CHEMISTRY LETTERS, pp. 813-816, 1973. Published by the Chemical Society of Japan

THE NICKEL-CATALYZED ISOMERIZATION OF METHYLENECYCLOPROPANE TO BUTADIENE[1]

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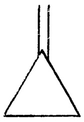
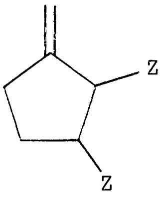
Methylenecyclopropane under the influence of nickel catalysts dimerizes to give 2-vinylmethylenecyclopentane. The intervention of butadiene intermediate has been determined on the basis of the isotope incorporation into the product and the asymmetric transformation.

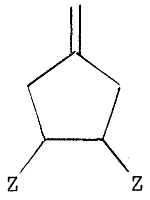
The course of the transition metal catalyzed reaction of strained molecules profoundly depends not only on the type of metal, but also the coordinated ligands and the oxidation state.[2] Methylenecyclopropane (I) is known to cycloadd to electron-deficient olefins in the presence of bis(acrylonitrile)nickel(0) leading to the $[_{\sigma}2 + _{\pi}2]$-type adducts II and III (Z = electron-withdrawing group).[3] Upon treatment with bis(1,5-cyclooctadiene)nickel(0) I undergoes dimerization to afford the spiro-fused hydrocarbons IV and V.[4] With the aid of triphenylphosphine (1.1 equiv to the nickel complex), I cycloadds to norbornadiene to produce selectively the $[_{\pi}2 + _{\pi}2]$-type adduct VI.[5] This paper describes a new, clean skeletal change of I in the presence of nickel catalysts.



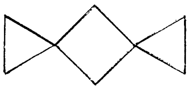
I



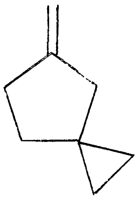
II



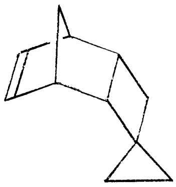
III



IV

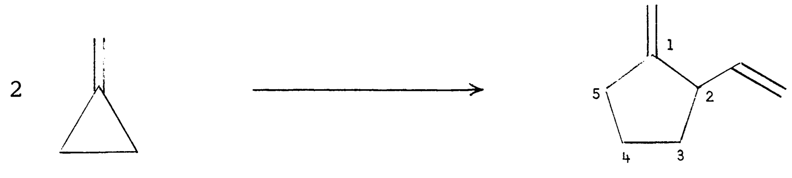


V



VI

Utilization of the catalyst system developed by Furukawa and his coworkers[6] led to the selective conversion of I to 2-vinylmethylenecyclopentane (VII). When I (4.0 mmol) was mixed in a sealed tube with the nickel catalyst prepared from bis(tri-n-butylphosphine)nickel(II) dibromide (0.2 mmol), n-butyllithium in n-hexane[7] (0.2 mmol), and methanol (5 mmol) in benzene (3 ml), and heated at 60°C for 48 hr under nitrogen atmosphere, a single dimer VII was obtained in 91% yield. No other dimers were detected.



I VII

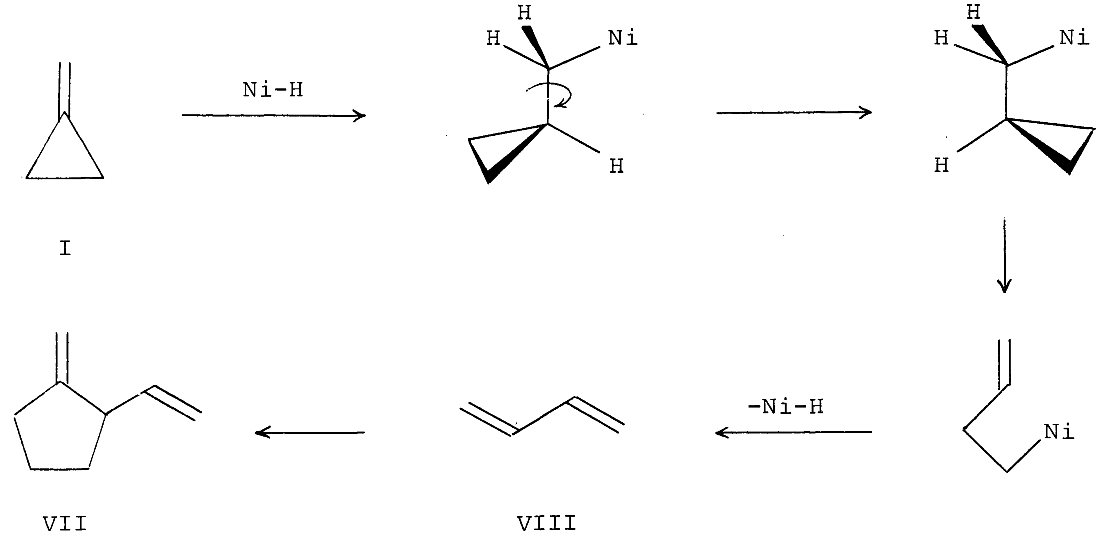
Because the present catalytic conditions are those adopted for the facile dimerization of butadiene (VIII) to VII,[6] a reasonable reaction path for such a conversion was considered to involve the intervention of VIII as intermediate. Monitoring the reaction by glpc analysis could in fact detect VIII in the mixture, but only in varying amounts, since its dimerization to VII competed considerably with the isomerization I → VIII. The following experiments, however, revealed the operation of a single mechanism, that is, the dimerization of I occurs only by way of butadiene intermediate.

Firstly, when methanol-O-d was used in place of methanol, deuterated VII (5% $\underline{d}_3$, 12% $\underline{d}_2$, 45% $\underline{d}_1$, and 38% $\underline{d}_0$ by mass spectral analysis) was obtained. Nmr analysis indicated that the deuterium was located mainly in the allylic C-5 position. Dimerization of VIII under similar isotopic conditions has been reported to induce deuterium incorporation at the same position.[6]

The second evidence rests on the observation of a novel type of asymmetric reaction caused by a nickel catalyst containing chiral tertiary phosphine ligands. Treatment of I with the catalyst derived from bis[(-)-methylphenyl-n-propylphosphine]nickel(II) dibromide[8] at 60°C for 72 hr afforded the dimer VII (30% yield) in an optically active form, $[\alpha]_D^{25}$ +0.51° (c 2.8, ethanol). At this point the absolute configuration and the optical purity of the product remain unknown, because the authentic, optically pure substance is not readily available. By comparison, under the same chiral conditions, VIII gave VII (35% yield) with optical rotation $[\alpha]_D^{25}$ +0.50° (*c* 2.4, ethanol).[9]

Thus the intermediacy of VIII in the conversion of I to the dimer VII was definitely confirmed by the similarities in the reactions of both C_4 hydrocarbons I and VIII, *i.e.*, the product, the position of deuterium incorporation, and the extent of asymmetric induction. The most reasonable pathway of producing VIII from I would consist of (1) addition of nickel hydride species to double bond of I,[10] (2) conformational change, (3) cyclopropylcarbinyl—allylcarbinyl rearrangement, and (4) elimination of the nickel hydride catalyst, as outlined in Scheme I.[11]

Scheme I



NOTES AND REFERENCES

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5) R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, J. Amer. Chem. Soc., 95, 1674 (1973).

6) J. Kiji, K. Masui, and J. Furukawa, Tetrahedron Lett., 2561 (1970).

7) Prepared from *n*-butyl chloride and lithium [H. Gilman, F. W. Moore, and O. Baine, J. Amer. Chem. Soc., 63, 2479 (1941)]. Each ml of the solution contains 0.62 mmol of *n*-butyllithium and 0.75 mg-equiv of total base.

8) Obtained from $NiBr_2$ and (-)-methylphenyl-*n*-propylphosphine [optical purity 83%; K. Nauman, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 91, 7012 (1969)] according to the standard procedure [K. Yamamoto, Bull. Chem. Soc. Japan, 27, 501 (1954)].

9) Asymmetric induction in homogeneous catalysis forming carbon—carbon bonds: H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, Tetrahedron, 24, 3655 (1968); R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, Can. J. Chem., 47, 1242 (1969); W. R. Moser, J. Amer. Chem. Soc., 91, 1135 (1969); M. Tanaka, Y. Watanabe, T. Mitsudo, K. Yamamoto, and Y. Takegami, Chemistry Lett., 483 (1972); I. Ogata and Y. Ikeda, ibid., 487 (1972); B. Bogdanović, B. Henc, B. Meister, H. Pauling, and G. Wilke, Angew. Chem., 84, 1070 (1972). See also reference 5.

10) For a review on nickel hydride species, see D. R. Fahey, Organometal. Chem. Rev. A, 7, 245 (1972).

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(Received June 1, 1973)