H_2O, and dried (Na_2SO_4). Evaporation of the solvent yielded a viscous oil which solidified on addition of a few mL of EtOH. The two crops of solids were combined and recrystallized from toluene to give the 1:1 clathrate which was decomposed under vacuum (15 Torr) and heating (100 °C) to yield the pure host compound; 53%, mp 209–211 °C (lit.[16] mp 208–209 °C).

Crystal Structure Determination. Data Collection and Processing. The inclusion compounds 1–4 were obtained by dissolving the host (H) in a minimum amount of chloroform and adding an excess of the appropriate guest liquid.

The solutions were allowed to evaporate slowly for 3–4 days until crystals formed. These were mounted in capillary tubes and sealed under an atmosphere of mother liquor. Details of the crystallographic data collection and refinement for compounds 1–4 are summarized in Table I. Preliminary cell dimensions were determined photographically. Data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo K_α ($\lambda = 0.7107$ Å) radiation and the $\omega - 2\theta$ method. Crystal stabilities were checked by periodic monitoring of three reference reflections. Data were corrected by Lorentz and polarization factors, and absorption corrections were applied.[17] Final refinements were based on those observations that satisfied the condition $I > 2\sigma I$.

Solution and Refinement. The structures were solved by direct methods using SHELXS-86.[18] They were then refined by full-matrix least-squares using the SHELX76 program system.[19] Non-hydrogen atoms were treated anisotropically, and non-hydroxyl hydrogens were constrained to 1.00 Å from their parent atoms. Approximate positions for the hydroxyl hydrogens were found in difference Fourier maps, and these were then included in the structures at fixed distances from their parent oxygens. The final difference Fourier maps showed no indication of incorrectly placed or missing atoms.

Thermal Analysis. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed using a Perkin-Elmer PC7 series system. Before analysis, crystals were removed from their mother liquor, blotted dry on filter paper, and crushed. Sample weight, in each case, was approximately 5 mg. A constant stream of nitrogen (flow rate 40 mL min^{-1}) was passed over the samples. The temperature range for the DSC was typically 30–250 °C at a heating rate of 10 °C min^{-1}.

TG was used to confirm the host to guest stoichiometry determined by crystal structure analysis. It was also used to calculate an approximate value for the activation energy of guest desorption, using the method described by Flynn and Wall.[11] Various heating rates in the range 1–35 °C min^{-1} were used.

Acknowledgment. L.N. and S.B. thank the University of Cape Town and the Foundation for Research Development (Pretoria) for research grants. E.W. thanks the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for financial support. K.S. thanks the Konrad Adenauer Foundation for a scholarship.

Registry No. 1, 139276-41-8; 2, 139276-42-9; 3, 139276-43-0; 4, 139276-44-1; tri(1-naphthyl)silanol, 18919-22-7; 1-bromonaphthalene, 90-11-9.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates, figures of DSC traces of 1–4 (onset temperatures of endotherms are marked), and TG curves of 1–4 (showing the change in onset temperatures with heating rate) (42 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors are available directly from L.N.

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Proximity Effects in Fused Cyclobutanones. Facile Formation of Cage Systems†,[1]

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Received May 21, 1991

Chlorobicyclooctanone **3** on reaction with H_2O–Et_3N in acetonitrile at 20 °C produced in high yield four complex dimeric compounds **4–7**. The novel structures produced by C–C bond formation between tertiary centers were revealed by NMR and X-ray diffraction. Pathways leading from **4** or its diastereomer **14** to cage compounds **5–7** indicate the importance of proximity effects in these transformations.

α-Halocyclobutanones[2] have found wide synthetic application in the synthesis of tropolones,[3] α-methylene γ-lactones,[4] substituted cyclopentanones,[5] and even cyclopropane derivatives.[6] Reaction of bicyclic α-halocyclobutanones with nucleophiles can lead to ring opening,[7] ring contraction,[6] or cine substitution.[6c,8]

Recently,[9] we have shown that α-chlorobicyclooctanone **1** on reaction with hydroxide ion at room temperature (24 h) produced a cine substitution product **2** as well as a dimeric compound **2a**. The facile formation of a C–C bond between two tertiary centers can be attributed to coupling of an enolate with an oxidoallyl cation generated from **1**.

When we tried to test the generality of this coupling process by applying it to the oxabicyclooctane analogue

† Dedicated to Prof. H. C. Brown on the occasion of his 80th birthday.

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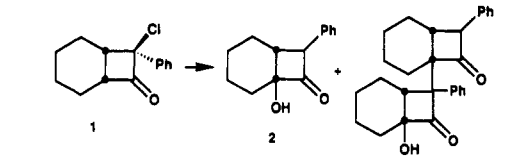
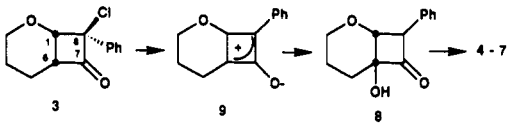
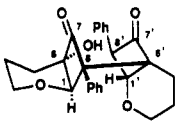
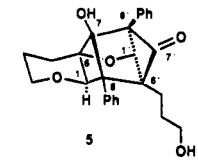




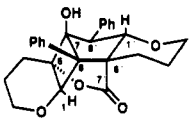
Long-range C–H coupling data for 4–7



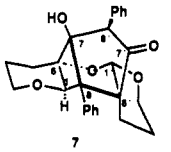
C_6-H_1,C_7-H_1,C_6'-H_1,C_7'-H_5',C_1'-H_6'



C_7-H_1,C_8-H_1,C_8'-OH,C_6'-H_1'



C_7-H_1,C_7-H_8',C_8-H_8'



C_7-H_1,C_7-H_8',C_7'-H_8'

3, we found that only dimeric products had formed. But in addition to expected dimer **4**, we were able to isolate three isomeric compounds possessing unexpected rearranged and cage structures. The reaction of **3** with H_2O–Et_3N in acetonitrile proceeded remarkably fast (within a few minutes) at room temperature and led to compounds **4–7** in 80% overall yield and in variable ratios depending on reaction conditions. After 5-min reaction time mainly **4** was isolated, whereas after 30 min and workup with dilute HCl mainly isomer **5** was obtained together with small amounts of **4**, **6**, and **7**. Ultimately, all four isomers were isolated and identified. Acetal **7** was formed only after acid workup and was found to be the main product of exposure of **5** to dilute HCl.

The Structures of 4–7.[13] The structures of the four isomers were determined from ^{1}H- and ^{13}C-correlated 1D-NMR spectra, as well as various (^{1}Hx–^{1}H, ^{1}Hx–^{13}C one-bond and long-range) COSY experiments, mass spectra, and elemental analyses, and in the case of **5** and **6**, these were verified by X-ray diffraction studies.

Dimer **4** showed characteristic cyclobutanone absorptions in the IR at 1790 cm^{-1}, in ^{13}C NMR two carbonyl peaks at 210.8 (C-7) and 209.6 ppm (C-7′), and in the proton spectrum two doublets (J = 8 Hz) at 5.27 (H-1′) and 5.14 (H-8′), a singlet at 4.07 (H-1, next to ether), and a high-field multiplet at 0.11 ppm ($CDCl_3$). This unusual position for an aliphatic hydrogen is due to shielding of H-4′ (ax) by the aromatic ring current of the phenyl group at C-8. Some relevant long-range C–H couplings from a hetero COSY experiment are given for **4–7**. Compound **4**, even after chromatography, usually still contained ~10% of a diastereomer **14** as evidenced by NMR (see below).

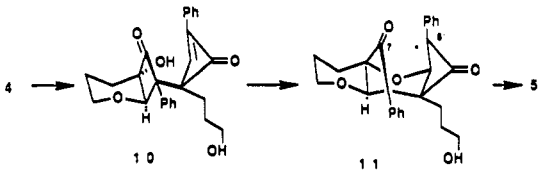
Dimer **5** exhibited a characteristic carbonyl resonance at 198.4 (C-7′) ppm, IR at 1780 cm^{-1}, and five quaternary carbons of which one is a tertiary alcohol (singlet at 96.1 ppm). The ^{1}H NMR spectrum showed three singlets at 5.25 (OH), 4.78 (H-1′), and 4.35 (H-1) and a two-proton triplet at 3.49 ppm, the latter implying that one ether ring had opened to an alcohol side chain. Structure **5** was unequivocally established by X-ray diffraction.

Dimer **7** showed only one low-field carbonyl peak (C-7′) at 213.7 ppm and IR absorption at 1731 cm^{-1} consistent with a cyclopentanone. A very low-field sp^3 carbon (C-1′) at 98.28 ppm bearing a hydrogen at 4.64 ppm implies the presence of an acetal function. There are further three singlets at 5.50 (H-1), 4.22 (H-8′), and 3.95 ppm (OH), as well as three quaternary carbons.[14]

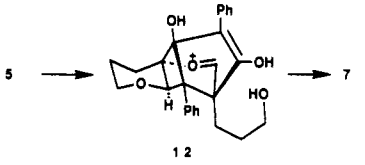
In the dimer **6** a carbonyl peak at 170.3 (C-7) ppm and IR at 1747 cm^{-1} indicated a lactone. A tertiary alcohol was suggested by a peak at 87.27 ppm (C-7). There were further two doublets (J = 11 Hz) at 4.18 (H-1′) and 3.84 (H-8′) and a singlet at 4.22 ppm (H-1). H-5′ (ax) absorbed at high field (0.96 ppm) because of the shielding effect of the 8-phenyl ring. Structure **6** was verified by X-ray diffraction studies.

Mechanistic Pathways. The first dimer **4** presumably derives from the primarily formed, but nonisolable, cine substitution product **8**, resulting from trapping of oxidoallyl cation[9,10] **9** with HO$^-$. The enolate of **8** apparently competes successfully even with hydroxide ion for another molecule of the oxidoallyl cation. We envision this process to be initiated by complex formation between the enolate of **8** and the oxidoallyl cation **9**, which due to the immediate proximity of the two species is followed by electron transfer and collapse to dimer **4**, in spite of the unfavorable geometry leading to formation of a bond between two tertiary C centers. This is reminiscent of bond formation between stabilized carbocations like the triphenylmethyl or tropylium ion and relatively stable but hindered carbanion species like methyl dimedone, which has been observed by Arnett and others.[11] It is remarkable that in our case *both cation and anion are generated in the same*

Scheme I



Scheme II



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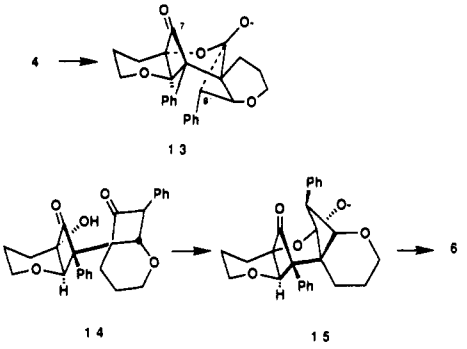
(13) Our numbering of carbons in dimers **4–7** is based on connecting two monomeric species in which the nonhydroxylated monomeric species is referred to by prime numbers.

(14) One of the quaternary carbons in **7** was not detectable, presumably being hidden among the other signals (quaternary carbons give notoriously weak signals).

Scheme III



solution from the same species. Since the enolate of **8** can approach the oxidoallyl cation **9** from 2 enantiofaces, **4** (8*R*,6*S*) and **14** (8*R*,6′*R*) are expected.[15]

The formation of isomers **5**–**7** from primary products, such as **4**, is most likely due to a chain of chemical events brought about by relief of strain and proximity effects. Reversible and facile base-catalyzed opening of an oxabicyclic ring system to produce a cyclobutenone has been demonstrated.[5] Hence, the first step in the formation of **5** from **4** must be reversible opening, under reaction conditions, of one of the tetrahydropyran rings with concomitant formation of a cyclobutenone (see intermediate **10**). This may lead to some relief of steric compression. Michael addition of the *tert*-alkoxide to the cyclobutenone in **10** to produce a six-membered ring ether **11**, though probably a reversible process, brings the resulting enolate carbon (C-8′) into immediate proximity to the C-7 carbonyl (the atoms being in a near 1,3-diaxial relationship) and leads to ring closure with formation of the rather strained cage compound **5** (Scheme I).

Formation of isomer **7** from **5** can be explained by an acid-catalyzed ring opening (demonstrated as occurring during acid workup) of the cyclobutanone ring. This ether-assisted cleavage of the C-1′ to C-8′ bond can be initiated by protonation of the C-7′ carbonyl and relieves strain present in the cage structure **5**. The resulting oxonium ion **12** undergoes ring closure to **7** through the propanol side chain (Scheme II).

Generation of lactone **6** from either **4** or **14** apparently must include intramolecular attack of the *tert*-alkoxide on the C-7′ carbonyl group (due to proximity effects) leading to an intermediate such as **13**.

Examination of molecular models indicated that **13**, generated from **4**, cannot possibly bring about ring closure to **6**, because the benzylic C-8′ is located on the opposite side of C-7. Instead, diastereomer **14** is required for the formation of **6**, as indicated by **14** → **15** → **6** (Scheme III). Furthermore, molecular models reveal that if dimer **14** were to undergo ether formation, similar to conversion of **4** to **10** to **11**, then the benzylic carbon C-8′ and the C-7 carbonyl would be out of reach of each other, so that *only isomer 4 can lead 5* and *only isomer 14 can lead to 6*. Hence, the structure verification of **5** and **6** by X-ray diffraction also confirms the structures of **4** and **14**.

On the basis of these conclusions, we decided to follow the conversion of chloro ketone **3** and of dimer **4** to products by means of ^{1}H NMR, in order to obtain a clearer insight into these unusual transformations. This was possible by integration of peaks in the 3.8–5.5 ppm region (see Figure 1). The reaction of chloro ketone **3** with 1

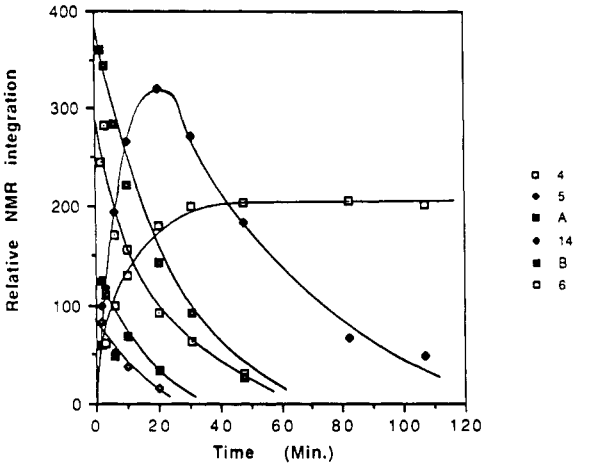


Figure 1. Product evolution with time in the reaction of **3** with TEA as measured by NMR.

molar equiv of Et_3N in CD_3CN–D_2O at 20 °C revealed that within 2 min all starting chloro ketone had disappeared. The presence of dimers **4** and **14** was detected, as well as the presence of new intermediates A and B apparently derived from **4** and **14**. ^{1}H NMR indicated a diastereoselectivity in favor of **4** over **14** of ca. 4:1. The benzylic position (C-8′) in all compounds had been deuterated within the first 2 min. As decay of **4** and A proceeded, isomer **5** became the major new component formed (see Figure 1). At the same time the disappearance of **14** and B was rapid and accompanied by formation of lactone **6** (half-life approx. 5 min). Further transformations of **5** to new products occured with time, whereas **6** remained more or less constant.

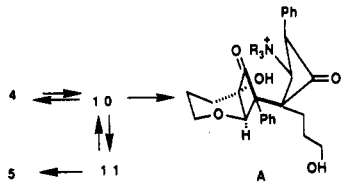
We then monitored by ^{1}H NMR the rapidly disappearing mixture of diastereomers **4** and **14** (85:15) in the presence of Et_3N or in the presence of $Et_3NH^+Cl^-$. The distinction between the two diastereomers is the high field axial proton (H-4′ ax) at 0.23 ppm in **4** (in CD_3CN–D_2O) due to shielding by a phenyl group. Furthermore, the benzylic H-8′ proton is observed as a doublet (J = 8 Hz) at 5.30 ppm (in CD_3CN–D_2O) for isomer **4**, while in its diastereomer **14**, it is shifted upfield to 3.96 ppm (d, J = 9 Hz). Molecular models indicate that this paramagnetic shift may be due to the fact that the benzylic H-8′ in **14** is located in the shielding cone of the C-7 carbonyl group, if one assumes a preferred conformer with H-bonding between the *tert*-hydroxyl and the C-7′ carbonyl group. Other readily identifiable protons of **14** appear at 5.18 (d, H-1′, J = 9 Hz) and 4.68 (s, H-1).

Dimer **4** was found to undergo a slow reaction in the presence of 1 mol equiv of $Et_3NH^+Cl^-$ in CD_3CN–D_2O at 20 °C. The half-life for disappearance of **4** is approx. 2 h and only very slow D-exchange of H-8′ was observed. As **4** disappeared an intermediate, presumably **10**, was observed (the vinylic proton of the cyclobutenone appears as a singlet at 8.42 ppm) and soon isomer **5** appeared. The approximate half-life for conversion of **10** to **5** was calculated to be 25 min. **5** was stable for 24 h under these conditions as was dimer **14** which remained unchanged.

When the reaction of **4** and **14** in CD_3CN–D_2O in the presence of 1 mol equiv of Et_3N was monitored by ^{1}H NMR, immediate D-exchange of H-8′ was observed as well as fast formation of intermediates A (singlets at 4.88 and 4.17 ppm) and B (singlets at 4.48 and 4.03 ppm) different from **10**. Within a few minutes both **4** and A disappeared and mainly isomer **5** was present as well as unidentified transformation products of **5**. At the same time disappearance of **14** and B led to lactone **6**. When the same

(15) We assume that the ring junction of the fused cyclobutanone will always be cis and that approach of the bicyclic system will be preferentially from the convex side.

Scheme IV



reaction was monitored in the presence of the more hindered diisopropylethylamine, all transformations including D-exchange were slower than with Et_3N and the ratio of 4/A was much larger.

These NMR experiments suggest that ring opening of **4** to an enone **10** is both acid and base catalyzed (faster with base and reversible). In the presence of base, reversible Michael addition of R_3N to enone **10** produces an adduct, presumably of structure A. A competing intramolecular Michael addition of the tertiary alcohol to the enone moiety drains **10** via **11** (Scheme IV) into the cage compound **5**. The latter reacts further with base.

A similar scenario converts **14** via a cyclobutenone isomer of **10** to B, an analogue of A, except that here **14** is drained off to lactone **6** via intermediate **15**. Apparently, lactone **6** is stable to further transformations under reaction conditions.

In conclusion, we have shown that chlorobicyclooctanone **3** undergoes a fast transformation in which a dimeric product **4** (major) and its diastereomer **14** (minor) are formed efficiently, apparently via an oxidoallyl cation and a derived enolate, leading to a bond between two quaternary carbons. Further transformations of **4** and **14** are guided by proximity effects and relief of strain and lead to novel cage molecules **5**, **6** and **7**.

Experimental Section

8-Phenyl-8-chloro-2-oxa-*cis*-bicyclo[4.2.0]octan-7-one (3). A three-neck flask equipped with a reflux condenser, addition funnel, and gas inlet was charged with 5 g (0.026 mol) of 2-chloro-2-phenylacetyl chloride and 25 mL of dihydropyran. To this refluxing mixture under Ar was added dropwise a solution of 4.4 mL (0.026 mol) of TEA in 15 mL of dihydropyran over a 30-min period. Stirring was continued for 1 h and the $Et_3N^+HCl^-$ salt was filtered, and the filtrate was washed successively with 5% HCl, 10% $NaHCO_3$, and saturated NaCl and dried ($MgSO_4$). Removal of the solvent in vacuum gave a solid which was recrystallized from MeOH to give (4.6 g) white crystals of **3** (75%): mp 74 °C; ^1H NMR ($CDCl_3$) δ 7.58 (m, 2 H), 7.35 (m, 3 H), 4.65 (d, J = 5.5 Hz, H-1), 4.09 (dddd, J = 7.5, 5.5, 2, 0.5 Hz, H-6), 3.77 (dq, J = 11, 2.5 Hz, H-3 eq), 3.31 (ddd, J = 11, 8, 6 Hz, H-3 ax), 2.22 (dddd, J = 14.5, 5.5, 3.5, 2.5 Hz, H-5 eq), 1.73 (ddt, J = 14.5, 10.8 Hz, H-5 ax), 1.47 (m, H-4 eq, ax); ^{13}C NMR ($CDCl_3$) δ 201.4 (C-7), 133.8, (ipso), 128.7, 128.4, 128.1, 73.9 (C-1), 65.1 (C-3), 54.1 (C-6), 21.7 (C-5), 18.6 (C-4); IR (KBr) 1770, 1440 cm^{-1}; MS (CI) m/e 237 (MH^+), 203 (MH^+ - Cl), 201 (M - HCl), 173 (M - CO). Anal. Calcd for $C_{13}H_{13}O_2Cl$: C, 65.98; H, 5.54. Found: C, 65.99, H, 5.61.

To 0.2 (0.85 mmol) of chloro ketone **3** and 0.1 g of $LiClO_4$ in CH_3CN/H_2O (9:1), was added 1.1 equiv of Et_3N. The mixture was stirred at 20 °C for 5–30 min, and then a few drops of 5% aqueous HCl were added and the solvent was removed in vacuum. The residue was dissolved in CH_2Cl_2 and the solution washed successively with water and saturated NaCl and dried ($MgSO_4$). Removal of the solvent left a mixture of dimers that was chromatographed on silica gel (EtOAC/hexne (1:4 to 1:2)), and each dimer was crystallized separately. After 5-min reaction time and repeated crystallization, **4** was isolated in 35% yield, **5** in 17%, and **7** in 12% yield.

After 30-min reaction time and chromatography, dimer **5** was isolated in 43%, dimer **7** in 10%, and a mixture of **4** and **6** in 30% yield.

6-Hydroxy-8-phenyl-8-[8′-phenyl-2′-oxa-*cis*-7′-oxobicyclo[4.2.0]oct-6′-yl]-2-oxa-*cis*-bicyclo[4.2.0]octan-7-one (4) was recrystallized from CH_2Cl_2/petroleum ether to give white crystals: mp 140 °C; IR (KBr) 3500, 1790, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40 (m, 10 H), 5.27 (d, J = 8 Hz, H-8′), 5.14 (d, J = 8 Hz, H-1′), 4.07 (d, J = 1.5 Jz, H-1), 3.74 (td, J = 12, 2.5 Hz, H-3-ax), 3.61 (dm, J = 12 Hz, Hx-3 eq), 3.40 (m, H-3′ ax, eq), 2.68 (dm, J = 16 Hz, H-5′ eq), 1.90 (ddd, J = 14.5, 13, 4.5, H-5′ ax), 1.85–1.40 (m, H-5 ax, eq, H-4 ax eq), 1.09 (d quin, J = 14, 2.5 Hz, H-4′ eq), 0.11 (qt, J = 12, 4.5 Hz, H-4′ ax); ^{13}C NMR ($CDCl_3$) δ 210.84 (C-7), 209.65 (C-7), 133.91 (ipso), 132.31 (ipso), 128.9, 128.4, 128.4, 127.9, 127.6, 127.00, 84.5 (C-6), 79.3 (C-1), 69.7 (C-1′), 69.6 (C-8), 64.2 (C-6′), 62.8 (C-3), 60.4 (C-3′), 59.6 (C-8′), 24.2 (C-5), 22.6 (C-5′), 20.3 (C-4′), 17.1 (C-4); MS CI (isobutane) m/e 419 (MH^+), 447 (M + C_2H_5+), 401 (M - H_2O), 391 (M - CO). Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.32; H, 6.22.

4,7-Diphenyl-6-(3′-hydroxypropyl)-13-hydroxy-2,9-dioxa-5-oxopentacyclo[5.5.1.0^{1,8}.0^{3,6}.0^{4,13}]tridecane (5). The dimer was recrystallized from EtOAC–hexane to give needles of mp 153 °C: IR (KBr) 3420, 1780, 1715, 1685 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.57 (m, 2 H), 7.45–7.15 (m, 8 H), 5.25 (OH), 4.78 (s, H-1′), 4.35 (s, H-1), 3.70 (dm, J = 11 Hz, H-3 eq), 3.49 (t, J = 5.5 Hz, H-3′), 3.34 (td, J = 11, 1.5 Hz, H-3 ax), 2.10–1.30 (m, H-2, H-3, H-2′, H-3′); ^{13}C NMR δ 198.39 (C-7′), 134.9 (ipso), 133.0 (ipso), 129.9, 128.1, 128.9, 128.3, 128.0, 127.1, 96.1 (C-7), 83.0 (C-6), 78.7 (C-1), 76.3 (C-6′), 75.1 (C-1′), 74.5 (C-8), 65.3 (C-3), 62.4 (C-3′), 55.6 (C-8′), 29.2 (C-5′), 24.8 (C-5), 22.9 (C-4), 20.4 (C-4′); MS CI (NH_3) m/e 436 (M + NH_4^+), 419 (MH^+). Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.59; H, 6.16.

1-Hydroxy-2,8-diphenyl-4,11,16-trioxa-17-oxopentacyclo-[8.5.1.2^{8,15}.0^{3,8}.0^{10,15}]octadecane (6). Dimer **6** was recrystallized from CH_2Cl_2/petroleum ether to give crystals of mp 180 °C: IR (KBr) 3492, 1745, 1597, 1492 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60–7.00 (m, 10 H), 4.21 (s, H-1), 4.18 (d, J = 11 Hz, H-1′), 3.96 (dd, J = 7.5, 3.5 Hz, H-3′ eq), 3.87 (dm, J = 9.5 Hz, H-3 eq), 3.80 (d, J = 11 Hz, H-8), 3.39 (m, H-3 ax), 3.35 (m, H-3′ ax) 2.64 (qt, J = 9, 3.5 Hz, H-4′ ax), 2.32 (dm, J = 9.5 Hz, H-5 eq), 2.11 (broad dt, J = 9.5, 3 Hz, H-5′ eq), 1.97 (m, H-4 ax), 1.87 (td, J = 8, 4 Hz, H-5 ax), 1.72 (m, H-4 eq), 1.29 (dm, J = 9 Hz, H-4′ eq), 0.96 (td, J = 9, 3.5 Hz, H-5′ ax); ^{13}C NMR ($CDCl_3$) δ 170.3 (C-7), 135.1, (ipso) 131.9 (ipso), 129.7 129.0, 128.7, 128.4, 127.8, 127.4, 87.3 (C-6), 83.3 (C-1′), 80.4 (C-7′), 78.2 (C-1), 69.2 (C-3′), 65.6 (C-3), 63.0 (C-6′), 56.3 (C-8), 47.8 (C-8′), 27.8 (C-5′), 23.7 (C-5), 22.8 (C-4), 21.1 (C-4′). MS CI m/e 419 (MH^+), 447 (M + C_2H_5), 401 (M - H_2O). Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.44; H, 6.07.

9,16-Diphenyl-15-hydroxy-2,4,11-trioxa-17-oxopentacyclo[6.6.3.0^{1,10}.0^{9,15}.0^{3,8}]heptadecane (7). Dimer **7** was recrystallized from CH_2Cl_2/petroleum ether, mp 183 °C: IR (KBr) 3506, 3055, 1731, 1654 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40 (m, 10 H), 5.50 (s, H-1), 4.64 (s, H-1′), 4.22 (s, H-8′), 4.11 (dm, J = 11 Hz, H-3 eq), 4.04 (broad dd, J = 11, 5 Hz, H-3′ eq), 3.95 (OH), 3.57 (m, H-3′ax, H-3 ax), 2.05 (td, J = 14, 5 Hz, H-5 ax), 2.00–1.5 (m, 6 H), 1.28 (dm, J = 11 Hz, H-4 eq), 1.08 (dm, J = 15 Hz, H-5 eq); we cannot distinguish between the H's and C's in the two ether rings; ^{13}C NMR δ 213.70 (C-7′), 134.64 (ipso), 132.4 (ipso), 128.4, 128.2, 127.4, 127.0, 98.2 (C-1′), 92.6 (C-7), 80.7 (C-6), 77.7 (C-1), 66.6, 66.5 (C-3, C-3′), 61.4 (C-8), 60.2 (C-8′), 26.0, 23.9, 23.3, 20.8 (C-4, C-5, C-4′, C-5′); MS CI m/e 419 (MH^+). Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.33; H, 6.27.

NMR Studies. Spectra were taken at 300.13 (^1H) and 75.47 (^{13}C) MHz, respectively. In the kinetic runs all the peaks in the δ 3.8–5.5 were integrated except for the benzylic protons (H-8′) which had experienced exchange. All the other proton signals were singlets or broad singlets under these conditions. The error in the integration is estimated to be ±10%.

Supplementary Material Available: Tables 1–4 giving crystallographic data, fractional coordinates, bond lengths, and bond angles for dimer **6** and crystal structure analysis (17 pages). Ordering information is given on any current masthead page.