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Expedient and Simple Method for Regeneration of Alcohols from Toluenesulfonates Using Mg-MeOH

Madabhushi Sridhar,* B. Ashok Kumar and R. Narender

Organic Division-II, Indian Institute of Chemical Technology, Hyderabad-500 007, India.

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Abstract : Efficient conversion of toluenesulfonates to corresponding alcohols with Mg-MeOH is discribed.

In the present communication we wish to report that treatment of toluenesulfonates with magnesium in methanol constitutes an ideal procedure for regeneration of corresponding alcohols through S-O bond cleavage. This transformation has importance not only in carbohydrate chemistry and steroid chemistry but also in view of the recent developments in the area of hypervalent iodine chemistry where new reagents such as **I** and **II** have been developed (**Figure-1**). These reagents produce optically active toluenesulfonates by introducing the toluene sulfonyloxy group directly into the molecules.[1] Conversion of resulting toluenesulfonates into the corresponding alcohols is essential for enhancing the synthetic utility of such reagents and thus exploration of convenient methods for this transformation is highly desired.

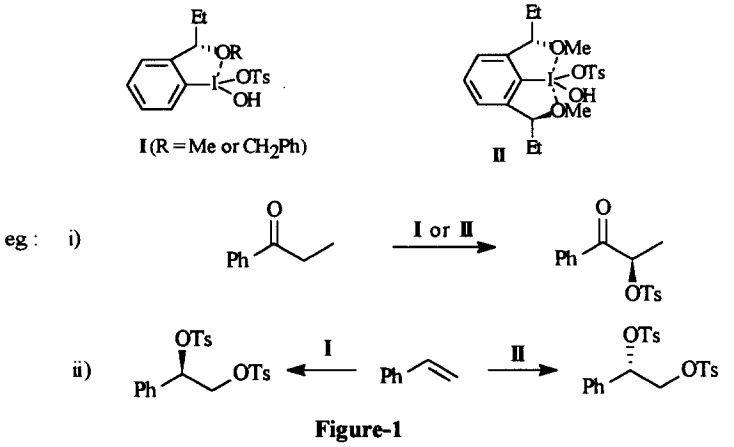

Figure-1

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As sulfonates are labile and undergo elimination and substitution reactions very easily, convenient methods for this transformation are scarce in literature. The earlier methods for conversion of toluenesulfonates to alcohols include: i) reduction with sodium amalgam in ethanol,[2] ii) hydrogenolysis with nickel,[3] iii) reduction with sodium in liquid ammonia[4] and iv) sodium naphthalene in tetrahydrofuran.[5] Except method, iv the remaining methods are not suitable for cleavage of optically active sulfonates as they cause epimerisation of the resulting alcohol. The latter procedure, however, is inconvenient for preparative purposes and involves a complicated procedure. When compared to these processes, the present method is a simple, mild and efficient approach for conversion of toluenesulfonates to alcohols. Some typical results are presented in **Table-I**.

Further, aryl toluenesulfonates, which are highly stable when compared to alkyl toluenesulfonates, are widely in use as protective agents for hydroxyl group of phenols.[6] These sulfonates resist reduction with $LiAlH_4$ and their deprotection requires reflux with aqueous-alcoholic KOH, which produces phenols only in moderate yields.[7] When compared to this process, the present method is found to be more reliable as a variety of aryl toluenesulfonates (entries **9-15**) were cleaved to phenols in excellent yields (90-95%). Deprotection of electron poor aromatics (e.g. 11), however, is harder by this method (it required more eq. of Mg and reaction time) when compared to the electron rich aromatics (10) and (12).

The alkyl and aryl toluenesulfonates used in this study were easily obtained from corresponding alcohols (purchased from Aldrich or Fluka) using standard procedure for toluenesulfonylation.[8] The optical rotation values of alcohols obtained from chiral toluene sulfonates (entries **1-3**) after reduction with Mg-MeOH are compared with the corresponding values of starting (purchased) alcohols and found to be identical. It shows that the resulting alcohols have not undergone epimerisation under the reaction conditions. The mechanism of reduction of toluenesulfonates to alcohols under Mg-MeOH is not clear and will require further study. In our preliminary study we have identified formation of toluene in this process from gc-ms analysis of the pentane extract of the reaction mixture. This observation suggests the involvement of a reaction mechanism which is similar to that suggested by Kovacks and Ghatak[9] for cleavage of toluenesulfonamides with sodium in liquid ammonia. In our study, sulfonamides (entries **15-18**) have, however, not shown any appreciable reaction with Mg-MeOH.

In conclusion, we have demonstrated a simple and convenient method for conversion of alkyl and aryl toluenesulfonates to the corresponding alcohols in high yields using Mg in methanol.

Table-1 : Cleavage of toluenesulfonates to alcohols using Mg-MeOH

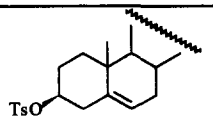
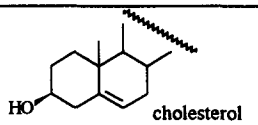
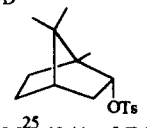
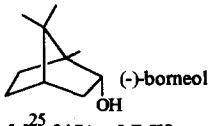
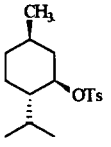
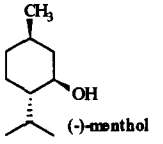
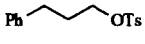
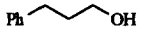
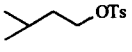
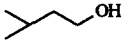
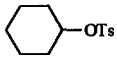
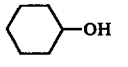
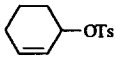
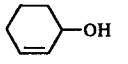
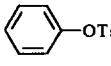
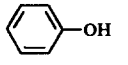
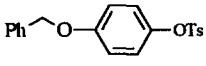
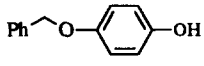
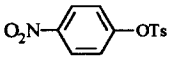
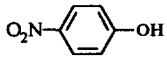
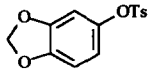
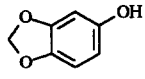
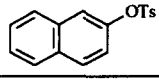
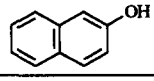
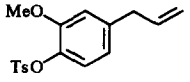
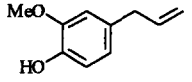
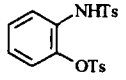
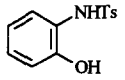
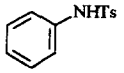
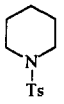
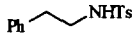
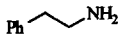
Entry	R-OTs	R-OH	Mg (equivalents)/ (Reaction time, h.)	Yield[a](%)
1.	 $[\alpha]_D^{25}$ -35.9(c=2; $CHCl_3$)	 cholesterol $[\alpha]_D^{25}$ -39.4(c=2; $CHCl_3$)	10 (6h)	95
2.	 $[\alpha]_D^{25}$ -13.4(c=5; EtOH)	 (-)-borneol $[\alpha]_D^{25}$ -34.7(c=5; EtOH)	10 (6h)	90
3.	 $[\alpha]_D^{25}$ -62.6 (c=5; $CHCl_3$)	 (-)-menthol $[\alpha]_D^{25}$ -42.3 (c=5; $CHCl_3$)	10 (6h)	90
4.			10 (6h)	95
5.			9 (5h)	90
6.			8 (6h)	85
7.			10 (6h)	90
8.			10 (5h)	80
9.			10 (6h)	95
10.			8 (4h)	95
11.			12 (5h)	95
12.			8 (4h)	95
13.			8 (4h)	90

Table continued.

14.			10 (6h)	95
15.			10 (8h)	90
16.		N.R	10 (10h)	—
17.		N.R	10 (10h)	—
18.			10 (10h)	trace

a : All the products gave satisfactory ^1H NMR, Mass spectrometry and IR spectral data and were identical to that of the authentic samples.

General method used for the reduction of toluenesulfonates to alcohols using Mg-MeOH:

Cholesteryl toluenesulfonate (1g, 1.8 x 10^{-3} mol) and magnesium (437mg, 1.8 x 10^{-2} mol) in dry methanol (15ml) in a r.b. flask fitted with condenser and calcium chloride guard tube and stirred at room temperature keeping flask in a water bath for 6h. When the reaction was complete, the reaction mixture was neutralized with chilled 5% HCl and extracted with diethyl ether (3x15ml) and the combined organic layers were washed with water and brine and dried over anhyd.Na_2SO_4 and concentrated. Crystallisation from ethanol yielded pure cholesterol (680mg, 95%; m.p. 148°C). Its ^1H NMR, IR and mass spectral data were identical to that of the authentic sample.

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