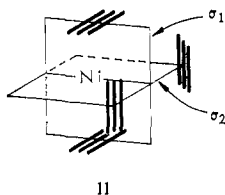


Figure 2.

π orbitals (Figure 2). The ligands seated at the corners of σ_2 comprise set 1 and the ligands positioned on the edges of σ_1 constitute set 2. The members of each set



interact yielding the following combinations. Orbitals in set 1 will interact with orbitals in set 2 of the same symmetry yielding a new set, half the members of which are bonding in the region of space between the sets and the other half antibonding. The SS and SS orbitals, for example, combine giving two orbitals, both of SS symmetry, one bonding in the region of the incipient cyclooctatetraene σ bonds and the other antibonding in that region. The four bonding members of the final set correspond in symmetry to the incipient σ bonds of cyclooctatetraene. If the interaction between the orbitals of the metal system and the olefin combinations results in the electronic population of these four molecular orbitals, then an orbital pathway to the concerted cycloaddition exists.

The application of symmetry conservation concepts to the selected reactions¹⁰ introduces a novel mechanism involving a role for the transition metal unique in catalysis. The results suggest that certain metal systems containing orbital configurations of the prerequisite energy are capable of rendering otherwise forbidden cycloaddition reactions allowed by providing a template of atomic orbitals through which electron pairs of transforming hydrocarbon ligands and metal systems can interchange and flow into the required regions of space.

Acknowledgment. We are grateful to Drs. J. Merritt, F. S. Mortimer, Isaac Dvoretzky, and J. H.

(10) Electronic involvement by a transition metal is suggested in other systems. The cobalt-catalyzed isomerization of allylbenzene to β -methylstyrene is an example.¹¹ Back donation of d electrons converts the suprafacial [1,3] sigmatropic change of order¹⁰ to an allowed process.

(11) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

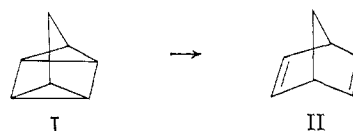
Raley for stimulating discussions and helpful comments.

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Received December 9, 1966

Valence Isomerization of Quadricyclene^{1a} to Norbornadiene^{1b} Catalyzed by Transition Metal Complexes

Sir:

The thermal isomerization of quadricyclene (I) to norbornadiene (II) is known to proceed slowly ($t_{1/2} > 14$ hr at 140°).² It has now been found that the rate of this reaction is dramatically increased by transition metal-olefin complexes. For instance, $t_{1/2}$ at -26° was found to be 45 min for a 0.7 M solution of I in CDCl_3 in the presence of 2 mole % of di- μ -chloro-bis(bicyclo[2.2.1]hepta-2,5-diene)dirhodium(I).



Complexes such as di- μ -chloro-tetrakis(ethylene)dirhodium(I), dichloro(1,5-cyclooctadiene)palladium(II), di- μ -chloro-bis(π -methallyl)dipalladium(II), and dichloro(bicyclo[2.2.1]hepta-2,5-diene)platinum(II) behave similarly. For all complexes a quantitative conversion of I into II was observed. The isomerization catalyzed by di- μ -chloro-bis(bicyclo[2.2.1]hepta-2,5-diene)dirhodium(I) was followed kinetically by integration of the olefinic triplet (δ 6.82 ppm) in the nmr spectrum of the norbornadiene formed. The samples were prepared at about -60° in CDCl_3 , warmed up rapidly to the desired temperature, and then transferred to the cavity of the nmr spectrometer (being at the same temperature).

The reaction proved to be first-order in quadricyclene and, as shown in Table I, about first order in catalyst.

Table I. Pseudo-First-Order Rate Constants of the Reaction^a Quadricyclene \rightarrow Norbornadiene

[Rh ₂ (norbornadiene) ₂ Cl ₂], M	10 ² k, sec ⁻¹
0.02	0.025
0.06	0.068

^a At -26°; [quadricyclene] = 0.7 M (CDCl_3).

The apparent values of the activation parameters (inaccurate because of experimental difficulties, such as temperature control and instability of the catalyst solution) are $\Delta H^\ddagger = 21 \pm 5$ kcal mole⁻¹, $\Delta S^\ddagger = 45 \pm 18$ eu (catalyst concentration 0.036 M).

The mechanism of the reaction is thought to involve a coordination of quadricyclene to the transition metal either *via* an exchange with the originally coordinated olefin or by extension of the coordination around the metal. For the rhodium-olefin complexes and for the

(1) (a) IUPAC designation tetracyclo[3.2.0.0.4².7.0⁴.6]heptane; (b) IUPAC designation bicyclo[2.2.1]hepta-2,5-diene.

(2) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

π -allyl-palladium complex coordination is possible with either the binuclear or the mononuclear species. This coordination of quadricyclene (I) may well be due to the π character of the cyclopropane bonds common to the three- and four-membered rings.³

The valence isomerization I \rightarrow II described is, by the Woodward-Hoffmann rule for cycloadditions,⁴ thermally forbidden. The catalysis observed might well be caused by the presence in the complex of occupied molecular orbitals with symmetries that make the isomerization an allowed process.⁵

(3) A. D. Walsh, *Nature*, **159**, 165, 712 (1947); C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947).

(4) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(5) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967).

H. Hogeveen, H. C. Volger

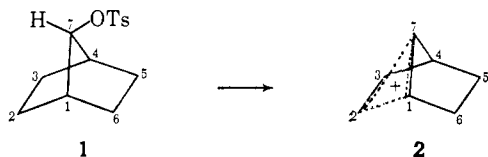
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The 7-Norbornyl Cation

Sir:

The nature of the cation formed in the solvolysis of 7-tosyloxybicyclo[2.2.1]heptane (1) has not been clearly established. Winstein and co-workers have described the ionization of 1 as an "example of carbon participation in solvolysis" in which the delocalized ion, 2, is formed.¹ In contrast, Foote² and Schleyer³



have used the solvolysis of 1 as an example of a system which solvolyzes without anchimeric assistance.⁴

We have found that solvolysis of *exo,exo*-2,3-dideuterio-*anti*-tosyloxybicyclo[2.2.1]heptane (3), in acetic acid buffered with sodium acetate, gave the mixture of products previously reported in the literature.¹ Isolation of the 7-acetoxycyclo[2.2.1]heptane, which constituted greater than 90% of the reaction product, provided a mixture of deuterium labeled compounds. Infrared analysis *vs.* standard mixtures showed that the solvolysis product consisted of $90 \pm 3\%$ of 4 and $10 \pm 3\%$ of 5.

Both the tosylate, 3, and the acetate, 4, were prepared from 6. The synthesis of 6 involved dideuterio-diimide^{5,6} reduction of *anti*-7-hydroxybicyclo[2.2.1]heptene.⁷ The acetate, 5, was synthesized from 7, which

(1) S. Winstein, F. Gadiest, E. T. Stafford, and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **80**, 5895 (1958).

(2) C. S. Foote, *ibid.*, **86**, 1853 (1964).

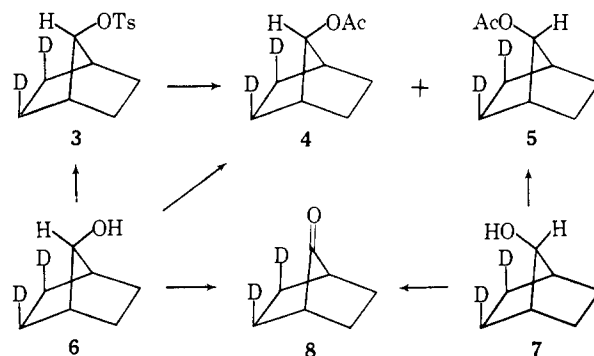
(3) P. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(4) It is assumed in this paper that anchimeric assistance and participation of neighboring groups are interrelated phenomena. For discussion of this relationship see P. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, and J. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(5) We wish to thank Professor J. Berson for providing us with experimental details for dideuteriodiimide reductions.

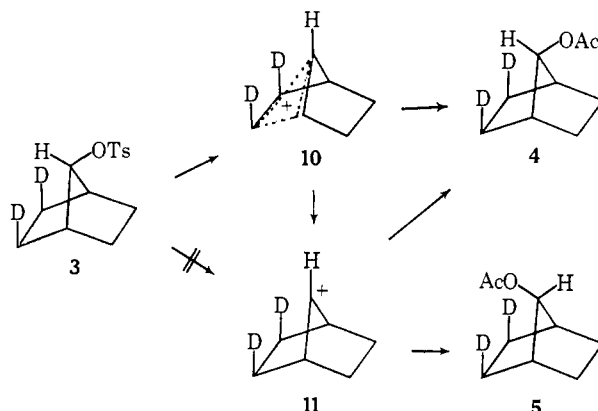
(6) The acetate prepared from 6 was shown to contain 90% of the theoretical amount of deuterium. All deuterium analyses were performed by J. Nemeth, Urbana, Ill.

(7) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).



had been prepared *via* diimide reduction of the known⁸ *exo,exo*-2,3-dideuterio-*syn*-7-hydroxybicyclo[2.2.1]hept-5-ene.⁹ In order to ascertain that the dideuterio-diimide reduction occurred from the *exo* side, both 6 and 7 were oxidized to the same ketone, 8. Whereas the ketones obtained from 6 and 7 were identical in all respects, the infrared and nmr spectra of each member of the epimeric pairs, 6 and 7, 4 and 5, and 3 and 9, were different.

We propose that the large degree of retention of configuration observed in the solvolysis of 3 is most consistent with concerted participation of the 1,2 σ electrons to form the delocalized ion, 10. Unlike certain explanations of the formation of the 2-nor-



bornyl cation,¹⁰ the formation of 10 may not be postulated to proceed *via* an initially formed classical ion such as 11 since, if 11 were an intermediate, approximately equal amounts of 4 and 5 should be formed.¹¹ Thus, it appears likely¹² that concerted ionization and carbon participation occur in the acetolysis of 3.

(8) B. Franzus and E. I. Snyder, *ibid.*, **87**, 3423 (1965).

(9) A tosylate, 9, prepared from 7, was shown to contain 95% of the theoretical amount of deuterium.

(10) It has been suggested that the initial step in the solvolysis of 2-tosyloxybicyclo[2.2.1]heptane is formation of a classical carbonium ion at C-2 of the bicyclo[2.2.1]heptyl system. For a discussion of this point of view see H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962.

(11) It is assumed that the steric requirements of deuterium *vs.* hydrogen would not be sufficiently different to cause the observed product distribution.

(12) An alternate rationalization of the observed results would invoke a front-side displacement on the ion pair by solvent. Indeed, Brown has suggested¹³ the possibility "that even static classical ions, where the structure inhibits approach from the back side, may well undergo substitution with retention." Obviously, special classes of molecules, such as bridgehead tosylates where back-side approach is impossible, can only solvolyze with retention.¹⁴ However, we doubt whether the tosylate, 3, can be justifiably classified as one in which solvent approach from the back side is hindered to the extent that the mechanism of acetolysis becomes one of "front-side displacement." In the absence of such steric hindrance to back-side approach of solvent we see no obvious reason for suggesting front-side displacement of solvent on any ion pair derived from 3.