

An Efficient Desulfonylation Method Mediated by Magnesium in Ethanol

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Summary: *An extremely convenient desulfonylation method of primary, secondary, tertiary alkyl and vinyl phenyl sulfones was developed by using magnesium in ethanol in the presence of catalytic amount of mercuric chloride to give the corresponding alkanes and alkene in almost quantitative yields.*

Although a number of reagents are available for cleaving benzenesulfonyl group sodium amalgam either in alcohol or buffered with anhydrous disodium hydrogen phosphate is the most frequently employed one among other electron transfer agents such as lithium in aliphatic amine, sodium in alcohol, aluminum amalgam in aqueous THF and Grignard reagents with nickel or palladium catalysts.¹ Previously magnesium in methanol was utilized for desulfonylation of primary, secondary alkyl phenyl sulfones^{2a,c} and 1,1-bis(benzene sulfones)^{2b,c}, however, it was necessary to use a large excess amount of highly activated magnesium (20-30 equiv) in methanol at 50 °C to complete the reaction. In order to carry out desulfonylation under controlled manner and to avoid handling of annoying active alkali metals it is desirable to develop a milder and efficient desulfonylating agent.

In our continuing effort to expand synthetic utility of magnesium in methanol as an electron transfer agent³, we have found that magnesium in ethanol in the presence of catalytic amount of mercuric chloride facilitate the cleavage reaction. Here we report the results of reductive cleavage of alkyl and vinyl phenyl sulfones with 3.0 equiv of magnesium powder without activation in absolute ethanol in the presence of catalytic amount of mercuric chloride at room temperature (Table I).

At first these sulfones were subjected to the standard condition^{3a} with 3.0 equiv of magnesium in methanol (8 ml) at -23 °C, however, no reaction took place even in the presence of mercuric chloride until the magnesium was completely consumed. Although the reaction proceeded at an elevated temperature (0 °C-25 °C) in the presence of mercuric chloride, magnesium reacted with methanol so fast (almost explosively !) that excess amount of magnesium (>20 equiv) was required to complete the reaction. In an attempt to facilitate the reaction and to control the consumption of magnesium less reactive ethanol was substituted for methanol. Reaction proceeded smoothly at room temperature in ethanol in the presence of mercuric chloride consuming less than 3.0 equiv of magnesium within 2 hr. In the absence of mercuric chloride, the reaction was so slow that even after 24 h the reaction was not completed. Regardless of size of alkyl group, the cleavage reaction underwent cleanly to give the corresponding alkanes in excellent yields. Even the tertiary alkyl sulfone (entry 4) sometimes suffering from low yield by conventional reagent⁴ was cleaved smoothly. Vinyl sulfone (entry 1) was also cleaved nicely to give the corresponding alkene⁵. While benzyl ester of secondary sulfone (entry 5) underwent desulfonylation smoothly without transesterification, in case of primary sulfone (entry 8) complete deacetylation of benzyl acetate occurred simultaneously resulting benzyl alcohol and ethyl acetate in quantitative yield. When allylic sulfone (entry 9) was subjected to the above condition, a mixture of di- and tri substituted olefin, in a ratio of 1.26 : 1, was obtained in quantitative yield as expected from the previous

cleavage reactions^{6,2a}. Concomitant deacetylation took place even under the buffered condition (Method B, entry 10). Unlike aluminum amalgam or samarium (II) iodide, β -keto sulfone (entry 7) was inert to magnesium in ethanol.

Table I. Reductive Cleavage of Sulfones by Magnesium in Absolute Ethanol

Entry	Sulfones ^a	Products	Method ^b	Isolated Yield (%)
1	Ad*—SO ₂ Ph	Ad*—H	A	99
2	Ad—SO ₂ Ph	Ad—	A	99
3	Ad—SO ₂ Ph	Ad—	A	100
4	Ad—SO ₂ Ph	Ad—	A	100
5	Ad—CO ₂ Bn SO ₂ Ph	Ad—CO ₂ Bn	A	98
6	3,4-(MeO)PhCH ₂ SO ₂ Ph	3,4-(MeO)PhCH ₃	A	98
7	Ph—C(=O)—SO ₂ Ph		B	no reaction
8	Ph—O—C(=O)—SO ₂ Ph	PhCH ₂ OH	A B	100 ^c 100 ^c
9	Ph—CH(OH)—SO ₂ Ph	Ph—CH(OH)—	A	98
10	Ph—CH(OH)—SO ₂ Ph	Ph—CH(OH)—	A B	98 98

^a Ad*: 2-adamantylidenyl, Ad; 2-adamantyl. ^b Method A; 3.0 equiv Mg, cat. HgCl₂, EtOH, rt, 2 h. Method B; 3.0 equiv Mg, cat. HgCl₂, EtOH, 6.0 equiv NaH₂PO₄, rt, 4 h. ^c Benzyl alcohol was obtained instead of benzyl acetate.

A typical procedure is as follows. A mixture of substrate (2.0 mmol), Mg (146 mg, 6.0 mmol, powder, -50 mesh, Aldrich[®]), and a few crystals of HgCl₂ in dry EtOH (10 mL) [or dry EtOH-THF (3/1, 10 mL) for entry 5-8] was stirred for 2 h at room temperature. The reaction mixture was poured into cold 0.5 N HCl and extracted with pentane (or ether for entry 5-10). The organic layer was washed with saturated aqueous NaHCO₃ solution, dried (MgSO₄), filtered, and concentrated *in vacuo* to give crude product which was purified by flash column chromatography (SiO₂).

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