

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

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Summary $\text{TiCl}_3 \cdot 3\text{THF}$ 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 $\text{TiCl}_3 \cdot 3\text{THF}$ –Mg in THF system¹ reacts with molecular nitrogen to give $\text{TiNMg}_2\text{Cl}_2 \cdot \text{THF}$, hydrolysis of which gives ammonia. Under nitrogen, this system reacts with acetone to give Pr^iOH , Pr^iNH_2 , $\text{Me}_2\text{C}=\text{CMe}_2$, and $\text{Me}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$.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 $\text{TiCl}_3 \cdot 3\text{THF}$ –Mg system is one of the most useful of the reagents proposed recently⁵ for reducing halogen derivatives, reducing unreactive bromides and iodides

almost quantitatively at room temperature. The reactivity order ($\text{I} > \text{Br} > \text{Cl} > \text{F}$) is similar to that for LiAlH_4 and unlike that for $\text{S}_{\text{N}}2$ reactions ($\text{F} \gg \text{Cl} \sim \text{Br} > \text{I}$), 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 $\text{Cl} < \text{Br} < \text{I}$.

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 $\text{TiCl}_3 \cdot 3\text{THF-Mg}^a$

Substrate	Atmosphere	Conditions		Product	Yield (%)
		t_1/h	t_2/h		
$\text{C}_6\text{H}_5\text{F}$	$\left\{ \begin{array}{l} \text{N}_2 \\ \text{N}_2 \\ \text{N}_2/\text{H}_2 \\ \text{Ar} \end{array} \right.$	24	24	C_6H_6	2—13
		24	24 ^b		8—28
		24/120	24		1—4
		48	24		5—20
$\text{C}_6\text{H}_5\text{Cl}$	$\left\{ \begin{array}{l} \text{Ar} \\ \text{Ar} \\ \text{H}_2 \end{array} \right.$	1	24	C_6H_6	50—55
		48	24		62—81
		24	24		20
$\text{C}_6\text{H}_5\text{Br}$	Ar	48	24	C_6H_6	89
$\text{C}_6\text{H}_5\text{I}$	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	$\text{C}_6\text{F}_5\text{H}$	27—30

^a Standard procedure: $\text{TiCl}_3 \cdot 3\text{THF}$ (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. Yamamoto¹ reported that in the presence of excess of Mg (Ti:Mg 1:10) the $\text{TiCl}_3 \cdot \text{THF-Mg}$ 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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