SELECTIVE REDUCTION OF ALKYNES BY THE REAGENT Sml₂ - TRANSITION METAL CATALYSTS - PROTON DONORS

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Summary: Alkynes were selectively reduced to cis-olefins under mild conditions by Sml₂ in admixture with first-row transition metal catalysts and appropriate proton donors, in which the corresponding transition metal hydrides are presumed as the reactive species. The conditions also effected the conversion of 1,6-diynes to the corresponding five-membered carbocycles.

A number of methods have been reported for selective reduction of alkynes to the corresponding alkenes. Among them, catalytic hydrogenation¹ and transition metal hydride reduction² have been widely used to obtain *cis*-olefins.^{3,4} In both cases, however, the concomitant formation of over-reduced products and/or undesirable *trans*-olefins are often inevitable.

Since most transition metal salts can easily be reduced to the corresponding lower-valent species with a Sml₂ solution in THF under mild conditions, the combined use of a catalytic amount of transition metal complexes and Sml₂ seems to have great potential for such reactions that low-valent transition metals are required as catalysts.⁵ As such a reaction, we examined the system, Sml₂-transition metal catalysts-proton donors, for the selective reduction of alkynes (Eq. 1).⁶

$$\mathbf{R}^{1} - \equiv -\mathbf{R}^{2} \xrightarrow{\text{transition metal catalyst}}_{\text{Sml}_{2}, \text{ proton donor, rt}} \mathbf{R}^{1} \xrightarrow{\mathbf{R}^{2}} \mathbf{R}^{2} + \mathbf{R}^{1} \xrightarrow{\mathbf{R}^{2}} \mathbf{R}^{2}$$
(1)

In the first instance diphenylacetylene was selected as the substrate for evaluation of different catalysts. The results are summarized in Table 1.

Among six transition metals (Fe, Co, Ni, Ru, Rh, and Pd) examined, only first-row elements have shown catalytic activity and the cobalt complex, CoCl₂•4PPh₃, was found to be the most effective catalyst in terms of stereoselectivity (entry 5). It is interesting from the mechanistic point of view that the addition of HMPA not only accelerated the reaction but also gave rise to a reversal of the senese of stereoselection thus affording thermodynamically more stable *trans*-stilbene as the major product (entries 6 and 9).

The reduction did not take place in the absence of proton donors and as shown in Table 2 a remarkable effect of proton sources on the cobalt(II)-catalyzed reduction of diphenylacetylene was realized: Both the reaction rate and product yields were increased in the order of 2-propanol < ethanol < methanol at the sacrifice of stereoselectivity and when acetic acid was employed rapid and quantitative formation of *cis*-stilbene was accomplished

in Table 3 are shown the results of the reduction of other substrates (1-4).

Ph—≡—Ph		catalyst, Sml ₂ , ROH		- Ph /-		n A Ph	+ ph A Ph
		additive, THF, rt		A A		B	C C
Run	Catalyst		Additive	ROH	Time(h)	Yield(%) ^{b)}	Ratio(A·B:C) ^{c)}
1	none		none	i-PrOH	24	N.R.	
2	11		HMPA	11	16	97	45 · 10 : 45
3	FeCl ₃ •4PPh ₃		none	MeOH	6	46	87.13
4	CoCl ₂ •(H ₂ O) _x		"	none	2	84	78 · 21 · 1
5	CoCl ₂ •4PPh ₃		"	/-PrOH	2	59	>99:1
6	п		HMPA	If	05	87	14 80 6
7	NiCl ₂ •(H ₂ O) _x		none	none	2	80	74 · 19 · 7
8	NICl2•4PPh3		n	/-PrOH	2	68	91 9
9	11		HMPA	11	0.5	89	1 · 90 : 9

Table 1. Reduction of Diphenylacetylene^{a)}

a) General procedure: A Sml₂-THF solution (0.1 mol dm⁻³, 5 ml, 0 5 mmol) was added to a solution of diphenylacetylene (35 mg, 0.2 mmol), a THF solution of the catalysts (0 025 mol dm⁻³, 240 μ l, 3 mol%), and ROH (0.5 mmol) in THF (0.5 ml) in the presence or absence of HMPA (0 4 ml) and the mixture was stirred at room temperature under argon. The crude products were purified by chromatography on silica gel b) isolated yield of the mixture (A+B+C) c) Determined by ¹H NMR (400 MHz) analysis

Run	ROH	Time (h)	Yield (%) ^{b)}	A . B
1	i-PrOH	2	59	> 99 · 1
2	EtOH	1	78	99.1
3	MeOH	0.5	99	96.4
4	AcOH	05	99	>99 : 1
5	t-BuCO ₂ H	8	56	96 : 4

Table 2. Effect of Proton Sources on the Reduction of Diphenylacetylene a)

a) CoCl₂•4PPh₃ (3 mol%) was used as the catalyst b) Isolated yield

≡ — Bu 1)	Ph ==TMS (2)	$C_5H_{11} - \equiv -C_5H_{11}$ (3)		$Bu - \equiv -CH(OH)C_6H_{13}$ (4)	
Alkyne	Catalyst	ROH	Time	%Yield ^{b)}	Z : E ^{c)}
1	CoCl ₂ •4PPh3	MeOH	Зh	97	>99 : 1
2	11	MeOH	2 h	96	97:3
11	**	i-PrOH	2 h	92	6 · 94
3	CoCl ₂ •(H ₂ O) _x		Зh	22 ^{e,f)}	
71	CoCl ₂ •4PPh ₃	MeOH	5 h	52 ^{e)}	> 99 : 1
11	11	AcOH	5 min	88 ^{e)}	> 99 : 1
4	FeCl ₃ •4PPh ₃	MeOH	15 min	95 ^{g)}	>99: 1
11	CoCl ₂ •4PPh ₃	AcOH	5 min	80 ^{h)}	> 99 :1
	E — Bu 1) Alkyne 1 2 3 4	 Bu Ph- = -TMS (2) Alkyne Catalyst 1 CoCl₂*4PPh₃ 2 " 3 CoCl₂*(H₂O)_x GoCl₂*(H₂O)_x CoCl₂*4PPh₃ " 4 FeCl₃*4PPh₃ " CoCl₂*4PPh₃ 	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 3. Sml₂-Promoted Reduction of Alkynes (1-4)^{a)}

a) The reactions were carried out at room temperature by using 3 mol% of catalyst. b) Isolated Yield of olefins. c)Determined by ¹H and/or ¹³C NMR analysis. d) HMPA was added. e) GLC yield f) Hexapentylbenzene (18 %) was also produced. g) 5,6-Tridecadiene (5 %) was also isolated. h) A mixuter fo the corresponding allene and acetylene derivatives was also produced (ca. 20 %)

The present method seems superior in suppressing the over-reduction to the conventional semihydrogenation utilizing various types of doping Lindlar catalysts (e.g., entry 1) ^{1a} It is noted that the reduction of **2** afforded the corresponding *cis*-olefin in appreciablly high purity. In the presence of HMPA a stereochemical reversal was again realized. When Co(II) chloride polyhydrates was used as a catalyst in the reduction of **3**, a considerable amount of hexapentylbenzene was produced as the result of reductive trimerization⁷ (entry 4). The corresponding dimer was also detected on the reaction of entry 5. However, such oligomerization could be diminished by the use of acetic acid as a proton donor (entry 6). The reduction of **4** proceeded faster than that of diaryl or dialkyl acetylenes and the Fe(III) complex turned out to be most effective in this case (entry 7).

While the mechanistic details remain to be explored, formation of the transition metal hydrides is highly presumable because the reduction did not take place either in the absence of catalysts or proton donors.⁸ *cis*-Addition of the metal hydride to alkynes followed by further reduction of the resulting adducts with Sml₂ would produce the corresponding vinyl anions⁹ and low-valent transition metals, from which the *cis*-olefins and metal hydrides would be produced, respectively.

Reduction of alkynes with transition metal hydrides, prepared from the corresponding metal halides or clusters by reducing with NaBH₄,^{2b,e,f} LiAlH₄,^{2a} NaAlH₄,^{2d} or Grignard reagent,^{2c} has been reported. Few of them are, however, catalytic reactions and the chemo- and stereoselectivity is not always high. These problems could be overcome in the present reduction, in which only a

catalytic amount of metal hydrides and metal alkene intermediates might be present to minimize the over-reduction and isomerization of the products. Isomerization of the vinylic anion intermediates seems fast in HMPA and this might be the reason why *E*-isomer became major when diphenyl-acetylene or **2** was reduced in the presence of HMPA.

When the method was applied to the reaction of 1,6-diynes, intramolecular carbon-carbon bond formation took place to give fivemembered carbocyclic compounds as a mixture of stereoisomers ¹⁰ ¹¹



 $R^{1}=R^{2}=Ph$ (62 %); $R^{1}=Ph$, $R^{2}=TMS$ (37 %)

References and Notes

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- 7. J P Collman and L S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, ed by A Kelly, University Science Books, Mill Valley (1980), p. 523
- 8 The possibility of alkyne-samarium or alkyne-transition metal complex as an intermediate may be excluded by the fact that alkynes did not react with electrophiles such as alkyl halides, aldehydes, ketones, or chlorotrimethylsilane under the present conditions even in the absence of proton donor while it has been reported that such alkyne-metal complexes were produced by low-valent zirconium, niobium, or tantalum reagent, and reacted with electrophiles, see, for example, K Takai, Y Kataoka, and K Utimoto, J. Org. Chem, 55, 1707 (1990) and references cited therein
- 9. In order to clarify the origin of hydrogen atom incorporated in the products, diphenylacetylene was reduced in the presence of CD₃OD or CH₃COOD as a 'proton' source. The products obtained were subjected to catalytic hydrogenation to give 1,2-diphenylethane, ¹³C NMR (100 MHz) analysis of which revealed that totally ca. 80 % of D atom was incorporated in a mixture of mono- and dideuterated stilbene. On the other hand, the reaction in THF-d₈ without proton donor or in the presence of Bu₃SnD did not produce any trace of deuterated stilbene, indicating that hydrogen atom-transfer process is not involved.
- For similar transformations, see a) T. V RajanBabu, W A Nugent, D F Taber, and P J. Fagan, J. Am. Chem. Soc., 110, 7128 (1988), b) B M. Trost and D C Lee, *ibid.*, 110, 7255 (1988); c) E Negishi, S J. Holms, J M Tour, J A Miller, F E Cederbaum, D. R Swanson, and T Takahashi, *ibid.*, 111, 3336 (1989).
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