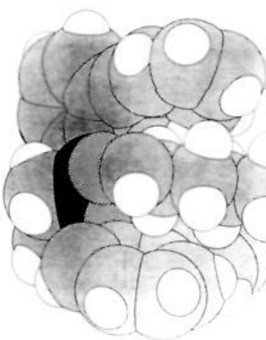

Figure 1. Space-filling model of the valeraldehyde–MAPH complex.

2 and **3** (Nu = Bu; 41% combined yield) in a ratio of 1:1.4, which is similar to the ratio (1:1.9) in the absence of MAD. This result suggests that MAD is not employable as a protection agent of sterically less hindered aldehyde carbonyl by coordination complex formation. In marked contrast, however, methylaluminum bis(2,6-diphenylphenoxide) (MAPH),[8] on treatment of an equimolar mixture of valeraldehyde and cyclohexanecarboxaldehyde, is capable of stabilizing the sterically less hindered valeraldehyde carbonyl as confirmed by the subsequent addition of BuLi, giving the carbinols **2** and **3** (Nu = Bu; 76% combined yields) in a ratio of 1:6.5. Furthermore, use of excess MAPH (2 equiv) resulted in greater selectivity (1:14), indicating that decomplexation of the more hindered cyclohexanecarboxaldehyde and MAPH is more readily facilitated by the action of BuLi. Other selected examples included in Table I clearly demonstrate the effectiveness of MAPH in the recognition and stabilization of structurally less hindered aldehydes based on the selective Lewis acid–base complex formation, thereby allowing chemoselective functionalization of more hindered aldehydes. Discrimination even at the β-carbon of aldehydes can be achieved by pairing valeraldehyde with 3,3-dimethylbutyraldehyde (entries 7 and 8). The opposite chemoselectivity is easily accessible to a moderate or great extent using $RTi(OPr^i)_3$ reagents.[2] Excellent chemoselective alkylation is observable between aldehydes and ketones (entries 12–14).[5,6]

The existence of hypothetical aldehyde–MAPH complexes was verified by carrying out a ^1H NMR spectral study of several coordination complexes in $CDCl_3$, where *the upfield shift of aldehyde protons in the aldehyde–MAPH complexes from free aldehydes is always observed* [e.g., 0.82 (CH_3), 0.98 (γ-CH_2), 0.50 (β-CH_2), 1.13 (α-CH_2), and 6.93 (CH=O), respectively, in the valeraldehyde–MAPH complex in $CDCl_3$ at 25 °C].[9] Since dimethylaluminum 2,6-diphenylphenoxide and methylaluminum bis(2-phenylphenoxide) as MAPH analogues are totally ineffective for recognition and stabilization of aldehydes,[9] the origin of the remarkable effect of MAPH on such stabilization is worthy of comment. In a space-filling model of the valeraldehyde–MAPH complex (Figure 1), each phenyl group of the two phenoxy ligands is parallel to the other in front of the Lewis acidic aluminum, so that the valeraldehyde carbonyl by coordination to MAPH is electronically stabilized by a sandwich structure between these two phenyl groups. This inference is in accord with the ^1H NMR data on the upfield shift of aldehydic protons in the aldehyde–MAPH complexes. A more sophisticated design of aluminum ligands and a more detailed characterization of aldehyde recognition by the designer aluminum reagents are subjects of our ongoing study.

Supplementary Material Available: Listings of structural information for complexes of aldehyde–MAPH and aldehyde–MAPH analogues by ^1H NMR spectroscopy (2 pages). Ordering information is given on any current masthead page.

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(9) For details, see the supplementary material.

A Novel Star-Shaped Crown Ether: Spontaneous Isomerization of a Macrocyclic Polyketone to a Spirobicyclic Polyketal

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We have been interested for many years in the synthesis and properties of [1_n]orthocyclophanes. Since the benzylic methylenes of these cyclophanes are susceptible to chemical reactions, these substances are expected to be precursors to novel macrocycles. Although we have reported the synthesis of [1_3]-,[1] [1_4]-, and [1_5]orthocyclophanes,[2] higher homologs have not been synthesized to date. However, the methoxy derivative of [1_6]orthocyclophane *has been reported*[3] *recently. This communication describes the* synthesis and functionalization of [1_6]orthocyclophane. During the oxidation of [1_6]orthocyclophane we discovered a new reaction in which the direct conversion of a cyclic polyketone to an isomeric polyketal takes place.

The condensation of reagent **1**, prepared by dilithiation of 1,2-bis(2-bromobenzyl)benzene,[4] with dialdehyde **2**,[5] followed by oxidation of the resultant cyclic diol with PCC, afforded dioxo-[1_6]orthocyclophane (**3**).[6] Reduction of **3** was attempted using various reducing agents, but [1_6]orthocyclophane could not be obtained in pure form because of the insolubility of the hydrocarbon. On the other hand, when oxidation of **3** was attempted using a variety of oxidizing agents in order to prepare the corresponding polyoxo derivative, an extraordinary reaction took place. Thus, oxidation of **3** by heating with ceric ammonium nitrate (CAN) in acetic acid for 7 days did not give the expected hexaketone **5**, but resulted in the isomeric polyketal **7** with mp > 350 °C (Scheme I).

The generation of polyketal **7** from the oxidation of diketone **3** was surprising, and the reaction was therefore carefully examined. Mild oxidation of **3** with CAN for 7 days at room temperature furnished pentaoxo[1_6]orthocyclophane (**4**) as the main product. Further oxidation of **4** with the same oxidant at 80 °C for 7 days generated the polyketal **7**. The reaction sequence is presumed to involve successive oxidation of **3** to the corresponding tri-, tetra-, penta-, and finally hexaketone **5**, which then rearranged to **7**.

The polyketal **7** was characterized by spectral and X-ray analyses. The IR spectrum of **7** did not contain a carbonyl frequency, but showed strong vibrations at 1150–1050 cm^{-1}, revealing the presence of the ether linkages. The ^1H NMR showed only aromatic proton resonances at δ 7.52–7.27, and the ^{13}C NMR displayed four resonances, three at δ 142.51, 128.99, and 123.11 (attributable to aromatic carbons) and one at δ 113.18 (attributable to ketal carbons). The simplicity of the ^{13}C NMR spectrum discloses the high symmetry of the compound. The EIMS gave the molecular ion (M^+) m/z 624 as the base peak, and HRMS revealed the exact mass to be 624.1666 (calcd for $C_{42}H_{24}O_6$ 624.1573). From these spectral data, we deduce that the oxidation product must be the spiropolycyclic ketal **7**. An X-ray analysis confirmed the structure **7**.[7] An ORTEP diagram of the molecular

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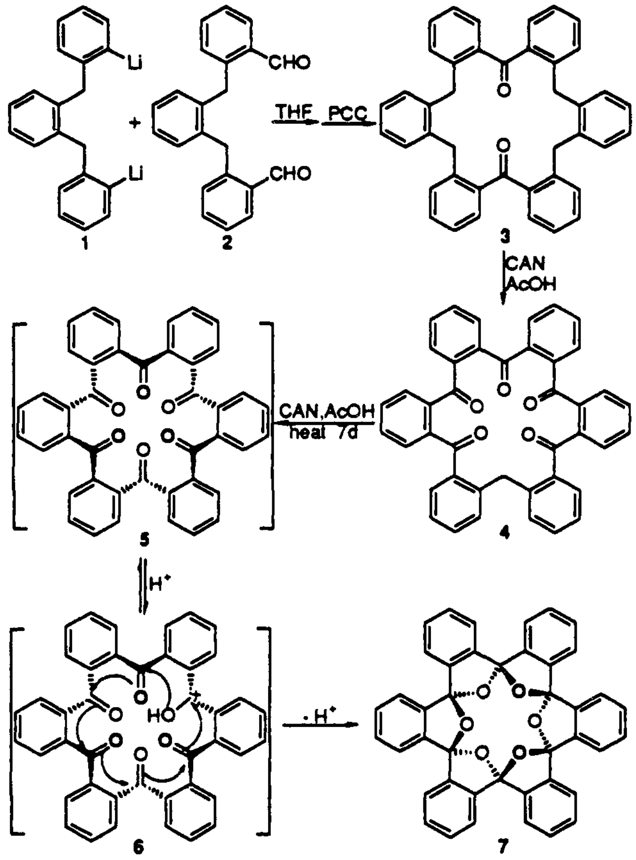
(6) The cyclic diketone **3** is a powder: mp >290 °C dec; IR 1660 cm^{-1}; ^1H NMR δ 7.34–6.90 (m, 24 H, Ar*H*), 4.02 (s, 8 H, ArCH_2); HRMS; found M^+ 568.2368, calcd for $C_{42}H_{32}O_2$ M 568.2402.

0002-7863/93/1515-1184$04.00/0

Scheme I



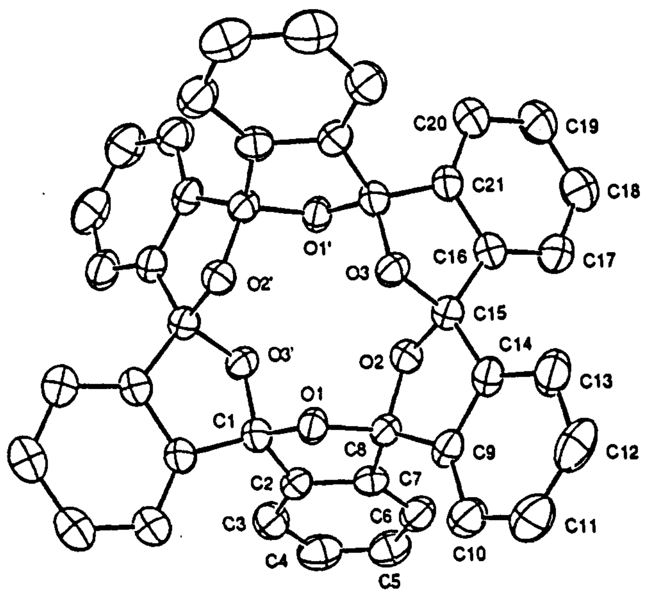


Figure 1. ORTEP diagram of 7.

geometry is presented in Figure 1. The polyketal 7 contains a 12-crown-6 moiety incorporated with a $[1_6]$orthocyclophane inside the macrocycle. The up-down-up conformation of the six oxygen atoms gives rise to a preorganized spherical cavity of diameter 1.02 Å. The six benzylic carbon atoms in 7 form a plane (rms 0.0085 Å), from which oxygen atoms deviate by about 0.8 Å.

Inspection of the CPK model of hexaketone **5** indicates that the preferred conformation has an up-down-up arrangement of the six carbonyl functions, causing serious steric strain in the molecule. It appears therefore that, as soon as it is produced, **5** undergoes rapid rearrangement, probably via the oxonium ion **6**, resulting in sp^2-to-sp^3 rehybridization in each ketonic carbon to give the strain-free **7**. This is an unprecedented reaction. The cyclic hexaketal **7** is a novel coronand containing the 2*n*-crown-*n* moiety. When viewed from above, the oxygen atoms of **7** form a six-pointed star. Although a number of coronands have been synthesized[8] during the last two decades, in most cases the oxygens are separated by hydrocarbon spacers having two or more bridging atoms, such as dimethylene, trimethylene, or *o*- or *m*-phenylene units. The 2*n*-crown-*n*-type coronands, whose oxygens are separated from one another by one carbon atom, have not been reported. Although $(CH_2O)_n$ cyclic structures (e.g., paraformaldehyde) are labile, the polyketal **7**, which is composed of $(CR_2O)_6$ units incorporated with a $[1_6]$orthocyclophane, is stable. Generation of homologs of the star-shaped coronand **7** can be anticipated from oxidation of other even-number $[1_n]$orthocyclophanes.

Acknowledgment. This work has been supported by a grant from the Nondirected Research Fund, Korea Research Foundation, 1992. The authors are grateful to Professor D. J. Cram for his advice.

Supplementary Material Available: NMR and EIMS spectra for 1,2-bis(2-bromobenzyl)benzene, **3**, **4**, and **7** and an IR spectrum, crystallography data, and ORTEP, and a stereoview for **7** (31 pages); tables of structure factors for **7** (48 pages). Ordering information is given on any current masthead page.

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(7) X-ray analysis: 7 crystallizes in the monoclinic space group $P2_1/c$ (No. 14); a = 15.813(6), b = 13.108(1), c = 20.257(7) Å; β = 109.35(2)°; V = 3961.6 Å^3; $d_{\rm calcd}$ = 1.25 g/cm^3; Z = 4. Data were collected on an Enraf-Nonius CAD4 diffractometer. Of the 5142 unique data collected with Mo Kα radiation (λ = 0.71073 Å), the 4212 with $F_o > 1.0\sigma(F)$ were used in the least-squares refinement to yield R = 5.2%, R_w = 6.9% after an empirical absorption correction based on Ψ-scan data was applied.

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Electrocrystallization and ESR Spectra of the Single Crystal $[N(P(C_6H_5)_3)_2]\cdot C_{60}$

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Since the discovery of superconductivity at 18 K for K_3C_{60},[1] the alkali-metal fullerides have been the object of considerable research. So far, however, the solid-state properties of fulleride single-crystals have not yet been clarified. The preparation of

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