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SKELETAL ISOMERIZATION OF DIENES BY NICKEL HYDRIDE COMPLEXES*

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Although positional isomerization of olefins is well studied[1] and skeletal isomerization of strained hydrocarbons is receiving much current attention,[2] there have been few reports of skeletal isomerization of unstrained olefins by homogeneous catalysts. One of the most interesting examples is the isomerization of cis-1,4-hexadiene (1) to trans-2-methyl-1,3-pentadiene (2) catalyzed by a mixture of $(n\text{-}Bu_3P)_2NiCl_2$ and $(i\text{-}Bu)_2AlCl$.[3-5] The reports of this reaction contain a strong presumption that it is catalyzed by a nickel hydride but the possibility remains that this reaction, like a number of other olefin isomerizations,[6] is catalyzed by an alkylaluminum compound.

1 → 2

We have now observed that the skeletal isomerization of 1 to 2 is catalyzed by nickel hydrides[7] generated by addition of protonic acids to zero-valent nickel complexes. The best catalyst of this type, a combination of $[(o\text{-}Tol\text{-}O)_3P]_3Ni$[8] (o-Tol = ortho-tolyl) and HCl in tetrahydrofuran, gave a 60-65% yield of 2 in 1 hr. at 25°. Other hydride-generating systems, including the $(R_3P)_2NiCl_2\text{-}NaBH_4$ combination,[9] are less effective (Table 1). The nickel and palladium complexes were ineffective in the absence of cocatalyst (HCl, $NaBH_4$ or H_2).

The presence of a metal hydride seems to be a necessary but not sufficient qualification for catalysis of carbon skeletal isomerization. All the systems shown in Table 1 are believed to contain or generate M-H bonds, but

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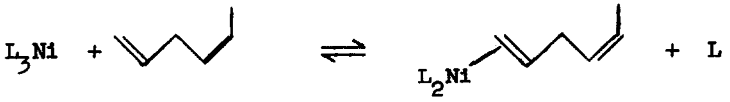
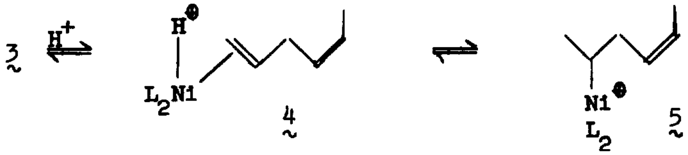
three of the better characterized hydride-forming systems yield no branched chain products. The combination of $[(EtO)_3P]_4Ni$ and HCl[7] isomerized cis-1,4-hexadiene to a mixture of 2,4-hexadienes. The combinations, $[(C_6H_{11})_3P]_2$-$NiCl_2/NaBH_4$ and $[(C_6H_5)_3P]_4Pt/HCl$, which give the isolable hydrides $[(C_6H_{11})_3P]_2NiHCl$[10] and $[(C_6H_5)_3P]_2PtHCl$,[11] were largely inert to cis-1,4-hexadiene at 100°.

The $[(o\text{-}Tol\text{-}O)_3P]_3Ni$ - HCl catalyst also isomerized 1,4-pentadiene to 2-methyl-1,3-butadiene in 70% yield at 32% conversion. Under identical conditions trans-1,4-hexadiene was isomerized to 2,4-hexadienes in 98% yield at 50% conversion with no detectable formation of 2-methyl-1,3-pentadiene. The $(n\text{-}Bu_3P)_2NiCl_2$ - $Al(i\text{-}Bu)_2Cl$ catalyst system is reported to behave similarly.[3,4]

The particular merit of the $[(o\text{-}Tol\text{-}O)_3P]_3Ni$ catalyst system is probably due to the exceptional ease with which this complex coordinates olefins and dienes. The equilibrium constant for reaction (1) is probably several orders of magnitude greater than that for reaction with $[(p\text{-}Tol\text{-}O)_3P]_4Ni$.[12] The olefin complex 3 may be expected to protonate readily to form a hydride species (4) which can rearrange to give the alkyl compound (5). (The same compound would result if protonation preceded olefin coordination in the reaction sequence.) Compound 6 is the key intermediate for carbon skeletal rearrangement via cyclopropylcarbinyl species such as 7 as proposed by Miller et al.[2,3] The present findings are fully consistent with Miller's proposal. The behavior of trans-1,4-hexadiene with these catalysts is strikingly different from that of the other 1,4-dienes examined. This difference may be due to the diminished tendency of trans olefins to form metal complexes. This could allow nickel hydride elimination to predominate in the two choices available to the trans analog of 5 in equation (3).

(1) 

L = $(o\text{-}Tol\text{-}O)_3P$ 3

(2) 

4 5

(3)

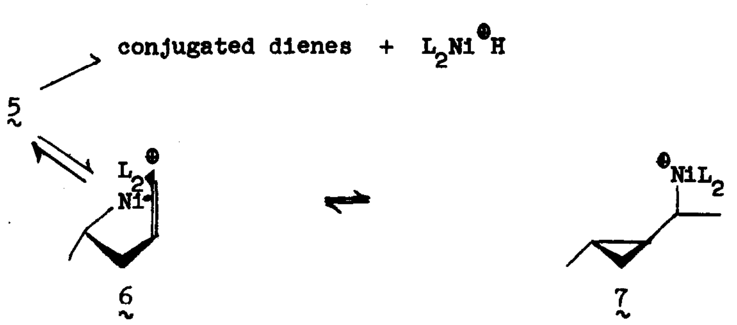


Table 1

Skeletal Isomerization of Cis-1,4-Hexadiene (1)

Catalyst Combination	Temp.	Yield of 2 (%)	Conversion of 1 (%)
$[(o\text{-Tol-O})_3P]_3Ni$ - HCl	25°	62	100
$[(PhO)_3P]_4Ni$ - HCl	25°	20	45
$[(p\text{-}CH_3OC_6H_4O)_3P]_4Ni$ - HCl	27°	14	43
$[(EtO)_3P]_4Ni$ - HCl	25°	0	83
$(Ph_3P)_4Ni$ - HCl	25°	19	29
$(Ph_3P)_4Pd$ - HCl	100°	24	20
$(Ph_3P)_4Pt$ - HCl	100°	0	1
$(Bu_3P)_2NiBr_2$ - $NaBH_4$	100°	61	18
$(Ph_3P)_2NiBr_2$ - $NaBH_4$	100°	49	35
$[(C_6H_{11})_3P]_2NiBr_2$ - $NaBH_4$	100°	0	47
$(Ph_3P)_2PdClC_6H_5$ - H_2	100°	8	13
$(Ph_3P)_3(CO)OsHCl$	70°	3	33

Experimental

L_3Ni-HCl Catalyst - In a typical experiment, a 22 ml glass pressure bottle sealed with an O-ring to a cap containing a valve and a rubber septum was charged (under N_2) with 0.15 g tris(tri-o-tolyl phosphite)nickel, 0.25 ml cis-1,4-hexadiene, and 2.5 ml 0.14M-HCl solution in THF (anhydrous). The mixture was stirred magnetically at room temperature for 1 hr. Gas chromatographic analysis was performed on a liquid sample which was separated from the catalyst by vacuum transfer. In this instance the chromatogram showed the presence of 27% cis-1,4-hexadiene, 44% trans-2-methyl-1,3-pentadiene, and 37% 2,4-

hexadienes in the hydrocarbon fraction. The 2-methyl-1,3-pentadiene was isolated by preparative gas chromatography and its ir and nmr spectra were compared with those of authentic material.

$(R_3P)_2NiCl_2$-$NaBH_4$ Catalyst - In a typical experiment a glass pressure bottle as above was charged (under N_2) with 0.10 g $(n\text{-}Bu_3P)_2NiBr_2$, 0.05 g $NaBH_4$, 0.25 ml cis-1,4-hexadiene, and 2.5 ml THF. The mixture was stirred magnetically at 100°C for 3 hr. Sample treatment and analysis as above showed the presence of 82% cis-1,4-hexadiene, 11% trans-2-methyl-1,3-pentadiene and 6% 2,4-hexadienes.

Control experiments showed that the isomerization of cis-1,4-hexadiene to 2-methyl-1,3-pentadiene was not produced by HCl, $NaBH_4$, nickel or palladium halide, nickel or palladium metal, the organometallic complexes without cocatalysts, or by combinations of $[(ArO)_3P]_4Ni$ or $[(ArO)_3P]_3Ni$ and nickel halide.

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