# UNUSUAL REACTIVITY OF ALLYLMAGNESIUM BROMIDE

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Abstract : Reaction of allylmagnesium bromide with trifluoromethyl oximes is different than with other Grignard reagents. On the other hand, allylmagnesium bromide acted as a reducing agent towards trifluoromethyl ketones. By using an excess of this Grignard reagent, an exclusive addition reaction is obtained. A single electron reaction is suggested to explain the reductive process.

We wish to report on a novel behaviour of allylmagnesium bromide towards oximes and ketones when substituted by a trifluoromethyl group.

We have previously shown (1) that ethylmagnesium bromide reacted with benzyltrifluoromethyl ketone oxime **1a** to give aziridine **3a** by reduction of the 2H-azirine intermediate **2a**. No addition product (of the ethyl group) was formed. The reduction of azirine **2a** is comparable to the reduction of hemiperfluorinated
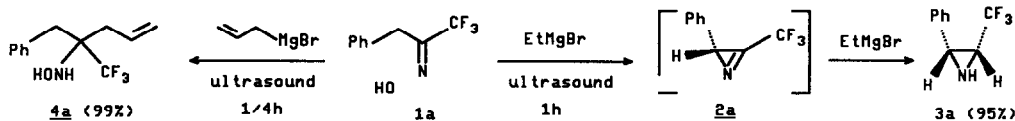
ketones with the same Grignard reagent (2) which acted mainly as a reducing agent. Like with typical reducing Grignard reagents, such as isobutylmagnesium bromide, the hydrogen atom transferred on the carbon atom of the carbonyl group is provided by the alkyl group.
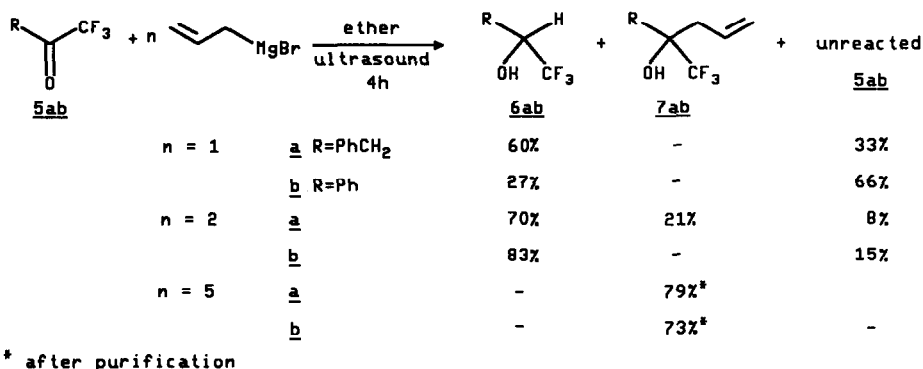
Interestingly, under similar reaction conditions, allylmagnesium bromide did not give any aziridine. This Grignard reagent added to the oxime to produce hydroxylamine **4a** (3). To our knowledge, the formation of hydroxylamines of type **4** by addition of a Grignard reagent has not been previously reported (4). However such compounds have already been obtained with organolithium compounds (5). The same reaction was observed with other trifluoromethylketone oximes **1a-d** ; hydroxylamines **4a-d** were isolated in almost quantitative yields. The use of ultrasonic stirring increased the rate of reaction.
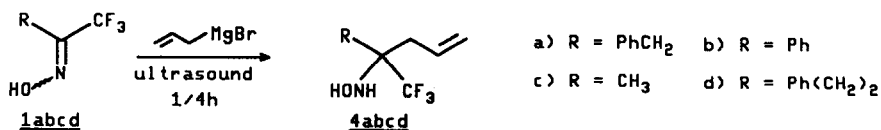
The discrepancy between the behaviour of ethyl and allylmagnesium bromides towards oximes of trifluoromethyl ketones may be due to their difference in basicity or to the possibility for the allylic Grignard reagent to add to a substrate *via* a cyclic transition state.

By reacting allylmagnesium bromide and trifluoromethyl ketones it was expected to form addition

products ; however under stoichiometric conditions (or with a slight excess of Grignard reagent), reduction alcohols $\underline{6}$ were obtained from trifluoromethylacetophenone $\underline{5b}$ and benzyltrifluoromethyl ketone $\underline{5a}$. This is the first example in which allylmagnesium bromide acted as a reducing Grignard reagent.

			6ab	7ab	5ab
n = 1	$\underline{a}$	R=PhCH$_2$	60%	–	33%
	$\underline{b}$	R=Ph	27%	–	66%
n = 2	$\underline{a}$		70%	21%	8%
	$\underline{b}$		83%	–	15%
n = 5	$\underline{a}$		–	79%*	
	$\underline{b}$		–	73%*	–

* after purification

Addition products $\underline{7a,b}$ can be exclusively formed by adding a large excess (5 molar equivalents) of allyl Grignard reagent to ketones $\underline{5a,b}$.

Since Ashby's work (6) it was demonstrated that the Grignard reagent addition is preceeded by a single electron transfer to form a ketyl radical anion $\underline{8}$ which reacts with the alkyl radical $\underline{9}$ to give the addition alcohol.
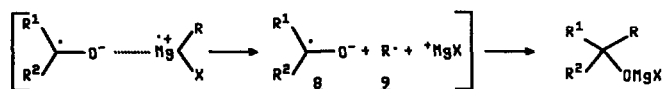
Recently (7), such a ketyl intermediate was postulated to explain the hydrogen atom transfer during the reduction of trifluoroacetophenone with dihydronicotinamides.

The reduction alcohols $\underline{6a,b}$ are almost certainly not formed from a reduction reaction involving the allyl group, because in that case a vinylic hydrogen atom transfer (in the cyclic transition state) would be implied. Such a hydrogen atom is probably provided by the solvent of the reaction (8). Further work is now under way to try to elucidate the mechanism of formation of alcohols $\underline{6}$ and $\underline{7}$. In particular, we hope to find if they derive from a common intermediate, such as a ketyl radical anion.

References and notes

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