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Tetrakis(dimethylamino)ethylene (TDAE) as a potent organic electron source: alkenylation of aldehydes using an Ni/Cr/TDAE redox system

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Abstract

Tetrakis(dimethylamino)ethylene (TDAE) was found to be a potent organic electron source which could promote alkenylation of several kinds of aldehydes in the presence of a catalytic amount of $NiBr_2$ and $CrCl_3$. © 1999 Elsevier Science Ltd. All rights reserved.

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A combination of a transition metal salt with a proper electron source (reductant) constitutes an electron transfer system in which the transition metal behaves as an electron transfer catalyst. The reactivity and product selectivity are highly dependent on the components of the system, e.g., electron source, transition metal, and solvent. Metals such as Zn,[1a] Mg,[1b] and Mn[1c] and metal hydrides such as $LiAlH_4$[1d] have been used as an electron source. Organic reductants are expected to have several advantages over inorganic reductants: (1) the redox potential is easily tunable by designing and modifying the molecular structure; and (2) organic reductants are soluble in organic solvents, thus shortening the induction period. Tetrakis(dimethylamino)ethylene (TDAE) is known as an organic reductant having reducing power close to that of zinc,[2] and is used in reduction of organofluorine compounds.[2,3] However, there has been no report on a combination of metal catalysts and TDAE used in organic synthesis. Herein we describe that the catalytic Nozaki–Hiyama reaction proceeds by use of TDAE as a reductant for regeneration and recycled use of the Cr(II) reagent.

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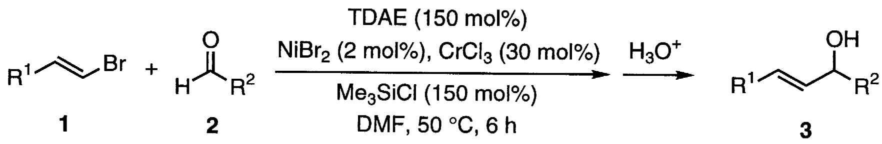
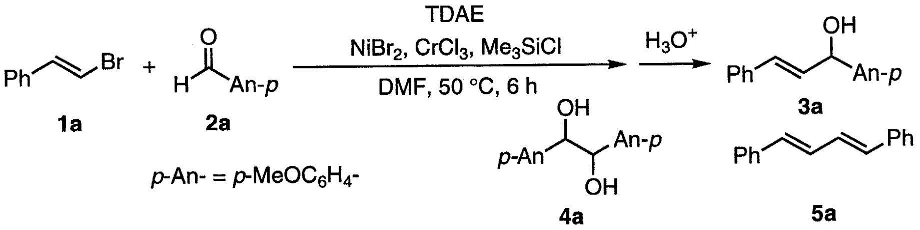


The Cr–Ni promoted alkenylation of carbonyl compounds (Nozaki–Hiyama reaction) proceeds in a highly chemoselective manner under very mild conditions,[4] and has been used in the synthesis of complex natural products.[5] The serious drawback of this system, however, is that a large excess (400 mol%) of $CrCl_2$ is usually used, which may cause environmental problems. Therefore, the regeneration and recycled use of a catalytic amount of a Cr reagent are subjects of keen interest, and have been successfully performed by reduction with metals such as Mn[6a] and Al[6b] and by electro-reduction.[6c,d] In most of these procedures, $CrCl_2$ was used, which is expensive and difficult to handle because of its high sensitivity to moisture and O_2. Systems using stable $CrCl_3$ are more preferable.[7]

A typical procedure for alkenylation of aldehydes is as follows (Table 1, Entry 1): To a mixture of β-bromostyrene **1a** (2.0 mmol), *p*-anisaldehyde **2a** (1 mmol), $CrCl_3$ (30 mol%, Katayama Chemical Co.), $NiBr_2$ (2 mol%, Katayama Chemical Co.), Me_3SiCl (150 mol%) in freshly distilled DMF (5 mL) was added TDAE (150 mol%). The mixture was stirred at 50°C under argon atmosphere for 6 h. After usual workup, the corresponding allyl alcohol **3a** was obtained in 96% yield. Alkenylation hardly proceeded at room temperature even with excess TDAE (Entry 2). A notable feature of this process is that the alkenylation proceeded with $CrCl_3$. The yield of **3a** decreased to 51% when 100 mol% of TDAE was used (Entry 3). The yield of **3a** was decreased to 40% when $CrCl_3$ was decreased to 0.15 mmol (Entry 4). When no $CrCl_3$ was used, homo-coupling of β-bromostyrene occurred predominantly to give 1,4-diphenyl-1,3-butadiene **5a** (Entry 5).

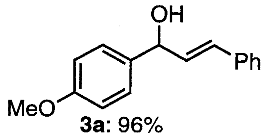
Table 1
Cross-coupling of *p*-anisaldehyde **2a** and β-bromostyrene **1a**



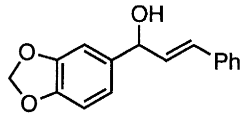
Entry	Additives / mmol				Temp / °C	Products / %[a]			
	$NiBr_2$	$CrCl_3$	Me_3SiCl	TDAE		3a[b]	4a[b]	5a[c]	2a
1	0.02	0.3	1.5	1.5	50	96	-[d]	-[d]	-[d]
2	0.02	0.3	4.0	4.0	room temp.	8	trace	trace	16
3	0.02	0.3	4.0	1.0	50	51	5	-[d]	23
4	0.02	0.15	1.5	1.5	50	40	-[d]	6	23
5	0.10	0	4.0	4.0	50	-[d]	-[d]	90	70

[a] Isolated yields. [b] Based on **2a**. [c] Based on **1a**. [d] Not detected.

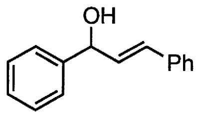
Representative results of alkenylation of aldehydes **1** in the TDAE/$CrCl_2$/$NiBr_2$/DMF system are shown below. The alkenylation of aromatic aldehydes proceeded smoothly to give the corresponding allyl alcohol derivatives (**3a**, **3b**, **3c**) in good yields, whereas electron-poor aromatic aldehydes such as *p*-cyanobenzaldehyde gave poor results (**3e**), resulting in predominant formation of the corresponding pinacol derivatives. These results are almost comparable to those obtained in Al/Cr/Ni-promoted[6b] alkenylation. It is noteworthy that alkenylation of *p*-chlorobenzaldehyde gave the product **3d** in better yields,[8] whereas aliphatic aldehydes such as 3-phenylpropanal[9] gave no alkenylated product **3f**, most of which was recovered unchanged. This significant change would be caused by a Lewis-acidic species generated in situ: in Al-promoted alkenylation, Lewis-acidic Al salts accumulate which would facilitate either alkenylation or pinacolization of aldehydes. On the other hand, a strong Lewis-acidic species would not be produced in the TDAE/Cr/Ni system.



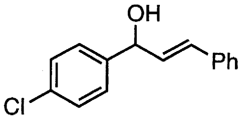
3a: 96%



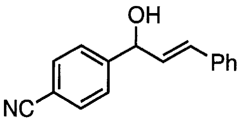
3b: 73%



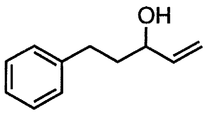
3c: 75%



3d: 66%

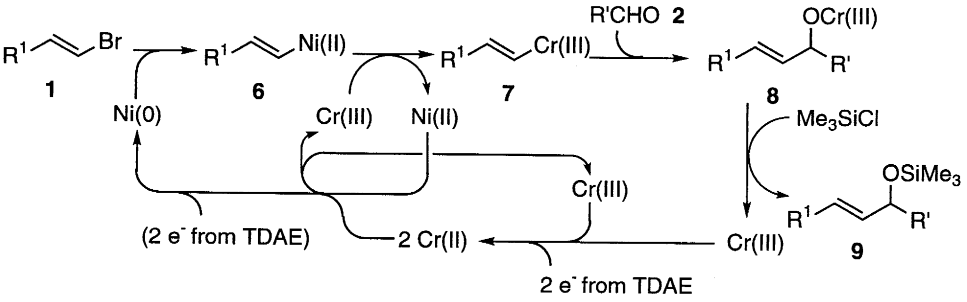


3e: 5%



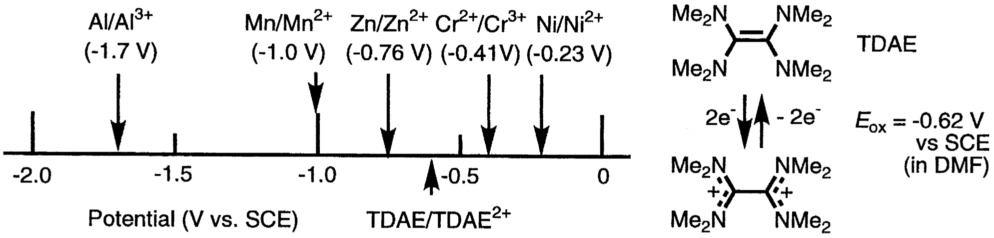
3f : 0%

Although the reaction mechanism is not clear at present, taking the well-established mechanism of the Hiyama–Nozaki reaction into consideration, a plausible catalytic cycle of this reaction is illustrated in Scheme 1. Standard redox potential of TDAE was measured in DMF to be −0.62 V versus SCE (a two-electron reversible peak), which is less than those of Al^{3+}/Al, Zn^{2+}/Zn, and Mn^{2+}/Mn but is adequate for reduction of both Cr(III) (Cr^{3+}/Cr^{2+} −0.41 V) and Ni(II) (Ni^{2+}/Ni^{0} −0.23 V) (Scheme 2). The purple $CrCl_3$ suspension in DMF immediately turned into a green solution on addition of TDAE, suggesting that TDAE smoothly reduces Cr(III) into Cr(II). Ni(II) would be reduced to Ni(0) by either Cr(II) or directly by TDAE, which would react with alkenyl halide to produce alkenylnickel species **6**. Transmetallation between **6** and Cr(III) would afford alkenylchromium **7** which would react with aldehyde to yield Cr-alkoxide **8**. Subsequent reaction of the alkoxide **8** with Me_3SiCl would liberate the Cr(III) salt with forming silyl ether **9**, which would be hydrolyzed during workup to give the corresponding homoallyl alcohol **3**. The thus-generated Cr(III) salt would be reduced with TDAE to regenerate Cr(II).



Scheme 1. A plausible mechanism of Cr/Ni/TDAE promoted alkenylation of aldehyde

In conclusion, TDAE can act as a potent electron source, and an electron transfer system consisting of TDAE and a catalytic amount of $CrCl_3/NiBr_2$ effectively promotes alkenylation of aromatic aldehydes. $CrCl_3$ can be used as a chromium source. As TDAE shows a reversible redox peak in its cyclic voltammogram, TDAE itself is expected to be an electron transfer catalyst. Electrochemical recycling of TDAE is now under study in our laboratory.



Scheme 2. Redox potentials of metals, metal salts, and TDAE

Acknowledgements

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7. In the previous paper (Ref. 6b), we reported that in the presence of a small amount of Zn, $CrCl_3$ can promote the alkenylation reaction using Al as an electron source.
8. Upon reaction of *p*-chlorobenzaldehyde and vinyl bromide under Al/$CrCl_2$/$NiBr_2$ conditions, 1-(4-chlorophenyl)-2-propen-1-ol was obtained in 25% (Ref. 6b).
9. 5-Phenyl-1-propen-3-ol was obtained in 34 and 64% yield from 3-phenylpropanal and vinyl bromide under electro-reduction (Ref. 6d) and Al/$CrCl_2$/$NiBr_2$ (Ref. 6b) conditions, respectively.