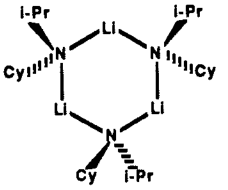
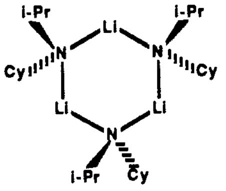
have been isolated and crystallographically characterized on three occasions (viz $[(PhCH_2)_2NLi]_3$, $[(Me_3Si)_2NLi]_3$, and $[Me_2C(CH_2)_3CMe_2NLi]_4$), they are all void of coordinating solvents. In contrast, the etherates of $(PhCH_2)_2NLi$ and $(Me_3Si)_2NLi$ crystallize as disolvated cyclic dimers[4,5] (as do other related lithium amide derivatives) while an etherate of $Me_2C(CH_2)_3CMe_2NLi$ remains uncharacterized.[2,3,6] By noting the symmetry of stereoisomeric trimers i and ii, further arguments can be made supporting dimers rather than trimers (or higher oligomers) as the predominant forms of LICA in THF solution. The ^{15}N–^{6}Li coupling patterns of i and ii would exhibit as many as three ^{6}Li resonances, three ^{15}N resonances, and three separate resonances for each carbon atom in the skeleton. Such spectral complexities were not detected by three quite different forms of NMR spectroscopy. Thus, we concur with Snaith and co-workers[19] that the higher order cyclic oligomers are probably restricted to ligand-free lithium amides and, in turn, assign the observed aggregates of LICA as *cis*- and *trans*-**1**.



i



ii

The invariance of the ^{6}Li shift of LICA over THF concentrations spanning 0.2–12.0 M, taken in conjunction with crystallographic studies of N-lithiated species solvated by simple monodentate donors, is consistent with a single coordinated THF per lithium in dimers *cis*- and *trans*-**1**. However, Seebach and co-workers have crystallographically characterized an unsymmetrical trisolvated dimer of a related N-lithiated species.[6c] In addition, solution structural studies of lithium diphenylamide dimer and the corresponding lithium diphenylamide–lithium bromide mixed dimer in THF/hydrocarbon solutions uncovered evidence of higher degrees of solvation.[10b] Thus, the solution solvation states of *cis*-**1** and *trans*-**1** are not evident at this time.

As evidence of the relative importance of aggregated, mixed aggregated, and monomeric forms of lithium dialkylamides in determining reactivity and selectivity begins to accumulate,[20] detailed solution structural information will become an increasingly important component of predictive models.

Acknowledgment. We thank the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643) for support of the Cornell Nuclear Magnetic Resonance Facility. E.M.M. would like to thank the National Science Foundation REU program (CHE-8712498) for an undergraduate research fellowship and D.B.C. expresses thanks to the A. P. Sloan Foundation for unrestricted support.

Registry No. LICA, 32400-20-7; THF, 109-99-9; toluene, 108-88-3.

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(20) For example, aggregate reactivity has been addressed theoretically (McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 7284). Residual lithium amides (or the secondary amine byproducts) appear to alter the outcome of a number of reactions utilizing lithium amide derivatives as bases (see references cited in ref 10). Williard and co-workers have successfully characterized a number of lithium diisopropylamide–enolate complexes crystallographically (ref 2a and unpublished results). We have recently observed and studied the direct N-alkylation of lithium diphenylamide dimer and lithium diphenylamide–lithium bromide mixed dimer with *n*-butyl bromide (ref 10b). The general principles of mixed aggregation effects on reaction outcomes has been discussed previously (Seebach, D. In *Proceedings of the Robert A. Welch Foundation Conferences on Chemistry and Biochemistry*; Wiley: New York, 1984; p 93).

Interactions of Dialkylmagnesium Compounds with 15-Crown-5: Formation in Solutions and Solids of $RMg(15\text{-crown-}5)^+$ and Magnesiate Ions[†]

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Received December 24, 1987

Magnesiate ions, formed by equilibria such as that in eq 1 but in amounts too small to detect by NMR spectroscopy, were

$$3R_2Mg + 15\text{-C-}5 \rightleftarrows RMg(15\text{-C-}5)^+ + R_5Mg_2^- \quad (1)$$

suggested as being the species responsible for the striking chemical behavior of solutions resulting from addition of 15-crown-5 to EtOEt or THF solutions of dialkylmagnesium compounds.[1] Subsequent studies showed that appropriate cryptands, far more effective than crown ethers as coordinating agents for Mg, form substantial amounts of such ions. Structures of solid $NpMg(2,1,1\text{-cryptand})^+Np_3Mg^-$ (Np = neopentyl) and $[EtMg(2,2,1\text{-cryptand})^+]_2Et_6Mg_2^{2-}$ were determined,[2] and ^1H NMR spectra of solutions prepared from several diorganomagnesium compounds showed absorptions attributed to similar species.[2–5] This communication now reports *direct observations* of the species in eq 1.

Crystals (mp 129 °C) suitable for X-ray analysis slowly formed when an EtOEt solution of Me_2Mg (2 mL, 1.5 M) was layered over a benzene solution of 15-crown-5 (2 mL, 0.5 M). X-ray analysis[6] revealed $MeMg(15\text{-crown-}5)^+$ units and $(Me_5Mg_2^-)_n$ chains, presumably having the indicated charges. As shown in Figure 1, the Mg of the cation is bonded in an equatorial fashion to all crown ether oxygens and lies just 0.42 Å out of their mean plane. This Mg also is bonded to an apical methyl group (Mg–C 2.140 (7) Å). The other apical position is occupied by one methyl group of the anionic polymer chain, though at a Mg–C distance of 3.28 Å.[7] Within the four-membered ring, bond angles are similar to and bond lengths slightly longer than those in the Me_2Mg structure, which has adjoining Mg's linked by two bridging methyl groups.[8]

Solutions now have been prepared, many of which are stable for days or weeks at room temperature, whose ^1H NMR spectra indicate the presence of significant amounts of $RMg(crown)^+$ and magnesiate ions. The spectrum in Figure 2, of a benzene solution containing approximately 5.2 Np groups per 15-crown-5 residue, is a convenient example to consider. This spectrum shows two crown ether absorptions (A, δ 2.99; C, δ 3.31) and two sets of Np absorptions (A, δ −0.40 for the CH_2 and δ 1.22 for the CH_3's; B, δ 0.34 for the CH_2 and δ 1.54 for the CH_3's). For several

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[†] Dedicated to Professor Paul D. Bartlett on the occasion of his 80th birthday.

(1) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.

(2) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

(3) Richey, H. G. Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.

(4) Squiller, E. P. The Pennsyvania State University, unpublished observations.

(5) Kushlan, D. M. The Pennsylvania State University, unpublished observations.

(6) Crystal data for $MeMg(15\text{-crown-}5)^+Me_5Mg_2^-$, $C_{16}H_{38}O_5Mg_3$: a = 10.736 (2) Å, β = 18.454 (3) Å, c = 11.923 (3) Å; V = 2362 (2) Å^3, Z = 4, D_{cacd} = 1.078 g cm^{-3}; space group $Pna2_1$, R = 0.077 for 1470 reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromatized Mo Kα radiation, the $\omega/2\theta$ scan method, and variable scan speed. The structure was solved by direct methods and refined by full-matrix least-squares calculations.

(7) The positions of the H's are not revealed by the analyis so it is not evident if this can be regarded as a particularly feeble Me–C bond or if H's of the methyl group lie between the C and the Mg.

(8) Weiss, E. *J. Organomet. Chem.* **1964**, *2*, 314. In polymeric Me_2Mg, C–Mg–C is 105 (2)°, Mg–C–Mg is 75 (2)°, Mg–C is 2.24 (3) Å, and Mg–Mg is 2.72 (2) Å.

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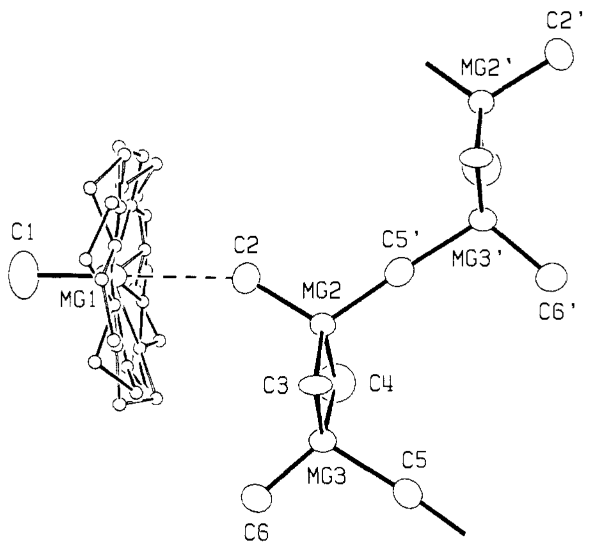

Figure 1. ORTEP drawing of the crystal packing of $MeMg(15\text{-crown-}5)^+$ units and $(Me_5Mg_2^-)$ chains. For clarity, atoms of the crown ether are assigned arbitrary radii; other atoms are shown with 50% probability thermal ellipsoids. The crown ether is disordered over two essentially identical sites, both of which are shown. In the polymeric anion bond lengths are as follows: Mg(2)–C(2) 2.170 (6), Mg(2)–C(3) 2.302 (9), Mg(2)–C(4) 2.334 (11), Mg(2)–C(5)' 2.258 (6), Mg(3)–C(3) 2.251 (9), Mg(3)–C(4) 2.309 (11), Mg(3)–C(5) 2.395 (6), and Mg(3)–C(6) 2.170 (6) (Mg(2)–Mg(3) 2.811 (2) Å). Bond angles are as follows: C(2)–Mg(2)–C(3) 110.9 (4), C(2)–Mg(2)–C(4) 109.3 (4), C(2)–Mg(2)–C(5)' 114.0 (4), C(3)–Mg(2)–C(4) 103.3 (3), C(3)–Mg(2)–C(5)' 112.9 (4), C(4)–Mg(2)–C(5)' 105.7 (4), Mg(2)–C(3)–Mg(3) 76.2 (3), Mg(2)–C(4)–Mg(3) 74.5 (3), C(3)–Mg(3)–C(4) 105.7 (3), C(3)–Mg(3)–C(5) 110.0 (4), C(3)–Mg(3)–C(6) 115.2 (4), C(4)–Mg(3)–C(5) 103.7 (4), C(4)–Mg(3)–C(6) 114.3 (5), C(5)–Mg(3)–C(6) 107.4 (2), and Mg(2)–C(5)'–Mg(3)' 174.1 (3)°. (Primed atoms are related to unprimed atoms by the symmetry $1/2 + x$, $1/2 - y$, z.).

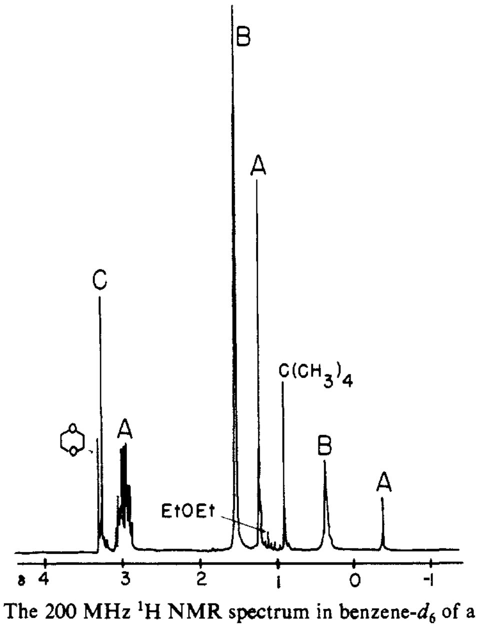

Figure 2. The 200 MHz ^1H NMR spectrum in benzene-d_6 of a solution formed from Np_2Mg and 15-crown-5. Chemical shifts are relative to benzene-d_5 (∂ 7.15). The absorptions labeled A are assigned to $NpMg(15\text{-crown-}5)^+$.

reasons we attribute the absorptions labeled A to $NpMg(15\text{-crown-}5)^+$, having a structure like that of the cation in Figure 1: (1) absorption areas have the appropriate ratios; (2) absorption positions are relatively insensitive to the solution composition; (3) absorptions of the α-H's (average ∂ −0.41) and the ligand H's (average ∂ 3.02) are shifted upfield, as in spectra of $RMg(\text{cryptand})^+$ ions; (4) the crown ether absorption is an AA'BB' multiplet, as expected for a crown ether with different faces.[9]

The absorptions labeled B are due to Np groups, interchanging rapidly on the NMR time scale, of magnesiate ions, and we think also of a species $Np_2Mg(15\text{-crown-}5)$, to which we assign the crown ether absorption labeled C. At Np to crown ether ratios between 0 and nearly 2, the single crown ether absorption shifts in position from that (∂ 3.51) characteristic of free crown ether to that (∂ 3.31) of C in Figure 2; throughout that range, however, the position of the single Np CH_2 absorption is relatively constant (∂ 0.09),[10] suggesting that the Np groups are in a single species. $NpMg(15\text{-crown-}5)^+$ absorptions first are seen as the ratio approaches 2; between ratios of approximately 2 and 6, the position of the original crown ether absorption now is constant (∂ 3.32 ± 0.01), consistent with all crown ethers responsible for it residing in a single species. By contrast, between these ratios, the original Np CH_2 absorption shifts steadily, consistent with its being due to Np groups of both $Np_2Mg(15\text{-crown-}5)$ and magnesiate anions. $Np_2Mg(15\text{-crown-}5)$ may have the "threaded" structure suggested[3] for $Ar_2Mg(\text{crown})$ species, in which the crown ether oxygens surround the Mg in an equatorial fashion and the organic groups occupy apical positions.[11]

At Np to crown ether ratios above about 6, only the crown ether absorption attributed to $NpMg(15\text{-crown-}5)^+$ remains. With an excess of crown ether, the ratio of Np absorptions B to those (A) for Np in $NpMg(15\text{-crown-}5)^+$ falls to but never drops below 5. Although solutions with a ratio of 5 might contain equilibrating mixtures of Np_3Mg^-, other magnesiate anions, and Np_2Mg, the major species probably are magnesiate ions of composition $Np_5Mg_2^-$. In spectra of solutions of various R_2Mg's with 15-crown-5 or 2,2,1-cryptand (a less than optimal cryptand), the ratio 5 has been observed frequently but also has been the lowest observed. $R_5Mg_2^-$ must have sufficient stability that its conversion to $(R_3Mg^-)_n$ and $RMgC^+$ ordinarily requires a more effective coordinating agent than 15-crown-5.

Other R_2Mg's (R = ethyl, hexyl, *sec*-butyl, *tert*-butyl) form solutions that exhibit $RMg(\text{crown})^+$ ^1H NMR absorptions, but equilibrium constants and equilibration rates vary.[4,5,12] Some $(\text{hexyl})Mg(15\text{-crown-}5)^+$ is evident, for example, even at hexyl to crown ratios near 0.

^1H NMR absorptions due to $RMg(15\text{–crown–}5)^+$ were not noted in our initial work because the solvent always was an ether. We have now observed that addition of some EtOEt or THF to benzene solutions prepared from Np_2Mg and 15-crown-5 reduces $NpMg(15\text{-crown-}5)^+$ absorptions. In fact, $EtMg(15\text{-crown-}5)^+$ absorptions are not detected in solutions of Et_2Mg and 15-crown-5 in pure EtOEt-d_{10}.

Acknowledgment. We are indebted to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers. We thank Professor Lloyd Jackman for help in analysis of NMR spectra and Professor Jeffrey Peterson for help in designing the glove box used for mounting crystals for X-ray diffraction.

Registry No. $MeMg(15\text{-crown-}5)^+Me_5Mg_2^-$, 113379-68-3; $NpMg(15\text{-crown-}5)^+Np_5Mg_2^-$, 113379-71-8; $Np_2Mg(15\text{-crown-}5)$, 113379-72-9; Me_2Mg, 2999-74-8.

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[9] For a particular solution with a Np to crown ratio of 3.5, ∂_A = 3.033, ∂_B = 3.069, $J_{AB} = J_{A'B'}$ = 4.1 Hz (gem), $J_{AA'}$ = 6.3 Hz (cis), $J_{BB'}$ = 6.2 Hz (cis), and $J_{AB'} = J_{A'B}$ = −9.9 Hz (trans). This absorption changes in appearance from solution to solution, often looking like a singlet. These differences apparently are due to small changes in ∂_A and ∂_B, particularly as concentrations change, rather than to exchange processes. Note that the spectra would be more complicated if the ring did not retain conformational mobility.

[10] A slight variation (∂ ± 0.03) is noted but at least in part is related to concentration level.

[11] Results obtained from NOE difference spectroscopy, although not definitive, also are consistent with this structure. Irradiation of the crown ether absorption enhanced (34.3%) the Np CH_2 absorption, indicating that the Np CH_2 is in close proximity to the crown ether. An enhancement involving R and the crown ether is noted in other situations where a threaded species seems likely (e.g., ref 3) but not observed in other situations where such a structure is unlikely, for example, for solutions of Np_2Mg and 12-crown-4.

[12] Pajerski, A. D. The Pennsylvania State University, unpublished observations.

Supplementary Material Available: ORTEP drawings of the cation of $MeMg(15\text{-crown-}5)^+Me_5Mg_2^-$ and tables for this salt of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters (5 pages); tables of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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n-Pentenyl Glycosides Permit the Chemospecific Liberation of the Anomeric Center[1]

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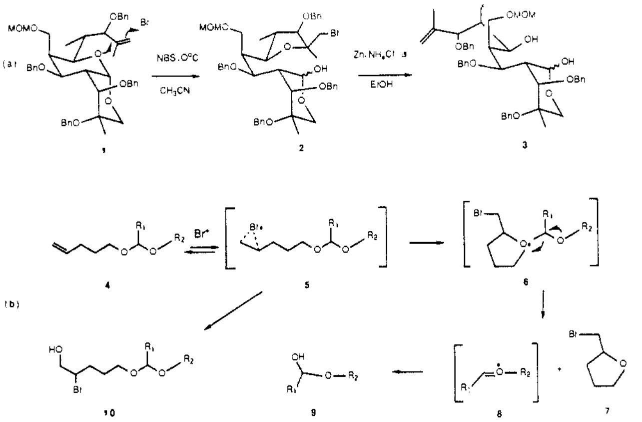
Synthetic manipulations of carbohydrate derivatives rely on efficient differential protecting group strategies, and excellent protocols have been developed which discriminate between various hydroxyl groups on the basis of their steric, electronic, or reactivity demands.[2] In this context, the anomeric center is particularly important, since it usually plays a key role in the syntheses, whether the sugar is used as a building block for oligosaccharides[3] or as a chiron[4] for natural products.[4,5] Therefore, a procedure for chemospecific liberation of the glycosidic oxygen would be advantageous, and in this manuscript, we describe such a reaction.

Our approach to this problem grew out of the serendipitous finding[6] that reaction of the dipyranoside **1** with NBS/CH_3CN/H_2O led not to the expected bromohydrin but to the bromomethyl tetrahydrofuran **2**[6] (Scheme Ia). We had failed in attempts to open the dipyranoside directly or indirectly (i.e., **1** → **3**) by use of protic or Lewis acid protocols. Hence, the ready formation of **2** was welcomed, particularly since reduction with zinc led readily to **3**.[6] With respect to the key step, a mechanistic rationale, summarized by the arrows in **1**, implied a unique case of "RO5 participation"[7] by the ring oxygen[8] in the opening of the putative cyclic bromonium ion.

The mechanistic proposition can be fleshed out by using the generalized structural element **4** (Scheme Ib). Thus, the process is driven by a cascade of ionic intermediates **5**, **6**, and **8**, which requires involvement of both oxygens. In effect, the overall transformation, **4** → **8**,[9] suggests a generalized protocol for "hydrolysis" of an acetal without the use of an acid, as is the customary requirement. The promise for sugar chemistry, therefore, was the possibility to cleave specifically the glycosidic oxygen under conditions that would leave a wide array of commonly used protecting groups unaffected.

Scheme I



Scheme II

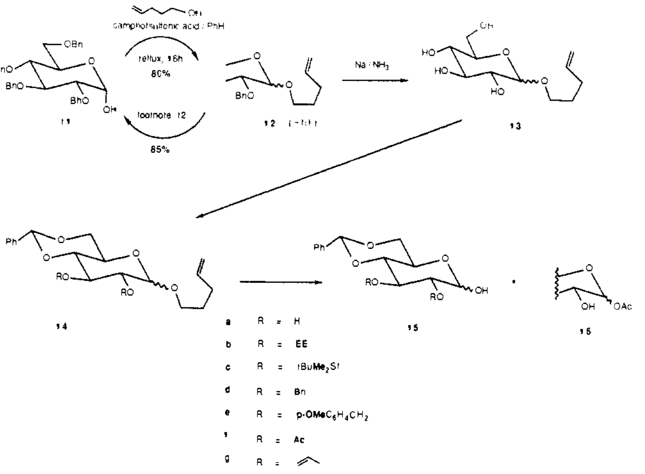


Table I. Deglycosidation of Protected *n*-Pentenyl α,β-D-Glucopyranosides with NBS[a]

entry	substrate	product	reaction time (h)	yield (%)
i	**12**	**11**	3	85
ii	**14a**	**15a**		complex mixture
iii	**14b**	**15b**	16	63
iv	**14c**	**15c**	7	90
v	**14d**	**15d**	6	70
vi	**14e**	**15e**	6	68
vii	**14f**	**15f**	36	62[b]
viii	**14g**	**15g**	9	72[b]

[a] For experimental conditions, see footnote 12. [b] These yields were not optimized. The reactions were stopped at ~50% completion, and the yields are based on recovered starting material.

Accordingly, the perbenzylated *n*-pentenyl glycoside **12**[10] was prepared by Fischer glycosidation of **11**[11] (Scheme II).

(1) Reaction either the α or β anomer of **12** with NBS in wet acetonitrile[12] regenerated **11** cleanly in 85% yield (Table I, entry i).

In order to examine a more discriminating substrate, the benzylidene derivative **14a** was prepared via **13** and converted into various diprotected derivatives, **14b** → **14g**.[10]

(2) Reaction of **14a** itself did not give high yields of **15a**, owing to complex side reactions.

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(1) This work is supported by a grant from the National Science Foundation (CHE 8703916).

(2) (a) Nanasi, P. *Magy. Kem Lapja* **1985**, *40*, 184. (b) Gigg, R. *ACS Symp. Ser.* **1976**, *39*, 253.

(3) See, for example: Sinay, P. *Pure Appl. Chem.* **1987**, *59*, 445. Sadozai, K. K.; Ito, Y.; Nukada, T.; Ogawa, *Carbohyd. Res.* **1986**, *150*, 91. Paulsen, H.; Lorentzen, J. P. *Carbohyd. Res.* **1986**, *150*, 63. Fugedi, P.; Binberg, W.; Garegg, P. J.; Pilotti, A *Carbohyd. Res.* **1987**, *147*, 297. Lemieux, R. U.; Bundle, D. R.; Baker, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4076. Nashed, M. A.; Anderson, L. *Carbohydr. Res.* **1983**, *114*, 43.

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(6) Mootoo, D. R.; Date, V.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1987**, 1462.

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(8) Mootoo, D. R.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1986**, 1570.

(9) At the present time, the formation of bromomethyltetrahydrofuran **7** is only postulated. A search for the compound is underway.

(10) All new compounds were characterized by 300 MHz ^1H NMR and by HRMS and/or elemental analysis.

(11) Schmidt, O. T.; Auer, T.; Schmadel, H. *Chem. Ber.* **1960**, *93*, 556.

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