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Stepwise Reduction of Acetals to the Corresponding Hydrocarbons. A Mild and Effective Transformation via Carbinyl Bromides

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Synopsis. Stepwise reduction of two alkoxyl groups in acetal was effected by the action of triethylsilane along with acetyl bromide and $SnBr_2$ and then of tributyltin hydride (or lithium aluminium hydride) providing methyl or methylene compounds in good yields under very mild conditions.

The dealkoxylation of aldehyde- or ketone-acetals to the corresponding methyl or methylene compounds is one of the reactions of potential usefulness in organic synthesis. Although a methodology similar to this transformation via dithioacetals has been well-established,1) dealkoxylative reduction of dialkyl acetals usually leads to the mono-dealkoxylated products2) which are sluggish to further reduction.3)

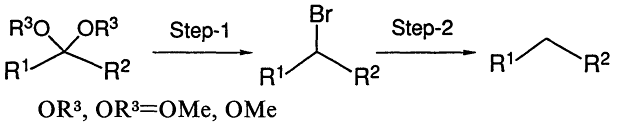
Now we wish to report a mild and convenient procedure to effect stepwise reduction of two alkoxyl groups in acetals to give the corresponding methyl or methylene compounds.

Our previous investigation4) on the halogenative reduction of acetals to corresponding carbinyl halides with triethylsilane promoted by SnX_2/AcX5) suggested that the subsequent reduction of thus obtained halides to alkanes would provide a two-step conversion of acetals to alkanes, which would constitute a mild and convenient alternative to Wolff-Kizhner6) or Clemmensen reduction7) of the parent carbonyl compounds.

In the first place, we undertook to examine the reduction of 1-naphthaldehyde dimethyl acetal to 1-methylnaphthalene. First reduction of acetal to 1-bromomethylnaphthalene was carried out according to the procedure described in the previous paper.4) Subsequent reduction of the bromide to 1-methylnaphthalene was effected by tributyltin hydride in benzene. The two-step conversion either with or without the purification of the intermediate, 1-bromomethylnaphthalene, invariably afforded 1-methylnaphthalene in 85% overall yield. A one-pot operation with an intermediary manipulation for solvent exchange has proved to be satisfactory enough with a minimal loss of yield (77% overall). While the tin hydride reduction for the second step is most mild and effective, less selective lithium aluminium hydride may also be employed as an alternative reagent of choice in cases where the radical reduction is hampered by undesirable side reactions.

The reaction was conducted with various acetals under the optimum conditions and the results are summarized in Table 1. Higher yields were obtained in the cases of aromatic aldehyde acetals (Entries 1—7). Ketone acetals also gave the corresponding methylene compounds in good yields (Entries 9—14). In the case of aliphatic ketone acetals, a small amount of olefin (9—25%) was obtained as a by-product (Entries 12, 13, and 14). The reaction was also effective to ethylene acetal to result in the corresponding hydrocarbon (Entries 3 and 11).

Table 1. Stepwise Reduction of Acetals to the Corresponding Hydrocarbonsa)



OR^3, OR^3=OMe, OMe
$O(CH_2)_2O$

Method A: Step-1, $Et_3SiH/SnBr_2$-$AcBr/CH_2Cl_2$; Step-2, n-Bu_3SnH/AIBN/benzene
Method B: Step-1, $Et_3SiH/SnBr_2$-$AcBr/CH_2Cl_2$; Step-2, $LiAlH_4$/THF

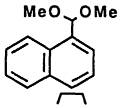
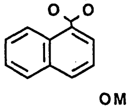
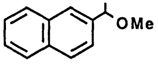
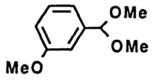
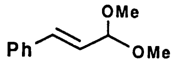
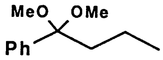
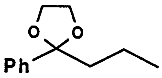
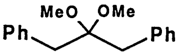
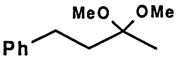
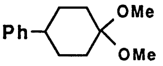
Entry	Acetal	Method	Step-1		Step-2		Yieldb)/%
1		A	0 °C,	1.5 h	Reflux,	0.5 h	85
2		B	0 °C,	1 h	R.T.,	2.5 h	84
3		A	R.T.,	4 h	Reflux,	0.75 h	72
4		A	0 °C,	3.5 h	Reflux,	0.75 h	85
5		B	0 °C,	3.5 h	R.T.,	2.5 h	86
6		A	R.T.,	2.5 h	Reflux,	0.5 h	90
7		B	R.T.,	2.5 h	R.T.,	2.5 h	92

Table 1. (Continued)

Entry	Acetal	Method	Step-1	Step-2	Yield[b]/%
8		B	0 °C, 5 h	R.T., 3.5 h	92
9		A	0 °C, 2 h	Reflux, 0.5 h	79
10		B	0 °C, 2.5 h	R.T., 15 h	82
11		A	R.T., 2 h	Reflux, 0.5 h	77
12		A[c]	R.T., 24 h	Reflux, 0.5 h	55[d]
13		A	R.T., 4 h	Relux, 0.5 h	60[e]
14		A	R.T., 24 h	Reflux, 0.5 h	67[f]

a) All the products gave satisfactory ^{1}H NMR and IR spectra. b) Isolated yield from acetal. c) Sn(OTf)$_2$ was used in place of SnBr$_2$. d) 1.3-Diphenylpropene was obtained in 9% yield. e) 1-Phenyl-2-butene was obtained in 25% yieid. f) 4-Phenylcyclohexene was obtained in 14% yield.

Experimental

Followings are the typical procedures for the reduction of 1-naphthaldehyde dimethyl acetal.

Method A: To a suspension of tin(II) bromide (6.9 mg, 0.02 mmol) and 1-naphthaldehyde dimethyl acetal (135 mg, 0.67 mmol) in dichloromethane (2 ml) were added triethylsilane (107 mg, 0.92 mmol) in dichloromethane (1.5 ml) and acetyl bromide (187 mg, 1.52 mmol) in dichloromethane (1.5 ml), successively at ice-bath temperature under argon atmosphere. The mixture was stirred for 1.5 h at this temperature and quenched with a phosphate buffer (pH 7). The organic materials were extracted with dichloromethane, dried over Na$_2$SO$_4$, and evaporated to leave the crude 1-bromomethylnaphthalene as an oil. The crude bromide was dissolved into benzene (3 ml) and *n*-Bu$_3$SnH (304 mg, 1.04 mmol) and a catalytic amount of azobisisobutyronitrile was added to it. After the mixture was refluxed for 30 min, the solvent was evaporated and 1-methylnaphthalene (80.7 mg, 85%) was isolated from the residue by thin layer chromatography over silica gel.

Method B: First step reduction was the same as that of Method A. To a suspension of LiAlH$_4$ (36.2 mg, 0.95 mmol) in THF (1 ml) was added a THF (4 ml) solution of the crude bromide from 1-naphthaldehyde dimethyl acetal (128 mg, 0.63 mmol). The mixture was stirred for 2.5 h. The reaction was quenched with a phosphate buffer (pH 7), and the precipitates were removed by Celite filtration. The organic materials were extracted with Et$_2$O and dried over MgSO$_4$. Filtration and concentration in vacuo gave an oily residue which was purified by thin layer chromatography over silica gel to afford 1-methylnaphthalene (74.9 mg, 84% from acetal).

One-Pot Operation: After completion of first-step reduction of acetals, solvents and volatile materials were removed from reaction flask using water-jet aspirator. The resultant residue was dissolved into benzene and subjected to the second-step reduction as described in the method A procedure.

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References

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