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RAPID, HIGH-YIELD CLEAVAGE OF ENOL AND DIENOL METHYL ETHERS UNDER MILD CONDITIONS USING CHLOROTRIMETHYLSILANE/SODIUM IODIDE

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Abstract: A number of enol and dienol methyl ethers are rapidly cleaved to aldehydes and ketones in quantitative yields by the use of chlorotrimethylsilane/sodium iodide.

In connection with our work on the preparation and Diels-Alder reactions of dienes substituted with methoxy and phenylthio groups[1,2] we required, for purposes of structural proof, a method of cleavage of these dienes to aldehydes and ketones. These dienes are very susceptible to acid catalyzed polymerization and this is the reason that they are prepared and used in the presence of diisopropylethylamine.[1] Thus, it is not surprising that the usual aqueous acid conditions for the hydrolysis of enol ethers failed to yield hydrolysis product, leading instead to polymer.[3]

Morita[4] and Olah[5] and their co-workers have recently introduced the convenient reagent chlorotrimethylsilane/sodium iodide for the cleavage of esters and ethers; aryl alkyl ethers are cleaved in generally satisfactory yields when treated with the reagent for at least two hours at elevated temperatures. These publications followed earlier reports by Jung and Lyster[6] and by Ho and Olah[7] of the cleavage of aryl alkyl ethers by trimethylsilyl iodide and by phenyltrimethylsilane/iodine, respectively.

We have now found that a number of dienol methyl ethers as well as enol methyl ethers are cleaved in less than five minutes at ambient temperature by the use of chlorotrimethylsilane/sodium iodide in acetonitrile. Aqueous work-up or treatment with alumina provides the aldehydes and ketones in quantitative yields (Table).[8] We have not tried the far more expensive and difficultly storable iodotrimethylsilane in this cleavage but its success is not assured since this reagent is reported[9] to undergo attack on enones.

The procedure for preparing synthetically useful quantities of aldehydes and ketones follows. One equivalent of chlorotrimethylsilane[10] is injected into a dry, argon-filled flask containing anhydrous acetonitrile which is 0.05 M in both the enol ether and sodium iodide. The deep orange mixture containing a white precipitate is stirred at ambient temperature (20°C) for 5 min and then partitioned between 0.5 N aq. sodium thiosulfate solution and ether. The dried ($MgSO_4$) organic phase is concentrated and diluted with carbon tetrachloride. The solution is redried with fresh $MgSO_4$; removal of the solvent in vacuo provides the carbonyl compound in quantitative yield.

An alternative procedure, which is more convenient for small scale (0.1 - 0.3 mmol) reactions performed for structural proofs, utilizes a non-aqueous work-up. The reaction mixture is rapidly passed through an alumina column (activity III) and eluted with 5 column volumes of acetonitrile. The solvent is removed in vacuo to provide the carbonyl compound in quantitative yield.

The reaction conditions are surprisingly mild, far milder in fact than those in any published procedures for the cleavage of ethers (including phenolic ethers) by chlorotrimethylsilane/sodium iodide or related reagents.[4-7] The brevity, simplicity, and mild, non-acidic conditions as well as the quantitative yields should designate this procedure as the first to be tried for the hydrolysis of methyl enol ethers and it should be particularly welcome when the reactants or products contain acid sensitive groups. In some cases, such as in the production of the type of aldehydes shown in entries 3-5 of the table, the synthesis of the diene[2] and its cleavage may constitute a viable preparative method.[11]

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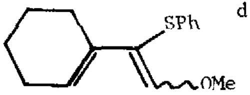
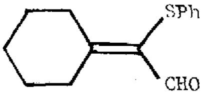
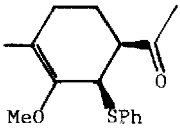
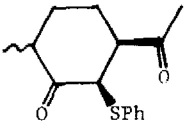
Table. Cleavage of Dienol and Enol Methyl Ethers by Means of Chlorotrimethylsilane/Sodium Iodide in Acetonitrile

Ether (ref. to preparation)	Product[a]
(Z)-CH_2=CHC(OMe)=CHSPh (1a,b)	CH_2=CHCOCH_2SPh
(Z)-CH_2=C(Me)C(OMe)=CHSPh (2)	CH_2=C(Me)COCH_2SPh
MeCH=CHC(SPh)=CHOMe[b] (2)	C_2H_5CH=C(SPh)CHO[c]
MeCH=C(Me)C(SPh)=CHOMe[b] (2)	C_2H_5C(Me)=C(SPh)CHO[d]
 [d] (2)	
(Z)-PhCH=CHOMe (11)	PhCH_2CHO
 (12)	

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[a] The yields were quantitative in all cases.

[b] Two isomers, presumably E,E and Z,E; see ref. 2.

[c] A single isomer of unknown stereochemistry.

[d] An approximately 1:1 mixture of E and Z isomers.

References and Notes

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12. This enol ether is the Diels-Alder adduct of methyl vinyl ketone with the diene[2] in the second entry of the Table. Details will be published at a later date.

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