A novel hydride rearrangement of the acetal group of tetraacetal tetraoxa-cages mediated by Lewis acids

Hsien-Jen Wu* and Jyh-Haur Chern

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, China

Treatment of tetraoxa-cages 1a-1f with Lewis acids such as TiCl4, AlCl3, BF3·OEt2, and MeSO3H in dichloromethane at 25 °C gives the rearrangement products 2a-2f in 90% yields regioselectively and stereoselectively; a novel hydride rearrangement of the acetal group of tetraacetal tetraoxa-cages mediated by Lewis acids.

The reaction chemistry of acetals has been greatly expanded by the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.

Recall, for example, the hydride rearrangement,10–1211 the use of Lewis acidic promoters, particularly in conjunction with silicon-containing nucleophiles.1,2 Usually, acyclic and monocyclic acetals, especially the acetal groups in monosaccharide derivatives, are the objects for study. Recently, we accomplished the synthesis of novel oxo-cage compounds, such as diacetal trioxa-cages,3 triacetal trioxa-cages,4 tetraacetal tetraoxa-cages,5 tetraacetal pentaoxa-cages6 and pentaacetal pentaoxa-cages (the pentaoxa[5]peristylanes).7 All these oxacages contain acetal and ketal groups. As part of a program that involves the synthesis, chemistry and applications of new heterocyclic cages, we report here a novel hydride rearrangement of the acetal group of the tetraacetal tetraoxa-cages 1 mediated by Lewis acids.
the stereoisomer 12 and a subsequent (fast) intramolecular hydride transfer gives 2.

In summary, we have discovered a novel hydride rearrangement of the acetal group of tetraacetal tetraoxa-cages mediated by Lewis acids. The hydride rearrangement is found to be regio- and stereo-selective. We attribute the highly regioselective hydride rearrangement to the unusually large bond angle of C(2)–O(13)–C(8) of the tetraoxa-cages 1.

Financial support from the National Science Council of the Republic of China is gratefully acknowledged. We thank Miss F. L. Liao and Dr S. L. Wang (at the Department of Chemistry, National Tsing Hua University) for their help in carrying out the X-ray crystallographic analysis.

Footnote
† Crystal data: for 9b: C_{10}H_{14}O_{4}, M = 198.2, monoclinic, space group P2_1/n, a = 5.4843(2), b = 13.6462(7), c = 12.2570(6) Å, β = 91.865(2)°, U = 916.8(4) Å^3, Z = 4, R = 0.0422, Rw = 0.0517. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/371.

References
7 H. J. Wu and C. Y. Wu, unpublished results.

Received, 30th October 1996; Com. 6/07403K