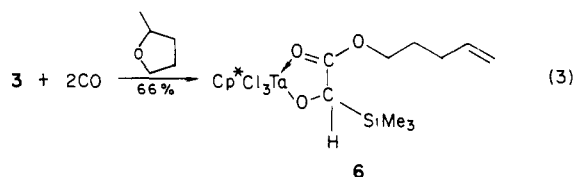


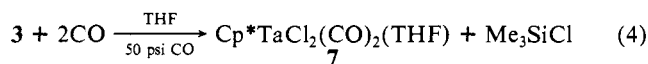
ligand (or insertion of CO into the Ta-COSiMe<sub>3</sub> bond) to produce a ketene intermediate, analogous to the transitory ketene Cp\*<sub>2</sub>Ta[OC(CO)CH<sub>2</sub>CMe<sub>3</sub>]Cl formed from CO and the acyl Cp\*<sub>2</sub>Ta(η<sup>2</sup>-COCH<sub>2</sub>CMe<sub>3</sub>)Cl.<sup>11</sup> The SiMe<sub>3</sub> and oxygen substituents should stabilize resonance structures C and D, imparting significant electrophilic character to the ketene α-carbon.<sup>12</sup> Nucleophilic attack by ether may be promoted by concurrent Ta-O bonding (E). Zwitterionic species similar to E have been proposed as intermediates in analogous reactions in which ethers are cleaved by arynes.<sup>13</sup> We are unaware of any such reactions involving ketenes, however. A mechanism involving ether cleavage by an acidic tantalum center seems unlikely, since this would be expected to produce a stable Ta-OCH<sub>2</sub>CH<sub>3</sub> derivative.<sup>1</sup> Further studies on the mechanism of this reaction are in progress.

The formation of silacyl intermediate A was observed by NMR and IR spectroscopy. A benzene-*d*<sub>6</sub> solution of **3** absorbed 1 mol of CO to produce an orange solution containing two new signals in the <sup>1</sup>H NMR at 2.15 and 0.42 ppm; if <sup>13</sup>CO is used, the peak at 0.42 ppm appears as a doublet (<sup>3</sup>J<sub>CH</sub> = 2.4 Hz). The acyl carbon atom of A\* appears as a singlet at 351 ppm in the <sup>13</sup>C NMR spectrum.<sup>3</sup> The C-O stretching frequency of A (1462 cm<sup>-1</sup>; 1428 cm<sup>-1</sup> for <sup>13</sup>C-labeled A\*) is relatively low.<sup>11a</sup> Complex A is stable for hours at room temperature in solution but rapidly reacts further in the presence of excess CO. Attempts to isolate A have so far proven unsuccessful.

Also consistent with the mechanism in Scheme I is the reaction of **3** with CO (50 psi) and 2-methyltetrahydrofuran (as solvent or with 1 equiv in pentane, eq 3), leading to the ring-opened product **6**.<sup>6</sup>



In tetrahydrofuran as solvent, no evidence for the analogous CO insertion chemistry was obtained. Instead, the products appear to result from a ligand-induced reductive elimination of Me<sub>3</sub>SiCl (identified by GC/MS) to form the Ta(III) product **7**<sup>6</sup> (eq 4).



Apparently the β-hydrogens of tetrahydrofuran are not sterically accessible for abstraction via a mechanism analogous to Scheme I. Alternatively, diethyl ether and 2-methyltetrahydrofuran, being poorer ligands toward tantalum(V), cannot induce elimination of Me<sub>3</sub>SiCl.<sup>14</sup>

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Research Corporation, and to the Air Force Office of Scientific Research for support of this work. We thank Prof. M. A. Battiste for helpful discussions.

**Supplementary Material Available:** Spectroscopic and analytical data for **4-7** (1 page). Ordering information is given on any current masthead page.

(11) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393. (b) Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1983**, *105*, 5696.

(12) We thank a reviewer for comments regarding the ketene intermediate's structure. A further possibility with respect to activation of the ketene toward nucleophilic attack is an interaction of the terminal oxygen with a Lewis acid center,<sup>11a</sup> since unsaturated Ta species are expected to be present in solution.

(13) (a) Franzen, V.; Joscheck, H. I.; Mertz, C. *Ann.* **1962**, *654*, 82. (b) Hellmann, H.; Eberle, D. *Ann.* **1963**, *662*, 188. (c) Hayashi, S.; Ishikawa, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 642. (d) Richmond, G. D.; Spindel, W. *Tetrahedron Lett.* **1973**, 4557.

(14) In the reaction involving diethyl ether (eq 1) traces of tantalum carbonyl species were detected (by ir), implying that loss of Me<sub>3</sub>SiCl and ether cleavage are competing reaction pathways which are heavily influenced by the ether solvent.

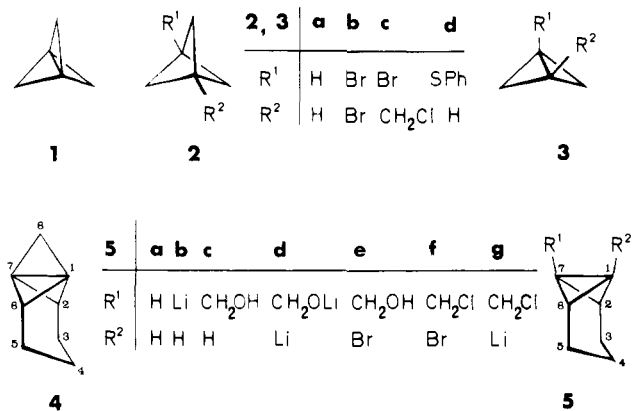
## Tetracyclo[5.1.0.<sup>1.6</sup>.0<sup>2.7</sup>]octane, a [1.1.1]Propellane Derivative, and a New Route to the Parent Hydrocarbon

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Recently Wiberg has shown that the heat of hydrogenation of [1.1.1]propellane (**1**) leading to bicyclo[1.1.1]pentane (**2a**) is



virtually the same as the one of cyclopropane affording propane.<sup>1,2</sup> As a consequence, formation of **1** by reduction of 1,3-dibromobicyclo[1.1.1]pentane (**2b**) is an energetically feasible reaction, as has been demonstrated by Wiberg and Walker.<sup>3</sup> It is interesting to note that bicyclo[1.1.1]pentane (**2a**) and bicyclo[1.1.0]butane (**3a**) have similar strain energies (66.6 kcal/mol<sup>4</sup> vs. 63.9 kcal/mol<sup>5</sup>). This suggests that it might be possible to construct the [1.1.1]propellane framework starting from a properly substituted bicyclo[1.1.0]butane derivative, as **3c**. In this paper we wish to report our results on the synthesis of tetracyclo[5.1.0.<sup>1.6</sup>.0<sup>2.7</sup>]octane (**4**), a derivative of **1**. In addition, we present a facile route to **1**.

Tricyclo[4.1.0.0<sup>2.7</sup>]heptane-1-methanol (**5c**),<sup>6</sup> obtained in 70% yield from **5a** after metalation to **5b** by *n*-butyllithium (BuLi) in ether at room temperature for 24 h and subsequent addition of formaldehyde, was converted to **5d** by 2 equiv of BuLi in ether, followed by bromination of **5d** with *p*-toluenesulfonyl bromide<sup>7</sup> giving rise to a 55% yield of 7-bromotricyclo[4.1.0.0<sup>2.7</sup>]heptane-1-methanol (**5e**): <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.40 (broadened s, 6 H), 1.90 (br s, 1 H), 2.80 (s, 2 H), 4.10 (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 19.8 (t, 2 C), 20.3 (t), 22.1 (s), 26.0 (s), 49.0 (d, 2 C), 62.2 (t); HRMS calcd for C<sub>8</sub>H<sub>11</sub><sup>79</sup>BrO 201.9993, found 201.999. Anal. C, H. 1-Bromo-7-chloromethyltricyclo[4.1.0.0<sup>2.7</sup>]heptane (**5f**) was prepared from **5e** by refluxing the carbinol with 1.1 equiv of triphenylphosphine in carbon tetrachloride for 12 h (yield 65–90%).<sup>8</sup> <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.42 (narrow m, 6 H), 2.75 (broadened s, 2 H), 3.88 (s, 2 H); <sup>13</sup>C NMR (CCl<sub>4</sub>/C<sub>6</sub>D<sub>6</sub>) δ 19.5 (t, 2 C), 20.1 (t), 21.8 (s), 27.1 (s), 44.5 (t), 49.3 (d, 2 C); HRMS calcd for C<sub>8</sub>H<sub>10</sub><sup>79</sup>Br<sup>35</sup>Cl 219.96545, found 219.965.

(1) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227–1233.

(2) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379–386.

(3) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239–5240.

(4) Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679–5686.

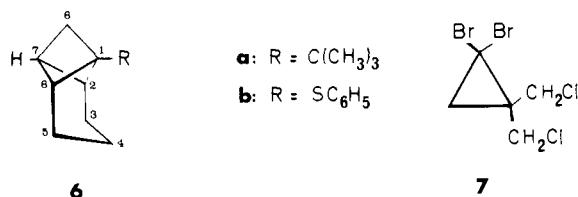
(5) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395–3397.

(6) Properties of **5c**: bp 31–32 °C (10<sup>-3</sup> torr); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.40 (m, 7 H), 2.25 (t, 1 H), 2.50 (m, 2 H), 4.00 (d, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 8.9 (d), 19.7 (s), 20.4 (t, 2 C), 20.9 (t), 42.6 (d, 2 C), 63.2 (t); MS (70 eV), *m/e* 124 (13%, M<sup>+</sup>).

(7) For previous use of *p*-toluenesulfonyl bromide as brominating reagent, see: Szeimies-Seebach, U.; Schöffner, A.; Römer, R.; Szeimies, G. *Chem. Ber.* **1981**, *114*, 1767–1785.

(8) Appel, R.; Halstenberg, M. In "Organophosphorus Reagents in Organic Chemistry"; Cadogan, J. I. G., Ed.; Academic Press: London, New York, Toronto, Sydney, San Francisco, 1979; pp 387–431.

Whereas the reduction of **5f** by sodium in triglyme at 100 °C or by sodium-potassium alloy in boiling ether did not lead to a C<sub>8</sub>H<sub>10</sub> hydrocarbon fraction, the reaction of **5f** with *tert*-butyllithium (*t*-BuLi) was more successful. When 2.2 equiv of *t*-BuLi was added to a solution of **5f** in pentane/ether (3:2) at -35 °C, aqueous workup after 30 min afforded a 35% yield of 1-*tert*-butyltricyclo[4.2.0.0<sup>2,7</sup>]octane (**6a**). The structure of **6a** is based



**a:** R = C(CH<sub>3</sub>)<sub>3</sub>  
**b:** R = SC<sub>6</sub>H<sub>5</sub>

on its spectroscopic data: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.85 (s, 9 H, CH<sub>3</sub>), 1.25 (s, 2 H, 8-H<sub>2</sub>), 1.45-1.80 (m, 6 H, 3-H<sub>2</sub>, 4-H<sub>2</sub>, 5-H<sub>2</sub>), 2.25 and 2.27 (s on top of broadened s, 3 H, 7-H, 2-H, 6-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 17.8 (t, C-4), 22.0 (t, C-3, C-5), 27.7 (q, CH<sub>3</sub>), 28.5 (d, C-7), 32.2 (s, CMe<sub>3</sub>), 42.7 (t, C-8), 53.5 (s, C-1), 54.8 (d, C-2, C-6); MS (70 eV), *m/e* 164 (5%, M<sup>+</sup>).

As the addition of *t*-BuLi to the central bond of highly strained small-ring propellanes<sup>9</sup> has been observed previously,<sup>10</sup> the precursor of **6a** is probably the [1.1.1]propellane **4**, which is formed by ring closure of **5g** and which reacts with the excess of the base leading to **6a**. When the reduction of **5f** was repeated with 1.3 equiv of *t*-BuLi under otherwise identical conditions, a new hydrocarbon was produced in 30% yield, which could be purified by preparative GC (column 4 m, 20% Silicon GE SE-30 on kieselgur, 65 °C). The spectroscopic properties of the hydrocarbon are in accord with structure **4**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.05-1.28 (m, 4 H, 3-H<sub>2</sub>, 5-H<sub>2</sub>), 1.35-1.63 (m with s at 1.55, 4 H, 4-H<sub>2</sub>, 8-H<sub>2</sub>), 2.75 (narrow m, 2 H, 2-H, 6-H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 9.4 (s, C-1, C-7), 18.9 (t, C-4), 20.8 (t, C-3, C-5), 66.6 (t, *J*(<sup>13</sup>C-H) = 162 Hz, C-8), 86.5 (d, *J*(<sup>13</sup>C-H) = 159 Hz, C-2, C-6); MS (70 eV), *m/e* 106 (40%, M<sup>+</sup>), 91 (100), 78 (55), 65 (20), 51 (30), 39 (35); IR (pentane) 595 cm<sup>-1</sup>.<sup>3</sup>

The yield of **4** was raised to 55-65% when BuLi, instead of *t*-BuLi, was chosen as a reducing agent for **5f**. **4** proved to be stable against BuLi in ether at -30 °C; in contrast, when **4** was exposed to an excess of *t*-BuLi in pentane/ether (3:2) in the presence of lithium bromide at -30 °C, **6a** after aqueous workup was obtained in high yield. Thiophenol and **4** afforded the thioether **6b**,<sup>11</sup> probably via a radical chain process. The propellane **4** shares with the parent hydrocarbon **1**<sup>3</sup> an unexpected thermal stability: the <sup>1</sup>H NMR spectrum of a sample of **4** in C<sub>6</sub>D<sub>6</sub> in a sealed NMR tube was unchanged after the sample had been kept at 105 °C for 30 min.

Recently Skattebøl, Baird, et al.<sup>12</sup> have shown that treatment of 1,1-dibromo-2-(chloromethyl)cyclopropanes with methylolithium leads to the formation of 1-bromobicyclo[1.1.0]butanes.<sup>13</sup> This observation combined with the facile ring closure of **5g** giving **4** suggested an efficient synthesis of **1** starting from **7** and proceeding via the bicyclo[1.1.0]butane **3c** as an intermediate: To a solution of **7**<sup>14</sup> in pentane/ether (3:2) at -50 °C, 2.2 equiv of BuLi was

added and the mixture was kept for 30 min at this temperature. Aqueous workup followed by distillation of the volatile organic material from a 30 °C bath into a dry-ice trap under vacuum afforded a solution of **1** in pentane/ether.<sup>15</sup> Addition of thiophenol to this fraction produced a 34% yield (based on **7**) of thioether **2d**,<sup>16</sup> indicating that **1** had been formed in a reasonable yield.

Finally we would like to point out that the reaction sequence leading to **4** could be applied to any bicyclo[1.1.0]butane hydrocarbon carrying hydrogen at the bridgehead positions.<sup>17</sup>

**Acknowledgment.** This investigation was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. We thank Dr. R. Römer for the mass spectrum of **4**.

(15) In addition to **1**, the pentane/ether fraction contained some 1-bromobutane.

(16) Properties of **2d**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.90 (s, 6 H), 2.65 (s, 1 H), 7.10-7.30 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 28.6 (d), 45.6 (s), 54.0 (t, 3 C), 127.3, 128.6, 133.4 (3 d), 134.1 (s); HRMS calcd for C<sub>11</sub>H<sub>12</sub><sup>32</sup>S 176.06592, found 176.067.

(17) **Note Added In Proof:** Tetracyclo[4.1.0.0<sup>1,5</sup>.0<sup>2,6</sup>]heptane, the lower homologue of **4**, was obtained in 45% yield from 1-bromo-6-(chloromethyl)tricyclo[3.1.0.0<sup>2,6</sup>]hexane and methylolithium in ether at -30 °C: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.54 (s, 4 H), 2.32 (s, 2 H), 2.73 (s, 2 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 11.8 (s), 25.1 (t, 2 C), 70.7 (t), 84.1 (d, 2 C).

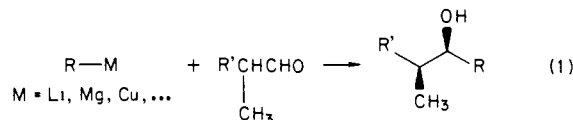
### Organometallic-Crown Reagents. Anti-Cram Selectivity via R<sub>2</sub>CuLi-Crown and Enhanced Cram Selectivity via RLi-Crown and RMgX-Crown

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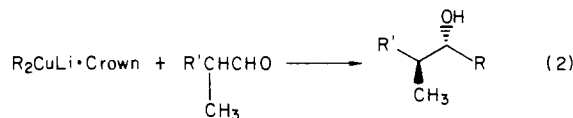
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It is widely agreed that the reaction of organometallic reagents with ordinary chiral aldehydes having no ability to be chelated produces the Cram (or Felkin) type isomer predominantly (eq 1). We report herein the surprising stereochemical behavior



exhibited by R<sub>2</sub>CuLi-crown reagents; the anti-Cram isomer is produced preferentially (eq 2). We have also discovered that



the Cram selectivity is enhanced with RLi (or RMgX)-crown reagents.<sup>1</sup> These findings provide not only a new useful method for 1,2-asymmetric induction but also a conceptual advance in empirical models to rationalize the stereoselectivity in reactions of chiral aldehydes. The results are summarized in Table I.

(1) For organolithium reactions in the presence of crown ethers and cryptates, see: (a) Pierre, J. L.; Handel, H.; Perraud, R. *Tetrahedron Lett.* **1977**, 2013. (b) Biellmann, J. F.; Vicens, J. J. *Ibid.* **1974**, 2915. (c) Atlani, P. M.; Biellmann, J. F.; Dube, S.; Vicens, J. J. *Ibid.* **1974**, 2665. (d) Chassaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399. (e) Maruoka, K.; Yamamoto, H. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 437. For reduction with metal hydrides, see: (f) Handel, H.; Pierre, J. L. *Tetrahedron Lett.* **1976**, 741; *Tetrahedron* **1975**, *31*, 997; **1975**, *31*, 2799. (g) Pierre, J. L.; Handle, H.; Perraud, R. *Ibid.* **1975**, *31*, 2795. (h) Loupy, A.; S-Penne, J. *Tetrahedron Lett.* **1978**, 2571. (i) Loupy, A.; S-Penne, J.; Tchoubar, B. *Ibid.* **1976**, 1677. (j) Lee, H. S.; Isagawa, K.; Toyoda, H.; Otsuji, Y. *Chem. Lett.* **1984**, 363 and 673. For Grignard reactions, see: (k) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672 and references cited therein.

(9) For definition, see: Ginsburg, D. "Propellanes", Verlag Chemie: Weinheim, 1975.

(10) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638-3641 and references therein.

(11) Properties of **6b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.45-1.75 (m with s at 1.63, 8 H, 3-H<sub>2</sub>, 4-H<sub>2</sub>, 5-H<sub>2</sub>, 8-H<sub>2</sub>), 2.43 (narrow m, 2 H, 2-H, 6-H), 2.58 (s, 1 H, 7-H), 7.05-7.42 (m, 5 H, Ar H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 18.1 (t, C-4), 20.7 (t, C-3, C-5), 30.7 (d, C-7), 48.4 (s, C-1), 49.7 (t, C-8), 58.1 (d, C-2, C-6), 126.8, 128.3, 133.6 (3 d, Ar C), 133.7 (s, Ar C); HRMS calcd for C<sub>14</sub>H<sub>16</sub><sup>32</sup>S 216.09727, found 216.096.

(12) Nilsen, N. O.; Skattebøl, L.; Baird, M. S.; Buxton, S. R.; Slowey, P. *Tetrahedron Lett.* **1984**, 2887-2890.

(13) Düker, A.; Szeimies, G. *Tetrahedron Lett.* **1985**, 3555-3558.

(14) **7** was obtained in 45% yield from commercially available 3-chloro-2-(chloromethyl)-1-propene by addition of dibromocarbene (from bromoform and 50% aqueous sodium hydroxide in dichloromethane at 25 °C under the conditions of phase-transfer catalysis). Properties of **7**: mp 45-46 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.80 (s, 2 H), 3.91 (s, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 32.0 (s), 33.9 (t), 35.2 (s), 47.6 (t, 2 C). Anal. C, H.