Smith) to the cyclopropyl ether **16** which hydrolytically rearranges in high yield to the spirocyclobutanone **17**, a system which has already been shown to be amenable to further transformations.[17]

Metalation of monosubstituted enol ethers is also possible. Thus the cis and trans mixture of methylpropenyl ether **18**, with *tert*-butyllithium in the presence of tetramethylethylenediamine (1 equiv) followed by benzaldehyde gave, after hydrolysis, ketol **19** (55% isolated).[18] The crotonyl anion equivalent **20** was obtained by metalation (conditions as for MVL) of 1-methoxy-1,3-butadiene which after reaction with benzaldehyde and hydrolysis provided ketol **21** (30% recrystallized).

In summary, metalated enol ethers are versatile and efficient acyl anion equivalents which provide simple routes to some otherwise difficulty accessible functionalities.

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(17) See B. M. Trost, *Accounts Chem. Res.*, **7**, 85 (1974), and references cited therein.
(18) We have not yet been able to successfully α-metalate β,β-disubstituted enol ethers.

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The Effect of Oxygen on Rhodium-Catalyzed Ring Openings of Bicycloalkenes[1]

Sir:

There is considerable current interest in the metal-catalyzed valence isomerization and ring opening of strained cyclic hydrocarbons. Attention in most of these systems has been directed to the detailed mechanisms involved, including the nature of the active catalytic species and whether the processes are stepwise or concerted.[2-6] During the course of our studies of metal complex catalyzed rearrangements of the 6-substituted bicyclo[3.1.0]hex-2-enes of the general formula I,[7] we have discovered a dramatic effect of oxygen on the reaction rates. Our results unequivocally demonstrate the necessity of O_2 for efficient ring opening when the catalyst employed is $(PPh_3)_3RhCl$ or $(PPh_3)_2Rh(CO)Cl$. Reported herein are the preliminary results of this study.

(1) Presented in part at the Eighth Great Lakes Regional Meeting of the American Chemical Society, West Lafayette, Ind., June 3–5, 1974, Abstract No. 114.
(2) Pertinent reviews include: (a) F. D. Mango and J. H. Schachtschneider in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971; (b) J. Halpern, "Collected Accounts of Transition Metal Chemistry," Vol. 1, F. Basolo, J. F. Bunnett, and J. Halpern, Ed., American Chemical Society, Washington, D. C., 1973; (c) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).
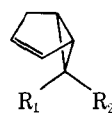(3) P. G. Gassmann and R. R. Reitz, *J. Amer. Chem. Soc.*, **95**, 3057 (1973).
(4) G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, **95**, 4456 (1973).
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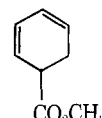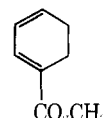(7) D. L. Garin and K. O. Henderson, *Tetrahedron Lett.*, 2009 (1970).

Ia, $R_1 = CO_2CH_3$; $R_2 = H$
b, $R_1 = H$; $R_2 = CO_2CH_3$
c, $R_1 = CO_2CH_3$; $R_2 = CH_3$
d, $R_1 = CH_3$; $R_2 = CO_2CH_3$

II — CO_2CH_3
III — CO_2CH_3

All reactions were performed in nmr tubes for the purpose of monitoring reaction progress by proton nmr spectroscopy.[8] Typically, 1.0 mmol of the organic substrate and 0.1 mmol of rhodium catalyst were dissolved in 1.0 ml of $CHCl_3$, and the solution was charged to an nmr tube which was subsequently capped and stored in the dark at room temperature. Spectra were recorded at appropriate intervals. In all cases the reported reactions were catalytic.

The system we have studied most intensively to date is the endo ester Ia. Regardless of the rhodium catalyst employed, the major products (95% yield) are the conjugated cyclohexadienes II and III. Both major products were isolated in pure form by preparative vpc (6 ft × $^1/_4$ in. Carbowax on Chromasorb W) and characterized by mass spectrometry, uv, and proton nmr spectroscopy.[9] Compounds II and III were obtained in an approximately 40:60 ratio when Ia was completely consumed. Although nmr traces of the reaction mixtures very accurately portray the extent of reaction, other methods are needed to show the presence of small amounts of the other cyclohexadiene products.[9-12] If the reaction is not terminated by quenching with hexane and subsequent removal of the precipitated rhodium catalyst when Ia has completely reacted, a slow conversion ($t_{1/2} \cong 5$ days)[12b] of II to III is observed.

When samples of Ia with $(PPh_3)_3RhCl$ are prepared under inert atmosphere with argon-purged solvent, no ring opening is observed after 48 hr, but the reaction may be initiated by bubbling oxygen through the system for 15–20 sec. Intentional oxidation of a methylene chloride solution of $(PPh_3)_3RhCl$ by the method reported by Bennett and Donaldson[13] affords the O_2-containing complex $[(PPh_3)_2RhCl(O_2)]_2$. This complex was isolated in solid form and placed in an nmr tube equipped with a vacuum fitting and the endo-ester Ia was added. The tube was placed under high vacuum, and chloroform, which had been rigorously degassed on the vacuum line, distilled into the nmr tube, which was sealed under vacuum. Ring opening was found to occur at a rate comparable to that observed when O_2 was bubbled through a chloroform solution of Ia and $(PPh_3)_3RhCl$. This rate is approximately seven times faster than the rate of reaction of Ia with $(PPh_3)_3RhCl$

(8) We have observed catalyst poisoning due to small amounts of acid in several commercial samples of deuteriochloroform. For this reason all experiments were carried out in freshly distilled $CHCl_3$ solvent using tubes which had been washed with dilute sodium bicarbonate.
(9) W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *J. Org. Chem.*, **27**, 1851 (1962).
(10) R. Grewe and I. Hinrichs, *Chem. Ber.*, **97**, 443 (1964).
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(12) (a) Ia and Ib ring-open to give all five possible cyclohexadiene isomers as shown by vpc. Regardless of the extent of reaction, II and III constitute at least 95% of the product mixture. (b) Values of $t_{1/2}$ represent time required for conversion of 50% of starting material, based on nmr integrations.
(13) (a) M. J. Bennett and P. B. Donaldson, *J. Amer. Chem. Soc.*, **93**, 3307 (1971); (b) We find that an essentially stoichiometric amount of triphenylphosphine oxide is formed in this reaction.

under conditions of strict air exclusion. Qualitative rates for the conversion of Ia to II and III (approximate $t_{1/2}$ in parentheses) decrease in the order: oxidized $(Ph_3P)_3RhCl$ (2 days) > oxidized $(PPh_3)_2Rh(CO)Cl$ (5 days) > $(PPh_3)_3RhCl$ (14 days) > $(PPh_3)_2Rh(CO)Cl$ (30 days).[12b]

One possible explanation of this oxygen effect is that $[(PPh_3)_2RhCl]_2$ is formed by oxidation of one of the Ph_3P ligands of $(PPh_3)_3RhCl$ to triphenylphosphine oxide[13b] with the dimeric complex being catalytically active. This has been ruled out by synthesis of $[(PPh_3)_2-RhCl]_2$[14] and demonstrating that it is unreactive toward Ia (in $CHCl_3$ solution) over a period of 72 hr. Upon bubbling O_2 through the solution, ring opening to give II and III was initiated, with $t_{1/2} < 48$ hr.

It would thus appear that the O_2-containing complex is the actual catalyst precursor. The report that $(PPh_3)_2Rh(CO)Cl$ also forms an O_2 complex[15] suggests that the mode of activation may be similar to that of the trisphosphine complex. We wish to emphasize that the actual catalytic species in these systems is very much in doubt and we make no claims that the O_2 complexes are in themselves catalytically active—only that they more accurately describe the catalyst precursors. Our results demonstrate that great caution should be exercised in interpreting results based on these and related catalyst systems unless the "O_2-history" of the catalyst is well-defined.[16]

The nature and stereochemistry of the substituents at C_6 exert considerable influence on the rate of the ring opening process. Using the oxidized $(PPh_3)_3RhCl$ catalyst, Ib opens very slowly $(t_{1/2} \cong 9$ days)[12b] to give III in 95% yield, while Ic is converted rapidly $(t_{1/2} \cong 12$ hr)[12b] to 5-methyl-5-carbomethoxy-1,3-cyclohexadiene.[19,20] Under identical conditions Id is recovered unchanged after 10–12 days. The reasons for these rate differences are not obvious, apparently reflecting a delicate balance of steric and electronic influences on the tendency of the C_1—C_5 σ bond to open in the presence of the catalyst.

In view of the uncertainty of the catalytically active species, mechanistic speculation at this time would seem premature. However, a rhodium–olefin interaction appears to be an important part of the ring-opening process since the dihydro derivatives of Ia and Ic are completely unreactive even at 55–60° over periods of several weeks.

Further studies designed to elucidate the nature of the active catalysts and influences of ring size and nature and stereochemistry of substituents on these reactions are in progress.

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An External Heavy Atom Effect on Excited State Quenching and Exciplex Decay

Sir:

Photoisomerization of olefins related to stilbene has been the subject of extensive investigation.[1] In various compounds both singlets and triplets can isomerize,[1-4] and in several cases induced olefin photoisomerization has proved to be a useful mechanistic probe in determining excited state decay channels.[5-8] An area of interest to both photochemists and spectroscopists has been the induction of singlet–triplet intersystem crossing by external and internal heavy atoms.[9-11] It has recently been shown that the stilbene system can be strongly perturbed by internal halogen atoms.[1,3,12,13] In the present paper we report an investigation of the external heavy atom effect in some stilbene-like olefins using cis–trans isomerization as a probe.

The stilbene-like olefins used in the present study are the dimethylfluoroborates of *trans*-1,2-bis(3-pyridyl)-ethylene (**1**) and *trans*-1,2-bis(4-pyridyl)ethylene (**2**). The possibility for investigating induced intersystem crossing pathways was suggested by the finding of contrasting photochemistry for these compounds in the presence and absence of oxygen. Irradiation of degassed acetonitrile solutions of **2** led to no isomerization, and only a small amount ($\phi \ll 0.01$) of as yet unidentified product (possibly an adduct) could be detected. In contrast an air equilibrated solution showed very rapid ($\phi \sim 0.4$) isomerization of **2** to the cis isomer with subsequent cyclization to the phenanthrene derivative at a slightly slower rate. Similar results were obtained with **1** although a small amount of trans → cis isomerization ($\phi = 0.13$) occurred even in degassed solutions.

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(15) C. T. Mortimer and S. J. Ashcroft, *Inorg. Chem.*, **10**, 1326 (1971).
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(20) The oxygen effect is also dramatic for this system. Argon-purged solutions of Ic and $(PPh_3)_3RhCl$ exhibit $t_{1/2} \cong 5$ days.

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