Selective Cleaving Reagents



Iodotrimethylsilane

Iodotrimethylsilane (1) has recently been introduced by Jungi and Olah² as an efficient and convenient reagent for the cleavage of esters and ethers under neutral conditions. Iodotrimethylsilane has advantages over other dealkylating agents in that mild, homogeneous reaction conditions can be employed.² Hence, a mixture of 1 and a carboxylic ester, either neat² or in an aprotic solvent, gave the corresponding acid on heating and subsequent aqueous hydrolysis.

$$RCO_2R'$$
 + Me_3SiI $\xrightarrow{-R'I}$ 1

 RCO_2SiMe_3 $\xrightarrow{H_2O}$ RCO_2H

tert-Butyl and benzyl esters were rapidly dealkylated at 25°C, whereas methyl, ethyl, and isopropyl esters required higher reaction temperatures.

Iodotrimethylsilane has also been used to cleave alkyl and aryl ethers.^{2,3} Jung and Lyster³ have recently examined cleavage conditions for a wide variety of ethers. For example, heating an excess of iodotrimethylsilane with alkyl aryl ethers gave good yields of aromatic trimethylsilyl ethers (2). These may be converted to their respective alcohols by simple hydrolysis.

ArOR
$$\frac{1}{-RI}$$
 ArOSiMe₃ $\frac{H_2O}{}$ ArOH

Certain alkyl ethers are selectively and quantitatively cleaved, as shown in the following equation:

$$C_6H_{11}OR$$
 $\xrightarrow{1}$ $C_6H_{11}OSIMe_3$ $\xrightarrow{H_2O}$ $C_6H_{11}OH$

R = t-Bu, CH_2Ph , CPh_3

The ester and ether cleavages with iodotrimethylsilane apparently do not affect isolated double bonds, ketones, thioethers, amines, or amides.1

Aldrich offers iodotrimethylsilane in 5- and 25-g units, stored over copper.

References:

M.E. Jung and M.A. Lyster, J. Am. Chem. Soc., 99, 968 (1977).
 T.-L. Ho and G.A. Olah, Angew. Chem., Int. Ed. Engl., 15, 774 (1976).

3) M.E. Jung and M.A. Lyster, J. Org. Chem., in press.

19,552-9 Iodotrimethylsilane

5g \$9.60; 25g \$32.00

Cyssor I

Cyssor I [2-methyl- N^1 -benzenesulfonyl- N^4 -(bromoacetyl)quinonediimide, 1] is a new reagent designed by R.G. Lawton and T.J. Holmes for cysteine modification and selective cleavage of proteins. The term Cyssor I is an acronym for "cysteine-specific scission by an organic reagent" which appropriately describes the reagent's function.

Cyssor I offers potential applications in protein modification and structure determination. It has the advantage that it can be employed under mildly acidic conditions, thereby suppressing complications arising from the use of strongly alkaline conditions.

The incubation of ovalbumin or reduced bovine pancreatic ribonuclease with Cyssor I resulted in fragmentation believed to occur at the sulfhydryl sites. Evidence for this selective protein cleavage is based on the reaction of Cyssor I with a model substrate, N-acetylcysteine (2). The reaction in-

volves regiospecific alkylation (easily monitored by ultraviolet spectroscopy) and subsequent cleavage to yield 4, isolated as a solid in 75% yield. Degradation of 3 can occur via either of two proposed routes, both of which result in cysteine-specific cleavage.

Aldrich offers Cyssor I as a stable, yellow, crystalline solid.

Reference:

1) T.J. Holmes, Jr. and R.G. Lawton, J. Am. Chem. Soc., 99, 1984 (1977).

19,584-7 Cyssor I

1g \$12.00; 5g \$48.00

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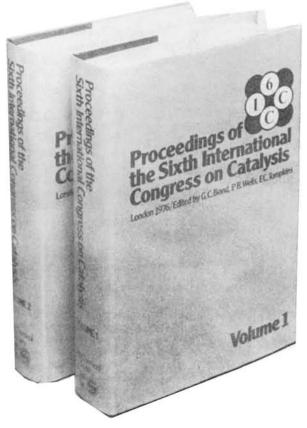
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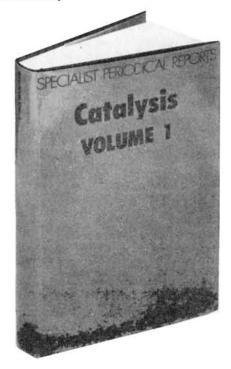
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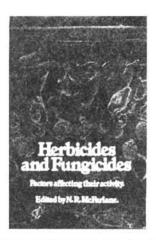


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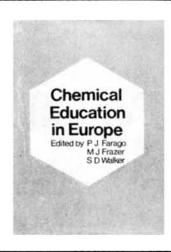
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ITS STUDY BY CRYSTAL DIFFRACTION

J. Clare Speakman



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