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ISOMERIZATION OF OLEFINS CATALYSED BY A $CoCl_2/Ph_3P/NaBH_4$ SYSTEM

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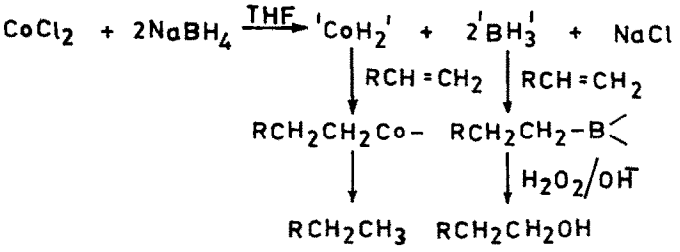
Summary

The catalyst generated in situ using $CoCl_2/Ph_3P/NaBH_4$ in 1/3/1 ratio in THF at −10°C isomerizes 1-decene into predominantly *cis*-2-decene or *trans*-2-decene. Allyl benzene and safrole have been converted into the corresponding β-methylstyrenes. The catalyst also isomerizes *cis,cis*-1,5-cyclooctadiene to *cis,cis*-1,3-cyclooctadiene.

Many transition metal complexes isomerize olefins [1,2]. However, in many cases the process is not a useful one since mixtures of products are formed and severe conditions may be necessary. Further, many isomerization procedures utilize the relatively expensive second row transition metal complexes or the toxic metal carbonyl derivatives [1,2]. We have found that the reagent prepared in situ simply by the addition of $NaBH_4$ to a mixture of anhydrous $CoCl_2$ and Ph_3P in THF catalyses isomerization of some olefinic subtrates.

We recently reported that a mixture of anhydrous $CoCl_2$ and $NaBH_4$ in THF undergoes reactions characteristic of 'CoH_2' and 'BH_3' species [3].

We attempted the in situ carbonylation of the organocobalt species generated via hydrocobaltation in this way by passing carbon monoxide for 3 h at 0°C into a mixture of $CoCl_2$ (10 mmol), CH_3OH (60 mmol) and 1-decene (10 mmol) while



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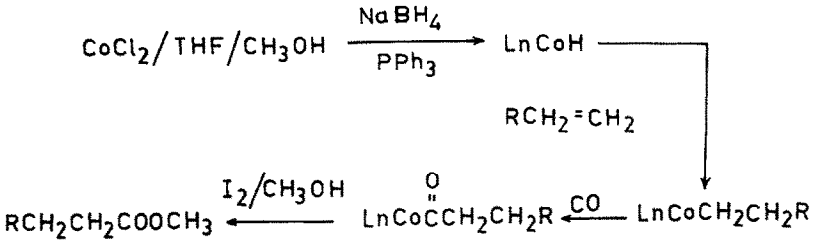


adding a mixture of $NaBH_4$ (20 mmol) and Ph_3P (30 mmol) in portions by use of a solid addition flask. After I_2/CH_3OH treatment, methyl undecanoate was isolated in 20% yield [4].

In the course of the efforts to optimize the conditions for the above transformation, we have observed that the complex prepared in situ under nitrogen by the addition of $NaBH_4$ (10 mmol) to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and Ph_3P (30 mmol) in THF (80 ml) at $-10°C$ during 15 min followed by further stirring for 30 min at $-10°C$ isomerizes alkenes (Table 1).

Whether the reaction of 1-decene will give predominantly *cis*-2-decene or *trans*-2-decene can be determined by simple control of the experimental conditions. The results indicate that the *cis*-2-decene is initially formed and then undergoes conversion into *trans*-2-decene. The ease of the isomerization falls in the sequence: 1-decene > *cis*-2-decene > *trans*-2-decene. Allylbenzene and safrole gave only the corresponding *trans*-β-methyl styrenes, and efforts to stop the reaction at the *cis*-alkene stages were unsuccessful.

cis,cis-1,5-Cyclooctadiene gave small amount (~ 10%) of cyclooctene when the reaction temperature was raised to room temperature during 2 h following reaction for the time indicated in Table 1. Similarly when 5 mmol of *cis,-cis*-1,3-cyclooctadiene was used as the substrate and reaction carried out under the conditions indicated in Table 1 (8 h, $-10°C$) was followed by raising the temperature to 25°C during 2 h, the product isolated contained 30% of cyclooctene and 70% of *cis,cis*-1,3-cyclooctadiene. Similar reduction of 1,3-butadiene to butenes was previously observed with the $(Ph_3P)_2NiHCl$ system [5,6].

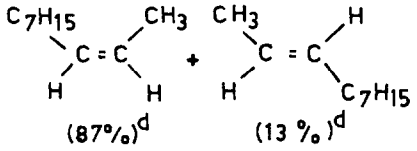
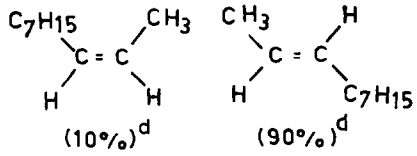
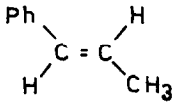
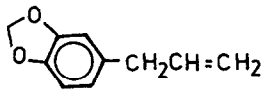
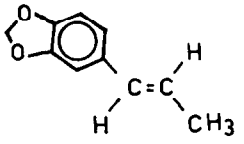
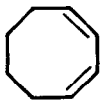
4-Vinylcyclohexene gave high boiling polymeric products under our conditions, while limonene and 1-methylcyclohexene did not react at all. Furthermore, no isomerization of 1-decene occurs at $-40°C$, and above 0°C the catalyst decomposes. When more than 20 mmol of an olefinic substrate was used a considerable amount of starting material remained unreacted under the usual conditions. These results serve to indicate the scope and limitations of the method.

The precise structure and composition of the active species in the present case are not clearly understood since it has been reported that the $CoCl_2/Ph_3P/NaBH_4$ system gives cobalt complexes of various compositions in alcoholic media [7]. Under our reaction conditions, the Ph_3PBH_3 complex was isolated in 70–80% yield. In view of this, the composition of the present catalytic species is tentatively suggested to be $(Ph_3P)_2CoHCl$ (**A**), and the isomerization of alkenes can be rationalized in terms of the hydrocobaltation-dehydrocobaltation sequence.

To our knowledge, the hydridocobalt(II) (**A**) has not been reported. The corresponding nickel(II) species has been shown to isomerize alkenes [5]. We should

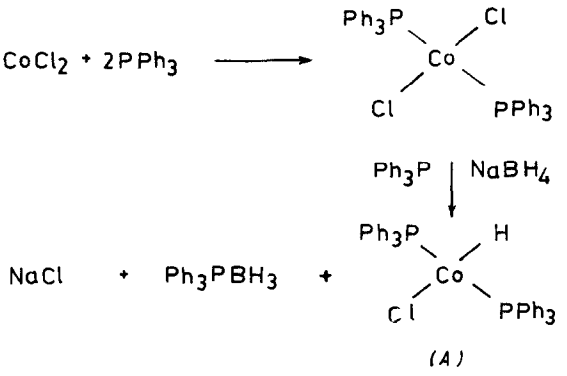
TABLE 1

ISOMERIZATION OF ALKENES [a]

Substrate	Reaction time [b]	Product	Yield [c] (%)
$C_7H_{15}CH_2CH=CH_2$	2h	 (87%)[d] + (13%)[d]	81
$C_7H_{15}CH_2CH=CH_2$	8h	 (10%)[d] (90%)[d]	78[e]
$PhCH_2CH=CH_2$	2h		81
	2h		80
	8h		78

[a] The reactions were carried out using anhydrous cobalt chloride (10 mmol), triphenylphosphine (30 mmol), sodium borohydride (10 mmol) and the olefinic substrate (20 mmol) in THF (80 ml) at $-10°C$ (bath temperature) under nitrogen. [b] Reaction time after the addition of the alkene following preparation of the catalyst as described in the text. [c] Yields are of the isolated and distilled products. The yields are based on the olefinic substrate (20 mmol). When more than 20 mmol of the olefinic substrates were utilized a considerable amount of starting material remained in many cases. The products were identified from their spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with literature data. [d] Percentage compositions were calculated from the intensities of the olefinic methyl group in the 270 MHz ^1H NMR spectra. [e] A new ^{13}C NMR signal begins to appear in the olefinic region at 129.5 ppm if the reaction mixture is stirred for a further 4 h at $-10°C$; presumably as the double bond migrates along the carbon chain.

emphasize, however that the hydridocobalt(II) (A) cannot be definitely regarded as the active spcies in our system. It may be relevant to note that the cobalt(II) complex, $CoH(N_2)(Ph_3P)_3$, isomerizes 1-butene into 2-butenes [8] and the cobalt(0) complex, $Co(N_2)(Ph_3P)_3$, isomerizes 1-hexene into 2-hexenes [9]. Formation of such cobalt(I) and cobalt(0) species from cobalt(II) species using $NaBH_4$ must involve hydrogen evolution, but we have not observed any gas evolution under our conditions and so cobalt(I) or cobalt(0) species cannot be the active species in our catalyst system [10].



Although the precise structure and concentration of the active species are still to be defined our procedure for isomerization of alkenes has good synthetic potential since it utilizes simple reagents under mild conditions.

Experimental

The THF was distilled over benzophenone-sodium immediately before use. Anhydrous cobalt(II) chloride was prepared by heating $CoCl_2 \cdot 6H_2O$ at 110°C for 24 h and further dried under vacuum for 1 h at 100°C. Triphenyl phosphine, sodium borohydride, and the olefins were commercial samples.

General procedure for isomerization

$NaBH_4$ (10 mmol) was added under nitrogen during 15 min to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and Ph_3P (30 mmol) in THF (80 ml) at −10°C and the mixture was stirred for a further 30 min. The alkene (20 mmol) was injected and the mixture stirred at −10°C for the time indicated in Table 1. Petroleum ether (200 ml) was added at −10°C folllowed by 2 *N* HCl (30 ml). The layers were separated and the aqueous layer was extracted with petroleum ether (2 × 25 ml). The combined organic extracts were 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 distilled to give the isomerized alkene (Table 1). ^{13}C NMR data (in ppm, $\delta = 0$ for TMS) for isomerized alkenes (in $CDCl_3$): *cis*-2-decene: 130.9, 123.5, 32.9, 32.2, 29.8, 29.6, 27.1, 23.0, 14.2, 12.7, *trans*-2-decene: 131.8, 124.5, 32.9, 32.2, 30.0, 29.5, 23.0, 17.96, 14.2; β-methyl styrene: 139.8, 133.2, 130.1, 128.4, 127.7, 126.8, 30.1, 20.0; 3,4-methylenedioxy-β-methylstyrene: 146.4, 145.0, 131.9, 129.1, 121.9, 118.5, 106.5, 103.7, 99.2, 16.6; *cis,cis*-1,3-cyclooctadiene: 131.0, 126.0, 28.3, 23.34.

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10 Dr. H. Kanai of Kyoto University, Japan, recently informed us of his kinetic study of the isomerization 1-butene with $(Ph_3P)_2MX_2/NaBH_4$(M = Ni, Co). Dr. Kanai and his coworkers found that the catalyst system was very efficient when $(Ph_3P)_2CoCl_2$ and $NaBH_4$ were present in a 1:1 ratio. They also invoked the possibility that complex **A** was the active species in the reaction. We thank Dr. Kanai for sending the preprint of his paper which is to be published elsewhere.