shifts clustered at ~1.5 or ~3.4 Å[16] and with mean plane separations of 3.30 Å upwards. Dimeric $[M(OEP^{\bullet})]_2^{2+}$ systems[17-19] are completely overlapped (zero lateral shift) and have mean plane separations of 3.25-3.35 Å.[20] The $[M(OEP^{\bullet/2})]_2^{+}$ derivatives have lateral shift values (0.8-1.0 Å) and inter-ring Ct···Ct distances that are about halfway between those of the oxidation extremes. These structural data, along with the recent observation of Le Mest et al.[21] that only certain dimeric, covalently linked, cofacial porphyrin systems can be electrochemically oxidized by 1 equiv per two rings, suggest that there are particular inter-ring geometries that stabilize the partially oxidized species and that are distinctly different from either the neutral or fully oxidized analogs. The importance of the inter-ring geometry in stabilizing a "special pair" is an intriguing question that is being further explored in these laboratories. Whether oxidation-reduction rates are also affected by the inter-ring geometry remains a question to be explored.

Acknowledgments. We thank the National Institutes of Health for support of this research (Grant GM-38401 to W.R.S. and GM-23851 to C.A.R.). W.R.S. thanks Dr. J. Fajer for helpful discussions on the spectra of photooxidized reaction centers.

Supplementary Material Available: Tables (SI-SIV) of atomic coordinates, bond distances, and bond angles for $[M(OEP^{\bullet/2})]_2SbCl_6$ (M = Ni, Cu) (8 pages); observed and calculated structure amplitudes (×10) (26 pages). Ordering information is given on any current masthead page.

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Chemoselective Functionalization of More Hindered Aldehyde Carbonyls with the Methylaluminum Bis(2,6-diphenylphenoxide)/Alkyllithium System

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Received October 23, 1992

The chemoselective functionalization between two different carbonyl substrates is a synthetically useful operation and is closely related to the chemistry of molecular recognition.[1] The discrimination between two different aldehydes or between aldehydes and ketones is commonly achievable by using bulky organometallic reagents or bulky Lewis acids to discriminate the structural or electronic environment of the carbonyl group, in which the sterically less hindered or electronically more labile aldehyde is more easily functionalized.[2-4] For example, titanium reagents of the type $RTi(OPr^i)_3$ offer the most satisfactory results for this selective transformation.[2] However, the opposite selectivity, i.e., chemoselective functionalization of the sterically more hindered aldehyde carbonyl, seems quite difficult to attain in view of the high reactivity of the paired aldehydes toward nucleophiles, and hence it has not yet been realized in spite of long-standing concern.[5,6] Here we wish to disclose our initial results on this subject using certain modified organoaluminum reagents, featuring a Lewis acidic molecular cleft for recognition and stabilization of structurally similar aldehydes based on the selective Lewis acid-base complex formation (Scheme I).

Scheme I

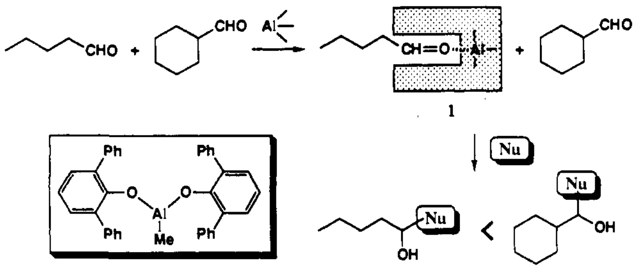
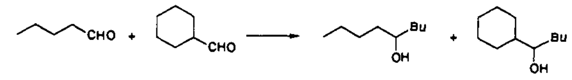
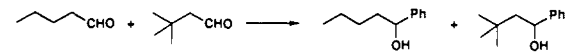
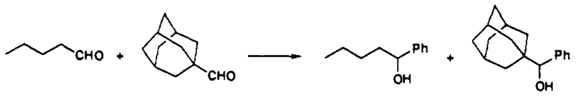
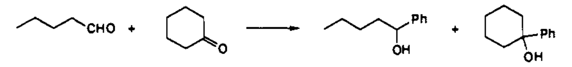


Table I. Chemoselective Functionalization between Two Different Carbonyl Substrates[a]

entry	reagent (equiv)	conditions (°C, h)	yield[b] (%)	ratio[c]
				
1	$BuTi(OPr^i)_3$ (1)	-40, 1; 28, 34	31	2.5 : 1
2	BuLi (1)	-78, 0.25	76	1 : 1.9
3	MAD (1)/BuLi (1)	-78, 0.3	41	1 : 1.4
4	MAPH (1)/BuLi (1)	-78, 0.3	76	1 : 6.5
5	MAPH (2)/BuLi (1)	-78, 0.3	45	1 : 14
				
6	$PhTi(OPr^i)_3$ (1)	-40, 1	60	3.3 : 1
7	MAPH (1)/PhLi (1)	-78, 0.5	80	1 : 4.3
8	MAPH (2)/PhLi (1)	-78, 0.5	60	1 : 10.8
				
9	$PhTi(OPr^i)_3$ (1)	-40, 2	80	10.1 : 1
10	MAPH (1)/PhLi (1)	-78, 0.5	60	1 : 2.9
11	MAPH (2)/PhLi (1)	-78, 1	58	1 : 24
				
12	$PhTi(OPr^i)_3$ (1)	-40, 1	83	>99 : 1
13	MAPH (1)/PhLi (1)	-78, 0.5	90	1 : 2.7
14	MAPH (2)/PhLi (1)	-78, 1	68	1 : 56

[a] The alkylation of two different carbonyl substrates (1 equiv each) was carried out in CH_2Cl_2. [b] Isolated yield. [c] Determined by capillary GLC and/or 200-MHz ^1H NMR analysis.

First, we examined the possibility of discriminating two different aldehyde carbonyls with the exceptionally bulky, oxygenophilic methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD), which was recently introduced for the selective reduction of one out of two different ketone carbonyls by combining certain hydride reagents.[7] Attempted treatment of a mixture of 1 equiv each of MAD, valeraldehyde, and cyclohexanecarboxaldehyde in CH_2Cl_2 at -78 °C with BuLi in hexane afforded two carbinols

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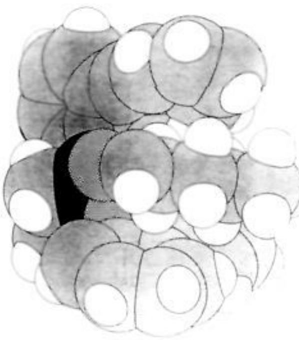

Figure 1. Space-filling model of the valeraldehyde–MAPH complex.

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 ^{1}H 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 ^{1}H 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 ^{1}H 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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Received November 18, 1992

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 ^{1}H 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}; ^{1}H NMR δ 7.34–6.90 (m, 24 H, Ar*H*), 4.02 (s, 8 H, ArC*H*$_2$); HRMS; found M$^+$ 568.2368, calcd for $C_{42}H_{32}O_2$ M 568.2402.

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