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Supplementary Material Available: Characteristic ¹³C 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-Dehydroquadricyclane

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

Schlosser⁴ and Brandsma⁵ 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 $4e^6$ in 40% yield and with 4-toluenesulfonyl chloride into 2-chloronorbornadiene 4f⁶ in 34% yield.



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.^{7,8} The ¹³C NMR spectrum of the precipitate in THF- d_8 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 5.9

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.8,10

Conversion of 4g and 4k into the quadricyclanes 3g¹¹ and 3k^{8,12} 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 31 in 60% yield. This result indicates that 3i 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 3i 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 anhydride¹³ afforded a 40% yield of an 84:16 mixture of **6a**^{8,14} and **7a**.^{8,15} **7a** was less

Harnisch, J.; Baumgärtel, O.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. J. Am. Chem. Soc. 1979, 101, 3370.
 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.; Kramař, J.; Schlosser, M. Chimia 1985, 39,

²²⁹

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

^{(6) 4}e and 4f are known compounds: see ref 2. For 4f, see also: Davies, D. 1. J. Chem. Soc. 1960, 3669. (7) 4g: bp 74-77 °C/12 Torr; ${}^{13}C$ NMR (CDCl₃) 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; ¹³C NMR (CDCl₃) δ 58.52 (d), 71.84 (t),

^{(10) 4}k: bp 85-86 °C/12 1orr; ¹³C NMR (CDCl₃) δ 58.52 (d), 71.84 (t), 132.91 (s), 141.09 (d). (11) 3g: bp 20 °C/0.01 Torr; ¹³C NMR (CDCl₃) 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; ¹³C NMR (CDCl₃) δ 24.84 (d), 30.93 (t), 35.04 (d), 39.19 (s); HRMS calcd for C₇H₉⁷⁹Br⁸¹Br 249.881, found 249.876. (13) Wittig, G. Organic Syntheses; Wiley: New York, 1963; Collect. Vol. 1V p.964.

⁽¹³⁾ Wittig, G. *Organic Syntheses*; Wiley: New York, 1965; Collect. Vol. IV, p 964. (14) **6a**: mp 151–153 °C; ¹³C NMR (CDCl₃) 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 diffraction¹⁶ and is depicted in Figure 1.¹⁷



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 °C to room temperature in the presence of 1,2,3-trimethylisoindole and, respectively, of 2,5-dimethylfuran. In the first case, aqueous workup afforded a 65% yield of adduct 6b;^{8,18} 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 919 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 10²⁰ and, respectively, 11²¹ 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 °C; ¹³C NMR (CDCl₃) δ 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** (C₂₇H₂₀O): 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)°; V (nm³) = 0.93462; D_{calcd} (g cm⁻³) = 1.281. The data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo K α radiation A total of 2792 referctions (+b + k) were collected in the range radiation. A total of 2792 refections $(\pm h, \pm k, l)$ were collected in the range $4^{\circ} < 2\theta < 46^{\circ}$ with 1322 having $l > 2\sigma(l)$ 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-sesquinor-(17) (Noted as of quark years) with the function of the funct

 $\begin{array}{l} 13.59 (4, C-3, C-7), 22.14 (4, C-2, C-6), 29.02 (NCH_3), 88.12 (8, C-1, C-9), \\ 119.16, 126.12 (2 d), 146.02 (s). \\ (19) 8: {}^{13}\text{C} \text{NMR} (\text{CDCl}_3) \delta 10.08 (d, C-3, C-7), 15.42 (q, CH_3), 24.20 \\ (d, C-4, C-6), 36.35 (t, C-5), 40.33 (s, C-2, C-8), 84.98 (s, C-1, C-9), 135.47 \\ (d, C-10, C-11). 9: {}^{13}\text{C} \text{NMR} (\text{CDCl}_3) \delta 14.99 (d, C-3, C-7), 16.29 (q, CH_3), \\ 24.41 (d, C-4, C-6), 37.72 (t, C-5), 39.20 (s, C-2, C-8), 86.21 (s, C-1, C-9), \\ 128.20 (d, C-10, C-11). \\ \end{array}$ 138.30 (d, C-10, C-11).

(20) 10: mp 193–196 °C; ¹³C NMR (CDCl₃) δ 43.65, 48.67 (2 d, C-1, C-9), 50.46 (1, C-9), 68.66, 78.34 (2 s, C-2, C-4). (21) 11: mp 180.5–182 °C; ¹³C NMR (CDCl₃) δ 46.10, 46.83 (2 d, C-1,

C-9), 52.61 (1, C-12), 67.93, 76.78 (2 s, C-2 C-4).

intermediates. The structure of 11 was established by X-ray crystallography.²²

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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 α -Alkoxy Organolead Compounds. S_E2-Retention Pathway

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 α -Alkoxy organometallic compounds (1; M = Sn,¹ Li,^{1,2} MgX,³ CuX⁴) 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 = Li, MgBr, CuX) with benzaldehyde produces a low syn diastereoselectivity especially in the case of primary and secondary R groups.³ Previously, we reported that tetraalkyllead compounds react smoothly with aldehydes.⁵ 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, α -alkoxy organolead compounds 1 (M = Pb) and investigated the condensation of 1 (M = Pb) with aldehydes. Here, we report that (i) the stereodivergent synthesis of 1,2-diol derivatives is accomplished by the condensation of 1 (M = Pb) with aldehydes by merely changing Lewis acids (eq 1) and also (ii) the reaction proceeds through S_E2 -retention.



 α -Methoxy organolead compounds 5⁶ were prepared by transmetalation of the corresponding α -methoxy organostannanes 4^{7} with *n*-butyllithium followed by trapping with *n*-Bu₃PbBr 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.

- 1. L.; McGarvey, G. J. J. Am. Chem. Soc. 1988, 170, 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. (3) McGarvey, G. J.; Kimura, M. J. Org. Chem. 1982, 47, 5420. (4) (a) Linderman, R. J.; Godfrey, A. J. Am. Chem. Soc. 1988, 170, 6249. (b) Linderman, R. J.; Godfrey, A. Home, K. Tetrahedron 1989, 45, 495. (5) Yamamoto, Y.; Yamada, J. J. Am. Chem. Soc. 1987, 109, 4395. (6) ¹H NMR (CDCl₃, 270 MHz): 5a, PbCH(OMe)CH₂ & 4.370 (1 H, dd, J = 5.5 and 7.5 Hz), ²⁰⁷Pb satellites gave $J_{H,Pb} = 82$ Hz; 5b, PbCH-(OMe)CH & 4.185 (1 H, d, J = 6.0 Hz), ²⁰⁷Pb satellites gave $J_{H,Pb} = 74$ Hz.

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