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RHODIUM CATALYZED ISOMERIZATION OF TRICYCLO[3.2.2.$0^{2,4}$]NONATRIENE

Thomas J. Katz and Steven A. Cerefice

Department of Chemistry, Columbia University, New York, New York 10027

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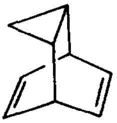
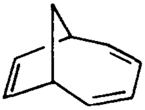
In 1966 it was first reported that rhodium catalyzes a cycloaddition reaction (norbornadiene + 5% Rh/C) (1). Subsequently similar reactions were found to occur not only with some other hydrocarbons and rhodium on carbon (2), but also with coordination complexes of rhodium (3,4,5). The effect of rhodium catalysts on tricyclo[3.2.2.$0^{2,4}$]nonatriene (I) (6,7) is reported here, and is remarkable as it was recently found that valence tautomerizations of this hydrocarbon are difficult to effect thermally, catalytically, or photochemically. Thus,(6) pyrolysis of I at 360° gave benzene and allylbenzene; pyrolysis at 240° over silica-alumina gave mainly benzene, about 5% of a substance tentatively assigned structure II, but no bicyclo[3.2.2]nonatriene (III); and photolysis in acetone-pentane gave a low yield of barbaralane (IV).


I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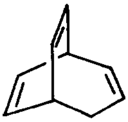

III


IV

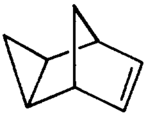
By contrast (Table 1), heating I with 5% rhodium on carbon or with $[Rh(CO)_2Cl]_2$ cleanly and quantitatively converts it into bicyclo[4.2.1]nonatriene (II) (8). Similarly, warming I with tris-triphenylphosphinerhodium(I) chloride also converts it into II (40% of the product),

Table 1. Rhodium Catalyzed Isomerizations of Tricyclo[3.2.2.$0^{2,4}$]nonatriene (I)

Catalyst	Mole % Catalyst	Time (Days)	Temp (°C)	Products (%)			
				I	II	III	IV
5% Rh/C	1.4	1.5	130	2	98	0	trace
$RhCl(Ph_3P)_3$	2.7	2.0	130	1	40	9	50
$[Rh(CO)_2Cl]_2$	9.0	0.25	60	0	100	0	0
$[Rh(CO)_2Cl]_2$	9.0	1.0	25	75	25	0	0
$[Rh(CO)_2Cl]_2$	9.0	7.0	25	28	72	0	0
none	---	1.0	130	100	0	0	0

but the major product is barbaralane (IV ,51%) (9) and a minor one is the bicyclononatriene III (9%) (10).

The path by which II is formed proceeds almost surely, by analogy with the known conversion by rhodium on carbon of V to VI (4d,5a) and of VII to VIII (5b), via IX,which presumably* is transformed into II. Although barbaralane (IV) is obtained from I both by photolysis (6) and by reaction with tris-triphenylphosphinerhodium(I) chloride, the pathways for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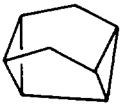
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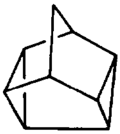
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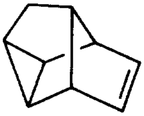
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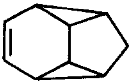
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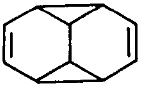
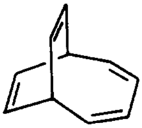

X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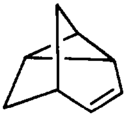
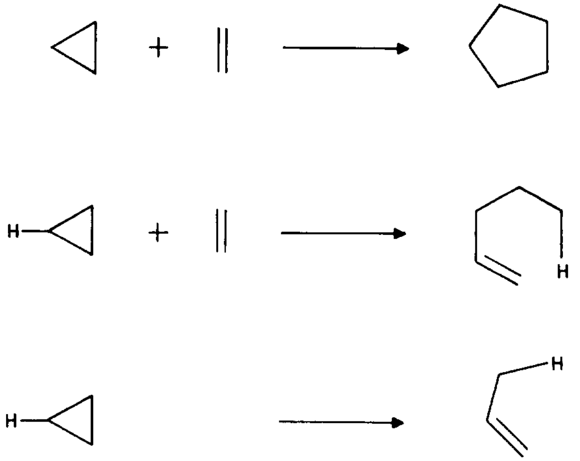

XII

the two transformations are probably very different, as close analogues of the former reaction take place without a hydrogen migration (12), while an analogue of the latter, the transformation of V to XII by tris-triphenylphosphinerhodium(I) chloride, does (5a). The formation of III is analogous to the transformation by tris-triphenylphosphinerhodium(I) chloride of V to bicyclo[3.2.1]octadiene (5a).

Thus the products formed here and in related systems can be accounted for if the reactions the rhodium catalysts effect are those in scheme 1. Moreover, the catalysts provide a

Scheme 1.



simple and efficient means for effecting these chemical transformations.

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* cf. the conversion at -15° of X to XI (11).

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REFERENCES

(1) J. J. Mrowca and T. J. Katz, J. Am. Chem. Soc., 88, 4012 (1966).

(2) T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, J. Org. Chem., 32, 1301 (1967).

(3) T. J. Katz, N. Acton, and I. C. Paul, J. Am. Chem. Soc., 91, 206 (1969).

(4) (a) H. Hogeveen and H. C. Volger, ibid., 89, 2486 (1967); (b) idem., Chem. Commun., 1133 (1967); (c) H. C. Volger and H. Hogeveen, Rec. Trav. Chim., 86, 830 (1967); (d) H. C. Volger, H. Hogeveen, and M. M. P. Gassbeek, J. Am. Chem. Soc., 91, 218 (1969).

(5) (a) T. J. Katz and S. Cerefice, ibid., 91, in press (1969); (b) idem., Tetrahedron Lett., submitted (1969).

(6) J. Daub and P. von R. Schleyer, Angew. Chem. Intern. Ed. Engl., 7, 468 (1968).

(7) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, Tetrahedron Lett., 5117 (1968); H. H. Westberg and H. J. Dauben, Jr., ibid., 5123 (1968).

(8) L. G. Cannell, ibid., 5967 (1966).

(9) U. Biethan, H. Klusacek, and H. Musso, Angew. Chem. Intern. Ed. Engl., 6, 176 (1967); W. von E. Doering, et al, Tetrahedron, 23, 3943 (1967).

(10) M. Jones, Jr. and S. D. Reich, J. Am. Chem. Soc., 89, 3935 (1967).

(11) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, ibid., 90, 5286 (1968).

(12) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, ibid., 90, 6096 (1968).