Selective Markovnikov's Addition of Trifluoroacetic Acid to Alkenes using Vanadium(v) Oxide†

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A simple and efficient method for trifluoroacetoxylation of alkenes using catalytic amounts of V_2O_5 in trifluoroacetic acid to give the Markovnikov's product selectively in excellent yields for the first time is described.

Selective functionalization of alkenes *via* acetoxylation is an important organic transformation, since esters formed in the reaction provide a variety of organic derivatives by simple nucleophilic exchange.[1] Earlier attempts of acetoxylation of higher alkenes by Lewis acids proceeded with concomitant isomerization to afford an isomeric mixture of acetoxylated derivatives[2–4]. Montmorillonite, an acid smectite clay designed to obtain higher selectivity due to its layered silicate structure showed only marginal improvement towards Markovnikov's product in the acetoxylation of higher alkenes.[5] Metal salts such as Tl^{III} trifluoroacetate,[6] Pb^{IV} acetate[7] and chromyl chloride,[8] employed for the acetoxylation of alkenes gave mixtures of products composed of ketones, epoxides, diacetates and diols. Selective Markovnikov's addition of acid to alkenes was achieved by mercuric salts involving a complicated procedure of oxymercuration of alkenes and subsequent *in situ* reduction of the organomercurial bond by alkaline sodium borohydride.[9,10] The use of molar quantities of toxic mercuric salts causing environmental problems, *in situ* reduction of organomercurial bond by expensive sodium borohydride render the reaction incompatible in the presence of other functional or reducible groups and poor selectivity in the case of internal disubstituted alkenes are inherent disadvantages in this method. Hence it was felt that there was a need to develop a catalytic methodology for the acetoxylation of alkenes to give the Markovnikov's product with high selectivity.

With the discovery of vanadium in bromoperoxidase[11] and nitrogenase,[12] intensive and vigorous research on vanadium chemistry is being persued. Dioxovanadium, a model for bromoperoxidase using H_2O_2 as reoxidant, catalysing the bromination of trimethoxybenzene with the liberated bromine from potassium bromide suggested a possible path for the biosynthesis of marine haloorganic products. In this communication, we report a simple and elegant method for trifluoroacetoxylation of various cyclic and acyclic alkenes catalysed by readily available V_2O_5 or freshly prepared vanadyl

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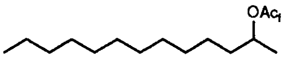
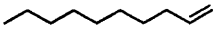
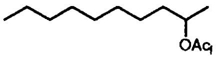
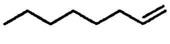
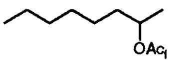
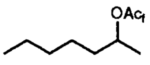
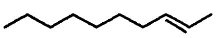
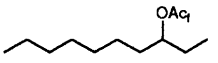
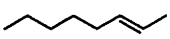
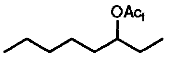
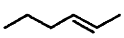
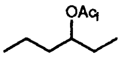
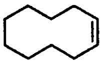
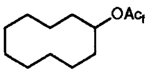
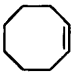
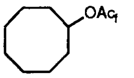
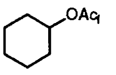
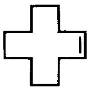
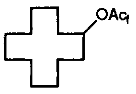
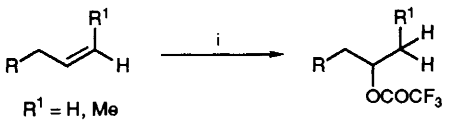
Table 1 Markovnikov's addition of trifluoroacetic acid to alkenes using vanadium(v) oxide.

Entry	Substrate	Product	Isolated[a] yield (%)
1			87
2			86
3			82
4			64
5			81
6			79
7			64
8			84
9			78
10			67
11			74

[a] Products were characterized by ^{1}H NMR, IR, mass spectrometry and GC.

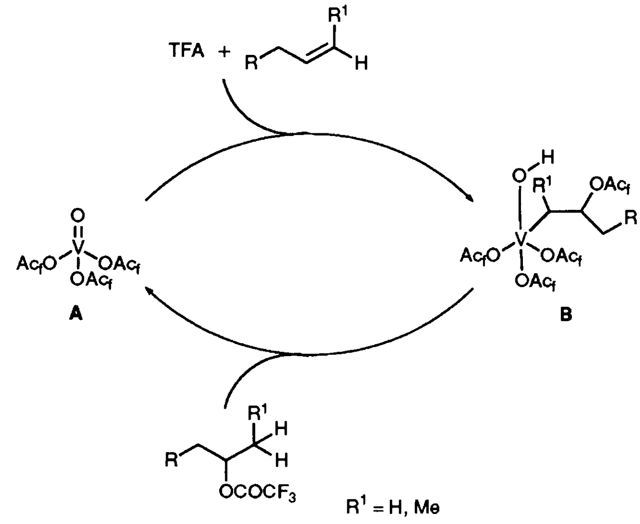


Scheme 1 *Reagents and conditions*: i, V_2O_5, TFA, 70 °C, 5 h

trifluoroacetate[13] (1 mol% of the catalyst to the substrate) in trifluoroacetic acid (TFA) under reflux conditions for the first time affording always the Markovnikov's product directly and exclusively (Scheme 1).

A typical experimental procedure is as follows, V_2O_5 (0.2 mmol) and dec-1-ene (10 mmol) in anhydrous trifluoroacetic acid (10 ml) were refluxed under moisture exclusion conditions for 5 h. The progress of the reaction was monitored by TLC. The reaction mixture was treated with saturated sodium hydrogencarbonate solution and extracted with diethyl ether. The residue obtained after spin drying of the ether extract was subjected to column chromatography (silica gel, hexane) to give 2-trifluoroacetoxydecane (86%, 2.18 g). The yield of the product is almost the same when 1 mol% of V_2O_5 to the substrate or vanadyl trifluoroacetate was used.

The selectivity towards Markovnikov's product in the case of the terminal alkenes (entries 1–4, Table 1) is comparable with mercuric acetate, the best system reported so far. However, the selective formation of Markovnikov's product



Scheme 2 Plausible mechanism for the reaction

in the trifluoroacetoxylation of alk-2-enes (entries 5–7) is very impressive and unusual because acetoxylation of alk-2-enes by mercuric acetate gave the mixture of 2- and 3-acetoxylated derivatives in the ratio of 6:4.[9] Incidentally, this forms the first report to the best of our knowledge of selective

Markovnikov's addition of acids to internal disubstituted alkenes.

In the plausible mechanism (Scheme 2) it is thought that the reaction is initiated by the attack of higher valent vanadium(v) oxotrifluoroacetate **A** acting as an electrophile on the double bond of the alkene followed by transfer of the acetate group to give an intermediate **B** which on subsequent transfer of the proton gives the acetoxylated product with the regeneration of vanadyl trifluoroacetate.

The simple, convenient and catalytic methodology described here for the acetoxylation leading to the formation of Markovnikov's product exclusively becomes a practical alternative to the best method using toxic mercuric(II) acetate as a reagent reported earlier.

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