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SELECTIVE HYDROGENATION OF THE CC-TRIPLE BOND IN PhC≡CPh BY TRIS(TRIPHENYLPHOSPHINE)COBALT ACTIVATED $NaBH_4$; DEUTERIUM TRACING EXPERIMENTS

B. STEINBERGER, M. MICHMAN *,

Institute of Chemistry, Hebrew University of Jerusalem, Jerusalem 91904 (Israel)

H. SCHWARZ and G. HÖHNE

Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 1000 Berlin 12 (Germany)

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Summary

Sodium borohydride does not on its own react with diphenylacetylene, but becomes an active hydrogenation agent in the presence of $(Ph_3P)_3CoCl$. Unlike systems involving other catalysts, e.g. cobalt halides in ethanol, this is a selective reagent for hydrogenation in which an alkyne is selectively hydrogenated to *cis* and *trans* alkenes. The role of $NaBH_4$ in this hydrogenation and isomerization has been studied by deuterium labelling. A brief comparison is made with other active catalysts in this system like $(Ph_3P)_3CoBH_4$.

The activation of hydrido reagents such as NaH, $NaBH_4$, $LiAlH_4$ by transition metal compounds has attracted considerable attention in recent years, and is described in several reviews [1,2]. Such reagents are important because of their versatility as hydrogenation, polymerization and desulphurization catalysts, their resistance in some cases to catalyst fatigue, their selectivity and, in connection with the latter, the many possible variations of the methods of the preparation of the catalysts [2]. That the origin of their reactivity and their structure are often unclear is further justification for their study.

In the case of sodium borohydride, activation is brought about by $CoCl_2 \cdot 6H_2O$ and $CoBr_2$ [3], Cobalt(III) porphyrine [4], and iron sulfides [5]. $NaBH_4$ also reduces the π-complex $[\eta^5\text{-}C_5H_5]Fe(CO)(Ph_3P)\ [\eta^2\text{-alkyne}]^+$ to a σ-derivative [6]. Double bonds in α,β-unsaturated ketones are hydrogenated by $NaBH_4$ in the presence of cobalt, iron and nickel salts but hardly at all in their absence [7–9]. Transition-metal hydrides are presumably the active intermediates [10]. Reductions of thioketones, nitro groups, nitriles, amides and other functional groups have been well documented [2]. The reaction between $NaBH_4$ and the transition-metal compound

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proceeds in various ways with formation of hydrido and borohydrido complexes [11–13] or of borides and reduced metal [2] with release of molecular hydrogen. Hence the sensitivity dependence on reaction conditions is very high. The reaction of $NaBH_4$ with cobaltous halides in the presence of Ph_3P yields $(Ph_3P)_3CoX$ [12] ($X = Cl$ or Br), $(Ph_3P)_3Co(BH_4)$ [13,14], $(Ph_3P)_3CoH_3$ or $(Ph_3P)_3Co(N_2)H$ [15] depending on the conditions used.

With a few exceptions, the reactions mentioned above were run under a hydrogen blanket and with the molecular hydrogen activated by the catalyst system. It was our aim to examine the hydrogen transfers within the reaction media in the absence of extraneous hydrogen.

$NaBH_4$ was chosen since on its own it does not react at all with diarylalkynes. We have used deuterium tracing to study its reaction with $PhC{\equiv}CPh$ under catalysis by $(Ph_3P)_3CoCl$. In a typical run (24 h at 25°C) the conversion of $PhC{\equiv}CPh$ to stilbene was approximately 60%. Bibenzyl was obtained as a side product in varying yields, not exceeding 5%.

$$PhC{\equiv}CPh + NaBH_4 + (Ph_3P)_3CoCl \xrightarrow[]{\substack{1)\ \text{THF, } 25^\circ\text{C} \\ 2)\ H_2O/HOAc}} \underset{c/t}{PhCH{=}CHPh}$$

In a preliminary experiment using $NaBD_4$ we isolated 100 mg stilbene by silica-gel chromatography. This sample was analysed by 70 eV electron impact mass spectrometry without separation of the stereoisomers. The following results were obtained for the deuterium incorporation: $d_0 = 32.9$, $d_1 = 48.2$ and $d_2 = 18.9\%$. The position of the deuterium (exclusively vinylic) was established by 100 MHz ^1H NMR spectroscopy.

Reactions with deuterated sodium borohydride or with D_2O, D^+ or both were studied, and the results are shown in Table 1. They show that:

(a) $NaBH_4$ in the predominant but not exclusive source of hydrogen appearing at the vinylic position of $PhCH{=}CHPh$.

(b) A significant contribution to vinylic hydrogen is made in the hydrolysis step. Since exchange of hydrogen between $NaBH_4$ and water takes place during hydrolysis, this process cannot be ruled out as a contributing factor. However the extent of deuteration due to D_2O/D^+ can be clearly distinguished from that due to $NaBD_4$.

(c) Some of the vinylic hydrogen must came from the solvent used since the amount of deuterium-free product would otherwise be too large.

It has already been observed that mixtures of H_2, HD and D_2 are obtained when D_2O is used for the hydrolysis [16–20]:

$$NaBH_4 + 3H_2O + H^+ \rightarrow 4H_2 + H_3BO_3 + Na^+$$

The composition of the $H_{2\text{-}n}D_n$ mixture ($n = 0, 1, 2$) is changed in the presence of transition metal salts [20]. This could influence our results because the reaction of the residual $NaBH_4$ during the hydrolysis with D_2O could form mixtures of isotopic hydrogen. However, hydrogen gas does not reduce $PhC{\equiv}CPh$ either in the presence of $NaBH_4$ or $(Ph_3P)_3CoCl$ in THF at low pH values. The considerable quantities of deuterium-free products in reaction 1 (Table 1) cannot be accounted for in terms of the protium content of the D_2O/D^+ (which is below the detection level of a 60 MHz NMR) and of $NaBD_4$ ($\simeq$ 16% protium), and the solvent must be a protium source. This is born out by reactions 1 and 3. Such exchange processes could also explain

TABLE 1

PRODUCTS OF REACTION BETWEEN $PhC{\equiv}CPh$, $NaBX_4$ ($X = H$, D) AND $(Ph_3P)_3CoCl$ in THF

Reaction	Reagent	Deuterium content of products	Stilbene	
			cis	*trans*
		d_0	27.2	26.4
1 [a]	$NaBD_4$	d_1	44.8	29.2
	D_2O, D^+	d_2	28.0	44.4
		d_0	79.7	79.4
2 [a]	$NaBH_4$	d_1	16.2	16.9
	D_2O, D^+	d_2	4.1	3.7
		d_0	12.8	38.1
3 [b]	$NaBD_4$	d_1	78.4	54.0
	(without hydrolysis)	d_2	8.8	7.9

[a] Reaction at 35°C for 5 h. [b] Reaction at 25°C for 21 h.

the formation of dideuterated stilbene, e.g. in reaction 2.

Deuterium incorporation into dodecene by use of labelled sodium borohydride and ethanol has recently been reported [3], the reactions being catalyzed by cobaltous halides; the extent of deuterations was high but so was the amount of scrambling over five positions. Both sodium borohydride and ethanol were shown to contribute.

A large number of alkenes and alkynes can be reduced in ethanol [3], and the addition of an aprotic ether solvent has an adverse effect. We have found that in our system this effect does not totally inhibit the reaction but is rather selective; in THF and even toluene or DMSO none of the alkenes examined were reduced to alkanes, yet diarylalkynes were smoothly and selectively hydrogenated [21] to the alkene stage. This is probably a result of the (expected) better ability of alkynes to coordinate the cobalt catalyst. This comment holds for a number of different related catalyst systems, all of which may be present (see Table 2). Obviously cobalt

TABLE 2

REAGENTS FOR REDUCTION OF $PhC{\equiv}CPh$

Reducing reagent	Solvent	Temp. (°C)	Time (h)	Stilbene		Bibenzyl (%)	Unreacted diphenyl-acetylene [a] (%)
				cis (%)	*trans* (%)		
$(PPh_3)_3Co(BH_4)$	THF	0	1.5	18	–	1	31
$(PPh_3)_3Co(BH_4)$	THF	0	2	22	–	1	37
$(PPh_3)_3CoCl + NaBH_4$	THF	0	2	15	7	6	8
$(PPh_3)_3Co(BH_4)$	Toluene	0	2	28	8	< 1	64
$(PPh_3)_3CoCl + NaBH_4$	Toluene	0	2	4	–	< 1	96
$(PPh_3)_3Co(BH_4)$	DMSO	25	2	20	3	< 1	64
$(PPh_3)_3CoCl + NaBH_4$	DMSO	25	2	17	9	4	–

[a] Amount actually recovered. Differences from 100% are due to condensation reactions.

TABLE 3

TIME DEPENDENCE OF THE PRODUCT FORMATION IN THE REDUCTION OF PhC≡CPh WITH $(PPh_3)_3CoCl$ AND $NaBH_4$ IN THF

Time (h)	Stilbene		Bibenzyl	Diphenylacetylene recovered
	cis	*trans*		
0.1	13.7	–	0.6	69.8
0.5	24.1	0.4	1.8	50.5
1	23.6	5.1	1.1	42.9
2	26.6	4.5	4.1	26.3
3	31.7	7.8	2.5	15.4
5	33.9	13.5	1.0	11.9

borohydrides may be the active intermediates, and the usual reference to active hydrides [1] may be an oversimplification. Indeed, the results in Table 2 show that the cobaltborohydride complex, also formed in the reaction of $NaBH_4$ and $(Ph_3P)_3CoCl$, can react as a hydrogenation reagent in THF as well as in other aprotic solvents.

With regard to the formation of *trans* stilbene the following comments can be made. The results in Table 3 demonstrate that formation of *cis* stilbene preceeds that of the *trans* isomer. This is substantiated by the results shown in Table 4, where the free *cis* olefin is shown to isomerize to the *trans* isomer under the reaction conditions. However, as indicated by the results in Table 1, reaction 2, isomerization in the catalyst-bound adduct cannot be excluded. Another feature concerns the role of the catalyst in the *cis-trans* isomerization of the free olefin. From the data given in Table 5 it can be seen that the reaction temperature is of crucial importance; when the reaction using $NaBD_4$ is run at 25°C no deuterium is incorporated into the reaction products, whereas at 35°C there is a significant d_1 incorporation and a minor amount of d_2. A similar temperature dependence is observed in the hydro-

TABLE 4

REACTION OF *cis* STILBENE[a] (IN THF) WITH $NaBH_4$ AND/OR $(Ph_3P)_3CoCl$

Reagent	Temp. (°C)	Time (h)	Stilbene		Bibenzyl (%)
			cis (%)	*trans* (%)	
$(PPh_3)_3CoCl+NaBH_4$	0	2	81	18	1
$(PPh_3)_3CoCl+NaBH_4$	room temp.	20	78	21	1
$NaBH_4$	room temp.	20	97–98	2–3	–
$(PPh_3)_3CoCl$	room temp.	20	97–98	2–3	–

[a] The starting *cis* stilbene contains 2–3% *trans* isomer.

TABLE 5

ISOMERIZATION OF *cis* STILBENE[a] IN THF CATALYZED BY $NaBD_4/(Ph_3P)_3CoCl$

Conditions	Isomerized mixture	%	*m/z*[b] 180	*m/z* 181	*m/z* 182
24 h, 25°C	*cis* stilbene	70	100.0	16.0	1.8
	trans stilbene	30	100.0	15.7	2.4
5 h, 35°C	*cis* stilbene	77	100.0	16.0	1.0
	trans stilbene	23	100.0	30.0	3.3

[a] Under the same conditions no isomerisation of *trans* stilbene was observed. [b] Both authentic isomers gave the following $CI(NO^+)$ mass spectra: *m/z* 180 (100.0); 181 (16.0); 182 (1.4).

genation reaction of PhC≡CPh (see Table 1, reaction 1 and 3).

It must be concluded that although an apparently selective system is chosen and studied with aprotic solvent, there are several ways in which active hydrides are formed and the formed olefins isomerize. Some of these routes have been partly clarified, but detailed mechanistic discussion is not appropriate at this stage.

Experimental

Instrumentations. Gas chromatography (GC), was carried out with 1/8" 3% and 5% SE-30 on Chromosorb columns. ^1H NMR spectra were recorded on Varian T 60 and Varian HA 100 instruments. Mass spectra were recorded on a Varian MAT 311 (70 eV electron impact ionization) and a Varian MAT 44 instrument (chemical ionization using NO^+), in combination with capillary GC, with data on-line to a SS 200 computer. The data given in Table 1 were corrected for natural ^{13}C isotope contribution; they are the average of at least three separate runs, and the relative errors are ±5%.

Solvents used were refluxed with sodium under argon. Ethanol was dried over $MgSO_4$ under argon.

Materials. The compounds $(Ph_3P)_3CoCl$ [12] and $(Ph_3P)_3CoBH_4$ [13,14] were prepared by literature methods, the former by reduction with zinc. Ph_3P was freshly crystallized. CH_3COOD was prepared by treating acetic anhydride with D_2O.

Reaction of PhC≡CPh with $NaBH_4/(Ph_3P)_3CoCl$

To a solution of PhC≡CPh (0.178 g; 1 mmol), $NaBH_4$ (0.038 g; 1 mmol) and Ph–Ph (0.0154 g; 0.1 mmol) in THF (50 ml) is added $(Ph_3P)_3CoCl$ (0.88 g; 1 mmol) at −50°C under argon. The stirred mixture is warmed immediately to 25°C unless otherwise stated. A gradual change in colour from green to brown is observed. Stirring is continued for 24 h unless otherwise stated, and the reaction is hydrolysed using aqueous HOAc at pH = 3 for 3 h. The organic products were extracted with diethyl ether. Similar conditions were used for the isomerization of the free stilbene.

Control experiments

(1) Reactions under the conditions described above were carried out in the absence of either $NaBH_4$ or $(Ph_3P)_3CoCl$. The starting material was fully recovered.

(2) No reduction of PhC≡CPh was observed when hydrogen gas (10 ml min^{-1}) was introduced over the solution described above in the presence of either $(Ph_3P)_3CoCl$ or $NaBH_4$.

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21 Note: Unsubstituted alkynes can react differently, e.g. $NaBH_4$ in presence of cobaltous salts is an efficient catalyst for polymerization of alkynes like PhC≡CH see ref. [2].