

Ionic Hydrogenations using Transition Metal Hydrides. Rapid Hydrogenation of Hindered Alkenes at Low Temperature

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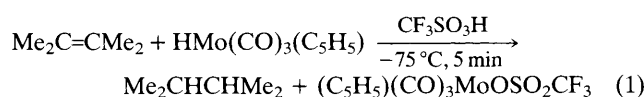
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Tetra-substituted, tri-substituted, and 1,1-disubstituted alkenes can be rapidly hydrogenated in high yield at -75°C using $\text{CF}_3\text{SO}_3\text{H}/\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ or $\text{CF}_3\text{SO}_3\text{H}/\text{HSiEt}_3$.

In contrast to the hydric reactivity of early transition metal hydrides¹ such as $(\text{C}_5\text{H}_5)_2\text{ZrH}_2$, many neutral metal hydrides such as $\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ and $\text{HMn}(\text{CO})_5$ are acidic. For example, $\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ ($\text{p}K_a$ 13.9 in MeCN)² is much more acidic than MeCO_2H ($\text{p}K_a$ 22.3 in MeCN) and the kinetics of proton transfer from $\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ to metal-,³ nitrogen-,³ and carbon-centred⁴ bases have been reported. While hydride can be removed from $\text{HMn}(\text{CO})_5$ by reaction with neat $\text{CF}_3\text{SO}_3\text{H}$,⁵ or from $\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ by reaction with Ph_3C^+ ,⁶ the hydric reactivity of these neutral species has not been studied in detail. We now report that $\text{HMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ can function as a net hydride donor in a reaction that accomplishes the facile stoichiometric hydrogenation of hindered alkenes at temperatures as low as -75°C .

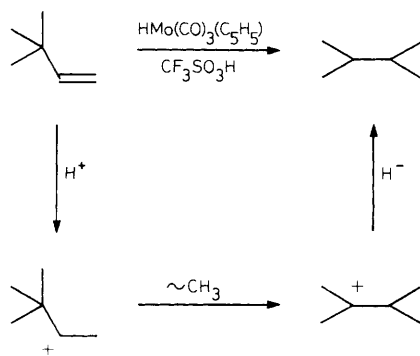
Addition of $\text{CF}_3\text{SO}_3\text{H}$ to a solution of $\text{Me}_2\text{C}=\text{CMe}_2$ and $\text{HM}(\text{CO})_3(\text{C}_5\text{H}_5)$ ($\text{M} = \text{Mo}, \text{W}$) at room temperature causes

an immediate colour change from pale yellow to wine-red, and 2,3-dimethylbutane is formed in $>85\%$ yield [equation (1)]. The C=C bonds of tri-substituted alkenes and 1,1-disubstituted alkenes are also readily hydrogenated (Table 1), giving high yields of alkane products along with $>85\%$ yields of red-purple $(\text{C}_5\text{H}_5)(\text{CO})_3\text{MOSO}_2\text{CF}_3$ ($\text{M} = \text{Mo}, \text{W}$). At room temperature, these reactions are complete within the time of mixing. Low temperature experiments in CD_2Cl_2 indicate that the reactions are $>95\%$ complete within ~ 5 minutes at -75°C .



The mechanism of these reactions apparently involves initial formation of a carbocation by protonation of the alkene, followed by trapping of the carbocation by the metal hydride. Evidence for carbocation intermediates comes from the observation of characteristic rearrangements. Ionic hydrogenation of *t*-butylethylene produces 2,3-dimethylbutane since the initially formed secondary carbocation rearranges to a more stable tertiary carbocation by methyl migration. Only those alkenes which can form a tertiary carbocation (by protonation or protonation followed by rearrangement) have been successfully hydrogenated by this method. While it is clear that the transition metal hydrides function as stoichiometric hydride donors, it remains to be established whether this involves direct H^- delivery or sequential electron transfer/hydrogen atom transfer steps (Scheme 1).

Related ionic hydrogenations involving sequential delivery of H^+ and H^- to organic substrates using $\text{CF}_3\text{CO}_2\text{H}/\text{Et}_3\text{SiH}$ have been reported, but typical conditions used are several hours at 50°C .⁸ The $\text{CF}_3\text{SO}_3\text{H}/(\text{C}_5\text{H}_5)(\text{CO})_3\text{MH}$ system



Scheme 1

Table 1. Alkene hydrogenations using $(\text{C}_5\text{H}_5)(\text{CO})_3\text{MH}/\text{CF}_3\text{SO}_3\text{H}$.^a

Alkene (conc./M)	$\text{CF}_3\text{SO}_3\text{H}$ /equiv.	M (equiv.)	Product ^b (% yield)	Conditions: $\theta/^\circ\text{C}$, t/min
Tetra-substituted alkenes				
$\text{Me}_2\text{C}=\text{CMe}_2$ (0.11)	1.3	W(1.4)	$\text{Me}_2\text{CHCHMe}_2$ (85)	$-75, 5^c$
$\text{Me}_2\text{C}=\text{CMe}_2$ (0.11)	1.3	Mo(1.4)	$\text{Me}_2\text{CHCHMe}_2$ (85)	$-75, 5^c$
Tri-substituted alkenes				
$\text{MeCH}=\text{C}(\text{Me})\text{Et}$ (0.09)	2.5	W(1.2)	$\text{MeCH}_2\text{CH}(\text{Me})\text{Et}$ (100)	$-80, 10^d$
$\text{MeCH}=\text{C}(\text{Me})\text{Et}$ (0.13)	1.1	Mo(1.0)	$\text{MeCH}_2\text{CH}(\text{Me})\text{Et}$ (100)	22, 5^e
$\text{Me}_2\text{C}=\text{CHEt}$ (0.09)	1.4	Mo(1.5)	$\text{Me}_2\text{CHCH}_2\text{Et}$ (96)	$-75, 5^c$
1,1-Di-substituted alkenes				
$\text{CH}_2=\text{C}(\text{Me})\text{Pr}^i$ (0.10)	1.4	Mo(1.5)	$\text{Me}_2\text{CHCHMe}_2$ (86)	$-75, 5^c$
$\text{CH}_2=\text{C}(\text{Me})\text{Pr}^n$ (0.13)	1.2	Mo(1.0)	Me_2CHPr^n (96)	22, 5^e

^a $\text{CF}_3\text{SO}_3\text{H}$ was added to a CD_2Cl_2 solution containing the alkene and $(\text{C}_5\text{H}_5)(\text{CO})_3\text{MH}$. ^b Yields were determined by n.m.r. spectroscopy with an internal standard. Products were identified by comparison of n.m.r. and g.c./m.s. spectra with those of authentic materials.

^c Experiment carried out at -75°C in a cold bath, then excess of pyridine was added (at -75°C) to quench the reaction after 5 min.

^d Reaction monitored by n.m.r. spectroscopy at -80°C . ^e Experiment carried out at room temperature. An immediate colour change was observed, and an n.m.r. spectrum was recorded after about 5 min.

Table 2. Alkene hydrogenations using HSiEt₃/CF₃SO₃H.^a

Alkene (conc./M)	CF ₃ SO ₃ H /equiv.	HSiEt ₃ /equiv.	Product (% yield)
Me ₂ C=CH ₂ Et	(0.09)	1.4	Me ₂ CHCH ₂ Et (98)
CH ₂ =C(Me)Pr ⁿ	(0.10)	1.4	Me ₂ CHPr ⁿ (93)
CH ₂ =C(Me)Pr ⁱ	(0.09)	1.4	Me ₂ CHCHMe ₂ (96)

^a CF₃SO₃H was added to a CD₂Cl₂ solution of the alkene and HSiEt₃ at -75 °C in a cold bath. After 5 min excess of pyridine was added (at -75 °C) to quench the reaction. Yields were determined by n.m.r. spectroscopy with an internal standard.

reported here enables rapid, high yield alkene hydrogenations to be accomplished at temperatures over 100 °C lower than with CF₃CO₂H/Et₃SiH. In the absence of alkenes, HMo(CO)₃(C₅H₅) reacts with CF₃SO₃H in CD₂Cl₂ at room temperature to give a good yield of (C₅H₅)(CO)₃MoOSO₂CF₃ within an hour. The analogous reaction of the tungsten hydride takes several days. It has been claimed⁸ that acids stronger than CF₃CO₂H cannot be used in the ionic hydrogenation of alkenes since they react with HSiEt₃. We have confirmed that CF₃SO₃H reacts quickly with HSiEt₃. Surprisingly, however, this reactivity does not preclude the use of this combination in analogous alkene hydrogenations. We have found that low temperature hydrogenations using CF₃SO₃H/HSiEt₃ give results comparable to those obtained with CF₃SO₃H/HMo(CO)₃(C₅H₅) (Table 2). Thus, while the demonstration of facile hydride transfer reactions of transition metal hydrides is of mechanistic importance, the ability to hydrogenate alkenes rapidly using readily available CF₃SO₃H and HSiEt₃ will undoubtedly be of more synthetic use.

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