The Titanium Trichloride–3Tetrahydrofuran Magnesium System. A New Reagent for Easy Reduction and Dehydrohalogenation of Organic Halides

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Summary $TiCl_3 \cdot 3THF$ is reduced by metallic magnesium in tetrahydrofuran (THF) under argon or nitrogen to a product which reductively removes halogen atoms from both sp^3 and sp^2 hybridised organic halides.

THE $TiCl_3 \cdot 3THF$–Mg in THF system[1] reacts with molecular nitrogen to give $TiNMg_2Cl_2 \cdot THF$, hydrolysis of which gives ammonia. Under nitrogen, this system reacts with acetone to give Pr^iOH, Pr^iNH_2, $Me_2C{=}CMe_2$, and $Me_2C(OH)C(OH)Me_2$.[2] When prepared under argon, the system reacts with carbonyl compounds giving olefins,[3] and it also reacts with CO and CO_2.[4]

We have now found that this system reduces organic halides of sp^3 or sp^2 hybridisation (see Table).

The $TiCl_3 \cdot 3THF$–Mg system is one of the most useful of the reagents proposed recently[5] for reducing halogen derivatives, reducing unreactive bromides and iodides almost quantitatively at room temperature. The reactivity order ($I > Br > Cl > F$) is similar to that for $LiAlH_4$ and unlike that for S_N2 reactions ($F >> Cl \sim Br > I$), indicating that the reaction is not a simple nucleophilic attack on carbon. Electron-releasing substituents such as *p*-methyl and *p*-methoxy result in a decrease of the yield. The reaction with aliphatic alicyclic halides gives alkanes accompanied by alkenes, the relative amount of the elimination products increasing in the order $Cl < Br < I$.

The reaction takes place under mild conditions, at room temperature, and under normal pressure. Low-boiling products can be isolated by distillation. Hydrolysis of the product is not necessary.

The compound which reduces the halogenoderivatives is formed under nitrogen and argon atmospheres but in the latter case the efficiency of the system is slightly higher. The yield is not improved by replacing nitrogen or argon

Table. Reduction of halides by $TiCl_3$·3THF–Mg[a]

Substrate	Atmosphere	Conditions		Product	Yield (%)
		t_1/h	t_2/h		
C_6H_5F	N_2	24	24	C_6H_6	2—13
	N_2	24	24[b]		8—28
	N_2/H_2	24/120	24		1—4
	Ar	48	24		5—20
C_6H_5Cl	Ar	1	24	C_6H_6	50—55
	Ar	48	24		62—81
	H_2	24	24		20
C_6H_5Br	Ar	48	24	C_6H_6	89
C_6H_5I	Ar	48	24	C_6H_6	100
1-Fluoronaphthalene	Ar	24	24[b]	Naphthalene	89
1-Chloronaphthalene	Ar	48	24	Naphthalene	34
Cyclohexyl chloride	Ar	48	48	Cyclohexane	79—88
				Cyclohexene	15—18
Cyclohexyl bromide	Ar	48	48	Cyclohexane	79
				Cyclohexene	21
Cyclohexyl iodide	Ar	48	48	Cyclohexane	61—66
				Cyclohexene	33—39
n-Pentyl bromide	N_2	24	24	n-Pentane	79
				Pent-1-ene	12
MeI	N_2	24	24	CH_4	55—60
4-Chloroanisole	Ar	48	24	Anisole	20—30
$PhCH_2Cl$	Ar	48	24	PhMe	96—100
p-Chlorotoluene	Ar	48	24	PhMe	64—70
C_6F_6	Ar	24	24	C_6F_5H	27—30

[a] Standard procedure: TiCl·3THF (0·01 mol) and Mg (0·02 mol) in THF (*ca.* 40 ml) were allowed to react under N_2 or Ar for time t_1. The organic halide (0·01 mol) was then added, and after time t_2 the mixture was evaporated to dryness and the distillate was collected and analysed by g.l.c. For the naphthalene derivatives, after time t_2 the mixture was hydrolysed with 1N-HCl and extracted with ether before g.l.c. analysis. [b] Heated under reflux for time t_2.

with hydrogen. Yamamoto[1] reported that in the presence of excess of Mg (Ti:Mg 1:10) the $TiCl_3$·THF–Mg system reacts with H_2 giving MgH_2. Our results indicate that MgH_2 is not the reducing agent. The origin of the hydrogen replacing halogen has not been elucidated. One source of reactive hydrogen could be the THF molecule, following its decomposition in the initial stages of the reaction.

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