

An Improved Procedure for the Deprotection of Acetals with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$

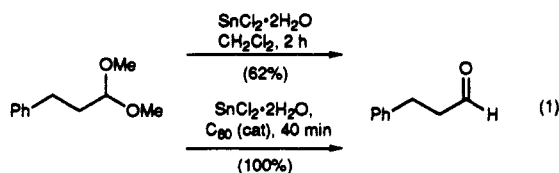
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Received February 16, 1993

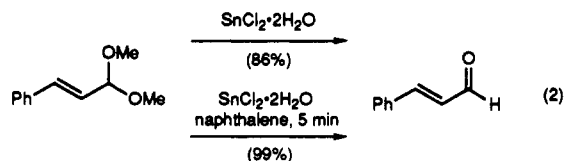
Recently, we described a new method for the deprotection of acetals using tin dichloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$).¹ Under neutral or even mildly basic conditions, both nonconjugated and conjugated acetals are converted to aldehydes when treated with 1 equiv of this stannylene. Yields range from 62–94% for dimethoxy and diethoxy acetals and 84–95% for conjugated dioxolanes; poorer yields were obtained for conjugated 1,3-dioxanes and nonconjugated dioxolanes.

During the course of this study, we observed that the reaction proceeded more rapidly and in higher yield when run in the presence of naphthalene.² For example, deprotection of the dimethoxy acetal of hydrocinnamaldehyde under our standard conditions was achieved in 62% yield after 2 h (Figure 1). When the same reaction was run in the presence of 1 equiv of naphthalene, however, an 84% yield was obtained after 2 h. Remarkably, addition of 1 equiv of C_{60} ³⁻⁵ resulted in a quantitative yield of hydrocinnamaldehyde in only 40 min (eq 1). Similarly,



addition of 10 mol% C_{60} or 10 mol% C_{60} -soot⁶ also resulted in quantitative yield of aldehyde in less than 1 h.

Similar improvements in yield and reaction time were also observed with conjugated acetals. The dimethoxy and diethoxy acetals of cinnamaldehyde, for example, were cleaved in quantitative yield in only 5 min in the presence of naphthalene (eq 2). We also were pleased to find that



(1) Ford, K. L.; Roskamp, E. J. *Tetrahedron Lett.* 1992, 33, 1135.

(2) Naphthalene was originally added as an internal standard in order to monitor the course of the reaction by gas chromatography.

(3) Pure crystalline C_{60} was used in these studies. More recently, we have repeated these experiments with a mixture of $\text{C}_{60}/\text{C}_{70}$ and with crude C_{60} soot with equally good results.

(4) For the preparation of fullerenes see: Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature*, 1990, 347, 354. Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* 1990, 1423. Ajie, H.; Alveraz, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Schriver, K. E.; Sen Sharma, D.; Whetten, R. L. *J. Phys. Chem.* 1990, 94, 8630.

(5) Recent reviews: McLafferty, F. W. *Acc. Chem. Res.* 1992, 25, 98–169. Kroto, H. W. *Angew. Chem. Int. Ed. Engl.* 1992, 31, 111. Schwarz, H. *Angew. Chem. Int. Ed. Engl.* 1992, 31, 293. *Ibid. Chem. Rev.* 1991, 91, 1213. *Ibid. Chem. Rev.* 1989, 89, 1713.

(6) This material was obtained by extraction of crude soot with toluene.

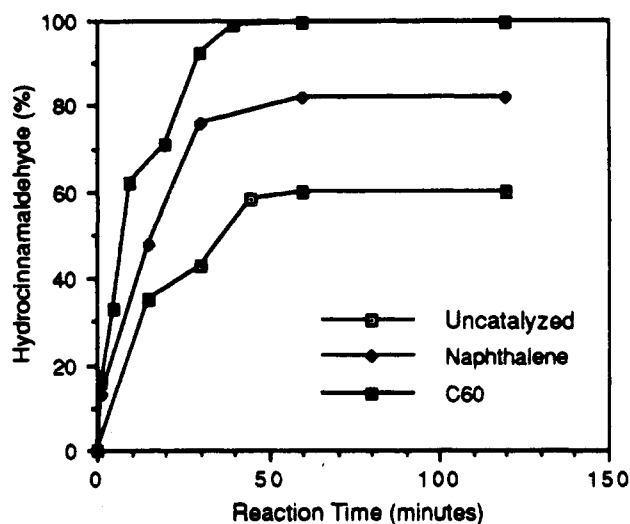


Figure 1. Effect of promoters on the deprotection of acetals by $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Table I. Effect of Promoters on the Deprotection of Acetals

acetal	% yield of aldehyde ^a (time, h) ^b		
	no promoter	naphthalene ^c	C_{60} ^c
	62(2)	84(2)	100(0.67) ^d
	80(2)	88(2)	100(0.58)
	15(16)	17(16)	22(4)
	86(1)	100(0.08) ^e	100(0.25)
	84(1)	100(0.08)	—
	38(16)	53(2)	63(3)

^a Following distillation of the crude product, the acetal/aldehyde ratio and the yield were determined by GC by using calibrated standards. ^b Reactions were run until no further change in aldehyde/acetal ratio was observed. ^c The data in Table I are based on 1 equiv of naphthalene or 1 equiv of C_{60} . ^d 100% Isolated yield was obtained in 1 h using 10 mol% C_{60} -soot (See Experimental Section). ^e 99% Isolated yield.

aromatic promoters improved the yield of deprotection reactions involving sluggish substrates, such as conjugated pyrans. The 1,3-dioxane of cinnamaldehyde was hydrolyzed in 38% under our original conditions, in 53% when naphthalene was added, and in 63% in the presence of C_{60} (Table I).

The aromatic compounds may be acting as phase-transfer catalysts by forming reversible arene complexes with tin dichloride.^{7,8} Under our standard conditions,

(7) Arene complexes of tin(II) chloride have been characterized by X-ray crystallography. These complexes readily lose their benzene or xylene ligands: Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* 1968, 90, 5941. Luth, H.; Amma, E. L. *J. Am. Chem. Soc.* 1969, 91, 7515. Weininger, M. S.; Rodesiler, P. F.; Gash, A. G.; Amma, E. L. *J. Am. Chem. Soc.* 1972, 94, 2135. Gash, A. G.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* 1974, 13, 2429.

(8) The possibility of an initial electron transfer step between tin dichloride and the aromatic compound exists. Since no color change was observed in reactions with either naphthalene or anthracene, the presence of highly colored radical anions seems unlikely.

SnCl_2 remained at the bottom of the flask, and the solution was both clear and colorless. Addition of naphthalene resulted in formation of an opaque white suspension, regardless of the rate of stirring or whether acetal was present. In reactions where C_{60} was added, the reaction mixture became a brown suspension, making it more difficult to assess the dispersion of tin dichloride. In both cases, the aromatic compounds were recovered unchanged and used in subsequent experiments without loss of activity.

Experimental Section

Spectra were recorded on a Varian Gemini 300-MHz spectrometer at a frequency of 300 MHz (^1H NMR). Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane. Coupling constants are reported in hertz (Hz). Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. Dichloromethane was distilled from calcium hydride. Acetals were prepared according to literature procedures.⁹ Reactions were monitored by capillary GLC analyses on an HP 5880A gas chromatograph equipped with a DB-5 (J & W Associates) fused silica 15-m capillary column and a flame-induction detector.

Deprotection of Dimethoxy Acetals. To a well-stirred suspension of 0.880 g (3.90 mmol) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.300 g

(0.39 mmol) of C_{60} -soot⁸ in 25 mL of methylene chloride at 0 °C was slowly added a solution of 0.700 g (3.90 mmol) of 1,1-dimethoxy-3-phenylpropane in 5 mL of methylene chloride. The ice bath was then removed and the reaction mixture allowed to warm to room temperature. After stirring for 45 min at room temperature, the reaction mixture was treated with 0.5 g of NaHCO_3 and then concentrated at reduced pressure. The residue was purified by Kugelrohr distillation (ca. 80 °C, 0.2 mmHg) to give 0.514 g (100%) of hydrocinnamaldehyde as a colorless oil: GC retention time 8.5 min; ^1H NMR (300 MHz, CDCl_3) δ 9.8 (s, 1 H), 7.3 (m 5 H), 3.0 (t, $J = 7$ Hz, 2 H), 2.8 (t, $J = 7$ Hz, 2 H).

Deprotection of Conjugated Dimethoxy Acetals. To a well-stirred suspension of 1.27 g (5.62 mmol) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.720 g (5.62 mmol) of naphthalene in 25 mL of methylene chloride at 0 °C was slowly added a solution of 1.00 g (5.62 mmol) of 1,1-dimethoxy-3-phenyl-2-propene in 5 mL of methylene chloride. The ice bath was then removed and the reaction mixture allowed to warm to room temperature. After stirring for 5 min at room temperature, the reaction mixture was treated with 0.5 g of NaHCO_3 and then concentrated at reduced pressure. The residue was purified by Kugelrohr distillation (ca. 80 °C, 0.2 mmHg) followed by column chromatography (silica gel 60, hexane then EtOAc) to give 0.734 g (99%) of cinnamaldehyde as a light yellow oil: GC retention time 9.5 min; ^1H NMR (300 MHz, CDCl_3) δ 9.7 (d, $J = 8$ Hz, 1 H), 7.4 (m 6 H), 6.6 (dd, $J = 16, 8$ Hz, 1 H).

Acknowledgment. We wish to thank both M.M. Kappes and C.A. Mirkin for samples of C_{60} and the National Institutes of Health (GM42732) for support of this research.

(9) Meskens, F. A. J. *Synthesis* 1981, 501.