

Preliminary communication

Importance of the transition metal in the catalysis of a diene rearrangement

ROY G. MILLER, PAUL A. PINKE, RICHARD D. STAUFFER and HARRY J. GOLDEN
Chemistry Department, University of North Dakota, Grand Forks, North Dakota 58201 (U.S.A.)
(Received March 2nd, 1971)

We have observed that catalysts derived from the reaction of diisobutylaluminum chloride with *trans*-dichlorobis(trialkylphosphine)nickel(II) complexes skeletally rearrange 1,4-dienes¹⁻³. A crucial factor in mechanistic studies of these transformations is the determination of the importance of the role of the transition metal component. We wish to report that some compounds of the general formula $C_2H_4Ni(PR_3)_2$, on combination with hydrogen chloride, afford extremely active catalysts for some of the same skeletal transformations as are provided by the catalyst prepared *in situ* from nickel and aluminum precursors.

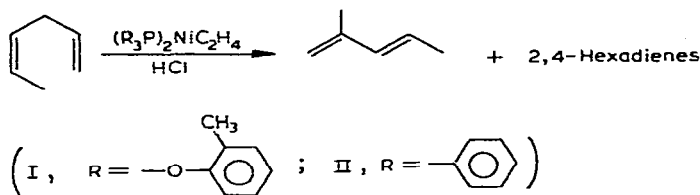
Ethylenebis(tri-*o*-tolylphosphite)nickel(0) (I) was prepared by treatment of tris(tri-*o*-tolylphosphite)nickel(0)⁴ with ethylene⁵. The product could be crystallized from benzene-methanol at 0° to afford yellow crystals which exhibited a PMR spectrum (C_6D_6) in agreement with that of I⁵. Treatment of a toluene solution of *cis*-1,4-hexadiene and I with hydrogen chloride at 25° (1,4-diene/I/HCl mole ratio 12/1/0.65) resulted in a 37% conversion of the 1,4-diene to isomeric products during a 30 sec period. The isomeric product mixture consisted of *trans*-2-methyl-1,3-pentadiene, 70%, *trans,cis*-2,4-hexadiene, 10%, *cis,cis*-2,4-hexadiene, 20%. Essentially 74% of the starting material had been converted to isomeric products within 2.5 minutes.

Utilization of ethylenebis(triphenylphosphine)nickel(0)^{6a} as the transition metal component led to the generation of a somewhat less active catalyst after its treatment with HCl in the presence of *cis*-1,4-hexadiene (1,4-diene/II/HCl 12/1.3/1.0). During 30 sec, 19% of the 1,4-diene was converted to products. Of the material reacted, 80% was converted to an isomeric product mixture consisting of *trans*-2-methyl-1,3-pentadiene, 73%, *trans,cis*-2,4-hexadiene, 14%, and *cis,cis*-2,4-hexadiene, 13%. The catalyst activity decreased rapidly with time, 31% of the *cis*-1,4-hexadiene being converted to products during 10 min and only a 49% conversion being realized during 4 hours.

In similar experiments, both *trans*- and *cis*-2-methylvinylcyclopropane² were rearranged by a combination of I and HCl to isomeric product mixtures which consisted of *trans*-2-methyl-1,3-pentadiene and the geometric isomers of 2,4-hexadiene. In each case,

*The compound was first prepared by G. Wilke^{5b}.

**Prepared by the procedure of Greaves *et al.*^{6a}; the compound was first described by Wilke and Herrmann^{6b}.



more than 60% of the starting material had been converted to isomeric products within 6 minutes, *trans*-2-methyl-1,3-pentadiene being the major product. The diene products in all of these reactions were isolated via preparative GLC and were identified by their PMR spectra.

Control experiments demonstrated that neither HCl nor the nickel(0) complexes, alone, catalyzed the rearrangements at 25° when the same reactant concentrations were employed. The three 2,4-hexadiene geometric isomers were not isomerized by HCl, by II or by a 1/1 combination of HCl and II under the conditions described above. Treatment of each of the 2,4-hexadiene isomers with the catalyst derived from nickel and aluminum precursors¹ has also afforded no isomerization. As was the case when *trans*-1,4-hexadiene was treated with the catalyst derived from nickel and aluminum precursors¹, a 1/1 mixture of II and HCl failed to cause its skeletal rearrangement, but afforded *trans,trans*- and *trans,cis*-2,4-hexadienes as products.

Treatment of II with an excess of HCl in the presence of *cis*-1,4-hexadiene provided an initial formation (during a few seconds) of small amounts of the isomerization products, followed by the rapid decomposition of the catalyst as evidenced by decolorization of the reaction mixture, deposition of solid material, and associated termination of diene isomerization.

Precedent exists for the formation of hydridonickel compounds via the reaction of hydrogen acids with trialkylphosphine and trialkylphosphite complexes of nickel(0). The relatively stable chloro(hydrido)bis(tricyclohexylphosphine)nickel(II) (III) has recently been synthesized and characterized^{7,8}. One of the routes for its preparation involved the addition of HCl to bis(tricyclohexylphosphine)nickel(0)⁷. The addition of hydrogen acids to tetrakis(triethylphosphite)nickel(0) has been shown to generate hydride complexes⁹ which catalyze double bond migration in alkenes¹⁰ and the addition of alkenes to 1,3-dienes¹¹. Compound III did not, however, catalyze the isomerization of *cis*-1,4-hexadiene in toluene solution at 25°. Also, the dichlorobis(tricyclohexylphosphine)-nickel(II)-diisobutylaluminum chloride system exhibited a very low activity for the isomerization of *cis*-1,4-hexadiene. Dichlorobis(triphenylphosphine)nickel(II) and diisobutylaluminum chloride afforded an active catalyst for the skeletal rearrangement only after ethylene was introduced to the reaction mixture. This "ethylene effect" on catalyst activity has been observed in other transformations².

The results demonstrate that the transition metal species plays a very significant role in the *cis*-1,4-hexadiene rearrangement and that an aluminum component is not required. They support the view that the catalyst is a nickel hydride or its chemical equivalent^{12,13}.

ACKNOWLEDGEMENT

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

- 1 R.G. Miller, *J. Amer. Chem. Soc.*, 89 (1967) 2785.
 - 2 R.G. Miller and P.A. Pinke, *J. Amer. Chem. Soc.*, 90 (1968) 4500.
 - 3 R.G. Miller, P.A. Pinke and D.J. Baker, *J. Amer. Chem. Soc.*, 92 (1970) 4490.
 - 4 L.W. Gosser and C.A. Tolman, *Inorg. Chem.*, 9 (1970) 2350.
 - 5 (a) W.C. Seidel and C.A. Tolman, *Inorg. Chem.*, 9 (1970) 2354; (b) G. Wilke, *Angew. Chem. Intern. Ed.*, 3 (1963) 105.
 - 6 (a) E.O. Greaves, C.J.L. Lock and P.M. Maitlis, *Can. J. Chem.*, 46 (1968) 3879; (b) G. Wilke and G. Herrmann, *Angew. Chem.*, 74 (1962) 693.
 - 7 K. Jonas and G. Wilke, *Angew. Chem. Intern. Ed.*, 8 (1969) 519.
 - 8 M.L.H. Green and T. Saito, *Chem. Commun.*, (1969) 208.
 - 9 C.A. Tolman, *J. Amer. Chem. Soc.*, 92 (1970) 4217.
 - 10 R. Cramer and R.V. Lindsey, Jr., *J. Amer. Chem. Soc.*, 88 (1966) 5534.
 - 11 C.A. Tolman, *J. Amer. Chem. Soc.*, 92 (1970) 6777. See also, R.G. Miller, T.J. Kealy and A.L. Barney, *ibid.*, 89 (1967) 3756.
 - 12 R. Cramer, *J. Amer. Chem. Soc.*, 87 (1965) 4717.
 - 13 F. Faraday, L. Bencze and L. Marko, *J. Organometal. Chem.*, 17 (1969) 107.
- J. Organometal. Chem.*, 29 (1971) C42-C44