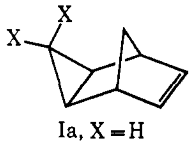
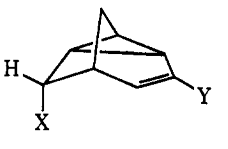
The Stereochemistry of a Rhodium-Catalyzed Rearrangement of a Cyclopropane to a Propylene

Sir:

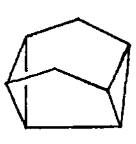
Cyclopropanes can be isomerized to propylenes by catalysts containing transition metals such as platinum,[1] palladium,[2] nickel,[3] rhodium,[4] and iridium.[5] The mechanism of the reaction, like that of the metal-catalyzed hydrogenolysis of small-ring compounds to which it is probably related, is unclear.[6] An opportunity to learn how these reactions work is provided by the observation that compound Ia below when warmed with $[(C_6H_5)_3P]_3RhCl$ gives IIa, III, and IVa.[4a] Although IVa comprises only a small part (about 6%) of the product, the reaction provides a means to discover the stereochemistry of the rearrangement. Thus if, as seems likely, the metal inserts into one of the cyclopropane bonds, metal hydride is eliminated, and the metal is extruded as in Scheme I below,[4,7-9] then the isomerization of Ib should yield IVb.[10] This scheme seems likely because a simple variant also accounts for the formation of IIa and for the demonstrated stereospecificity of the rearrangement of Ib to IIb.[4a,8] However, it is possible that the rearrangement of Ia to IVa proceeds by a mechanism very different from that by which Ia rearranges to IIa, and if it proceeds as depicted in Scheme II,[11] then the deuterium-labeled cyclopropane Ib should yield not IVb, but IVc instead.[12,13]



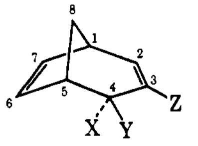
Ia, X = H
b, X = D



IIa, X = Y = H
b, X = Y = D

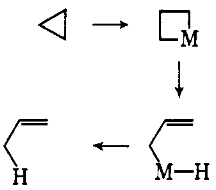


III

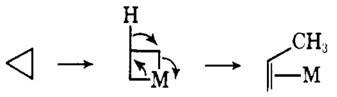


IVa, X = Y = Z = H
b, X = D; Y = H; Z = D
c, X = H; Y = D; Z = D
d, X = Y = D; Z = H

Scheme I



Scheme II



The starting material Ib required to distinguish between Schemes I and II was prepared from CD_2I_2[15] and norbornadiene using the Simmons–Smith reaction,[16] and purified by fractional distillation and repeated crystallization of a silver nitrate complex.[16a] The extensive purification was necessary because about[17] 18% of the product of the Simmons–Smith reaction of norbornadiene with CH_2I_2 is IVa and with CD_2I_2 IVd.[18] If this latter contaminant is not removed from the samples of Ib used for the study, the analysis of the location of the deuterium atoms in the IV produced in the rearrangement is difficult.

A 3.90-g sample of Ib (96.64 ± 0.51% d_2, 2.63 ± 0.02% d_1, 0.73 ± 0.02% d_0)[21] that was 99.5% isomerically pure, contaminated by 0.5% IVd,[22] was heated with 0.43 g of $[(C_6H_5)_3P]_3RhCl$ at 90° for 2 hr, giving, after distillation, 3.83 g of products consisting of deuterated II (54%), III (43%), and IV (3%). The proton nmr spectrum of the deuterated product IV, isolated by glpc,[23] and the spectrum of the undeuterated IV are compared in Figure 1. These spectra show that the product of the rearrangement is almost entirely IVb, that the amount of IVc is less than 3%, and that the product is contaminated with about 18% IVd (which

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(1) (a) V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," Macmillan, New York, N. Y., 1936, pp 154–155; (b) D. B. Brown, *J. Organometal. Chem.*, **24**, 787 (1970).

(2) R. J. Ouellette and C. Levin, *J. Amer. Chem. Soc.*, **90**, 6889 (1968).

(3) R. G. Miller and P. A. Pinke, *ibid.*, **90**, 4500 (1968).

(4) (a) T. J. Katz and S. Cerefice, *ibid.*, **91**, 2405 (1969); (b) T. J. Katz and S. A. Cerefice, *Tetrahedron Lett.*, 2561 (1969).

(5) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeeck, *J. Amer. Chem. Soc.*, **91**, 2137 (1969).

(6) (a) J. Newham, *Chem. Rev.*, **63**, 123 (1963); (b) C. H. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969); (c) E. I. Klabunovskii, *Russ. Chem. Rev.*, **35**, 546 (1966).

(7) See the footnotes in ref 4a.

(8) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6519 (1969).

(9) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).

(10) When cycloheptatrienemolybdenum or -chromium tricarbonyls are heated, the methylene hydrogen atom on the same face of the ring as the metal migrates [W. R. Roth and W. Grimme, *Tetrahedron Lett.*, 2347 (1966); M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *Chem. Commun.*, 843 (1970)].

(11) S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Amer. Chem. Soc.*, **87**, 2517 (1965).

(12) The assumption here is that this is a nucleophilic displacement.

(13) A similar mechanism may be involved in the oxidation of olefins by palladium salts.[14]

(14) (a) J. Smidt, W. Hafner, R. Gira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem., Int. Ed. Engl.*, **1**, 80 (1962); (b) E. W. Stern, *Proc. Chem. Soc.*, 111 (1963); (c) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964).

(15) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, **8** (II), 621 (1966).

(16) (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964); (b) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

(17) By proton nmr spectroscopy.

(18) That IVa and IVd are products of the Simmons–Smith reaction of norbornadiene was shown by identifying their characteristic olefin proton absorptions in the crude distilled products, by precipitating their $PdCl_2$ complexes by means of $(C_6H_5CN)_2PdCl_2$ (the complexes are orange crystalline solids, mp 180–185°, forming in 87–90% yield), by identifying the $PdCl_2$ complex of the undeuterated material with a complex prepared from $(C_6H_5CN)_2PdCl_2$ and authentic IVa,[19] and by decomposing the $PdCl_2$ complexes with aqueous sodium cyanide and isolating thereby IVa and IVd identical with hydrocarbons formed from bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde and undeuterated[19] or dideuterated[20] methylenetriphenylphosphorane.

(19) C. Cupas, W. E. Watts, and P. von R. Schleyer, *Tetrahedron Lett.*, 2503 (1964).

(20) (a) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. B*, 411 (1964); (b) R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968).

(21) K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, Chapter 5.

(22) Based on the amount of IVd detected by nmr in the reaction product with $[(C_6H_5)_3P]_3RhCl$.

(23) 12 ft × 3/8 in. 20% Apiezon L on 60–80 Chromosorb W.

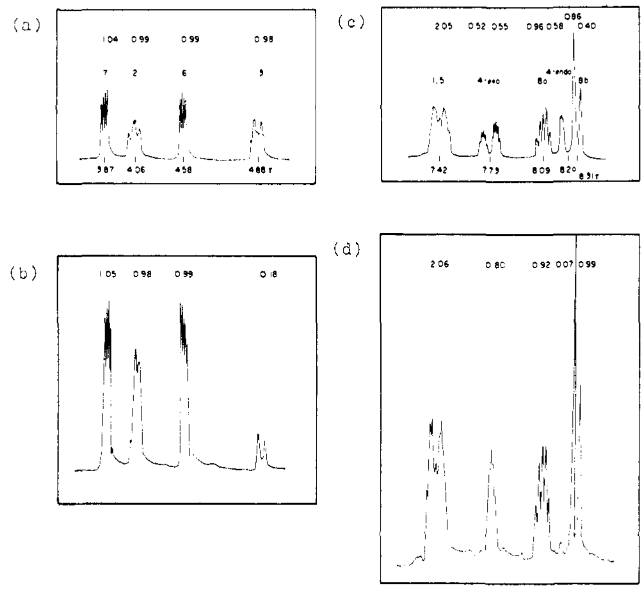

Figure 1. Proton nmr spectra (220 MHz) of IVa and of the product IV of the rearrangement of Ib. The solvent is CCl_4 and TMS is the internal standard. Intensities and assignments (integers) are above the peaks: (a and b) low-field portions of the spectra of IVa and product, respectively; (c and d), high-field portions of the spectra of IVa and product, respectively.

is expected because the starting material Ib contained 0.5% IVd). Thus, in the deuterated compound (1) the doublet ($|J|$ = 18.3 Hz) in the undeuterated compound at τ 8.24 (the upfield half of which is buried under the low-field peak of the doublet at τ 8.3), attributed to the 4-endo proton,[20a,24,25] is essentially absent, and the intensity of the singlet at τ 8.24 expected of IVc (but not observed) is estimated to be less than that of 0.03 proton; (2) the doublet ($|J|$ = 18.3 Hz) in the undeuterated compound at τ 7.73, attributed to the 4-exo proton,[20a,24,25] is collapsed to a singlet; (3) the multiplet in the undeuterated compound at τ 4.88, attributed to the proton at position 3,[20,26] is collapsed to a doublet ($|J_{2,3}|$ = 10 Hz) and of only small intensity; (4) the multiplet in the undeuterated compound at τ 4.06, attributed to the proton at position 2,[20,26] is collapsed to a doublet ($|J_{1,2}|$ = 7.0 Hz).

Thus, the rearrangement involves the stereospecific transfer of a hydrogen atom across that face of the molecule to which the metal is almost surely coordinated, and is in accord with the mechanism of Scheme I, not with that of Scheme II.

Acknowledgments. The 220-MHz spectra were measured at the Bell Telephone Laboratories. We are grateful to the National Science Foundation (NSF-GP7809) for its support.

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(24) (a) J. M. Brown and E. N. Cain, *J. Amer. Chem. Soc.*, **92**, 3821 (1970); (b) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967).

(25) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

(26) The resonances of protons 2 and 3 can be identified because in the spectrum of VIII, the resonance of 3 is a doublet ($|J_{2,3}|$ = 10 Hz) while that of 2 is a doublet of doublets ($|J_{2,3}|$ = 10 Hz, $|J_{1,2}|$ = 6.5 Hz).

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Book Reviews

Transition Metal Chemistry. A Series of Advances. Volume 6. Edited by RICHARD L. CARLIN, Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Ill. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1970. ix + 328 pp. 16 × 23.5 cm. $19.75.

This book is the sixth volume in the series under the general editorship of Richard L. Carlin which is "devoted to the science of the transition elements and is geared to research scientists, graduate students, and teachers of advanced inorganic chemistry." Volume 6 covers the two topics: (a) Theory of Bridge Bonding and the Structure of Binuclear Coordination Compounds (B. Jezowska-Trzebiatowska and W. Wojciehowski, 58 pages) and (b) Amine Complexes of Chromium(III) (C. S. Garner and D. A. House, 236 pages). Chapter 1 includes discussions of the magnetic properties of bi- and polynuclear complexes, the theory of bridge bonding, which includes both electron-donating and electron-accepting bridges, metal–metal interaction in coordination compounds, infrared spectra of bi- and polynuclear complexes, and the stereochemistry and structure of polynuclear complexes. The 203 references quoted by the authors appear to offer an adequate number of entries into the open chemical literature; unfortunately very few of the references cited are for material published after 1967. However, the authors have listed a few manuscripts as "in press" with the journal where the work is to appear so that the serious worker in the field can find more up-to-date material.

The section concerning the infrared spectra of bridged complexes contains a number of stretching frequencies for the M–O–X system where X is a group IV element as well as S–O–S, Se–O–Se, and X–O–X (X is a group V element). The section on stereochemistry and structure contains the results of a number of structural determinations for several polynuclear coordination compounds.

Chapter 2 is a monumental review which includes the general chemistry, structure, synthesis, kinetics and mechanisms, photochemistry, chemical effects of nuclear radiations, and optical and magnetic properties of chromium(III) complexes which have one or more primary, secondary, or tertiary amine groups as coordinated ligands. The chemical literature has been searched through June of 1969, and the 923 quoted references provide easy access to the open chemical literature. The entire review is well written and the authors have pointed to those synthetic methods which yield the desired product in poor yield as well as areas in which more work needs to be done.

Two sections of the review deserve special mention. The portion which deals with spectra and optical activity will be important to those chemists who are involved in preparative work, and the very complete table of visible absorption maxima and minima is a most welcome addition to the chemical literature.

The section on kinetics and reaction mechanisms is excellent, and again workers in this field will appreciate the extensive tabulation of data which appears in this section. Topics covered in this section are aquation, base hydrolysis, anation, isomerization, racemization, redox, reactions in nonaqueous or mixed solvents, reactions of polynuclear complexes, isotopic exchange, and tracer chemistry.

The diagrams which relate the rate constants for a number of aquation and isomerization reactions can be confusing at times because of the large amount of information contained in these drawings.

The entire book is printed on a good grade of paper and is relatively free of typographical errors. Volume 6 is a good but high-priced addition to the series.

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