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THE HYDROGENATION OF NORBORNADIENE

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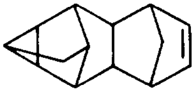
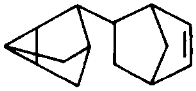
When norbornadiene (NBD) is combined with rhodium on carbon[1] or with $(NBD)_2Rh^+PF_6^-$ in acetone,[2] it is dimerized to two stereoisomers of structure I.[1,3,4] However Schröck and Osborn found that when hydrogen is combined with the reaction mixture of norbornadiene and $(NBD)_2Rh^+PF_6^-$, a different hydrocarbon, $C_{14}H_{18}$, is formed, consisting of two molecules of norbornadiene plus one molecule of hydrogen.[2] The nmr spectrum indicates that this hydrocarbon has a disubstituted double bond and the ir spectrum indicates that the double bond is probably in a norbornene ring system, but the spectra are so complex that further interpretation is difficult.[2,5]

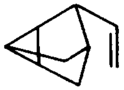
We have determined that the structure of the hydrocarbon is II. This was achieved by distilling it at 5 mm pressure through a 50 cm x 8 mm id quartz tube heated at 450°, which cleaved a molecule of cyclopentadiene[6] giving in 62% yield 3-vinylnortricyclane (III), whose structure is known and easily recognized.[7]



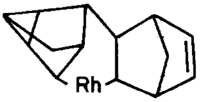
I



II

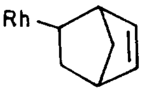


III

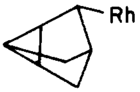


IV

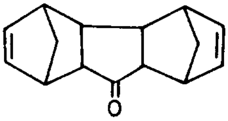
There are two ways II might be formed from norbornadiene, $(NBD)_2Rh^+PF_6^-$, and hydrogen. The metal might link two norbornadiene molecules to give IV, whose carbon-rhodium bonds are then cleaved by hydrogen, or metal hydride might add to norbornadiene to give either V or VI,[8] whose carbon-metal bond then adds to another molecule of norbornadiene before it is cleaved by hydrogen.



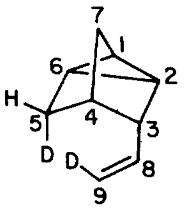
V



VI



VII



VIII

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The first possibility is in accord with the observation that when a ligand that can insert into a metal-carbon bond is attached to the metal, dimerized insertion products are formed, for example NBD and Fe(CO)$_5$ yield VII,[9] while when such ligands are absent only pure dimers, such as I, are formed.[1,2] The second possibility resembles the rhodium-catalyzed addition of ethylene to either butadiene or ethylene,[10] except that since *cis* elimination of rhodium hydride is impossible, the reaction is terminated by the hydrogenolysis of the carbon-metal bond.

When deuterium is used for the reduction in place of hydrogen, the product II is dideuterated,[2] as is the pyrolysis product III. That the deuterium atoms are in the expected positions, shown on structure VIII, is demonstrated by the 220 MHz proton nmr spectrum's differing from that of III[11] in the following respects: (1) there is no resonance for the 5-*syn* proton at τ8.53;[12] (2) the resonance of the 5-*anti* proton at τ8.98 is a singlet instead of a 5.5 Hz doublet; the resonance of H_9 is an 11 Hz doublet instead of a multiplet; the resonance of H_8 shows a 2.7 Hz splitting attributable to the *trans*-deuterium atom.[13]

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Footnotes

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

(2) R.R. Schrock and J.A. Osborn, *ibid.*, **93**, 3089 (1971).

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

(4) T.J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967).

(5) R.R. Schrock, Dissertation, Harvard University (1971).

(6) For analogies see reference 3 and L.G. Cannell, *Tetrahedron Lett.*, 5967 (1966).

(7) The nmr and ir spectra are identical with spectra of authentic samples provided us by Professor Ronald Sauers. See R.R. Sauers, S.B. Schlosberg, and P.E. Pfeffer, *J. Org. Chem.*, **33**, 2175 (1968). We are grateful to Professor Sauers for the spectra.

(8) *endo*-Norbornenyl- and nortricyclylpalladium complexes have been interconverted: D.R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969).

(9) (a) R. Petit, *J. Amer. Chem. Soc.*, **81**, 1266 (1959); (b) C.W. Bird, R.C. Cookson, and J. Hudec, *Chem. Ind. (London)*, 20 (1960).

(10) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

(11) The 220 MHz proton nmr spectrum of III in C_6D_6 shows peaks assigned as follows: τ9.01 (broad singlet, $H_{1,2,6}$), 8.95 (d, 5.5 Hz, $H_{5\text{-}anti}$), 8.78 (broad singlet, H_7), 8.53 (d, 5.5 Hz, $H_{5\text{-}syn}$), 8.37 (broad singlet, H_4), 7.88 (d, 6 Hz, H_3), 4.8 (m, H_9), 4.15 (m, H_8).

(12) Changing the solvent from CCl_4 to C_6D_6 shifts the resonance of $H_{5\text{-}syn}$ to lower field, while that of $H_{5\text{-}anti}$ is unaffected.

(13) The splittings of the H_8 resonance in III are: $J_{8,9\ trans}$ = 18 Hz, $J_{8,9\ cis}$ = 11 Hz, $J_{3,8}$ = 6 Hz.