A Convenient Method for *in situ* Generation of Deuterium Chloride and its Addition to Olefins[1]

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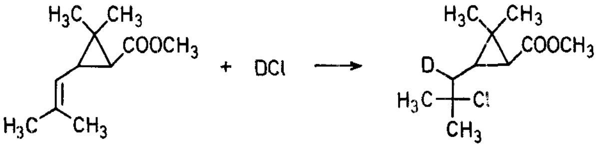
Recently we have shown that titanium(IV) chloride is an excellent catalyst for promoting the addition of hydrogen azide to certain olefins[2]. Although the ability of hydrogen chloride to add to multiple bonds is well documented, there have been only few studies of the use of titanium(IV) chloride to promote such reactions[3]. Hydrogen chloride is readily available; on the other hand, procedures for generating deuterium chloride in known molar quantities are few (reaction of deuterium oxide with phosphorus(III) chloride, acyl chlorides, or silicon tetrachloride), with deuterium chloride being distilled, trapped, and titrated or weighed[4].

We have developed a simple, *in situ*, procedure for the generation and addition of known amounts of deuterium chloride to activated olefins. Typically, one equivalent of the olefin and one equivalent of a deuterium source, usually methanol-O-*d* or deuterium oxide were mixed in a dichloromethane solution. This was followed by the addition of one-half of an equivalent titanium(IV) chloride. The reaction took 30 min to 1 h at 5 °C to reach completion and the yields were usually excellent (see Table). Mass spectra and ^{1}H-N.M.R. integration of the deuterium chloride adducts indicated incorporation of one deuterium and no methoxy incorporation was observed. Terminal monosubstituted and 1,2-disubstituted olefins did not give a deuterium chloride adduct, but rather polymerized under the reaction conditions.

That titanium(IV) chloride definitely promotes the reaction is apparent by comparing the reaction times necessary to reach complete reaction for gaseous deuterium chloride addition versus titanium(IV) chloride/methanol-O-*d* addition. The addition of gaseous deuterium chloride to chrysanthemate **1** required 30 h, while the catalyzed reaction was complete in 20 min, **2** was produced, and no rearrangement was observed (Scheme A). Similarly, addition of gaseous deuterium chloride to 2,3-dimethyl-2-butene required 19 h, while the catalyzed reaction was over in 30 min.



1 **2**

Scheme A

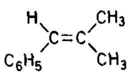
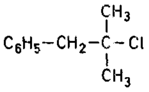
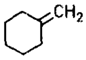
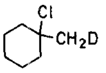
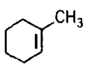
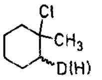
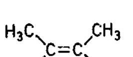
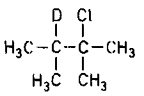
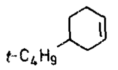
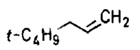
As a first rapid step, titanium(IV) chloride is expected to react with methanol-O-*d* (or deuterium oxide) according to Scheme **B**.

$$TiCl_4 + 2\ H_3C{-}OD \rightleftharpoons Ti(OCH_3)_2Cl_2 + 2\ D{-}Cl$$

Scheme **B**

As the next step, the results are consistent with complexation of the generated titanium species with the olefin. In the case of monosubstituted olefins this results in polymerization, while in the case of 1,1-disubstituted tri- and tetrasubstituted olefins, deuterium chloride addition takes place. Though stereochemical questions still remain to be elucidated, the procedure provides a simple, useful method for addition fo DCl to such olefins.

Table. Addition of Hydrogen Chloride and Deuterium Chloride (in Dichloromethane) to Olefins

Olefin	Product[a]	Proton Source	Reaction Time	Yield [%]
		CH_3OH	1 h	99
		CH_3OD	20 min	61 (91)[b]
		CH_3OD CH_3OD D_2O	< 1 h 30 min 1 h	77 64 74
		CH_3OD DCl	30 min 19 h	66 (100)[b]
1	**2**	CH_3OD DCl	20 min 30 h	87 90
	–	CH_3OD	18 h	0
	–	CH_3OD	14 days	0

[a] The products were distilled in a Kugelrohr oven at 0.1 mm Hg. The purity was > 95% as determined by G.L.C or by ^{1}H-N.M.R. integration.

[b] Yield by N.M.R. spectrometry.

General Procedure for *in situ* Generation and Addition of Deuterium Chloride to Olefins:

The olefin (10 mmol) and either methanol, methanol-O-*d*, or deuterium oxide (11 mmol) are mixed in dry dichloromethane (20 ml) under nitrogen and cooled in an ice bath. Titanium(IV) chloride (5 mmol) in dichloromethane (10 ml) is added dropwise to the cooled olefinic solution. After one hour the reaction mixture is passed down a 2 cm × 3 cm column of alumina, eluting with dichloromethane, and the solvent removed to yield the adduct in ≥ 95% purity. Further purification can be affected, if desired, by vacuum distillation. See Table for reaction times, yields, and the proton or deuterium sources.

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