along with transformation of the minor isomer to the major isomer clearly demonstrate the existence of stereoisomerism, due to slow pyramidal inversion at the apical nitrogen, in the birdcage compounds discussed above.

The *p*-nitrobenzoate **12** showed important fragments in its mass spectrum at *m/e* 381 (M^+), 366 ($M^+ - CH_3$), 350 ($M^+ - OCH_3$), and 202 ($M^+ - N(CH_3)COC_6H_4NO_2$). The presence of a strong fragment at *m/e* 202 (30%) coupled with the absence of a fragment at *m/e* 186 (<1%) corresponding to the loss of $-N(OCH_3)COC_6H_4NO_2$ for the *p*-nitrobenzoate derivative is very significant and rules out the alternative structure **13** for the product obtained by reacting **3** with lithium dimethylcuprate.

Substitution reactions of organocuprate reagents with alkyl/allyl halides and oxygen derivatives such as tosylates and acetates are well known.[8] There is, however, no report to our knowledge of transformation of $C-OCH_3$ or $N-OCH_3$ to their corresponding alkyl derivatives.[9] Formation of **6** from **3** represents a novel reaction and involves displacement of the methoxy group on nitrogen with the methyl group of the cuprate reagent.

Oxa-Birdcage Compounds. Addition of nucleophiles to cage diketone **1** and its homologues has been reported to give 4-oxa-birdcage compounds.[3] In our hands, however, treatment of **1** with either hydroxylamine or *tert*-butylamine failed to give a birdcage compound and afforded in near quantitative yield dioxime **14**[10] and the mono Schiff base **15**, respectively.



14, X = Y = NOH
15, X = H; Y = N-*t*-Bu

16 → **17**, R = R′ = OH
18, R = OH; R′ = OC_2H_5
19, R = R′ = NHOH

The diimine could not be obtained even under forcing conditions, such as excess amine in the presence of titanium tetrachloride,[11] presumably due to unfavorable steric interaction of the bulky *tert*-butyl groups. The monoimine was sensitive to moisture and gave the parent diketone quantitatively. Our failure to get oxa-birdcage compounds with nucleophiles is in accord with similar observations made by Sasaki and coworkers.[2b] Activation of the cage diketone with electron-withdrawing groups, as expected, rendered it very susceptible to transannular nucleophilic reactions. Thus, tetrachloro cage diketone **16**[3] afforded oxa-birdcages **17–19** in excellent yield when refluxed with aqueous 1,4-dioxane, ethanol, and hydroxylamine, respectively. The dihydroxy compound **17** was also obtained when the parent diketone was exposed to atmospheric moisture for a prolonged period. Structures of these oxa-birdcage compounds are in agreement with their analytical and spectral data (see Experimental Section). None of the dioxime analogous to **14** could be obtained by reacting **16** with hydroxylamine under a variety of conditions.

In summary, we have shown that transannular addition reactions of nucleophiles to appropriately functionalized cage compounds provide an easy access to otherwise difficult to prepare hetero-birdcage compounds. The tetrachloro cage diketone **16** is more reactive than the diketone **1** to nucleo-

philic additions and readily affords oxa-birdcage compounds. The higher susceptibility of the cage compound **16** to nucleophiles as compared to the diketone **1** is in accord with the expected increase in electrophilicity of α-halocarbonyl groups.

Experimental Section

Melting points of solids were determined in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Unless specified otherwise, solutions in organic solvents were dried over anhydrous magnesium sulfate and TLC analyses were performed on silica plates. UV spectra were recorded on a Cary-15 spectrophotometer, and IR spectra were run on a Perkin-Elmer instrument. The NMR spectra were recorded on a Varian T-60 machine, equipped with a permalock, and the values are given in (δ) parts per million downfield from tetramethylsilane as an internal standard.

Treatment of Cage Diketone 1 with Methoxyamine Hydrochloride. Formation of Di-*O*-methyloximes 2a and 2b. A solution of the cage diketone **1**[3] (500 mg) and methoxyamine hydrochloride (570 mg, 10% excess) in pyridine (15 mL) was stirred overnight. The solvent was removed, and the residue was washed thoroughly with water and filtered to afford **2** as a solid (510 mg). The filtrate was extracted with chloroform. The extract was washed with water, dried, and evaporated to afford more of the product (150 mg). Total yield of the product thus obtained was 660 mg (99%). TLC analysis of the product (silica, $CHCl_3$) showed two overlapping spots. The mixture was resolved by careful preparative TLC (developed twice with chloroform) to give isomers **2a** and **2b** in a relative ratio of 45:55. Sublimation of both of the isomers (0.1 mm and 60 °C bath temperature) afforded analytically pure colorless crystalline samples.

The faster moving isomer on the TLC plate, **2a,** melted at 80–81 °C and exhibited the following spectral data: NMR ($CDCl_3$) δ 1.4–2.0 (AB quartet centered at δ 1.7, J = 5 Hz, 2 H), 2.5–3.7 (m, 8 H) and 3.8 (s, 6 H, methoxy groups); IR (KBr) 1650, 1040 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.23; H, 6.98; N, 12.02.

The slower moving isomer on the silica TLC plate, **2b,** melted at 89.5–91.5 °C, exhibited NMR signals virtually identical with those of its isomer **2a,** and had IR absorbtion bands at 1655 and 1040 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.14; H, 6.99; N, 12.06.

Reaction of Di-*O*-methyloximes 2a and 2b with Methyllithium. Formation of Dimethoxy Aza-Birdcage 3. A solution of the unresolved mixture of dimethoxy cage compound **2** (2.32 g, 0.01 mol) in tetrahydrofuran (40 mL), dried and freshly distilled over lithium aluminum hydride, was added dropwise to an ice-cold stirring solution of methyllithium in ether (35 mL, 1 M solution) under nitrogen. The reaction mixture was stirred under an inert atmosphere at 0 °C, and after 2 h it was poured onto crushed ice and extracted with chloroform. The organic layer was washed with water, dried, and evaporated to afford **3** as an oil (2.7 g). The product was chromatographed on a silica column in benzene and eluted successively with benzene and benzene–ether (3:1). The benzene–ether eluents afforded the aza-birdcage compound **3** as a colorless liquid, 2.5 g (100%), which was found to be homogenous on silica TLC. Evaporative distillation at 0.1 mm pressure (bath temperature ca. 70 °C) afforded an analytically pure sample.

Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28. Found: C, 67.12; H, 8.06; N, 11.18.

The product **3** had the following spectral data: NMR ($CDCl_3$) δ 1.27 and 1.33 (singlets, 3 H), 1.4–1.9 (m, 2 H), 2.0–3.1 (m, 8 H), 3.58 and 3.65 (singlets, 6 H), and 6.0 (br singlet, 1 H, exchangeable with D_2O); IR (neat) 3260 cm^{-1} (weak); mass spectrum (70 eV), m/e 248 (M^+, base peak), 233 ($M^+ - CH_3$), 218 ($M^+ - 2CH_3$), 202 ($M^+ - NHOCH_3$), 187 ($M^+ - CH_3 - NHOCH_3$).

Treatment of a chloroform solution of **3** with *m*-chloroperbenzoic acid gave immediately a pink-colored solution which showed a distorted three-line ESR spectrum, with a splitting of 21.5 G. The radical had decayed in ca. 10 min.

Preparation of *p*-Nitrobenzoyl Derivative 4 of the Aza-Birdcage 3. A solution of the aza-birdcage **3** (248 mg, 1 mmol) in dry pyridine (3 mL) was heated on a steam bath with freshly crystallized *p*-nitrobenzoyl chloride (220 mg). After ~60 min, the reaction mixture was poured into ice-cold water (20 mL) and the product was extracted with chloroform. The organic extract was washed with cold, 2 N aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and water. The chloroform layer was dried, and removal of the solvent gave **4** as a TLC pure pale yellow solid (375 mg, 95%). The solid was chromatographed on a silica column, eluted with chloroform, and crystallized from benzene–petroleum ether to afford pale yellow microneedles of **4,** mp 170–171 °C.

Anal. Calcd for $C_{21}H_{23}N_3O_5$: C, 63.46; H, 5.83; N, 10.58. Found: C, 63.29; H, 5.87; N, 10.50.

The *p*-nitrobenzoate exhibited the following spectral data: IR ($CHCl_3$) 1650, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.32 and 1.39 (singlets, 6 H), 1.5–2.0 (m, 2 H), 2.0–3.0 (m, 7 H), 3.0–3.5 (m), 3.48 (s), and 3.5 (s) (total 7 H), 7.75–8.33 (A_2B_2 pattern, J = 8.5 Hz, $\Delta\nu_{AB}$ = 23.5 Hz, 4 H).

Treatment of Dimethoxy Aza-Birdcage 3 with Lithium Dimethylcuprate. Formation of Methoxy Aza-Birdcage Amine 6. A suspension of cuprous iodide (382 mg, 2 mmol) in dry ethyl ether (15 mL) charged into a three-neck flask, kept under nitrogen, was cooled (~0 °C), and to it was added a 2 M ethereal solution of methyllithium (2.5 mL, 5 mmol). The mixture was stirred for 15 min, during which time the solid had dissolved to give a clear ether solution of lithium dimethylcuprate. The temperature of the cuprate solution was now lowered to −70 °C, and to it was added dropwise a solution of aza-birdcage compound **3** (250 mg) in anhydrous ether (5 mL). During the course of addition, which took about 10 min, the reaction mixture was kept stirring. After 3 h, the reaction mixture was allowed to warm to 0 °C and then poured into a stirring aqueous, saturated solution of ammonium chloride. The product was extracted with ether; the ethereal layer was washed with 1% aqueous ammonium hydroxide and saturated aqueous brine. Removal of the solvent from the dried extract afforded an oil (190 mg) which showed at least four components on a TLC plate (silica, ether), with one being the major product. Preparative TLC on silica plates, developed twice with ether, gave aza-birdcage methylamine **6** as a liquid (117 mg, 50%). The product was found to be homogenous by TLC as well as by GLC (QF-1 column at 100 °C) and exhibited the following spectral data: NMR ($CDCl_3$) δ 1.27 and 1.32 (singlets, 3 H), 1.5–2.0 (AB quartet, J = 9 Hz, 2 H), 2.17 (s, ~1 H), 2.4–2.9 (m) and 2.57 (s) (total 11 H), 3.63 (s, 3 H). The position of the –NH singlet at δ 2.17 was concentration dependent, and the signal was absent when the sample was treated with D_2O.

Treatment of Methoxy Aza-Birdcage Amine 6 with *p*-Nitrobenzoyl Chloride. Formation of *p*-Nitrobenzoates 11 and 12. The aza-birdcage compound **6** (115 mg) in pyridine (3 mL) was heated on a steam bath with *p*-nitrobenzoyl chloride (300 mg, excess). After 2 h, the reaction mixture was poured into cold water (25 mL) and the product was extracted with chloroform. The extract was washed with 2 N aqueous hydrochloric acid, aqueous sodium bicarbonate, and saturated brine. The organic layer was dried, and removal of the solvent furnished a pale yellow solid (280 mg). Careful TLC analysis of the solid showed it to be a mixture of two compounds (overlapping spots). The mixture was resolved by preparative silica TLC, using benzene–ethyl acetate (4:1) as the solvent system. The faster moving major compound **12** was a solid (147 mg, 77%) and crystallized from benzene–petroleum ether as shining plates: mp 152–152.5 °C; NMR ($CDCl_3$) δ 1.37 (s, 3 H), 1.4–1.8 (AB quartet, J = 11 Hz, 2 H), 2.0–3.4 (m) and 3.1 (s) (total 11 H), 3.7 (s, 3 H), 7.63 (d, J = 9 Hz, 2 H), 8.22 (d, J = 9 Hz, 2 H); mass spectrum (70 eV), m/e 381 (M^+), 366 ($M^+ - CH_3$), 360 ($M^+ - OCH_3$, base peak), 202 ($M^+ - NCH_3 - CO - C_6H_4NO_2$); IR (KBr) 1650, 1602 cm^{-1}.

Anal. Calcd for $C_{21}H_{23}N_3O_4$: C, 66.12; H, 6.08; N, 11.02. Found: C, 65.82; H, 6.09; N, 10.87.

The minor fraction **11** (lower R_f value), a thick liquid (40 mg, 21%), was contaminated with compound **12** (NMR analysis): NMR ($CDCl_3$) δ 1.28 (s, 3 H), 1.45–2.05 (AB quartet centered at δ 1.78, J = 11 Hz, 2 H), 2.3–3.4 (m) and 3.1 (s) (total 11 H), 3.7 (s, 3 H), 7.63 (d, J = 9 Hz, 2 H), 8.22 (d, J = 9 Hz, 2 H).

The thick oil had solidified to a crystalline solid when set aside at room temperature. Analysis of the solid after 5 days by NMR spectroscopy showed it to be a mixture of **12** and **11,** with the former being the major component. The mixture was resolved on silica TLC plates to give **12** (27 mg, undepressed mixture melting point and spectral comparison with an authentic sample) and **11** (7 mg, TLC and spectral comparison) in a relative ratio of ca. 4:1.

Reduction of Dimethoxy Aza-Birdcage Compound 3 with Sodium in Liquid Ammonia. Formation of Cage Diamine 5. The dimethoxy cage compound **2** (260 mg) was placed in a 25-mL, three-neck flask equipped with a dry ice condenser and nitrogen and ammonia inlet tubes. Liquid ammonia (ca. 8 mL) was transferred to the reaction vessel. Sodium (ca. 100 mg) was added to the flask, and the reaction mixture was stirred under nitrogen. After 15 min, the solution had acquired a deep blue color. The solution was stirred for 1.5 h, the ammonia was evaporated, and the reaction was quenched by the careful addition of methanol (ca. 2 mL) followed by a large excess of

water. The reaction mixture was extracted with chloroform, and the extract was washed with brine, dried, and evaporated to afford a pale yellow, semisolid residue (176 mg). The residue was chromatographed on an alumina column (neutral, Woelm grade III, 18 g), and elution with chloroform–methanol (9:1) gave aza-birdcage diamine **5** as a thick oil (142 mg, 72%) which solidified when set aside for a prolonged period at room temperature. Sublimation, 0.01 mm/25 °C, afforded white crystalline diamine **5**, mp 65–66.5 °C, which showed the following spectral data: IR (neat)[12] 3300 cm^{-1} (strong, broad); NMR ($CDCl_3$) δ 1.3 (s, 3 H), 1.37 and 2.02 (AB quartet, J = 10 Hz, $\Delta\nu_{AB}$ = 19.6 Hz, 2 H), 2.0 (br s, concentration dependent, D_2O exchanged, 3 H), 2.3–2.9 (m, 8 H); mass spectrum (15 and 70 eV), m/e 188 (M^+), 173 ($M^+ - CH_3$).

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 86.24; H, 8.46; N, 14.59.

Reaction of the Cage Ketone 1 with *tert*-Butylamine. Formation of Monoimine 15. The cage diketone **1** (174 mg, 1 mmol) in dry benzene (10 mL) was heated under reflux over 4Å molecular sieves. After 5 days, the solution was cooled and filtered. Evaporation under reduced pressure afforded **15** as an oil which solidified on standing (220 mg, 95%). The product had the same characteristic on silica TLC, in different solvent systems, as that of its parent diketone **1** and had the following spectral data: NMR ($CDCl_3$) δ 1.2 and 1.26 (singlets, 9 H), 1.6–2.35 (m, 2 H), and 2.4–3.7 (m) (total 8 H); IR (neat) 1740, 1675 cm^{-1}.

On exposure to air it hydrolyzed back to the parent diketone **1** (IR and NMR analysis) with, very likely, the formation of *tert*-butylamine (strong basic smell).

When a benzene solution of **1** (174 mg) and *tert*-butylamine (2 mL, excess) was heated for 5 days in the presence of titanium tetrachloride, the monoimine **15** was the sole product obtained in quantitative yield. No trace of a diimine could be detected.

Addition of Water to Tetrachloro Cage Diketone 16. Formation of Oxa-Birdcage 17. A solution of the tetrachloro cage **16** (150 mg) in aqueous tetrahydrofuran (18 mL containing 3 mL of water) was refluxed. After 16 h, the solution was evaporated to afford **17** as a faint yellow solid (160 mg, 100%). The solid was dissolved in chloroform, decolorized with Norit A, and crystallized from chloroform–petroleum ether to afford white, shining needles of dihydroxy cage compound **17**.[13] After drying at 60 °C over P_2O_5 (0.1 mm), the crystals melted at 201–202 °C, resolidified, and remelted at 229–231 °C and exhibited the following spectral data: IR (KBr) 3500, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.85 (d, J = 11 Hz, 1 H), 2.53 (d, J = 11 Hz, 1 H), 2.8–3.3 (m) and 3.2–3.8 (m, exchangeable with D_2O) (total 6 H).

Anal. Calcd for $C_{11}H_8Cl_4O_3$: C, 40.00; H, 2.42; Cl, 43.03. Found: C, 40.09; H, 2.59; Cl, 42.02.

Addition of Ethanol to Tetrachloro Cage Diketone 16. Formation of Oxa-Birdcage 18. A solution of the cage diketone **16** (500 mg) in absolute ethanol (25 mL) was heated under reflux. After 16 h, the solvent was evaporated to give **18** as a white solid (530 mg). Attempts to recrystallize the solid from methylene chloride–hexane or chloroform–hexane resulted in the formation of white crystals, mp 116–121 °C, TLC analysis of which indicated a mixture of **16** and **18**. Further crystallizations increased the amount of **16** at the expense of **18** and did not give an analytically pure sample of the product. The parent diketone was also formed when the product was allowed to stand over a prolonged period (TLC analysis). Preparative TLC on silica of this mixture ($CHCl_3$–MeOH, 95:5) afforded **16** as the only isolable product. The crude ethanol adduct **18** had the following spectral data: IR (KBr) 3520, 1250 cm^{-1}; NMR ($CDCl_3$) δ 1.3 (t, J = 7 Hz, 3 H), 1.77 (d, J = 12 Hz, 1 H), 2.5 (d, J = 12 Hz, 1 H), 2.8–3.3 (m, 4 H), 3.4 (br s, exchangeable with D_2O) and 4.1 (q, J = 7 Hz) (total 3 H); mass spectrum (70 eV), m/e (359, M^+).

Treatment of Tetrachloro Cage Compound 16 with Hydroxylamine Hydrochloride. Formation of Oxa-Birdcage 19. A solution of the tetrachloro cage compound **16** (1.8 g) and hydroxylamine hydrochloride (6 g) in pyridine (20 mL) and ethanol (20 mL) was heated under reflux. After 90 min, the solution was cooled and evaporated to afford a dirty white, thick paste. The product was dissolved in chloroform and thoroughly washed with water. The organic layer was dried and evaporated to give TLC pure product **19** (1.7 g, 81%). Crystallization from ethyl acetate–hexane afforded white crystals: mp 219–220 °C; NMR ($CDCl_3$ + pyridine) δ 1.6 (d, J = 11 Hz, 1 H), 2.34 (d, J = 11 Hz, 1 H), 2.9–3.2 (m, 4 H), 6.34 (broad s, 4 H, exchangeable with D_2O); IR (KBr) 3560, 3400 (broad) cm^{-1}.

Anal. Calcd for $C_{11}H_{10}Cl_4N_2O_3$: C, 36.66; H, 2.77; Cl, 39.44; N, 7.77. Found: C, 36.84; H, 3.01; Cl, 39.01; N, 7.78.

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Registry No.—**1**, 2958-72-7; **2**, 68525-47-3; **3a**, 68525-48-4; **3b**, 68566-84-7; **4**, 68525-49-5; **5**, 68525-50-8; **6a**, 68525-51-9; **6b**, 68566-85-8; **11**, 68525-52-0; **12**, 68566-86-9; **15**, 68525-53-1; **16**, 68525-54-2; **17**, 68525-55-3; **18**, 68550-22-1; **19**, 68525-56-4; methoxyamine hydrochloride, 593-56-6; methyllithium, 917-54-4; *p*-nitrobenzoyl chloride, 122-04-3; lithium dimethylcuprate, 15681-48-8; *tert*-butylamine, 75-64-9; ethanol, 64-17-5; hydroxylamine hydrochloride, 5470-11-1.

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