

**Cleavage of Ethers and Geminal Diacetates Using the Boron  
Triiodide-N,N-Diethylaniline Complex**

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**Abstract:** The boron triiodide-N,N-diethylaniline complex, generated *in situ* from borane:N,N-diethylaniline and iodine cleaves ethers and regenerates carbox-aldehydes from the corresponding geminal diacetate derivatives under mild conditions in good yields.

Recently a simple procedure for the preparation of alkyl and alkenyl iodides in good yields using boron triiodide-N,N-diethylaniline complex and acetic acid was reported.<sup>1</sup> This prompted us to report our results on the cleavage of ethers and regeneration of aldehydes from geminal diacetates using the boron triiodide-N,N-diethylaniline reagent.

**Cleavage of Ethers:**

Phenolic hydroxy groups are generally protected<sup>2</sup> as alkyl ethers and esters; ether cleavage can then be affected by a variety of reagents.<sup>3</sup> There is continued interest in developing new reagents which dealkylate ethers under mild conditions.<sup>4</sup>

Addition of a solution of methyl 2-naphthyl ether (3.0 mmole) in dry benzene (10 ml) to a complex of boron triiodide-N,N-diethylaniline complex (3.0 mmole) [prepared from the borane-N,N-diethylaniline complex (3.0 mmole) and iodine (9.0 mmole)] under an argon atmosphere at room temperature resulted in a dark reaction mixture. After three hours 2-naphthol was isolated in 94% yield. Other aromatic ethers underwent cleavage to give the corresponding phenols in good yields. (Table)

Ortho substituents do not impede the cleavage (entry 4) but ethers bearing electron withdrawing substituents on the aryl nucleus (2- nitro and 4- nitro) are unreactive. The mode of dealkylation, presumably is analogous to that reported<sup>5</sup> for boron tribromide. As anticipated alkyl ethers produce iodinated products; thus ethers entry 6 and 7 produced benzyl iodide and diiodobutane respectively.

**Regeneration of Carboxaldehydes from Geminal Diacetates:**

Formation of 1,1-diacetates<sup>6</sup> from aldehydes has been the basis of the preparation of aldehydes from the corresponding toluenes. We found that addition of a solution of diacetate (entry 9, 1.0 mmol) in benzene (10 ml) to the BI<sub>3</sub> complex (1.0 mmol) in benzene (15 ml) under argon at room temperature

yielded 4-methylbenzaldehyde in 66% yield. Other diacetates were successfully cleaved. (Table) As in the ether cleavages, diacetates derived from aryl carboxaldehydes with electron withdrawing substituent (4-nitro) did not undergo the reaction.

Conversion of diacetates to the corresponding aldehydes has also been accomplished with both sodium hydroxide and potassium carbonate in aqueous tetrahydrofuran overnight.<sup>7</sup> Under our reaction conditions, the ester group was found to be unaffected. (entry 12) We are currently exploring the synthetic utility of the BI<sub>3</sub> reagent for other functional group transformations.

**Table: Cleavage of Ethers and Geminal Diacetates**

| Entry No. | Substrate                                                                                           | Time/h | Product                                                                               | Yield% <sup>a</sup> |
|-----------|-----------------------------------------------------------------------------------------------------|--------|---------------------------------------------------------------------------------------|---------------------|
| 1         | C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>                                                      | 3      | C <sub>6</sub> H <sub>5</sub> OH                                                      | 85                  |
| 2         | 4-BrC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>                                                  | 4      | 4-BrC <sub>6</sub> H <sub>4</sub> OH                                                  | 86                  |
| 3         | 3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OCH <sub>3</sub>                                  | 4      | 3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OH                                  | 67                  |
| 4         | 2-t-C <sub>4</sub> H <sub>9</sub> -5-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> OCH <sub>3</sub> | 3      | 2-t-C <sub>4</sub> H <sub>9</sub> -5-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> OH | 71                  |
| 5         | 2-C <sub>10</sub> H <sub>7</sub> OCH <sub>3</sub>                                                   | 3      | 2-C <sub>10</sub> H <sub>7</sub> OH                                                   | 94                  |
| 6         | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>        | 2.5    | C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> I                                       | 88                  |
| 7         | Tetrahydrofuran                                                                                     | 3      | I(CH <sub>2</sub> ) <sub>4</sub> I                                                    | 62                  |
| 8         | C <sub>6</sub> H <sub>5</sub> CH(OAc) <sub>2</sub>                                                  | 3      | C <sub>6</sub> H <sub>5</sub> CHO                                                     | 65                  |
| 9         | 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(OAc) <sub>2</sub>                                | 3      | 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO                                   | 66                  |
| 10        | 4-BrC <sub>6</sub> H <sub>4</sub> CH(OAc) <sub>2</sub>                                              | 3      | 4-BrC <sub>6</sub> H <sub>4</sub> CHO                                                 | 65                  |
| 11        | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(OAc) <sub>2</sub>                                | 2.5    | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CHO                                   | 60                  |
| 12        | 4-OHCC <sub>6</sub> H <sub>4</sub> COOCH <sub>3</sub>                                               | 1.5    | 4-OHCC <sub>6</sub> H <sub>4</sub> COOCH <sub>3</sub>                                 | 65                  |

<sup>a</sup>Unoptimized isolated yields.

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