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A SIMPLE SYNTHESIS OF TRANS, TRANS-1,3-DIENES FROM TERMINAL ALKYNES USING $CoCl_2/Ph_3P/NaBH_4$

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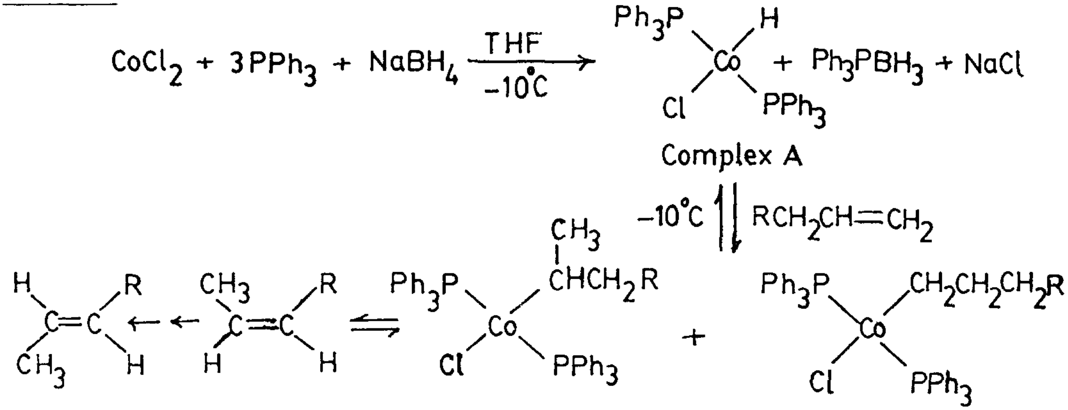
Abstract: The cobalt hydride reagent prepared in situ in THF at -20°C using $CoCl_2/NaBH_4$ Ph_3P in the 1:1:4 ratio hydrodimerizes terminal alkynes into the corresponding trans, trans-1,3-dienes in good yields (65 to 86%).

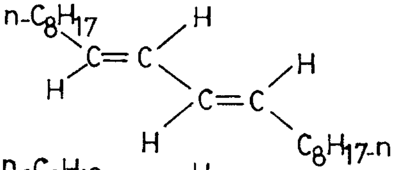
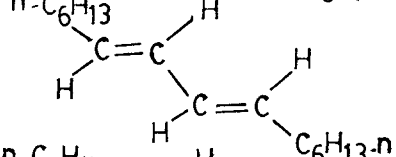
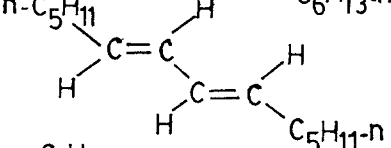
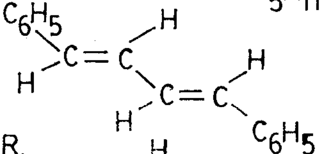
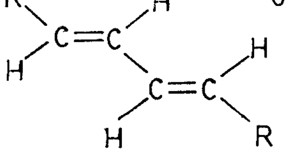
In the course of our studies[1,2,3] on the synthesis of transition metal organometallics via non-carbanionic routes, we have observed[2] that a 1:1:3 mixture of $CoCl_2/NaBH_4/Ph_3P$ in THF at -10°C isomerizes some olefins. The transformation can be visualized by the hydrometalation-dehydrometalation sequence (i.e. addition-β-elimination of Co-H moiety) via alkylcobalt intermediates as shown in Scheme 1. The β-elimination is a well known process in alkyl organometallics[4] and often a problem in the application of organometallics for organic synthesis.

Scheme 1



The complex A would most probably give vinylcobalt species with alkynes which would be more stable compared to the alkylcobalt species and hence would be suitable for investigating the reactions of such organocobalt species. The synthesis of such stable vinylcobalt species is yet to be realized. In the course of our efforts in this direction, we have observed that the reaction of the $CoCl_2/NaBH_4/Ph_3P$ system with terminal alkynes at -20°C in THF gives trans, trans-1,3-dienes in good yields (Table 1). The following is the general procedure.

Table 1. Conversion of terminal alkynes into trans, trans-1,3-dienes using $CoCl_2/Ph_3P/NaBH_4$.

Substrate[a]	Product[b]	Yield [%]
n-$C_8H_{17}C\equiv CH$		$86^{c,d}$
n-$C_6H_{13}C\equiv CH$		$82^{c,e}$
n-$C_5H_{11}C\equiv CH$		$78^{c,f}$
$C_6H_5C\equiv CH$		65^{g}
$RC\equiv CH$ ($R = CH_2(CH_2)_7COOCH_3$)		69^{h}

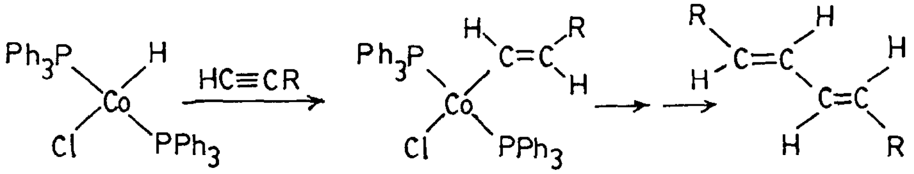
(a) The reactions were carried out using 10 mmol of alkyne, 10 mmol of anhydrous cobalt(II) chloride, 10 mmol of $NaBH_4$ and 40 mmol of Ph_3P in THF (80 ml). The reaction time and temperature were the same as those given in the text for all the substrates except phenylacetylene. In this case, the cobalt hydride reagent was prepared at -20°C as given in the text and the phenylacetylene was added after cooling the contents to -65°C and the mixture was further stirred for 3h at this temperature before workup. In this case, polymeric products were also formed at -20°C resulting in lesser yields of the trans, trans-1,4-diphenyl-1,3-butadiene. (b) The products were isolated by chromatography on a silica gel column using hexane or hexane/$CHCl_3$ as eluent. (c) Products are liquids at room temperature. (d) ^{13}C-NMR data (δ in ppm, $CDCl_3$): 132.3, 130.5, 32.7, 32.0, 29.8, 29.6, 29.5, 22.8, 14.2. (e) ^{13}C-NMR data: 132.4, 130.7, 33.0, 32.7, 29.5, 29.0, 22.7, 14.1. (f) ^{13}C-NMR data: 132.4, 130.5, 32.8, 32.6, 32.1, 29.4, 22.8, 14.3. (g) Mp. 150°C, Lit.[5] mp. 152.5°C, ^{13}C-NMR data: 137.3, 132.9, 129.4, 128.8, 127.7, 126.5. (h) Mp. 54°C, Lit.[6] mp. 54.5-55°C (Lit.[5] mp. ~40°C for cis, trans and trans, trans mixture); ^{13}C-NMR data: 174.0, 132.0, 130.6, 51.0, 33.7, 32.0, 28.9, 24.7.

Sodium borohydride (10 mmol) was added during 15 minutes into a magnetically stirred suspension of anhydrous $CoCl_2$ (10 mmol) and Ph_3P (40 mmol) in THF (80 ml) at -20°C (bath temperature) under nitrogen atmosphere and the mixture was further stirred for 45 minutes. The alkyne (10 mmol) was injected and the contents were further stirred for 3h at -20°C. Petroleum ether (200 ml) was added at -20°C followed by addition of 2N HCl (30 ml). The layers were separated and the aqueous layer was extracted with petroleum ether (2x25 ml). The combined organic extract was washed once with saturated sodium chloride solution (30 ml) and dried over anhydrous magnesium sulphate. The solvent was evaporated and pentane (10 ml) was added to the residue to precipitate the Ph_3PBH_3 complex and most of the Ph_3P. The solvent was evaporated from the filtrate and the residue was chromatographed on a silicagel column (hexane or hexane/chloroform as eluent) to isolate the trans, trans-1,3-diene.

We have utilized 40 mmol of Ph_3P here compared to the 30 mmol utilized for the isomerization of alkenes (Scheme 1) with this reagent system because when only 30 mmol of Ph_3P was utilized in the reaction with 1-decyne, some unidentified polymeric product (broad humps in the olefinic region in the ^{13}C-NMR spectra) was also formed besides 1,3-dienes. Presumably, the vinylcobalt species undergoes oligomerization via carbometalation of the alkyne substrate in the absence of excess Ph_3P. Such oligomerizations of alkynes are well-known with many transition metal complexes.[7]

The ^{13}C-NMR spectra of the products are free from signals corresponding to cis, cis or cis, trans dienes. Accordingly, these isomers (if any) cannot be present in significant amounts in the trans, trans-1,3-dienes obtained following the present procedure. Also, the formation of trans, trans-1,3-dienes indicates that the hydrocobaltation of 1-alkynes using the present reagent system takes place by the syn addition of the Co-H bond placing the cobalt at the terminal carbon atom (Scheme 2).

Scheme 2.



The internal alkynes, diphenylacetylene(tolan),1-phenylpropyne and 5-decyne remained unreacted even after 12h under the present reaction conditons. In addition to the carboxylic ester group (Table 1), n-octyl cyanide, n-octyl bromide and cyclohexanone were also not affected by the present reagent system. These observations may throw some light on the scope and limitations of the present method. Also, it should be pointed out that the Ph_3 PBH_3

and Ph_3P mixture obtained after workup can be converted entirely into Ph_3P for further utilization by treatment with $(C_2H_5)_2NH$ in methanol following a simple literature procedure.[8]

In conclusion, we would like to point out that the present method of the synthesis of trans, trans-1,3-dienes is a simple alternative method to the procedures available in the literature[5,6,9] for the conversion of terminal alkynes into trans, trans-1,3-dienes which are an important class of organic compounds with very rich chemistry.

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