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Hydrogen Transfer from Dioxane to an Olefin Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

Sir:

In transfer-hydrogenation[1] the donation of hydrogen to olefins by alcohols,[2] cyclohexene,[3] and partially hydrogenated aromatic compounds containing nitrogen atoms[4] has been observed. However, with the exception of alcohols there have been very few reports of double hydrogen abstraction by soluble complexes.[5]

We wish to report here that, with $RhCl(PPh_3)_3$[6] as a catalyst, a saturated cyclic ether, 1,4-dioxane, donated hydrogen to an olefin to give stoichiometric amounts of dioxene.

When a dioxane solution of cyclopentene (0.5 *M*) and the catalyst (0.02 *M*) was sealed in a Pyrex glass tube under vacuum (10^{-2} mm) and heated at 180° for 1 hr,[7] the formation of 0.43 *M* dioxene and 0.42 *M* cyclopentane in addition to the survival of 0.08 *M* cyclopentene[8] was shown by gas chromatographic analysis of the reaction mixture. Dioxene was identified by comparison with an authentic sample.[9] The following observations indicate that the reduction proceeded by hydrogen transfer from dioxane rather than by disproportionation. (1) The amount of the dioxene was almost equal to that of the cyclopentane.[10] (2) The total amount of the cyclopentane and the cyclopentene was equal to the amount of the charged cyclopentene. (3) Only a negligible amount of cyclopentadiene or the products of Diels–Alder reactions involving the diene was detected. (4) The reduction did not proceed in toluene without dioxane.[11]

The hydrogenation proceeded almost quantitatively and the observed initial rate of the formation of cyclopentane or of the consumption of cyclopentene was 1.2×10^{-2} mol l.$^{-1}$ min^{-1} at 180°, 6.2×10^{-3} at 170°, 3.7×10^{-3} at 160°, and 2.0×10^{-3} at 150°.

After the reactions, orange-red needles (A) were isolated by leaving the reaction mixtures at room temperature. The structure of A was inferred as $RhCl(PPh_3)_2(C_4H_8O_2)$, formed by replacing a triphenylphosphine of $RhCl(PPh_3)_3$ by a dioxane. The identification of the structure was based on the following grounds: (1) The value of the elemental analysis of A fitted the calculated value (*Anal.* Calcd for $C_{40}H_{38}ClO_2P_2Rh$: C, 66.72; H, 5.32 Found: C, 66.88; H, 5.16). (2) The ^1H nmr spectrum in $CDCl_3$ has a peak assignable to dioxane (singlet, τ 6.3) and peaks attributable to the aromatic hydrogens of triphenylphosphine (multiplet centered at τ 2.7). The ratio of the area of the former to that of the latter was about 1:4. (3) A was obtained also by dissolving $RhCl(PPh_3)_3$ in dioxane on warming and then cooling the solution. (4) Though $RhCl(PPh_3)_3$ has been reported to give the dimer, $[RhCl(PPh_3)_2]_2$ on heating in solvents such as toluene and ethanol,[6] the infrared spectrum of A is different from that of the dimer and has peaks attributable to coordinated dioxane at 870 and 890 cm^{-1}.

By analogy to the hydrogenation by molecular hydrogen[5,6,12] and the isomerization of olefins,[13] we should like to propose the following reaction scheme: $RhCl(PPh_3)_2(C_4H_8O_2) \rightleftarrows RhClH(C_4H_7O_2)(PPh_3)_2 \rightleftarrows RhClH_2(PPh_3)_2(C_4H_6O_2)$ (− dioxene) (+ olefin) $\rightleftarrows$ $RhClH_2(PPh_3)_2(\text{olefin}) \rightleftarrows RhClH(\text{alkyl})(PPh_3)_2$ (+ dioxane) $\rightleftarrows RhCl(PPh_3)_2\text{-}(C_4H_8O_2)$ + paraffin. The rate-determining step of the reaction is inferred to be the dehydrogenation step, that is, the formation of the monohydrido complex, $RhClH(C_4H_7O_2)(PPh_3)_2$ or $RhClH(C_4H_7O_2)(PPh_3)_2(S)$ (S = dioxane or olefin), by the oxidative addition of dioxane by the cleavage of a C–H bond, on the following grounds:[14] (1) The kinetic isotope effect at 180° was $k_H/k_D = 3.0$.[15] This value shows that a hydrogen transfer step is rate determining and exhibits a clear contrast to the reduction by molecular hydrogen in which the isotope effect is 0.78–

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(1) T. Nishiguchi and K. Fukuzumi, *Bull. Chem. Soc. Jap.*, **45**, 1656 (1972).

(2) (a) K. Sakai, T. Ito, and K. Watanabe, *ibid.*, **39**, 2230 (1966); (b) H. N. Basu and M. M. Chakrabarty, *J. Amer. Oil Chem. Soc.*, **43**, 119 (1966); (c) J. C. Bailar, Jr., and H. Itatani, *J. Amer. Chem. Soc.*, **89**, 1592 (1967); (d) S. Nanya, M. Hanai, and K. Fukuzumi, *Kogyo Kagaku Zasshi*, **72**, 2005 (1969).

(3) E. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *J. Chem. Soc.*, 3578 (1954).

(4) L. M. Jackman, *Advan. Org. Chem.*, **2**, 329 (1960).

(5) (a) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972); (b) G. N. Schrauzer, "Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971, pp 33, 41.

(6) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(7) This concentration of the olefin and the catalyst was used in every instance, unless otherwise noted.

(8) When cyclopentene and the catalyst (0.01 *M*) were heated for 1 hr at 180° in isopropyl alcohol, 0.18 *M* cyclopentane was obtained along with acetone.

(9) R. K. Summerbell and R. R. Umhoefer, *J. Amer. Chem. Soc.*, **61**, 3016 (1939).

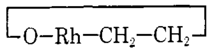
(10) Though the amount of dioxane was a little more than that of cyclopentane, the difference seems to be within experimental error.

(11) In this reaction, $[RhCl(PPh_3)_2]_2$ was isolated.

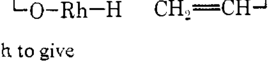
(12) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967).

(13) (a) J. F. Biellmann and M. J. Jung, *J. Amer. Chem. Soc.*, **90**, 1673 (1968); (b) A. S. Hussey and Y. Takeuchi, *ibid.*, **91**, 672 (1969); (c) G. C. Bond and R. A. Hillyare, *Discuss. Faraday Soc.*, **46**, 20 (1968); (d) R. L. Augustine and J. F. V. Peppen, *J. Amer. Oil Chem. Soc.*, **47**, 478 (1970); (e) C. H. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969).

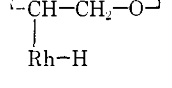
(14) A referee suggested another route instead of the C–H insertion. This is a C–O insertion to give



followed by Rh–H elimination to give



An insertion of O–Rh to give



followed by a second Rh–H elimination would give $RhClH_2(PPh_3)_2(C_4H_6O_2)$. According to this mechanism, the rate-determining step must be one of the Rh–H elimination steps from the observed isotope effect. We should like to point out the resemblance of the two steps to the steps involved in the isomerization of olefins under hydrogen which occurs under milder conditions.

(15) The initial rate of the reduction in which cyclopentene (0.25 *M*), dioxane (2.0 *M*), and the catalyst (0.02 *M*) in toluene were heated at 180[11] was 2.1×10^{-3} mol l.$^{-1}$ min^{-1}, while that of the one in which octadeuteriodioxane was used instead of dioxane was 6.9×10^{-4}.

$1.0^{6,12}$ or $1.10–1.17^{16}$ and the replacement of a solvent molecule from $RhClH_2(PPh_3)_2$(solvent) by an olefin is rate limiting. (2) While the reduction, the isomerization, and the hydrogen–deuterium exchange[17] of olefins under hydrogen take place rapidly at room temperature, the transfer–hydrogenation scarcely proceeded below 100°. Therefore, the steps which can correspond to the steps in the former reactions may not be rate determining in the latter. All the hydrogen transfer steps in the latter other than the oxidative addition step have the corresponding ones in the former which involve the steps $RhClH_2(PPh_3)_2$(olefin) $\rightleftarrows$ RhClH(alkyl)$(PPh_3)_2$ (+ solvent) $\rightarrow$ $RhCl(PPh_3)_2$(solvent). (3) The initial rate seems to be zero order in the concentration of cyclopentene. (4) The possibility of a radical mechanism may be eliminated because the transfer–hydrogenation was not retarded at all by the addition of pyrocatechol (1.0 *M*) which is an inhibitor of radical reactions.[18]

Notwithstanding the report that $RhCl(PPh_3)_3$ gave $RhCl(CO)(PPh_3)_2$ on warming in dioxane with excess triphenylphosphine and $[RhCl(PPh_3)_2]_2$ without the phosphine, we observed neither the formation of the carbonyl complex nor the dimer in the transfer–hydrogenation in dioxane. Moreover, the dimer gave $RhCl(PPh_3)_2(C_4H_8O_2)$ on warming in dioxane. Perhaps this is due to the ability of dioxane to cleave the chloro bridge of the dimer. Another indication of the strong complexing power of dioxane is the fact that the addition of 0.2 *M* triphenylphosphine did not depress the rate of the transfer–hydrogenation in spite of the strong inhibition by added phosphine in the hydrogenation by molecular hydrogen in benzene.[6]

(16) S. Siegel and D. W. Ohrt, *Chem. Commun.*, 1527 (1971).

(17) (a) A. I. Odell, J. B. Richardson, and W. R. Roper, *J. Catal.*, **8**, 393 (1967); (b) A. S. Hussey and Y. Takeuchi, *J. Org. Chem.*, **35**, 643 (1970); (c) G. V. Smith and R. Shuford, *Tetrahedron Lett.*, 525 (1970).

(18) D. C. Dittmer and P. A. Fonty, *J. Amer. Chem. Soc.*, **86**, 91 (1964).

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Subjacent Orbital Control. An Electronic Factor Favoring Concertedness in Woodward–Hoffmann "Forbidden" Reactions[1]

Sir:

The exceptionally fruitful ideas of Woodward and Hoffmann on the electronic control of chemical reactions have been summarized in the statement[2] "orbital symmetry is conserved in concerted reactions." It has been widely assumed that a "forbidden" process, in which orbital symmetry in the Woodward–Hoffmann sense was not conserved, would proceed by a nonconcerted two-step pathway involving discrete diradical or ionic intermediates.[3,4] By implication, the forbidden reaction would have a transition state with net antibonding character. It would be reasonable, therefore, to postulate that if extrasymmetric factors precluded the symmetry-allowed process, the system would shun the forbidden concerted pathway in favor of one in which the reactive sites tended to overlap as little as possible. This would have the important consequence that reactions proceeding by other than allowed pathways would tend to occur in two steps and stereorandomly. We wish to suggest that this conclusion is misleading and that there is a significant electronic factor favoring stereospecific, *concerted, forbidden* reactions.[6]

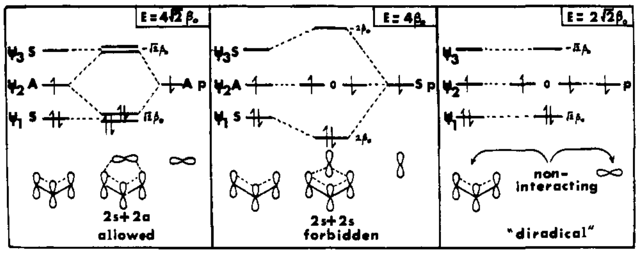

Figure 1. Schematic diagram of orbital energies and topologies of three different suprafacial 1,3-sigmatropic rearrangement transition states derived by interaction of an allyl unit with a carbon p orbital.

Figure 1 shows the essentials of the argument applied to the case of suprafacial 1,3-sigmatropic rearrangement of carbon. There are two idealized transition state geometries for concerted processes, one in which the migrating carbon retains configuration (a forbidden $2_s + 2_s$ reaction), another in which inversion occurs (an allowed $2_s + 2_a$ reaction). The energy level scheme is derived by permitting interaction between the allyl and p orbitals in the two topological combinations corresponding to the transition state geometries. We consider first, for didactic purposes, the case in which the energies themselves are derived from simple Hückel calculation on the assumption of equal nearest-neighbor interactions (all nonzero off-diagonal matrix elements $= \beta_0$).

Consider a hypothetical two-step rearrangement *via* a model diradical in which distance or orbital perpendicularity ensures zero interaction between the allyl and p orbitals and therefore favors stereorandomization of the products. It is clear from Figure 1 that the transition state for the allowed reaction is stabilized relative to that in such a diradical case largely because of the lowering of an antisymmetric nonbonding level, the highest occupied molecular orbital (HOMO) of the allyl unit, to a strongly bonding level.

However, Figure 1 also shows that there can be appreciable stabilization of the forbidden transition state. This results not from an effect on the HOMO but instead from the interaction of the carbon p orbital with a *subjacent*, bonding allyl orbital. Two of the four electrons involved thus can be accommodated in a more stable orbital than is the case in the separated fragments. The energies of the electrons in the allyl HOMO (ψ_2) and

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(1) The support of this work by the National Science Foundation (GP-11017X) and by the Hoffmann-LaRoche Foundation is gratefully acknowledged.

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 1.

(3) Reference 2, p 173.

(4) In some cases,[5] the "diradicals" may not represent true local potential minima.

(5) *Cf.* (a) R. Hoffmann, S. Swaminathan, B. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970); (b) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972); (c) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(6) For reasons different than those given here, concert in symmetry-forbidden processes has been invoked by W. Schmidt, *Tetrahedron Lett.*, 581 (1972), and by N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972).