plete inversion of one allyl residue, that increasing volume of R_3, R_4, and R_5 in compound **5** strongly depresses the rate, increasing polarity of the medium slightly increases the rate, and finally, that no intermolecular interchange of groups occurs.[11]

These facts are completely in accord with the interception by triphenylphosphine of the intermediate **3**, postulated to occur in the conversions **2** to **4**, *vide supra.* Thus, in transformations of type **5** to **7**, increasing bulk of R_3, R_4, and R_5 would reduce the amount of thiosulfoxide (**6**) available for reduction to **7**, whereas increasing size of R_1 and R_2 would favor this intermediate and thereby enhance the rate of formation of **7**. We have verified this prediction by measurement of the rate of reduction of the allylic disulfides **5**a–**e**[6] by triphenylphosphine at 60°, Table II.[13] The thioether products **7**a–**e** were formed quantitatively and were identical with authentic samples.

Table II. Pseudo-First-Order Rate Constants of the Reduction of Disulfides **5a–e** with Triphenylphosphine (Benzene, 60°)

	5				
	c	**e**	**d**	**a**	**b**
k, 10^{-4} sec^{-1}	0.70	8.6	8.9	140	190

The great tendency of the thiosulfoxide intermediate **6** to expel the thionsulfur may be observed in **5e** and **5f**, which lose sulfur spontaneously at 25° to yield sulfides **7e** and **7f**, respectively. The direct observation of **6** has not been achieved since methanol solutions of **5e** and **5f** showed no additional signals (>2%) and decomposed faster than neat samples into **7e** and **7f**.

Acknowledgments. We wish to thank the U. S. Public Health Service, The National Science Foundation, The Petroleum Research Fund administered by the American Chemical Society, Eli Lilly and Company, and Hoffmann-La Roche for support of this research.

[14] A. P. Sloan Fellow, 1969–1971.

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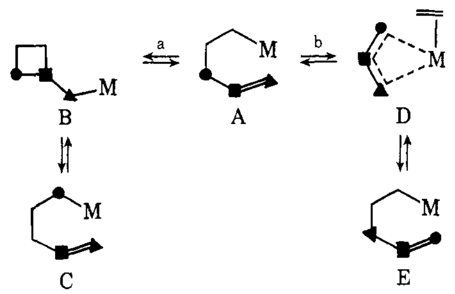
Homogeneous Catalysis of Diene Rearrangements *via* a Carbon–Metal β Elimination

Sir:

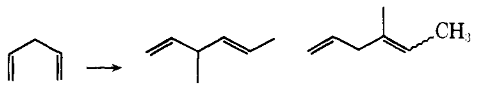
We wish to report extensive evidence for a new type of transformation in homogeneous catalysis, a carbon-metal β elimination. The nickel-catalyzed skeletal rearrangements of 1,4-dienes[1] are explained in terms of the chemistry of alkenylnickel species derived from 1,2 and 2,1 addition of nickel hydride to a terminal double bond.[2] The 1,4-pentadiene to isoprene rearrangement (herein referred to as the type I rearrangement) is pictured as involving a 2,1 nickel hydride adduct while the skeletal change exemplified by the 3-methyl-1,4-pentadiene to 1,4-hexadiene transformation (type II) is believed to involve a 1,2-nickel hydride adduct. For a given 1,4-diene, these are companion reaction paths, although in most cases only one type of reaction is detected. The competing route usually regenerates the carbon skeleton of the 1,4-diene reactant. We have reported evidence which suggests that the type I rearrangement proceeds *via* a cyclopropylcarbinylnickel derivative.[4]

Two reaction paths are considered to be serious candidates for the type II rearrangement (Scheme I). Path a entails the formation of a cyclobutylcarbinylnickel derivative, B, which on ring opening could afford rearrangement product C.[5] Path b is the reverse of the proposed addition step in the codimerization of alkenes and 1,3-dienes by nickel catalysts,[2a,3] a carbon–nickel β elimination. Scheme I describes the fates predicted by paths a and b for carbons in the 1,4-diene reactant.

Scheme I



While path a is intuitively attractive in view of results obtained in studies of the type I rearrangement, three lines of evidence have demanded serious consideration of path b. (1) Treatment of 3-methyl-1,4-pentadiene with the catalyst in the presence of propylene afforded significant quantities of 2-methyl-1,4-hexadiene,[1] the major product obtained when propylene is added to 1,3-butadiene by the same catalyst.[3] (2) We have discovered that product mixtures derived from treatment of 1,4-pentadiene with the catalyst over extended periods of time (1.5–3.0 hr) contain 3-methyl-1,4-hexadiene, 9–30% yields, and 4-methyl-1,4-hexadiene, 3–15% yields, in addition to the isomeric 1,3-pentadiene and isoprene. The yields of C-7 dienes were dependent upon the olefin-Ni ratio and reaction time employed. These C-7 dienes are those afforded by addition of ethylene to 1,3-pentadiene and isoprene, respectively, by the nickel catalyst.[3] (Thus, dienes seemingly



(1)

derived from *both* path b hydrocarbon fragmentation products, methylallyl from observation 1, and ethylene from observation 2 have been isolated.) (3) We have never observed the formation of 1,5-dienes which, in addition to the observed 1,4-dienes, are expected prod-

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(1) R. G. Miller, *J. Amer. Chem. Soc.*, **89**, 2785 (1967).

(2) Support for our supposition[1,3] that nickel hydride transfer plays an important role in these reactions has recently been advanced: (a) C. A. Tolman, *ibid.*, **92**, 6777 (1970); (b) R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, *J. Organometal. Chem.*, **29**, C42 (1971); (c) L. W. Gosser and G. W. Parshall, *Tetrahedron Lett.*, 2555 (1971).

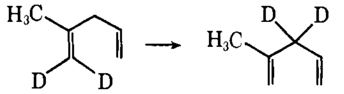
(3) R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Amer. Chem. Soc.*, **89**, 3756 (1967).

(4) R. G. Miller, P. A. Pinke, and D. J. Baker, *ibid.*, **92**, 4490 (1970).

(5) Evidence for this route in organomagnesium, sodium, and lithium chemistry: (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964).

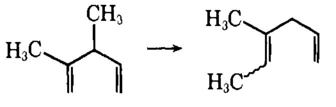
ucts from the rearrangements of 3-methyl- and 3,3-dimethyl-1,4-pentadiene by path a.

We have now labeled three carbons in the 1,4-pentadiene reactant with CH_3 or deuterium and have determined the fate of each label in the type II rearrangement product. 2-Methyl-1,4-pentadiene-*1*-d_2, 2.5% d_1, 97.2% d_2, 0.3% d_3 by mass spectrometry, was synthesized.[6] The position of the deuterium was unambiguously verified by the near absence of the C-1 proton resonance at τ 5.32. It was treated with the catalyst in chlorobenzene solution[8] for 120 min at 25°. The pmr spectrum of the recovered deuterio-2-methyl-1,4-pentadiene exhibited a multiplet resonance at τ 5.32 and a corresponding decrease in intensity of the doublet resonance of the C-3 allylic protons at 7.29. Very careful integration of the proton peak areas gave a C-1:C-2CH_3:C-3:C-4:C-5 proton ratio of 0.43:3.00:1.62:1.07:2.02 which may be compared to a ratio of 0.03:3.00:1.99:1.11:2.07 in the starting material. These values indicate that *ca.* 19% of the deuterium originally at C-1 now resided at C-3 and that little or no deuterium was present at other carbons. They imply that at least 38% of the molecules had fragmented *via* path b, Scheme I. Analysis by mass spectrometry demonstrated that the molecules were still predominantly d_2 (3.4% d_1, 94.3% d_2, 2.3% d_3). Therefore, little if any deuterium was lost by a MH addition–MD elimination sequence.[9] Similar analyses of the isomerization products indicated that they were *trans*-2-methyl-1,3-pentadiene (predominantly *1*-d_2) and 2,3-dimethyl-1,3-butadiene-*1*-d_2.



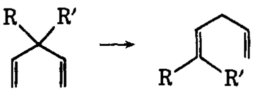
(2)

When 2,3-dimethyl-1,4-pentadiene was treated with the catalyst, it was converted to *only one* skeletally isomeric diene, 4-methyl-1,4-hexadiene (56% yield at 50% conversion). No 2-methyl-1,4-hexadiene or 2-methyl-1,5-hexadiene, the expected products from the Scheme I path a route, were detected.



(3)

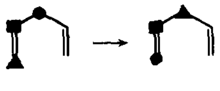
These experiments, along with the results from type II rearrangements of 3-methyl- and 3,3-dimethyl-1,4-pentadiene, eq 4, establish the nature of the skeletal



(4)

a, R = CH_3; R' = H
b, R = R' = CH_3

change in the type II rearrangement, eq 5. The results


(5)

are entirely consistent with path b of Scheme I and eliminate path a from consideration as a major route. Thus, the C–C σ bond-breaking steps in the type I and type II rearrangements appear to be mechanistically dissimilar. This conclusion is supported by our observation that the type I rearrangement can be accomplished by nickel species in the absence of an aluminum Lewis acid cocatalyst.[2b] The type II rearrangement has only been observed when the $(R_3P)_2NiCl_2$–R_2AlCl system is employed. Thus, the catalyst derived from ethylene bis(tri-*o*-tolyl phosphite)nickel and hydrogen chloride[2b] in toluene solution converted 3,3-dimethyl-1,4-pentadiene to only one isomeric product, 2,3-dimethyl-1,4-pentadiene. 2-Methyl-1,4-pentadiene-*1*-d_2, recovered after 5 hr treatment with these compounds, was unchanged, although 2,3-dimethyl-1,3-butadiene-*1*-d_2 and *trans*-2-methyl-1,3-pentadiene-*1*-d_2 were formed. 2,3-Dimethyl-1,4-pentadiene was not isomerized by the nickel(0) compound and hydrogen chloride. Experimental details and a complete discussion of these reactions will appear in our full paper which is in preparation.

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[6] 2-Methyl-4-penten-1-ol-*1*-d_2 was prepared in 88% yield by treatment of the ethyl ester of 2-methyl-4-pentenoic acid[7] with lithium aluminum deuteride. The corresponding acetate was prepared in 81% yield from the alcohol. Pyrolysis of 2-methyl-4-pentyl-*1*-d_2 acetate at 600° afforded a 17% yield of 2-methyl-1,4-pentadiene-*1*-d_2 after distillation of the product mixture and isolation of the diene by preparative glpc.

[7] G. I. Fray and N. Polgar, *J. Chem. Soc.*, 2036 (1956).

[8] Diene isomerization experiments were conducted in toluene or chlorobenzene solution at room temperature in a manner described previously.[4] All diene products described in the text were collected *via* preparative glpc and were identified by their pmr spectra.

[9] Further evidence shows that metal hydride addition to a methyl-substituted vinyl group in the 1,4-diene is not favored. (1) We have never detected the formation of a type I skeletal rearrangement product or a double bond migration product derived from initial addition of metal hydride to a methyl-substituted double bond. (2) Geometric isomerization of *trans*- and *cis*-1,4-hexadiene does not occur. (3) Deuteriums at positions 4 and 5 in *cis*-1,4-hexadiene are not exchanged with the catalyst hydrogen pool.[10] (4) Treatment of *trans*-1,4-hexadiene and 2-methyl-1,4-pentadiene with the catalyst at 50–85° has afforded hydrogenation products *trans*-2-hexene and 2-methyl-1-pentene, but hydrogenation of the more highly substituted double bond does not occur.

[10] P. A. Pinke, Ph.D. Thesis, University of North Dakota, 1970.

[11] (a) NSF Predoctoral Fellow, 1967–1970; (b) NDEA Predoctoral Fellow, 1965–1968; (c) PRF Predoctoral Fellow, 1969–1970.

A Novel Method for the Stereoselective Introduction of Olefinic Side Chains onto Cyclic Systems *via* the Hydroboration–Iodination of Alkynes[1]

Sir:

Recently we reported that addition of 6 *N* sodium hydroxide and iodine to the vinylborane derived from cis hydroboration of 1-hexyne with dicyclohexylborane results in a transfer of one cyclohexyl group from boron to the adjacent carbon followed by deboronoiodination to give the isomerically pure cis olefin.[2] It was suggested that migration of the cyclohexyl group proceeds

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[1] This research was supported by the National Science Foundation through Grant No. GP-9398.

[2] G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Amer. Chem. Soc.*, 89, 3652 (1967).