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ALKYLATION REACTIONS WITH ORGANOMETALLIC REAGENTS

III *. THE EFFECT OF OXYGEN ON ALKYLATION REACTIONS WITH COBALT(I) COMPOUNDS

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Summary

Methylmagnesium bromide reacts with diphenylacetylene in the presence of cobalt(I) and cobalt(II) complexes. Oxygen is shown to have a significant effect on the reaction. Under argon the alkyne is consumed either by formation of cyclisation products or by addition across the triple bond to yield stilbene derivatives and 1,2-diphenylpropene (by mono-alkylation of the triple bond). Under oxygen the consumption of the alkyne through condensation tends to be blocked while the yield of addition reactions to the triple bond increases and includes the formation of 2,3-diphenylbut-2-ene (by dialkylation of the alkyne). The same effect to a smaller extent is observed when $CH_3Co(Ph_3P)_3$ reacts with $PhC{\equiv}CPh$. An attempt to rationalize the oxygen effect is presented.

Introduction

In a study of alkylations of diarylacetylenes by organocobalt reagents a peculiar effect of oxygen has been observed. Under an argon atmosphere $(Ph_3P)_3$-CoCl and CH_3MgBr reacted with $PhC{\equiv}CPh$ to give very low yields of addition products ** [1] of which $PhC(CH_3){=}CHPh$ (*trans* and *cis*) was the main constituent. When, however, reactions were run under an oxygen atmosphere, the yields were raised and $PhC(CH_3){=}C(CH_3)Ph$ was obtained as the main product, while *cis*-diphenylpropene and *cis*-stilbene were not found at all. The effect of oxygen in this transformation seemed to justify further study. It was later observed that oxygen reacted with the cobalt reagents in other fashions as well.

Oxygen is usually considered to be a destructive agent for many transition

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* For part II see ref. 19, for a preliminary report see ref. 1.

** In these systems most of the diphenylacetylene forms cyclisation products. These however are not discussed in the present paper.

metal preparations whether compounds, reagents or catalysts. Hydrogenations with the well-known Wilkinson catalyst $(Ph_3P)_3RhCl$ are reportedly blocked by oxygen [2] and many homogeneously-catalyzed reactions are carried out in an inert atmosphere. There are however, some reports of a helpful effect of oxygen. Hydrogenation of cyclohexene with $(Ph_3P)_3RhCl$ was enhanced by small quantities of oxygen and H_2O_2 [3] and so were hydrogenations with $(Ph_3P)_2IrCl(CO)$ [4]. Oxygen affected rates of hydrogenations and isomerizations of alkenes in various solvents [5] and was also reported to enhance hydrosilylation [6], hydroformylation [7], activity of a Ziegler-type catalyst [8], formation of nitriles from amides [9] and alkyl coupling on alkylcopper compounds [10]. No satisfactory explanation was available in all cases and studies of the enhancement of reactions by oxygen are still scarce.

Results

Reactions of diphenylacetylene with CH_3MgBr and cobalt reagents were run with each of the following: $(Ph_3P)_3CoCl$ (I); oxidized $(Ph_3P)_3CoCl$ (Ia); $(Ph_3P)_2CoCl_2$ (II); anhydrous $CoCl_2$ (III) and $(Ph_3P)_3CoCH_3$ (IV) (no Grignard reagent used in this case). Runs were carried out under oxygen or argon. The yields are very low, 2—15%, based on diphenylacetylene and determined by gas chromatography with the aid of biphenyl as an internal standard. Since quantitative

TABLE 1

METHYLATION OF $PhC{\equiv}CPh$ WITH $(Ph_3P)_3CoCl + CH_3MgCl$ (I); $(Ph_3P)_2CoCl_2 + CH_3MgCl$ (II); $CoCl_2 + CH_3MgCl$ (III); $(Ph_3P)_3CoCH_3$ (IV); UNDER ARGON AND OXYGEN

Yields are based on $PhC{\equiv}CPh$ and calculated by using 1/10 molar ratio of biphenyl to diphenylacetylene as an internal standard. With this, low percentages but not high percentages could be determined accurately.

Product	I[a]		Ia	II		III		IV	
	Ar	O_2	Ar	Ar	O_2	Ar	O_2	Ar	O_2
cis-PhCH=CHPh	*b*	*c*	*b*	*b*	*b*	1.2	*b*	*b*	
cis-Ph$\overset{CH_3}{C}$=CHPh[a]	3	*c*	3	3	*b*	3.7	*b*	2	1
cis-Ph$\overset{CH_3}{C}$=$\overset{CH_3}{C}$Ph	*b*	5	4	*b*	*b*	4.2	*b*	*c*	1
trans-Ph$\overset{CH_3}{C}$=$\underset{CH_3}{C}$Ph	*b*	3	2	*b*	*b*	1	*b*	*c*	1
$PhC{\equiv}CPh$[d]	*b*	~90	*b*	15	80—90	*b*	~80—100	*c*	20
trans-PhCH=CHPh *trans*-Ph$\underset{CH_3}{C}$=CHPh	2	2	6	4	*b*	6	*c* *c*	*c* 8	
Total yield (%)	~5	10	15	7	<1	16	0	10	7

[a] Not the same run as in Fig. 1. [b] Detected in less than 1% yield. [c] Not detected. [d] Recovered.

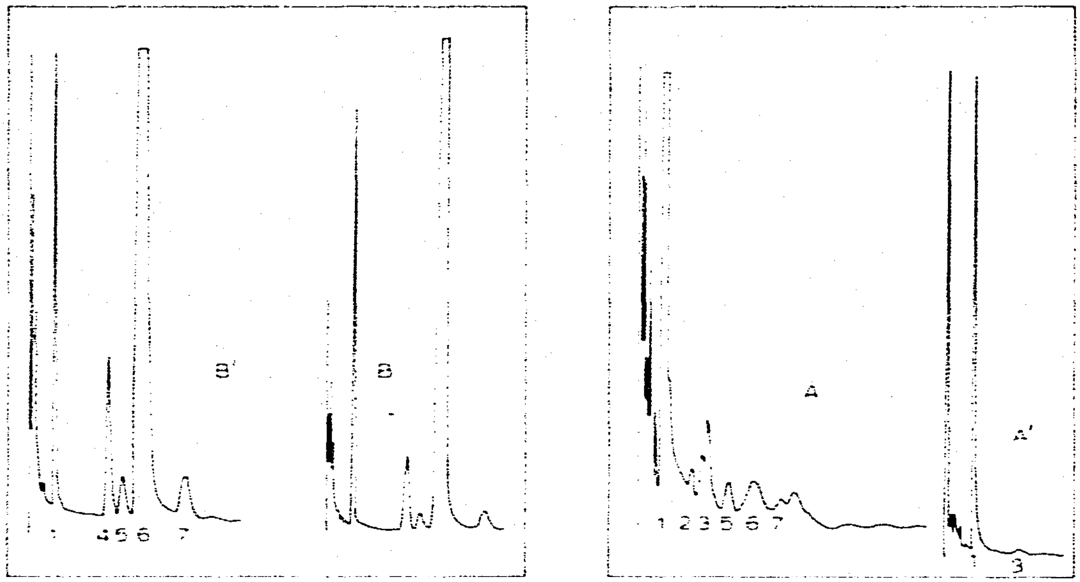

Fig. 1. A. System I, $(Ph_3P)_3CoCl + CH_3MgCl + PhC{\equiv}CPh$, under argon. A'. lower detector sensitivity. B. System I under oxygen. B'. higher sensitivity (A' is comparable to B').
Identification: 1 biphenyl; 2 *cis*-stilbene; 3 *cis*-1,2-diphenylpropene; 4 *cis*-2,3-diphenylbut-2-ene; 5 *trans*-2,3-diphenylbut-2-ene; 6 diphenylacetylene; 7 *trans*-stilbene and *trans*-1,2-diphenylpropene.

estimation of such yields is difficult, reactions were repeated several times and GC traces compared to ascertain reproducibility. All reactions were run in THF and under the same physical conditions. Characteristic results are given in Table 1. Fig. 1 represents a sample run with reagent I.

From Fig. 1, the following observations can be made:

a. Under argon, diphenylacetylene is practically consumed. However an almost insignificant amount (<1%) (1—5% was the range of yield in several runs), of products of addition to the triple bond is found; it consists mainly of *cis*-stilbene, *cis*-1,2-diphenylpropene, *trans*-stilbene and *trans*-1,2-diphenylpropene (overlapping peaks for the last two).

b. Under oxygen, a large part of the diphenylacetylene is recovered, no *cis*-stilbene or *cis*-1,2-diphenylpropene are detected, but the *trans* isomers are present. Two new main products appear: *cis*- and *trans*-2,3-diphenylbutene, and the total yield is increased to 5—10%.

When $(Ph_3P)_3CoCl$ was oxidized for 24 h in a stream of oxygen in solution or as a solid and the resulting blue complex allowed to react with $PhC{\equiv}CPh$ under argon, the isomeric 1,2-diphenylpropenes (9%) as well as the isomeric 2,3-diphenylbutenes (6%) were formed. In this case the $PhC{\equiv}CPh$ was fully consumed as in other reactions which were conducted under argon.

With reagent II under argon, about 15% of the acetylene was recovered and *cis*- and *trans*-1,2-diphenylpropene were practically the only addition products. Yields were about 5%. Under oxygen there was no reaction and almost all the alkyne was recovered. With system III both diphenyl-propenes and -butenes as well as stilbenes were obtained under argon; the yield was about 15% and no alkyne was left. Again there was a sharp drop in yield and in alkyne consumption with runs carried out under oxygen. Reagent IV yielded *cis*- and *trans*-1,2-diphenylpropene under argon, (~10%) with less than 1% *cis*-stilbene as the only other product. Both diphenylpropenes and diphenylbutenes were obtained under oxygen (7%), when no stilbene was formed, and about 20% of the alkyne was recovered.

Thus, oxygen influences alkylation in the cobalt(I) systems, while with the cobalt(II) reagents it mostly inhibits the reactions. In all systems, however, oxygen blocks consumption of the alkyne. Obviously, many of these reactions are of no consequence as far as yields are concerned, still the most pronounced effect of oxygen on alkylation is observed with system I, which gives the lowest yield under argon. It is noteworthy that under oxygen *cis*-stilbene and *cis*-methylstilbene decrease in yield or disappear completely while the *trans* isomers are still observable. Tests with $(Ph_3P)_3RhBr + CH_3MgBr$, in which addition products form in over 80% yield [11] showed no effect of oxygen other than inhibition of the reaction and complete recovery of $PhC{\equiv}CPh$. The same holds for $(Ph_3P)_3RhCH_3$.

Generally, in all reactions studied, under argon and oxygen some triphenylphosphine oxide was isolated in addition to free triphenylphosphine. On the one hand when $(Ph_3P)_3CoCl$ was oxidized by oxygen as described above the product could be shown by IR or mass spectroscopy to contain both triphenylphosphine and triphenylphosphine oxide. For reactions under argon, on the other hand, it was shown that CH_3MgBr reacts with free triphenylphosphine to yield the corresponding oxide after hydrolysis. There did not seem to be any specific correlation between the formation of phosphine oxide and the effect on alkylation.

Since the ratio of stilbene, diphenylpropenes and diphenylbutenes can be the result of competitive hydrogen and methyl group transfer reactions, tests were carried out to check the extent of hydrogen transfer in the formation of diphenylpropene and the possible effect of oxygen in such cases. With system I and with IV reactions were in some cases terminated by hydrolysis with D_2O/DCl or with D_2O/CH_3CO_2D. The results with system I do not include incorporation of deuterium into the $PhC(CH_3){=}CHPh$ formed, but are of doubtful significance due to the extremely low yields. Experiments with IV showed clearly that the 1,2-diphenylpropene retreived (10—20%) under argon contained no deuterium whatever. This strongly differs from $(PH_3P)_3RhBr + CH_3MgBr$ or $(Ph_3P)_3RhCH_3$ where at least 70% deuterium would be incorporated at the vi-

TABLE 2

REACTIONS OF HYDRIDOCOBALT COMPOUNDS WITH $PhC{\equiv}CPh$ UNDER ARGON [a] (20°C. THF solutions)

	$NaBH_4 + (Ph_3P)_3CoCl$	$(Ph_3P)_3Co(N_2)H$
cis-stilbene + dibenzyl	50%	3%
trans-stilbene	20%	1%
$PhC{\equiv}CPh$ residue	none	0.5—1%
Total yield	70%	4%

[a] In both cases, under O_2: no reaction, and complete recovery of $PhC{\equiv}CPh$.

TABLE 3

MASS SPECTRA OF TRIPHENYLPHOSPHINECOBALT COMPLEXES (% parent peak)

m/e	$(Ph_3P)_3CoCl$	$(Ph_3P)_2CoCl_2$	$(Ph_3P)_3CoCl$ oxidized	
278	2	0.72	4.3	(Ph_3PO)
277	4	0.36	9.3	
264	6	2.9	—	
263	60	21.8	23.6	
262	100	100	100	(Ph_3P)
261	34.7	13.8	16.4	
200	—	—	2.15	
198	—	—	2.15	
185	4.7	11.6	12.2	
184	43.2	16.5	17.2	
183	91	85.5	75	
108	90	49.3	40	
107	52	26	19	

nylic position of $PhC(CH_3){=}CHPh$ [11,12]. Evidently, with cobalt reagents, hydrogen- as well as methyl-transfer reactions take part in the formation of the olefinic products.

Next, $PhC{\equiv}CPh$ was treated with $NaBH_4$ and with $NaBH_4$ + $(Ph_3P)_3CoCl$ under argon. The latter two compounds were previously shown to yield cobalt hydrides [13]. $NaBH_4$ alone did not react with $PhC{\equiv}CPh$, which was fully recovered, but with $(Ph_3P)_3CoCl$ present *cis*- and *trans*-stilbene as well as dibenzyl were formed. This reaction was completely blocked when run under oxygen and only $PhC{\equiv}CPh$ was recovered. Finally, when a hydride $(Ph_3P)_3Co(N_2)H$ [14] was prepared and allowed to react with $PhC{\equiv}CPh$, stilbene was formed under argon but not under oxygen. The cobalt compound was indeed reported to react with oxygen [14]. These results are summarized in Table 2.

Discussion

Three specific reactions of oxygen have been observed: *1*. Oxidation of the phosphine ligand to phosphine oxide on direct reaction of oxygen with I. *2*. Inhibition of the greater part of alkyne consumption in the presence of oxygen. *3*. Increase in the extent of double alkylation of the triple bond with concurrent decrease in yields of *cis* isomers of stilbene and 1,2-diphenylpropene. The first two observations strongly suggest the coordination of oxygen to the cobalt compounds, a phenomenon often observed with cobalt complexes [15—17]. Free triphenylphosphine is not oxidized by oxygen under the experimental conditions used here and its catalysed oxidation to phosphine oxide in the presence of transition metal complexes is believed to involve an oxygen—metal complex as a key intermediate [18]. Since oxygen is present in excess its coordination to the cobalt compounds could compete significantly with the coordination of diphenylacetylene. Indeed those reactions of the alkyne in which extensive coordination is of utmost importance, i.e. condensation and cyclisation of two or three alkyne units, are the ones which are most effectively blocked by oxygen. Incidentally, with the very different reaction of hydrogenation of cyclohexene by rhodium catalysts [3] the presence of oxygen or H_2O_2 led to phosphine oxide formation which was considered most significant for the increase in the extent of cyclohexene coordination and the yields of hydrogenation. However, there may be no analogy at all between this and the case discussed here.

Systems such as L_2PdCl_2 + CH_3MgCl (L = C_6H_5CN, C_7H_7) were shown mainly to dimethylate diphenylacetylene [19] whereas mono-alkylation was observed with $(Ph_3P)_3RhCH_3$ and with $(Ph_3P)_3RhBr$ + CH_3MgCl [11]. Considering the relatively easy oxidation of L_3Co^IX to $L_2Co^{II}X_2$ [20] the possibility that I would yield cobalt(II) compounds which would behave in a manner similar to that of palladium(II) compounds is attractive but is not supported by our results, since the corresponding cobalt(II) compound (system II) did not lead to extensive dialkylation under argon and was inactive under oxygen. The direct oxidation of the cobalt(I) compound prior to reaction was sufficient to cause only a partial effect. In spite of the fact that in Ia $(Ph_3P)_3CoCl$ was exposed to oxygen for a longer time than in I, system Ia yielded, with PhC≡CPh under argon, products obtained from I both under argon and under oxygen though the yields were significantly increased. Most of the phosphine ligand seems to remain unoxidized in the preliminary oxidation of $(Ph_3P)_3CoCl$. Only when oxygen is present throughout the reaction as with system I is the change in the pattern of alkylation clearly observed.

The effect is not observed with cobalt(II) systems, although homolytic reactions caused by oxygen on cobalt(II) compounds [21] are well known, but system III which has been shown to give way to homolytic processes of CH_3MgCl under inert atmosphere [22] yields extensive monoalkylation and dialkylation of PhC≡CPh under argon. There is, however, no oxygen effect. It was also shown elsewhere that irradiation of $(C_5H_5)_2Ti(CH_3)_2$ in the presence of PhC≡CPh led to formation of 1,2-diphenylpropene [23]. Thus there exists a possibility of homolytic alkylation of PhC≡CPh perhaps not by free radicals but by alkyl groups trapped with the alkyne in a metal complex.

Increased alkylation in the presence of oxygen was reported in the coupling of alkyl and aryl groups in copper-catalysed alkyllithium systems [10]. Oxygen also led to increased yields of $ArCH_3$ from mixtures of ArBr and $L_2Ni(CH_3)Ar$ + $LiCH_3$ [24]. The possibility of one-electron transfer process invoked by oxygen and assisted by the metal ion: $R{-}M + O_2 \rightarrow (R{-}M)^{+\cdot}O_2^{-\cdot}$ (R = alkyl, M = metal) and eventually forming reactive alkylating agents has been suggested [24]. It is therefore likely that the oxidation of cobalt(I) to cobalt(II) compounds by oxygen is a one-electron transfer process which involves oxygen and the methyl groups on the Grignard reagent or on cobalt(I) as well, causing a metal-assisted homolytic reaction. Such electron transfer processes could offer, with the necessary variation for each specific case, a rationalisation of the ability of oxygen to enhance organometallic alkylation reactions, indicating a phenomenon which is perhaps of a wider scope than hitherto recognised.

This would be expected less with rhodium(I) complexes which oxidize to rhodium(III). However, another significant difference between the cobalt(I) and rhodium(I) system is observed. Termination of reactions of PhC≡CPh and the organometallic reagent (under argon) with D_2O led to formation of deuterated stilbene and 1,2-diphenylpropenes (especially at the vinylic position) when rhodium reagents were used [11,12] but not with $(Ph_3P)_3CoCH_3$ or $(Ph_3P)_3CoCl$ + CH_3MgCl. Thus with cobalt, but not with rhodium compounds, the formation of stilbene, 1,2-diphenylpropene and 2,3-diphenylbutene is the result of competitive methyl and hydrogen transfer processes within the reaction system. These processes may differ, e.g., in rates, in the availability of the transferable groups and in the rate of reaction with oxygen. The experiments with $(Ph_3P)_3CoCl$ + $NaBH_4$ and $(Ph_3P)_3Co(N_2)H$ were aimed to comprise systems of hydrogen transfer to PhC≡CPh having either transient or stable [Co—H] species similar to species which are to be expected in systems I and IV. The results show that oxygen efficiently blocks hydrogen transfer in the hydridocobalt systems. In addition to the possible enhancement of alkylations by oxygen there seems to be some selective interference of oxygen in hydrogen transfer reactions, and this can lead to the observed 'oxygen effect'. The reasons for such a selective interference by oxygen or for the fact that formation of *cis* but not *trans* isomers of stilbene and 1,2-diphenylpropene is affected are not clear at present.

Experimental

Materials. $CoCl_2 \cdot 6H_2O$ (Riedel de Haen) was used as supplied. Triphenylphosphine was freshly recrystallised from ethanol. Where necessary, argon and nitrogen were passed through freshly-prepared pyrogallol traps. CH_3MgBr was prepared and kept under argon in dry THF; its concentration was determined both by acid—base titration and volumetrically after addition of CH_3MgBr to dilute aqueous HCl.

Solvents for reactions were dried over sodium, refluxed and kept under argon then freshly distilled before use. THF was treated with alumina and dried on $LiAlH_4$. Solvents for the preparation of $(Ph_3P)_3CoCl$ and $(Ph_3P)_2CoCl_2$ [20] were used without special treatment.

Instrumentation. Gas chromatography was carried out on 5% or 10% SE-30 columns as in [11]. In all cases described, products were analysed at column temperatures of 120—140°C. IR spectra were taken on a Perkin—Elmer 337 spectrophotometer, NMR were recorded on varian T60, varian EM360 and HR-100 spectrometers. Mass spectra were taken on Varian M.A.T. 111 G.C.M.S. and Varian M.A.T. 311 spectrometers.

Reaction of $(Ph_3P)_3CoCl$ with CH_3MgCl and PhC≡CPh under argon

$(Ph_3P)_3CoCl$ was prepared by reaction of $CoCl_2 \cdot 6H_2O$ with Zn and Ph_3P in ethanol [20] and dried under a stream of argon. The cobalt compound 0.88 g (10^{-3} mol) was suspended in 40 ml THF at —70°C. 10 ml of CH_3MgBr 1.84 *N* were added dropwise with stirring, followed by addition of 0.178 g (10^{-3} mol) of diphenylacetylene containing 0.0154 g (10^{-4} mol) biphenyl, as an internal standard, in THF.

The mixture was let to warm to room temperature turning from green to dark brown, stirred for 24 h, hydrolysed with dilute acetic or hydrochloric acid (pH 3) and extracted with hexane after an additional 24 h.

The hexane extract was analysed by gas chromatography. From this extract the products and triphenylphosphine can be isolated by chromatography on silica with hexane [11]. The residue which is insoluble in hexane can be extracted with acetone from which triphenylphosphine oxide when present separates in crystalline form.

Reaction of $(Ph_3P)_3CoCl$ with CH_3MgBr and $PhC{\equiv}CPh$ under oxygen

The procedure was repeated as above and all operations were carried out under argon up to the stage in which $PhC{\equiv}Ph$ + PhPh were added, whereupon argon was substituted by a stream of oxygen. (It made no difference whether oxygen was bubbled through the reaction mixture or just led over it.) Termination and work-up were as above. The sequence of colour change was different under oxygen. During the warm-up period a transient brown colour appeared turning finally to green — also turning immediately to blue-green upon exposure to open air!

In all runs under oxygen, triphenylphosphine oxide was identified as an additional product. The reaction of CH_3MgBr with $(Ph_3P)_3RhBr$ and with $(Ph_3P)_3$-$RhCH_3$ [11] were carried out in the same manner. Diphenylacetylene was fully recovered in these cases.

Reactions of other cobalt compounds

Reactions of other cobalt compounds with CH_3MgBr and $PhC{\equiv}CPh$ were carried out similarly. The cobalt compounds were prepared according to literature: $(Ph_3P)_2CoCl_2$ [20], $CH_3Co(PPh_3)_3$ [14] and anhydrous $CoCl_2$ [25].

Control reactions on Ph_3P

a. Bubbling oxygen for 5 h through a suspension of triphenylphosphine in ethanol at 20° C yielded only starting material.

b. Benzoyl peroxide and triphenylphosphine in petroleum ether yielded triphenylphosphine oxide, in accord with [26].

c. Methylmagnesium bromide and triphenylphosphine (freshly recrystallized from ethanol) were let to react in THF for 24 h. When hydrolysed with dilute acetic-acid (pH 3), a white crystalline precipitate formed and was identified as triphenylphosphine, m.p. 80° C (IR (cm^{-1}): 1950, 1410, 1090, 1025, 740, 680, 510, 500). Extraction of the filtrate with CCl_4 yielded a white solid identified as triphenylphosphine oxide, m.p. 155° C (IR (cm^{-1}): 1430, 1195, 1125, 255, 720, 695, 535), also confirmed by mass spectrography.

Oxidation of $(Ph_3P)_3CoCl$ with oxygen

The green cobalt compound either as solid or in ethanol solution was kept for 24 h under a stream of oxygen. The colour changed into light blue. The mass spectrum test of the blue product showed an increased signal at $m/e = 277$ and 278 ($Ph_3P = 0$). The starting material as well as $(Ph_3P)_2CoCl$ also gave signals at m/e 277 and 278, however with weaker intensity: There may be differences in breakdown patterns of the cobalt compounds but apparently only a small part of the phosphine is oxidized (see Table 3).

Reaction of $(Ph_3P)_3CoCH_3$ + $PhC{\equiv}CPh$ under argon and deuterium incorporation test

The reaction was carried out as described earlier. One run was hydrolysed by dilute acetic acid. Another run was hydrolysed by a D_2O/CH_3CO_2D mixture (prepared by hydrolysis of acetic acid anhydride with D_2O and tested for deuterium purity in NMR). Gas chromatography—mass spectra tests showed a molecular peak pattern at m/e 194: [m/e, (% parent peak): 179 (100), 193 (28), 194

(79), 195 (20)] identical to that of synthetic $PhCH{=}C(CH_3)Ph$ (mass spectra were tested at several points of the GC peak). A sample of authentic $Ph(CH_3)$-$C{=}CHPh$ injected together with the sample worked up with D_2O/CH_3CO_2D, gave quantitatively the same result excluding any counting error. Similarly co-injection of a sample of di-deuterated diphenylpropene (obtained from rhodium reagents [11,12] gave a pattern of deuterated material in addition to the non-deuterated molecules [193 (5.9), 194 (19.5), 195 (36.4), 196 (76.7), 197 (37.7)].

Reaction of $(Ph_3P)_3CoCl$ *with* $NaBH_4$ *and* $PhC{\equiv}CPh$

a. Under argon. Diphenylacetylene 0.178 g (10^{-3} mol) in THF was added into a mixture of $(Ph_3P)_3CoCl$ 0.88 g (10^{-3} mol) and $NaBH_4$ 0.038 g (10^{-3} mol) in THF at −50° C. The reaction mixture was brought to room temperature (turning black) and stirred for 24 h. Hydrolysis with dilute acetic acid for another 24 h followed by extraction with hexane and CCl_4, yielded *cis*- and *trans*-stilbene and bibenzyl (GC NMR and GCMS analysis). No diphenylacetylene was left. Black and green residues of cobalt compounds were left over.

b. Under oxygen. The same procedure was repeated under oxygen. Analysis indicated the presence of diphenylacetylene exclusively. Neither were there any residues from decomposition of cobalt complexes left after hydrolysis.

Control: Under the same conditions and with argon, no reaction took place between $PhC{\equiv}CPh$ and $NaBH_4$.

Reactions of $(Ph_3P)_3Co(N_2)H$

$(Ph_3P)_3Co(N_2)H$ was prepared according to a procedure by Yamamoto [14], using di(isobutyl)aluminum hydride, which was added to a mixture of cobalt trisacetylacetonate [27] and triphenylphosphine in THF at −50° C. The mixture was left for 2 h at room temperature and cooled again to −50° C overnight. Rewarming the mixture to room temperature and filtering, yielded the orange-yellow hydride.

a. Under argon. To 3×10^{-3} mol of $(Ph_3P)_3Co(N_2)H$ (2.7 g), 0.53 g diphenylacetylene (3×10^{-3} mol) was added at −50° C, the mixture allowed to warm up (turning black) and worked up as in preceding procedures. The products were *cis*- and *trans*-stilbene in about equal quantities with a small amount of bibenzyl. Some diphenylacetylene (not more than 20%) was recovered.

b. Under oxygen. Reactions were run under oxygen as above and also with a two-fold excess of cobalt hydride over acetylene. No stilbene was formed and diphenylacetylene was fully recovered.

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