Acknowledgment. We wish to thank Larry Sklar for his skillful help in the synthesis and purification of some of the porphyrins described in the paper. This work was supported by grants from the National Institutes of Health and National Science Foundation.

(15) Note Added in Proof. It has been brought to our attention that the structure of the O-(Fe-TPP)$_2$ dimer has been independently determined by X-ray diffraction at Cornell University by A. B. Hoffman, D. M. Collins, V. M. Day, and J. L. Hoard. Their results are in agreement with ours; a future joint publication will result employing their more accurate and extensive data (3500 reflections with Mo Kα radiation).

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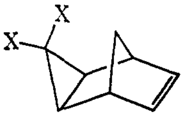
The Reaction of *exo*-Tricyclo[3.2.1.0^{2,4}]octene with Rhodium Catalysts

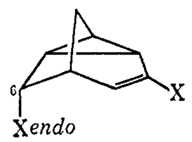
Sir:

Noble metal catalysts, which effect the hydrogenation and isomerization of olefins and cyclopropanes, in the absence of hydrogen effect other reactions. We have been studying such reactions and report below on the action of some rhodium catalysts on *exo*-tricyclo[3.2.1.0^{2,4}]octene (Ia).[1] Others have recently found that some transition metals catalyze valence tautomerizations,[2] and this catalysis has been attributed without evidence to molecular orbital symmetries, the assumption being that the reactions are concerted electrocyclic processes.[2,3] But the experiments described below show that this assumption may be false: at least in the case reported here products and intermediates are formed that have no place in the previous mechanistic scheme and must be accounted for in a different way.

When Ia is warmed (90°, 2 hr) with 1.3 mol % tris(triphenylphosphine)rhodium(I) chloride[4] it is quantitatively converted into a mixture[5] consisting of 62% IIa,[6] 32% III,[7] and 6% IV;[8] with 5% rhodium on carbon (130°, 2 days) a similar mixture forms (25% IIa, 55% III, 20% IV) plus a dimerization product consisting mainly of a substance that will be described separately, mp 131–132°, isolated in *ca.* 15% yield, and assigned structure V.[9] In the absence of the catalysts no reactions occur.

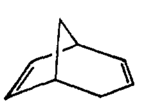


Ia, X = H
b, X = D

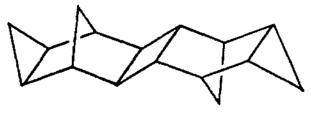


II

III



IV



V

Although III is formally related to I by an electrocyclic reaction, II is not. Nevertheless, with tris(triphenylphosphine)rhodium chloride the rearrangement of I to both II and III is intramolecular, and the conversion of Ib to IIb is stereospecific.

The evidence for the stereospecificity of the rearrangement is that the nmr spectrum of IIb formed from Ib (93.8% d_2, 5.4% d_1, 0.8% d_0)[1a,10] is similar to that of IIa except that the resonance of the 6-*endo* proton, which in IIa appears as a doublet (J = 11 Hz) at τ 9.31 of intensity 2,[6c,8b,11] appears as a doublet of exactly half the intensity (calcd 1.035; found 1.04),[12] and that the resonance of the olefinic protons, which in IIa appears as a triplet of peaks of relative intensity 2 separated by 7.2 Hz at τ 4.18, is replaced by a doublet of peaks of intensity 1.01 (calcd 1.035) separated by 4 Hz.[13]

The evidence that the rearrangement of I to II and III is intramolecular is that, as shown in Table I, the reaction of a mixture of unlabeled and doubly labeled I (Ia plus Ib) gave only unlabeled and doubly labeled II and III.[14]

Table I. Deuterium Distribution in Starting Material I and Products II and III[a]

	I, %	II, %	III, %
d_0	41	57	30
d_1	3	3	4
d_2	55	40	66
d_3			0.3

[a] The latter after 1 hr at 60° in the presence of 1.2 mol % tris(triphenylphosphine)rhodium chloride (16% reaction).

The implication of the facts described above is that the catalyst, [(C$_6$H$_5$)$_3$P]$_3$RhCl, reacts with I to give either

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(1) (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); (b) W. von E. Doering and W. Grimme, quoted in K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965), footnote 10; (c) K. Tori and M. Ohtsuru, *Chem. Commun.*, 886 (1966).

(2) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967); *Chem. Commun.*, 1133 (1967); H. C. Volger and H. Hogeveen, *Rec. Trav. Chim.*, **86**, 830 (1967); H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Am. Chem. Soc.*, **91**, 218 (1969); W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967).

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

(4) (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966); (b) M. A. Bennett and P.A. Longstaff, *Chem. Ind.* (London), 846 (1965).

(5) Each component is unchanged when similarly treated.

(6) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963); (c) R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968).

(7) (a) N. A. LeBel and R. N. Liesemer, *J. Am. Chem. Soc.*, **87**, 4301 (1965); (b) P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Lett.*, 3301 (1965).

(8) (a) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc., B*, 411 (1968); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (c) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Am. Chem. Soc.*, **89**, 3656 (1967); (d) C. Cupas, W. E. Watts, and P. von R. Schleyer, *Tetrahedron Lett.*, 2503 (1964).

(9) Related structures: T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, 32, 1301 (1967).

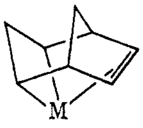
(10) CD$_2$I$_2$: S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, **8**, **Part II**, 621 (1966).

(11) C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Lett.*, 1185 (1966).

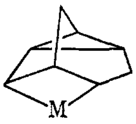
(12) Because the peak at τ 9.31 is a doublet, none of the product in which the positions of the hydrogen and deuterium at C-6 are interchanged can be significantly present.

(13) Whether one specifically labeled isomer IV is (like III) formed from Ib has not yet been determined, initial experiments having been thwarted because a minor side product of the Simmons–Smith reaction of norbornadiene[1a] seems to be IV!

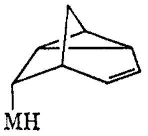
(14) With rhodium on carbon as catalyst, there was considerable intramolecular scrambling.



VI



VII



VIII

VI or VII,[15] or both (here M is $RhCl[(C_6H_5)_3P]_n$), that these give VIII,[16] and that VIII is converted into II.[17] This mechanism also accounts for the formation of III[18,19] if VII extrudes $[(C_6H_5)_3P]_nRhCl$;[4,20] the alternative, that III is formed from I independently of II and IV by a metal-catalyzed concerted electrocyclic reaction,[2,3] is not required by any of the data.

Acknowledgment. We are grateful to the National Science Foundation (NSF-GP7809) for its support.

[15] Metal insertion into cyclopropanes: (a) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Commun.*, 396 (1966); (b) D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *J. Chem. Soc.*, 738 (1961); (c) D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *ibid.*, *A*, 845 (1968).

[16] Transition metal hydrides: (a) A. P. Ginsburg, *Transition Metal Chem.*, **1**, 112 (1965); (b) M. L. H. Green and K. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965).

[17] Insertion into metal-hydrogen bonds: (a) G. W. Parshall, *J. Am. Chem. Soc.*, **90**, 1669 (1968); (b) W. H. Knoth, *ibid.*, **90**, 7172 (1968); (c) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965); (d) G. Hata, H. Kondo, and A. Miyake, *J. Am. Chem. Soc.*, **90**, 2278 (1968).

[18] It also can reasonably account for the observation that the kinetic deuterium isotope effects for the formation of II and III are in the ratio 2.4:1.

[19] The nmr spectrum (two multiplets at τ 8.33 and 8.75 in the intensity ratio 4.07:4.00) of the III formed from Ib is also consistent with the mechanism.

[20] (a) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1054 (1968); (b) D. R. Eaton and S. R. Suart, *J. Am. Chem. Soc.*, **90**, 4170 (1968).

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Free-Radical Chemistry and Photochemistry of Organophosphorus Intermediates. VII. Intermediacy and Configuration of Phosphoranyl Radicals in the Reaction of Labeled *t*-Butoxy Radical with Tri-*t*-butyl Phosphite

Sir:

The oxidation of trivalent phosphorus compounds, such as phosphines and phosphites, by alkoxy radicals has been shown to produce the product of oxygen transfer from the alkoxy radical to phosphorus.[1] Several

$$R_3P + R'O\cdot \longrightarrow \underset{A}{[R_3\dot{P}OR']} \longrightarrow R_3PO + R'\cdot$$

questions may be asked regarding the oxygen-transfer process. (1) Does the species A exist as a discrete intermediate, or is it simply the transition state for oxygen transfer? (2) If A is a discrete intermediate, is its formation reversible? (3) Again, if A is a discrete intermediate, what is its structure and lifetime? Although phosphoranyl radicals, such as A, are commonly proposed as possible intermediates in reactions of radicals with trivalent phosphorus, little or no information relating to these questions is available from past work.[1e] To help answer these questions, we have allowed di-*t*-butyl-2-^{14}C hyponitrite[2] to decompose completely at 65° in the presence of tri-*t*-butyl phosphite[4] (>95% pure) in deoxygenated benzene. The phosphate was produced almost quantitatively and was purified by multiple recrystallizations from hexane.

$$(C^*H_3)_3CON{=}NOC(C^*H_3)_3 \xrightarrow[\Delta]{} t\text{-Bu}^*O\cdot$$

$$t\text{-Bu}^*O\cdot + (t\text{-BuO})_3P \longrightarrow \underset{I}{[(t\text{-BuO})_4P\cdot]^*}$$

$$I \longrightarrow \underset{II}{[(t\text{-BuO})_3PO]^*} + (t\text{-Bu}\cdot)^*$$

As shown in Table I (expt 1–3), approximately 75% of the product phosphate is ^{14}C labeled. Controls (expt 4 and 5) showed that the label is not significantly incorporated into the unreacted phosphite or into the product phosphate after its formation.

Table I. Carbon-14 Product Labeling from the Decomposition of Labeled Di-*t*-butyl Hyponitrite in the Presence of Tri-*t*-butyl Phosphite[a]

Expt	[Phosphite][b]	[Hyponitrite][b]	*f*,[c] phosphate act.
1	0.35	0.37	0.76
2	0.45	0.45	0.73
3	0.40	0.05	0.75
4	0.18[d]	0.098	0.017[d]
5	0.40	0.05	0.003[e]

[a] In deoxygenated benzene at 65°. [b] Moles/liter. [c] Fraction of labeled product. The $(^{14}CH_3)_3COH$ used to produce the hyponitrite was employed as the standard of activity: *f* = [disintegrations/(min mmol of phosphate)]/[disintegrations/(min mmol of labeled *t*-butyl alcohol)]. [d] Decomposition of labeled hyponitrite in the presence of unlabeled phosphate. [e] Unreacted phosphite recovered as the thiophosphate.

These results suggest and are consistent with the essentially irreversible formation of a phosphoranyl radical *intermediate*, I, in a manner which allows a statistical scrambling of label. This could result either because the alkoxy groups are configurationally equivalent (as in III or a square-pyramidal intermediate) or because the intermediate, though unsymmetrical, *e.g.*, IV, has a lifetime sufficient to allow equilibration of configurationally nonequivalent groups by some process such as pseudorotation.[5,6] Alternatively, the groups in an asymmetric intermediate like IV might be reactionally equivalent.

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[1] (a) C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, **86**, 2262 (1964), and references to earlier work contained therein; (b) S. A. Buckler, *ibid.*, **84**, 3093 (1962); (c) J. B. Plumb, R. Obrycki, and C. E. Griffin, *J. Org. Chem.*, 31, 2455 (1966); (d) W. G. Bentrude, *Tetrahedron Lett.*, 3543 (1965); (e) J. I. G. Cadogan, *Advan. Free-Radical Chem.*, 3, 220 (1967).

[2] The labeled hyponitrite was prepared from labeled *t*-butyl chloride using the method of Kiefer and Traylor.[3] Labeled *t*-butyl-2-^{14}C chloride was prepared from $(^{14}CH_3)_3COH$ (New England Nuclear).

[3] H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 6163 (1966).

[4] V. Mark and J. R. Van Wazer, *J. Org. Chem.* 29, 1006 (1964).

[5] Esr studies have suggested that $\cdot PCl_4$ exists in a bipyramidal configuration at low temperature[7] and that the configuration of $\cdot PF_4$[8] approaches a bipyramidal configuration at low temperature while at room temperature rapid inversion (pseudorotationlike) allows equilibration of the fluorines to occur. Esr studies also suggest[7] that substitution of halogen for alkyl groups changes the configuration of substituents about phosphorus.

[6] We have been unable to write any kind of reasonable random attack mechanism whereby the labeling results might be accommodated by a simple displacement or a rigid asymmetric intermediate.

[7] G. F. Kokoszka and F. E. Brinckman, *Chem. Commun.*, 349 (1968).

[8] P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964).