

Preliminary Note

Reductive addition of trichlorofluoromethane to ketones initiated by the Mg/LiCl system

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Abstract

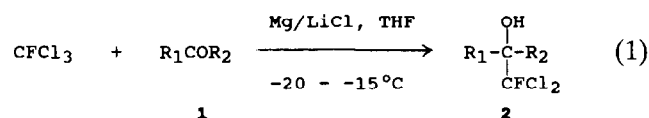
Reductive addition of trichlorofluoromethane to ketones initiated by the Mg/LiCl system at $-20\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$ gave dichlorofluoromethyl carbinols in moderate yield.

The accumulation of information about the depletion of the ozone layer in the stratosphere has led to a tighter control on chlorofluorocarbons (CFCs) and Halons. This control and the increasing popularity of the use of fluorine-containing building blocks in synthetic work has stimulated scientists to search for new applications of CFCs and Halons as chemical reagents in both the laboratory and industry.

CFCl_3 is one of the important and widely used CFCs in industry. Some of its applications in organic synthesis have been reported [1–7]. Reductive addition of polyhalomethanes to carbonyl compounds is one of the methods used to produce polyhalomethyl carbinols [8–10]. Using the HgCl_2/Al system, Zeifman *et al.* found that trichlorofluoromethane added reductively to electrophilic hexafluoroacetone to give a dichlorofluoromethyl carbinol [5]. Wheaton and Burton reported that ClCF_2Li formed *in situ* from the thermal decarbomethoxylation of $\text{ClCF}_2\text{COOCH}_3$ reacted with electrophilic polyfluoromethyl ketones, but the reaction failed with less electrophilic ketones such as acetophenone [11]. Herein, we describe the use of Mg/LiCl systems as initiators for the reactions of CFCl_3 with less electrophilic ketones to give dichlorofluoromethyl carbinols.

In a typical experiment, 0.11 mol of magnesium turnings, 0.10 mol of anhydrous LiCl, 40 ml of anhydrous THF, 0.10 mol of ketone **1** and 0.020 mol of CFCl_3 were placed in a three-necked flask equipped with a

magnetic stirrer, thermometer, Dry Ice condenser and a dropping funnel with a pressure-equalizing side-arm at $-20\text{ }^{\circ}\text{C}$. The mixture was stirred at $-20\text{ }^{\circ}\text{C}$ when heat was evolved. After the reaction was complete, a further 0.10 mol of CFCl_3 was added slowly through the dropping funnel and the mixture then stirred for 1 h at $-20\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$. The reaction was quenched by adding aqueous 5% hydrochloric acid and the mixture extracted with ether ($3 \times 15\text{ ml}$). The combined extracts were washed successively with 5% NaHCO_3 aqueous solution and brine, and then dried over anhydrous Na_2SO_4 . After removal of the solvent, the residue was distilled under reduced pressure and the distillate chromatographed on a silica gel column (petroleum ether (b.p. $30\text{--}60\text{ }^{\circ}\text{C}$)/EtOAc, 5:1) to give the dichlorofluoromethyl carbinol **2** as a colourless liquid. The results are listed in Table 1. All the carbinols were characterized by ^{19}F and ^1H NMR, MS and IR spectral methods and by elemental analysis.



Temperature played an important role in such reductive addition, the reaction proceeding smoothly at $-20\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$. Even at $0\text{ }^{\circ}\text{C}$ the reaction proceeded vigorously with pinacol being the main product.

As can be seen from Table 1, a ketone containing a large alkyl group such as $\text{CH}(\text{CH}_3)_2$ or $\text{C}(\text{CH}_3)_3$ reacted well with CFCl_3 to give dichlorofluoromethyl carbinol in moderate yield. However, no reaction took place if the carbonyl was flanked by two large $\text{CH}(\text{CH}_3)_2$ groups.

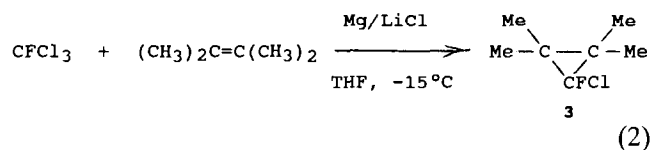
In the absence of anhydrous LiCl, the yield of **2** fell dramatically and a considerable amount of $\text{CFCl}=\text{CFCl}$ was formed. It seems that the $\text{CFCl}=\text{CFCl}$ is formed

TABLE 1. Reductive addition of trichlorofluoromethane to ketones promoted by the Mg/LiCl system

Ketone	R ₁	R ₂	Carbinol	Yield (%)
1a	CH ₃	CH ₃	2a	58
1b	CH ₃	CH ₂ CH ₃	2b	62
1c	CH ₃	CH(CH ₃) ₂	2c	65
1d	CH ₃	C(CH ₃) ₃	2d	45
1e	CH(CH ₃) ₂	CH(CH ₃) ₂	no reaction	
1f	CH ₂ CH ₃	CH ₂ CH ₃	2f	60
1g		-(CH ₂) ₅ -	2g	58
1h		-(CH ₂) ₄ -	2h	60

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via the coupling of chlorofluorocarbene, which can arise from the decomposition of dichlorofluoromethylmagnesium chloride. Chlorofluorocarbene could be trapped by tetramethylethylene to give 1,1,2,2-tetramethylchlorofluorocyclopropane (**3**) in 85% yield [eqn. (2)]. In the absence of anhydrous LiCl, **3** was obtained in poor yield.



Although the exact reaction mechanism utilized by the Mg/LiCl system has not yet been clarified, it presumably involves dichlorofluoromethyl lithium, which, in turn, would react with ketones to give the reductive adduct. Similar polyhalomethide ion intermediates were postulated in refs. 7 to 10.

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