Tetrahedron Letters No. 48, pp 4679 - 4680.

0040-4039/79/1122-4679$02.00/0

REACTION OF ACETALS AND TRIALKYLSILANES CATALYZED BY TRIMETHYLSILYL TRIFLUOROMETHANESULFONATE. A SIMPLE METHOD FOR CONVERSION OF ACETALS TO ETHERS[1]

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Summary: A mild, catalytic procedure for converting acetals to ethers is described.

Acetals, a masked form of carbonyl compounds, can be reduced directly to their lower oxidation state products under certain conditions.[2] Described herein is a procedure which effects such transformation leading to ethers under very mild reaction conditions.

This method utilizes trimethylsilane (or triethylsilane) as the reducing agent and trimethylsilyl trifluoromethanesulfonate as the catalyst. Apparently the trialkylsilyl moiety is playing a role of the chain-carrying cationic species. As shown in Table I, both aliphatic and aromatic substrates are employable.[3]

$$R_2C(OCH_3)_2 \quad + \quad (CH_3)_3SiH \quad \xrightarrow[-(CH_3)_3SiOCH_3]{(CH_3)_3SiOTf} \quad R_2CHOCH_3$$

The following experimental procedure is representative. A methylene chloride solution (0.5 ml) containing trimethylsilyl trifluoromethanesulfonate (11 mg, 0.05 mmol, 1 mol %) was covered under argon and cooled at 0 °C. To this were added successively trimethylsilane (420 mg, 5.7 mmol) and benzaldehyde dimethyl acetal (780 mg, 5.1 mmol) through a cooled syringe. The resulting mixture was stirred at 0 °C for 30 min and then allowed to stand at 28 °C for 13 h, and poured into a saturated $NaHCO_3$ solution (15 ml). The mixture was extracted three times with ether (20 ml). The combined ethereal solutions were dried over Na_2SO_4 and evaporated under reduced pressure (35 mmHg) to leave pure (NMR and GLC analysis) benzyl methyl ether as an oil (598 mg, 96% yield).

Acknowledgment. This work was supported in part by a grant from the Ministry of Education, Japanese Government (Grant-in-aid, No 403022).

Table I. Reaction of Acetals and Trialkylsilanes in the Presence of $(CH_3)_3SiOTf$[a]

acetal	product	% yield[b]
butyraldehyde dimethyl acetal	butyl methyl ether	100[c]
benzaldehyde dimethyl acetal	benzyl methyl ether	96
benzaldehyde dimethyl acetal[d]	benzyl methyl ether	90
3-pentanone dimethyl acetal	methyl 3-pentyl ether	100[c]
cyclohexanone dimethyl acetal	cyclohexyl methyl ether	76, 100[c]
4-*tert*-butylcyclohexanone dimethyl acetal[e]	4-*tert*-butylcyclohexyl methyl ether	89 (cis/trans = 44:56)

[a] The reaction was conducted in methylene chloride using an acetal, trimethylsilane, and trimethylsilyl trifluoromethanesulfonate (1:1.1:0.01 ratio) at 0 °C for 30 min and then 24–28 °C for 12–14 h. All products were identified by the spectral comparison with authentic samples. [b] Isolated yield. [c] Determined by GLC analysis. [d] Reaction using triethylsilane in place of trimethylsilane (0 °C for 30 min and 29 °C for 16 h). [e] Reaction using 3.4 mol % of $(CH_3)_3SiOTf$.

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3. When a ketone is used in place of acetals, a significant amount of dimeric ether is produced. For example, reaction of cyclohexanone with trimethylsilane under the comparable conditions gave dicyclohexyl ether in 86% yield.

(Received in Japan 31 August 1979)