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**Supplementary Material Available:** Characteristic  $^{13}\text{C}$  NMR data for free ethers and their complexes with MAD and experimental details and figures for complexation chromatography (6 pages). Ordering information is given on any current masthead page.

## Generation and Trapping of 1,5-Dehydroquadracyclane

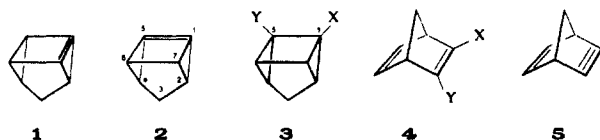
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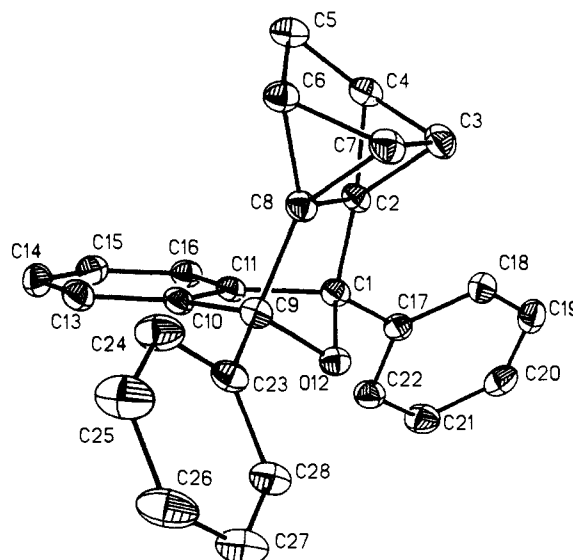
Several years ago evidence was provided for the existence of 1,7-dehydroquadracyclane (**1**) as a reactive intermediate.<sup>1-3</sup> **1** was generated by treatment of **3f** with lithium 2,2,6,6-tetramethylpiperidine in the presence of anthracene, 2,5-dimethylfuran, or trimethylisindole and trapped as a Diels-Alder adduct. Under these reaction conditions, no indications were obtained for the formation of 1,5-dehydroquadracyclane (**2**), whereas the reaction of **3f** with *n*-butyllithium proceeded via **1** as the major and **2** as the minor intermediate.<sup>1,2</sup> We now report on the controlled generation of **2** and on some trapping experiments of this highly strained pyramidalized bridgehead olefin.

Schlosser<sup>4</sup> and Brandsma<sup>5</sup> have shown independently that norbornadiene **4a** can be metalated at the vinylic position to give **4b** (or **4c/d**) by the mixture of *n*-butyllithium (BuLi) and sodium *tert*-butoxide or potassium *tert*-butoxide in tetrahydrofuran at -78 °C. We have used this reaction and converted **4d** with 1,2-dibromoethane into 2-bromonorbornadiene **4e** in 40% yield and with 4-toluenesulfonyl chloride into 2-chloronorbornadiene **4f** in 34% yield.



	3	4	a	b	c	d	e	f	g	h	i	j	k	l
X	H	Li	Na	K	Br	Cl	Br	Cl	Br	Cl	Br	Br	Br	Br
Y	H	H	H	H	H	H	H	Cl	Li	Li	K	Br	Br	SiMe <sub>3</sub>

With respect to **4a**, the acidity of C-3 in **4e** and **4f** should be enhanced by the vicinal halide. Indeed, treatment of **4f** with *tert*-butyllithium (*t*-BuLi) in THF/pentane at -78 °C for 45 min produced a yellow precipitate. Addition of 1,2-dibromoethane to the stirred suspension, warming to room temperature, and aqueous workup afforded a 44% yield of 2-bromo-3-chloronorbornadiene **4g**.<sup>7,8</sup> The  $^{13}\text{C}$  NMR spectrum of the precipitate in THF-*d*<sub>6</sub> was consistent with 2-chloro-3-lithionorbornadiene **4h** [58.22 (d), 60.28 (d), 72.18 (t), 139.91 (d), 144.45 (d), 159.47



**Figure 1.** ORTEP view of **6a**. The thermal ellipsoids are drawn at the 20% probability level. Hydrogens were omitted for clarity. Selected interatomic distances are as follows (Å): C1-O12, 1.481 (3); C1-C2, 1.519 (4); C1-C11, 1.520 (5); C1-C17, 1.500 (4); C2-C3, 1.516 (5); C2-C4, 1.492 (4); C2-C8, 1.546 (4); C3-C4, 1.529 (5); C3-C7, 1.536 (4); C4-C5, 1.517 (4).

(s), 178.55 (s)]. Mixtures of **4h** in THF were stable at room temperature, but decomposed in boiling THF in the presence of 2,5-dimethylfuran to a black solution, from which **4f** was isolated as the sole product. No evidence was observed for the formation of norbornenyne **5**.<sup>9</sup>

Fast lithium-bromine exchange excluded the use of *t*-BuLi as a base for the lithiation of **4e** to give **4i**. **4j** was obtained by reaction of **4d** with the bromide **4e** in THF at -65 to -55 °C for 2 h. Addition of 1,2-dibromoethane to the suspension of **4j** afforded a 65% yield of **4k**. The reaction sequence allows a one-pot synthesis of **4k** starting from **4a** without isolation of **4e**: After metalation of norbornadiene with BuLi/KO-*t*-Bu in THF at -105 to -35 °C, 0.50 equiv of 1,2-dibromoethane was added and the mixture kept at -35 °C for 1 h. Addition of the remaining 0.50 equiv of dibromoethane at -35 °C, warming to room temperature, and aqueous workup gave rise to a 53% yield of **4k**.<sup>8,10</sup>

Conversion of **4g** and **4k** into the quadracyclanes **3g**<sup>11</sup> and **3k**<sup>8,12</sup> was achieved in yields of 66 and 77% by irradiating 0.40 M solutions of the norbornadienes in ether at room temperature with a 150-W mercury high-pressure lamp in a glass apparatus in the presence of 5 mol % of acetophenone.

When a solution of **3k** in THF/pentane at -78 °C was treated with 2.0 equiv of *t*-BuLi and the mixture kept at this temperature for 1 h, addition of chlorotrimethylsilane led to bromosilane **3l** in 60% yield. This result indicates that **3l** was formed by lithium-bromine exchange, but that at -78 °C LiBr elimination to give **2** did not take place. However, when the cooled solution (-78 °C) of **3l** was transferred by syringe to a solution of diphenylisobenzofuran in THF and the mixture was allowed to warm to 20 °C and kept at this temperature for 30 min, aqueous workup and removal of excess diene with maleic anhydride<sup>13</sup> afforded a 40% yield of an 84:16 mixture of **6a**<sup>8,14</sup> and **7a**.<sup>8,15</sup> **7a** was less

(1) Harnisch, J.; Baumgärtel, O.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 3370.

(2) Baumgärtel, O.; Szeimies, G. *Chem. Ber.* **1983**, *116*, 2180.

(3) Baumgärtel, O.; Harnisch, J.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *Chem. Ber.* **1983**, *116*, 2205.

(4) Stähle, M.; Lehmann, R.; Kramář, J.; Schlosser, M. *Chimia* **1985**, *39*, 229.

(5) Verkruisje, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 66.

(6) **4e** and **4f** are known compounds: see ref 2. For **4f**, see also: Davies, D. I. *J. Chem. Soc.* **1960**, 3669.

(7) **4g**: bp 74-77 °C/12 Torr;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) δ 56.88 (d), 57.88 (d), 71.42 (t), 128.24 (s), 140.99 (d), 141.57 (d), 143.93 (s).

(8) Further spectral data are available as supplementary material.

(9) The intermediacy of 2-norbornyne has been established: Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6864.

(10) **4k**: bp 85-86 °C/12 Torr;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) δ 58.52 (d), 71.84 (t), 132.91 (s), 141.09 (d).

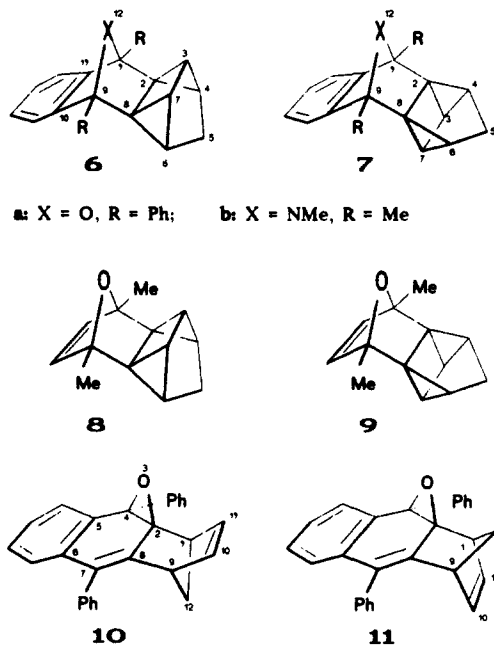
(11) **3g**: bp 20 °C/0.01 Torr;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) δ 24.17 (d), 24.93 (d), 30.68 (t), 34.38 (d), 35.17 (d), 39.07 (s), 49.80 (s).

(12) **3k**: bp 25 °C/0.01 Torr;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) δ 24.84 (d), 30.93 (t), 35.04 (d), 39.19 (s); HRMS calcd for C<sub>7</sub>H<sub>7</sub>Br<sup>81</sup>Br 249.881, found 249.876.

(13) Wittig, G. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 964.

(14) **6a**: mp 151-153 °C;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>) δ 15.45 (d, C-3, C-7), 25.75 (d, C-4, C-6), 36.26 (t, C-5), 42.01 (s, C-2, C-8), 87.93 (s, C-1, C-9), 118.98, 126.79, 127.09, 128.15, 128.27 (5 d), 136.21, 146.29 (2 s).

soluble in ether than **6a** and could be purified from that solvent, whereas **6a** was obtained pure after several crystallization from acetonitrile. The structure of **6a** was determined by X-ray diffraction<sup>16</sup> and is depicted in Figure 1.<sup>17</sup>



At 83:17, the ratio of **6a** to **7a** (total yield 36%) remained practically unchanged when the reaction sequence was carried out with **3g** instead of **3k**. The result is in accord with **2** as the common intermediate.

In two further experiments, a solution of **3i** in THF/pentane was allowed to warm from  $-78\text{ }^{\circ}\text{C}$  to room temperature in the presence of 1,2,3-trimethylisindole and, respectively, of 2,5-dimethylfuran. In the first case, aqueous workup afforded a 65% yield of adduct **6b**.<sup>8,18</sup> NMR spectroscopy of the crude material did not provide any evidence for the formation of the syn isomer **7b**. With dimethylfuran as a trap for **2**, a 3:1 mixture of **8** and **9**<sup>19</sup> was obtained in 23% yield as a liquid, the components of which could not be separated.

So far, several attempts at isomerizing the quadricyclanes **6a** and **7a** to the corresponding oxasesquinorbornatrienes were unsuccessful. After chromatography of **6a** or **7a** on a silica gel column, the epoxides **10**<sup>20</sup> and, respectively, **11**<sup>21</sup> were obtained as main products. In addition, **11** was formed after refluxing a solution of **7a** in acetonitrile for 1 h. Presumably, these rearrangements are effected by electrophilic catalysis via cationic

(15) **7a**: mp 186.5–188  $^{\circ}\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  16.20 (d, C-3, C-7), 27.57 (d, C-4, C-6), 36.48 (t, C-5), 40.59 (s, C-2, C-8), 89.39 (s, C-1, C-9), 118.74, 126.40, 126.47, 127.83, 128.32, (5 d), 137.17, 148.71 (2 s).

(16) X-ray crystal data of **6a** ( $\text{C}_{27}\text{H}_{20}\text{O}$ ):  $M = 360.460$ ; monoclinic; space group =  $P2_1$ ;  $Z = 2$ ;  $a$  (pm) = 801.4 (2);  $b$  (pm) = 835.4 (2);  $c$  (pm) = 1396.4 (4);  $\beta = 91.18$  (2) $^{\circ}$ ;  $V$  ( $\text{nm}^3$ ) = 0.93462;  $D_{\text{calc}}$  ( $\text{g cm}^{-3}$ ) = 1.281. The data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo  $K\alpha$  radiation. A total of 2792 reflections ( $\pm h, \pm k, l$ ) were collected in the range  $4^{\circ} < 2\theta < 46^{\circ}$  with 1322 having  $I > 2\sigma(I)$  being used in the structure refinement by full-matrix least-squares techniques (252 variables). Final  $R = 0.0286$ ,  $R_w = 0.0243$ .

(17) Molecules of quadricyclane frameworks related to *syn*-sesquinorbornatrienes have recently been synthesized: Paquette, L. A.; Künzer, H.; Kesselmayr, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 6521.

(18) **6b**: waxy solid, mp 46–52  $^{\circ}\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  11.54 (q,  $\text{CCH}_3$ ), 15.39 (d, C-3, C-7), 22.14 (d, C-2, C-8), 29.62 (NCH<sub>3</sub>), 68.12 (s, C-1, C-9), 119.16, 126.12 (2 d), 146.02 (s).

(19) **8**:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.08 (d, C-3, C-7), 15.42 (q,  $\text{CH}_3$ ), 24.20 (d, C-4, C-6), 36.35 (t, C-5), 40.33 (s, C-2, C-8), 84.98 (s, C-1, C-9), 135.47 (d, C-10, C-11). **9**:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.99 (d, C-3, C-7), 16.29 (q,  $\text{CH}_3$ ), 24.41 (d, C-4, C-6), 37.72 (t, C-5), 39.20 (s, C-2, C-8), 86.21 (s, C-1, C-9), 138.30 (d, C-10, C-11).

(20) **10**: mp 193–196  $^{\circ}\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  43.65, 48.67 (2 d, C-1, C-9), 50.46 (t, C-9), 68.66, 78.34 (2 s, C-2, C-4).

(21) **11**: mp 180.5–182  $^{\circ}\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  46.10, 46.83 (2 d, C-1, C-9), 52.61 (t, C-12), 67.93, 76.78 (2 s, C-2 C-4).

intermediates. The structure of **11** was established by X-ray crystallography.<sup>22</sup>

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**Supplementary Material Available:** Tables of atomic positional parameters, anisotropic thermal parameters, hydrogen atom positions, bond distances, and bond angles of **6a** and additional spectroscopic information for **4g**, **4k**, **3k**, **6a**, **7a**, **6b**, **10**, **11** (5 pages). Ordering information is given on any current masthead page.

(22) Details on the X-ray structure of **11** will be published at a later point.

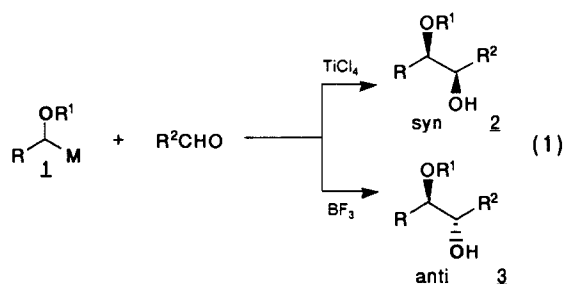
### Stereodivergent Synthesis of 1,2-Diol Derivatives via $\alpha$ -Alkoxy Organolead Compounds. $S_E2$ -Retention Pathway

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$\alpha$ -Alkoxy organometallic compounds (**1**;  $M = \text{Sn}, \text{Li}, \text{MgX}, \text{CuX}$ ) are versatile reagents in organic synthesis. However, access to 1,2-diols via these reagents produces some difficulties. For example, the condensation of **1** ( $M = \text{Li}, \text{MgBr}, \text{CuX}$ ) with benzaldehyde produces a low *syn* diastereoselectivity especially in the case of primary and secondary R groups.<sup>3</sup> Previously, we reported that tetraalkyllead compounds react smoothly with aldehydes.<sup>5</sup> If functionalized alkyl groups could be transferred stereoselectively to aldehydes in addition to such a simple alkyl group transfer, the synthetic utility of our Pb method would be enhanced. Accordingly, we prepared, for the first time,  $\alpha$ -alkoxy organolead compounds **1** ( $M = \text{Pb}$ ) and investigated the condensation of **1** ( $M = \text{Pb}$ ) with aldehydes. Here, we report that (i) the stereodivergent synthesis of 1,2-diol derivatives is accomplished by the condensation of **1** ( $M = \text{Pb}$ ) with aldehydes by merely changing Lewis acids (eq 1) and also (ii) the reaction proceeds through  $S_E2$ -retention.



$\alpha$ -Methoxy organolead compounds **5**<sup>6</sup> were prepared by transmetalation of the corresponding  $\alpha$ -methoxy organostannanes **4**<sup>7</sup> with *n*-butyllithium followed by trapping with *n*- $\text{Bu}_3\text{PbBr}$  at

(1) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842.

(2) (a) Cohen, T.; Maty, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900. (b) Cohen, T.; Lin, M.-T. *J. Am. Chem. Soc.* **1984**, *106*, 1130.

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(4) (a) Linderman, R. J.; Godfrey, A. *J. Am. Chem. Soc.* **1988**, *110*, 6249.

(5) Yamamoto, Y.; Yamada, J. *J. Am. Chem. Soc.* **1987**, *109*, 4395.

(6)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz): **5a**,  $\text{PbCH}(\text{OMe})\text{CH}_2$   $\delta$  4.370 (1 H, dd,  $J = 5.5$  and  $7.5$  Hz),  $^{207}\text{Pb}$  satellites gave  $J_{\text{H,Pb}} = 82$  Hz; **5b**,  $\text{PbCH}(\text{OMe})\text{CH}$   $\delta$  4.185 (1 H, d,  $J = 6.0$  Hz),  $^{207}\text{Pb}$  satellites gave  $J_{\text{H,Pb}} = 74$  Hz.