from the usual organic solvents. In the cases of the compounds **3c** and **3d** an additional purification was performed by fractional precipitation from CH_2Cl_2/Et_2O and $CH_2Cl_2/MeOH$, respectively. The yields, melting points, and spectral data are summarized in Tables I and II.

Method B. To a suspension of *p-tert*-butylcalix[4]arene toluene complex (1) (1.0 g, 1.36 mmol) in CH_3CN (300 mL) was added K_2CO_3 (0.38 g, 2.74 mmol). In the case of **2e**, a small amount of KI was added also. After being stirred for 30 min at reflux temperature (**2e**) or at room temperature (**2g**), a solution of the bridging reagent **2e**,**g** in CH_3CN (100 mL) was added dropwise to the reaction mixture. The addition times and reaction temperatures are given in Table I. In the case of **2e** the reaction mixture was refluxed for additional 16 h. After removal of the CH_3CN under reduced pressure, CH_2Cl_2 (150 mL) was added to the residue whereupon the organic layer was washed with brine (2 × 75 mL). After removal of the solvent under reduced pressure, the residue was purified by flash chromatography[16] [silica gel, CH_2Cl_2 (**3e**), $CHCl_3$:petroleum ether = 3:1 (**3g**)] to give pure compounds, which in the case of **3e** could not be recrystallized from the usual organic solvents. The yields, melting points, and spectral data are summarized in Tables I and II.

Method C. To a suspension of *p-tert*-butylcalix[4]arene (1) (0.65 g, 1.0 mmol) in CH_3CN (250 mL) was added CsF (0.61 g, 4.0 mmol). After the mixture was stirred for 30 min, a solution of compound **2f** (1.08 mmol) in THF (50 mL) was added dropwise to the refluxing reaction mixture in 24 h. After removal of the solvent under reduced pressure, CH_2Cl_2 (150 mL) was added to the residue whereupon the organic layer was washed with brine (2 × 75 mL). After removal of the solvent under reduced pressure, the residue was separated by flash chromatography[16] [silica gel, $CH_2Cl_2:Et_2O$ = 50:1]. The yields, melting points, and spectral data are summarized in Tables I and II.

X-ray Crystallography of Compound 3g. The crystal structure of compound **3g** was determined by X-ray diffraction. Crystal data: $C_{54}H_{70}O_6$, orthorhombic, space group $P2_12_12_1$; a = 10.026 (2) Å, b = 18.350 (3) Å, c = 26.679 (5) Å, V = 4908 (1) Å^3, $Z = 4$, d_{calc} = 1.103 g cm^{-3}, μ = 0.65 cm^{-1}. Reflections were measured in the $\omega/2\theta$ scan mode, using graphite-monochromated Mo Kα radiation [scan width (ω) 1.00 + 0.34 tan θ]. The structure was solved by direct methods and refined with full-matrix least-squares methods. A total of 2523 reflections with $F_o^2 > 3\sigma(F_o^2)$ was used in the refinement. The number of parameters refined was 361 [scale factor, positional and thermal parameters]. The final R factors were R = 8.0% and R_w = 9.1%. All calculations were done with SDP.[17]

In the crystal structure some disorder was found in the aliphatic chain, as evidenced by the high values of the thermal parameters in this part of the molecule. In order to keep the number of parameters small, thermal parameters were refined isotropically for C and O atoms, with the exception of the C atoms of the aliphatic bridge and the terminal C atoms of the *tert*-butyl groups, which were refined anisotropically. H atoms were added in their calculated positions and treated as riding atoms in the refinement. No hydrogens were added to the aliphatic chain carbon atoms, because of the disorder found. The phenolic H atoms could not be located from a difference Fourier synthesis and have not been included in the refinements.

Acknowledgment. This investigation was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Scientific Research (NWO) and EEC Twinning Project No. ST2J-0215. We also acknowledge J. M. Visser and J. L. M. Vrielink for recording the NMR, T. W. Stevens for recording the mass spectra, A. M. Montanaro-Christenhusz for performing the elemental analyses, and I. Jansen and W. T. Reinalda for their contributions.

Registry No. 1, 60705-62-6; **2a**, 17619-15-7; **2b**, 7357-41-7; **2c**, 6472-69-1; **2d**, 6423-26-3; **2e**, 24656-53-9; **2f**, 88-95-9; **2g**, 111-19-3; **3a**, 128217-27-6; **3b**, 128217-28-7; **3c**, 128217-29-8; **3d**, 128242-26-2; **3e**, 128217-30-1; **3f**, 128217-31-2; **3g**, 128217-32-3; **4a**, 128217-33-4; **4b**, 128217-34-5; **5**, 128217-35-6.

Supplementary Material Available: Figure showing **3a** with atom labels and tables of positional and thermal parameters, bond distances, and angles (9 pages). Ordering information is given on any current masthead page.

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[17] Structure Determination Package, B. A. Frenz and Associates Inc., College Station, TX, and Enraf-Nonius, Delft, The Netherlands, 1983.

C-Nitration of 2,6-Di- and 2,4,6-Tri-*tert*-butylpyridine with Nitronium Tetrafluoroborate[1]

George A. Olah,* Khosrow Laali, Omar Farooq, and Judith A. Olah

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

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Electrophilic substitution of pyridine occurs preferentially on the heteroatom (N-substitution). Nitration of pyridine with mixed nitric–sulfuric acid gives a low yield of the 3-nitro product, indicative that the nitration is that of the pyridinium ion formed by protonation in the acid medium.[2] The most convenient method of preparing 4-nitropyridine is that through nitration of pyridine *N*-oxide, followed by deoxygenation (for example with phosphorous trichloride).[3] Nitronium salts when reacted with pyridine gave *N*-nitropyridinium salts (N-nitration).[4] Nitration of 2,6-dimethylpyridine and 2,4,6-trimethylpyridine also occurred on nitrogen. The resulting pyridinium salts are effective transfer nitration reagents.[5,6] Whereas 2,6-di-*tert*-butylpyridine[7] has found extensive use as proton trap in synthetic chemistry,[8] electrophilic chemistry of hindered pyridines has not been explored.

We have now found that when reacting sterically crowded 2,6-di- and 2,4,6-tri-*tert*-butylpyridine with nitronium tetrafluoroborate nitration occurred exclusively in the ring. Thus, when 2,6-di-*tert*-butylpyridine was reacted with $NO_2^+BF_4^-$ in dry CH_2Cl_2 or CH_2Cl_2/sulfolane, apart from unreacted starting material, 28% 2,6-di-*tert*-butyl-4-nitropyridine and 6% 2,6-di-*tert*-butyl-3,4-dinitropyridine were formed.

Similarly, 2,4,6-tri-*tert*-butylpyridine when reacted with $NO_2^+BF_4^-$ in CH_2Cl_2 gave 36% 2,4,6-tri-*tert*-butyl-3-nitropyridine as the only product after workup.

Removal of the *tert*-butyl groups by acid-catalyzed transalkylation was also attempted in an attempt to obtain nitropyridines. *tert*-Butylnitropyridines were refluxed over superacidic Nafion-H or with CF_3SO_3H in excess benzene.

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[1] Aromatic Substitution. 59. For part 58, see: Olah, G. A.; Farooq, O.; F. Farnia, S. M.; Wu, A. *J. Org. Chem.* **1990**, *55*, 1516.

[2] Olah, G. A.; Malhotra, R.; Narang, S. C.; *Nitration: Methods and Mechanisms*; VCH Publishers: New York, 1989.

[3] Norman, R. O. C. In *Principles of Organic Synthesis*; Chapman and Hall: London, 1978; p 404.

[4] Olah, G. A.; Olah, J. A.; Overchuk, N. A. *J. Org. Chem.* **1965**, *30*, 3373.

[5] Cupas, C. A.; Pearson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 4742.

[6] Olah, G. A.; Narang, S. C.; Olah, J. A.; Pearson, R. L.; Cupas, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 3507.

[7] Scalzi, F. V.; Golob, N. F. *J. Org. Chem.* **1971**, *36*, 2541. 2,6-Di-*tert*-butyl- and 2,4,6-Tri-*tert*-butylpyridine are also commercially available (Aldrich).

[8] Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438. Stang, P. J.; Treptow, W. *Ibid.* **1980**, 283.

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However, no dealkylation was observed. Similar results were obtained in control experiments when 2,4,6-tri-*tert*-butylpyridine was treated with $CF_3SO_3H-SbF_5$ (1:1)/Freon-113 in excess benzene. Facile N-protonation substantially reduces the reactivity of the pyridine ring for further electrophilic attack and protonation ipso to the *tert*-butyl groups needed for transalkylation is prevented.

Experimental Section

2,6-Di-*tert*-butylpyridine (10 mmol) was reacted with 5 mmol of nitronium tetrafluoroborate in 30 mL of dry methylene chloride (or a 1:1 w/w mixture of methylene chloride and sulfolane) with good mixing at room temperature for 4 h. The reaction mixture was subsequently quenched with a solution of sodium bicarbonate/ice water and extracted with ether, and the organic layer was separated, dried, and analyzed by GC–MS using a Finnigan Model Incos-50 GC-MS spectrometer. Apart from unreacted starting material 28% (by GC), 2,6-di-*tert*-butyl-4-nitropyridine [*m/e* 236 (M, 2), *m/c* 191 (M – NO_2, 100)] and 6% (by GC) 2,6-di-*tert*-butyl-3,4-dinitropyridine [*m/c* 281 (M, 33)] were obtained.

Nitration of 2,4,6-tri-*tert*-butylpyridine under similar conditions gave apart from unreacted starting material 36% (by GC) 2,4,6-tri-*tert*-butyl-3-nitropyridine [*m/c* 292 (M, 3), *m/c* 247 (M – NO_2, 100)].

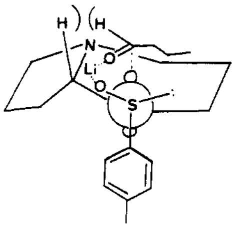
Acknowledgment. Support of our work by the US Army Office of Research and subsequently by the Office of Naval Research is acknowledged.

Additions and Corrections

Vol. 55, 1990

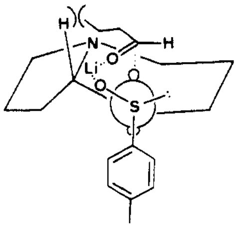
Duy H. Hua,* S. Narasimha Bharathi, Paul D. Robinson, and Atsuko Tsujimoto. Asymmetric Total Syntheses of Elaeokanines A and B via α-Sulfinyl Ketimine.

Page 2130, Scheme IV: structures "Transition State A_1" and "Transition State B_1" should be drawn as shown below



13a

Transition State A1



13a

Transition State B1

Page 2130, column 1, paragraph 2, line 7: the sentence "Greater repulsion ... product." should read "Transition state B_1 shows greater repulsion between the C-8a hydrogen of **13a** and the propyl group of butyraldehyde than with the formyl hydrogen in transition state A_1. And, greater repulsion between the C-6, C-7 hydrogens of **13a** and the propyl group of butyraldehyde in transition state B_2 than between these hydrogens and the formyl hydrogen of butyraldehyde in transition state A_2 accounts for the absence of the C-1′-(*R*) product."

B. Mario Pinto,* Michiel M. W. Buiting, and Kerry B. Reimer. Use of the [β-(Trimethylsilyl)ethoxy]methyl (SEM) Protecting Group in Carbohydrate Chemistry. Fully Functionalized Rhamnose Acceptors and Donors for Use in Oligosaccharide Synthesis.

Page 2177. Regarding the statement that the scope of the SEM protecting group has not been evaluated in the field of carbohydrate chemistry (ref 5), we wish to point out that the use of the β-(trimethylsilyl)ethyl group for protection of the anomeric center in carbohydrates is formally analogous and has been investigated.[1] Our work deals specifically with the protection of nonanomeric, secondary alcohol functions as SEM acetals.

The deprotection or manipulation of the β-(trimethylsilyl)ethyl glycosides by fluoride assisted reaction or by electrophilic catalysis has also been reported.[1]

Finally, we note that Lipshutz and Miller[2] have recently reported a new set of standard conditions for removal of SEM acetals.

(1) Lipshutz, B. H.; Pegram, J. H.; Morey, M. C. *Tetrahedron Lett.* **1981**, *22*, 4603. Jansson, K.; Frejd, T.; Kihlberg, J.; Magnusson, G. *Tetrahedron Lett.* **1986**, *27*, 753; **1988**, *29*, 361. Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G. *J. Org. Chem.* **1988**, *53*, 5629. Jansson, K.; Magnusson, G. *Tetrahedron* **1990**, *46*, 59.

(2) Lipshutz, B. H.; Miller, T. A. *Tetrahedron Lett.* **1989**, *30*, 7149.

Stanislaw Lochynski, Henry J. Shine,* Miroslaw Soroka, and T. Krishnan Venkatachalam. Evidence for Electron Transfer in Reactions of Thianthrene Cation Radical with Dialkyl Mercurials.

Page 2704, in Table I, column 14 headed 2-RTh^b, line 4 should read 6.3^e rather than 1.3^e.