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A Selective and Efficient Demesylation Using Methylmagnesium Bromide

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A SELECTIVE AND EFFICIENT DEMESYLATION USING METHYLMAGNESIUM BROMIDE.

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Abstract : The chemoselective regeneration of alcohols from mesylates was accomplished by using methylmagnesium bromide in THF.

Alcohols are easily regenerated from *p*-toluenesulfonates when they are irradiated either in the presence of sodium hydroxide in methanol ¹ or of amines ² or also under photo-sensitized electron-transfer conditions ³. In contrast, photolysis of methanesulfonates is not a viable method as the deprotection is accompanied by reduction ⁴. However, the irradiation of mesylate in methanol in the presence of potassium iodide leads to the formation of the corresponding alcohol in good yields, although the reaction is not selective as *p*-tolylsulfonyl, benzyl and acetyl groups are also cleaved ⁵. Likewise, the formation of alcohols from mesylates by using superoxide ion ⁶, sodium in liquid ammonia ⁷, sodium amalgam in 2-propanol ⁸ are efficient methods but in all these conditions, *p*-toluenesulfonates are also cleaved to the corresponding alcohols.

We report here a very simple and selective method that allows the conversion of mesylates to the corresponding alcohols in high yields by using methylmagnesium bromide in THF.

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$$\begin{array}{ccc} \text{ROSO}_2\text{CH}_3 & \xrightarrow{\text{CH}_3\text{MgBr}} & \text{ROH} & + & (\text{CH}_3)_2\text{SO}_2 \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & &$$

To a solution of methylmagnesium bromide (3M in ether, 1.5 mmol) in THF (2 mL) at 0°C was added the mesylate (1mmol) in THF (2mL). After 20 h at room temperature, the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl (3 mL). After extraction with ethyl acetate, and evaporation of the solvent, the alcohol was purified by flash chromatography.

The results are summarized in the Table.

Alcohols can be regenerated in good yields from primary (compounds 1 and 2), secondary (compounds 3, 4, 5) and tertiary (compound 6) mesylates. In these conditions tetrahydropyranyl and benzyl protecting groups are not affected. When compound 4 was treated by MeMgBr, the alcohol was recovered without any inversion ⁹. Furthermore in the case of compound 8, the reaction is chemoselective as the mesylate group is transformed to the alcohol and as the tosylate remains unchanged. However, in the case of compound 9, the expected tosyl alcohol 17 (41% yield) is accompanied by the bromoalcohol 18 with a yield of 40 %. No mesyl alcohol is detected. The formation of bromide 18, which is probably due to the reaction of the tosylate with the magnesium bromide present in the reaction medium ¹¹, indicates that the tosylate is not cleaved in these conditions.

We should point out that when N-tosyldicyclohexylamine and N-mesyldicyclohexylamine were treated by methylmagnesium bromide, these compounds remained unchanged.

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