(DMF). This correlation is not only compatible with the first step in the mechanistic scheme suggested, but offers the ability *to predict* both when the conjugate additions will be successful and when reduction of the C=C double bond will be a serious competing reaction. Specifically, all of the unsaturated carbonyl compounds studied that will accept an electron at potentials less negative than -2.4 V *vs.* sce react with lithium dimethylcuprate whereas carbonyl compounds with reduction potentials more negative than -2.4 V *vs.* sce are recovered unchanged. If the unsaturated carbonyl compound (*e.g.*, **7**) is able to accept a second electron at a potential less negative than *ca.* -1.2 V *vs.* sce, then the system is reduced beyond the anion radical stage to form a dianion (*e.g.*, **8**) which is protonated either by reaction with the solvent or during isolation to form a dihydro derivative (*e.g.*, **9**).

$$\underset{\mathbf{7}}{(EtO_2C)_2C{=}C(CO_2Et)_2} + [(CH_3)_2CuLi]_2 \xrightarrow{2e^-}$$

$$\underset{\mathbf{8}}{2Li^+(EtO_2C)_2\bar{C}{-}\bar{C}(CO_2Et)_2} + [CH_3Cu(I)]_n \xrightarrow{H_3O^+}$$

$$\underset{\mathbf{9}}{(EtO_2C)_2CHCH(CO_2Et)_2}$$

It is apparent that a number of previous observations[2,5] concerning organocopper(I) derivatives are qualitatively explained by the reaction scheme presented. Notable among these are the failure of methylcopper(I) derivatives to react with simple enones unless a negatively-charged ligand (*e.g.*, I^- or CH_3^-) is bound to the metal cluster and the loss of reactivity of cuprates LiR_2Cu with enones when R is a group such as allyl, or especially cyano or α-keto alkyl, that can allow electron density to be delocalized from the metal cluster into the R groups. One would expect that the net oxidation potential (and the electron density) of the cuprates would be diminished either by the absence of negatively-charged donor ligands or by the presence of R groups capable of delocalizing the electron density of the metal cluster. We hope to obtain a quantitative measure of these effects with cuprate oxidation potential measurements which are in progress. Such data should permit predictions concerning the success of conjugate addition reactions with a variety of dialkyl-, diaryl-, and other cuprates.

[6] This work is part of the Ph.D. thesis of M. J. Umen done *in absentia* from the Department of Chemistry, Massachusetts Institute of Technology.

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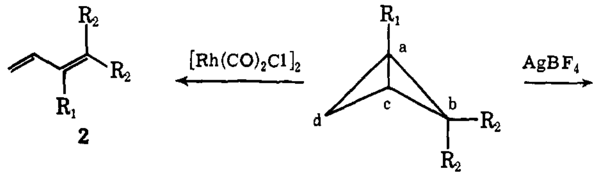
Solvent Determined Mechanisms in the Transition Metal Complex Promoted Rearrangement of Bicyclo[1.1.0]butanes[1]

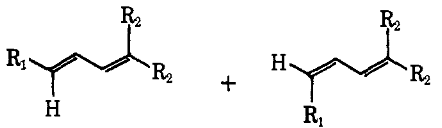
Sir:

Recently, it has been demonstrated that a change of solvent can result in significant changes in the ratio of products formed in transition metal complex promoted rearrangements of highly strained polycyclic molecules.[2,3] We now wish to report that the solvent can play a much more overwhelming role in these rearrangements than was previously anticipated.[4] In fact, a complete change of mechanism and (consequently) of products can result from a change of solvent.

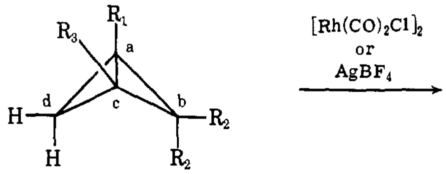
When either **1a** or **1b** was treated with rhodium dicarbonyl chloride dimer in nonprotic solvent, the only diene formed in the reaction was **2**.[5] It was demonstrated that **2** was derived *via* cleavage of the a–c and b–c bonds of **1**. In contrast, the presence of silver fluoroborate in nonprotic solvent promoted the formation of **3** and **4** from **1** *via* cleavage of the a–b and a–c bonds of **1**.[5,6] Changing from the nonprotic solvent, chloroform, to the protic solvent, methanol, resulted in a complete change in the mechanism and the products associated with the silver ion promoted reactions of **1**. When **1a** was treated with rhodium dicarbonyl chloride dimer[4] or silver fluoroborate[7] in methanol at 30°, **5a** was ob-



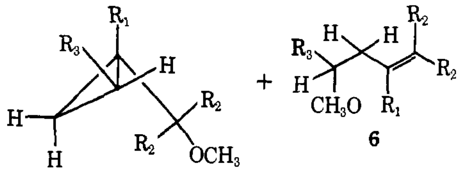
1a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = C_6H_5$



3 **4**



1a, $R_1 = R_2 = CH_3$; $R_3 = H$
1b, $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = H$
1c, $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$



5 **6**

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[1] Paper XXIX in a series on The Chemistry of Bent Bonds. For the previous paper in this series, see P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **94**, 2877 (1972).

[2] P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 4597 (1971).

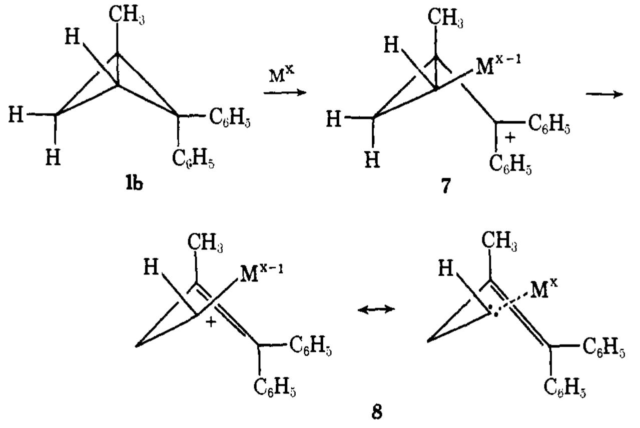
[3] W. G. Dauben and A. J. Kielbania, Jr., *ibid.*, **93**, 7345 (1971).

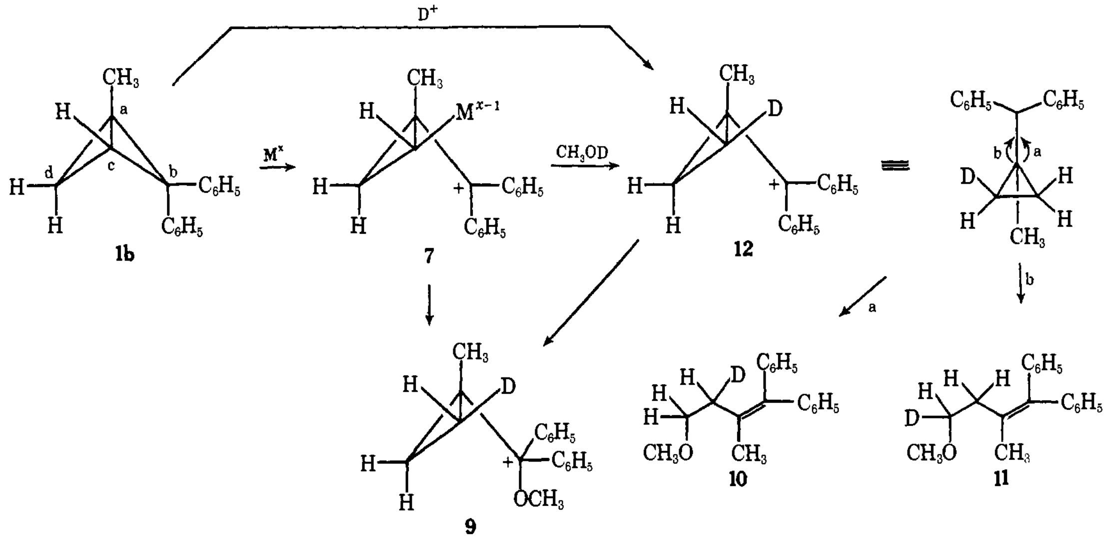
[4] We have previously cautioned that some of the results reported for the transition metal complex promoted rearrangement of highly strained ring systems could be due to the influence of solvent. This report indicates that the effect of solvent can be even more dramatic than was previously suggested: P. G. Gassman and F. J. Williams, *J. Chem. Soc., Chem. Commun.*, 80 (1972).

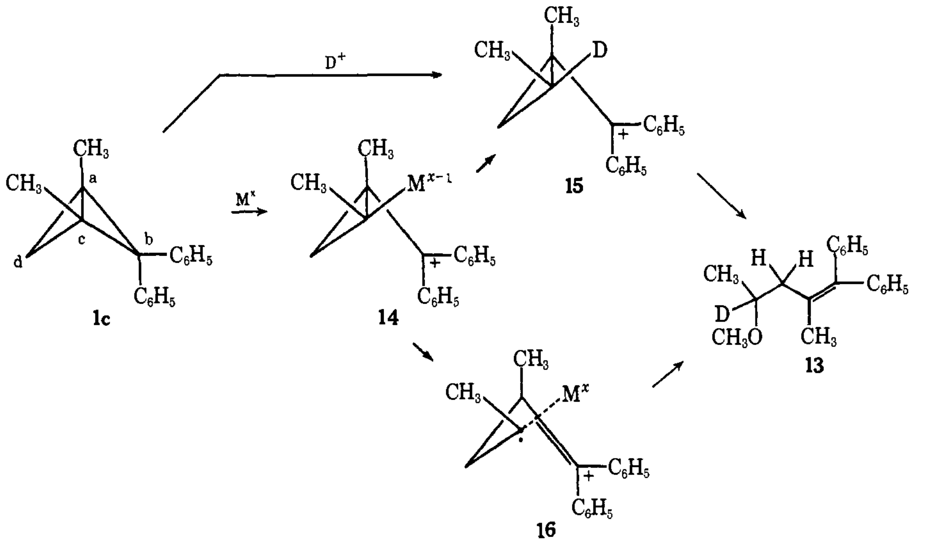
[5] P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, **93**, 5897 (1971); P. G. Gassman and F. J. Williams, *ibid.*, **92**, 7631 (1970).

[6] L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

[7] F. J. Williams, unpublished work. The reaction of **1a** with silver fluoroborate to give only **5** has also been observed in the laboratories of Professor S. Masamune. We wish to thank Professor Masamune for informing us of his results prior to publication.







tained as the only product in 97 and 95% yields, respectively. Similar treatment of **1b** with rhodium dicarbonyl chloride gave 61% **5b** and 33% **6b**. The effect of silver fluoroborate paralleled that of the rhodium complex in that **1b** gave 40% **5b** and 52% **6b**. Finally, the addition of *ca.* 4 mol % of either rhodium dicarbonyl chloride dimer or silver fluoroborate to a methanol solution of **1c** promoted rapid conversion of **1c** to **6c** in 92 and 90% yields, respectively.

These results show that, in methanol, the presence of silver ion promotes the cleavage of the same bonds as are cleaved with rhodium dicarbonyl chloride dimer. Thus, the presence of methanol results in a complete change in the bond which is initially cleaved in the silver ion promoted reaction. Furthermore, **1a** gave only cyclopropylcarbinyl ether, **1b** gave a mixture of cyclopropylcarbinyl ether and homoallylic ether, while **1c** gave only homoallylic ether. This change in products with substitution is consistent with what might be expected on the basis of known[8] carbonium ion theory. As Carey and Tremper have shown for the hydride capture of cyclopropylcarbinyl cations,[8] the presence of phenyl groups on the cyclopropylcarbinyl carbon leads to increased amounts of homoallylic products. The results of Pearson and Langer[9] would support the contention that the cyclopropylcarbinyl product is the kinetic product, while the homoallylic product is the thermodynamically more stable.[10] It is not completely clear whether the greater amount of opening to homoallylic product in the phenyl-substituted cases is due to the steric effect of the aryl groups[8] or to an increased

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(8) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, **91**, 2967 (1969).

(9) R. G. Pearson and S. H. Langer, *ibid.*, **75**, 1065 (1953).

(10) We have demonstrated that **5b** is not readily convertible to **6b** under the reaction conditions.

stability (decreased reactivity) of the cyclopropylcarbinyl cation.

In line with the strong supporting evidence for the intermediacy of a metal-bonded carbonium ion[6]–metal-complexed carbene hybrid intermediate[5,11] in the transition metal promoted rearrangement of derivatives of bicyclo[1.1.0]butane in nonprotic solvents, it is tempting to view the formation of **6b** and **6c** as resulting from solvent capture by a carbenoid type resonance hybrid. Such a hybrid would result from a **1b** → **7** → **8** type transformation as shown above. In order to test this concept, we studied the isomerization of **1b** in methanol-*O-d*. If **8** were the precursor of **6b**, the use of methanol-*O-d* would result in the methoxy group and the deuterium residing exclusively at the homoallylic position. In methanol-*O-d*, the addition of either rhodium dicarbonyl chloride dimer or silver fluoroborate resulted in the conversion of **1b** into **9** and an approximately *equimolar mixture of* **10** *and* **11**. The formation of both **10** and **11** required either that protonolysis of the intermediate, **7**, occur prior to the formation of homoallylic product or that **1b** be directly converted to **12** in an acid-catalyzed reaction. Either process would result in the formation of **12**, which can subsequently cleave *via* path a and path b to yield **10** and **11**,[12] respectively. These results indicated that, at least in the case of **1b**, *no metal-bonded carbonium ion-metal-complexed carbene resonance hybrid is formed in protic solvent*, in stark contrast to the formation of such a resonance hybrid in nonprotic solvents. Thus, protic solvents can completely change the mechanism of transition metal complex promoted rearrangements of highly strained ring systems.

We have also found that **1c** reacts readily on addition of small amounts of either rhodium dicarbonyl chloride dimer or silver fluoroborate in methanol-*O-d* to yield **13** as the only product. Current experimental results do not allow us to determine whether **13** is derived *via* the **1c** → **14** → **15** route, *via* the **1c** → **14** → **16** path, or directly through a **1c** → **15** process involving protonation. The question which remains to be answered in this case is whether the added transition metal derivatives are the active reagents or whether these complexes are reacting with solvent to generate protic acid or some other new reagent which promotes the observed reactions. We are continuing to investigate this problem.[13]

Acknowledgment. We are indebted to the National Science Foundation for partial support of this investigation.

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[11] P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971).

[12] The ratio of **10**:**11** was determined by nmr spectroscopy. The approximately equal amounts of **10** and **11** are consistent with secondary α and β deuterium isotope effects being small and approximately the same in carbonium ion reactions: E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 127 (1963).

[13] NOTE ADDED IN PROOF. Subsequent to the acceptance of this communication, it has been suggested that intermediates such as **7** and **14** would not be formed with rhodium complexes, but might be formed with silver(I) in methanol [W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972)]. If this suggestion can be substantiated, two different mechanisms would be implicated for the conversion of **1b** into a mixture of **9**, **10**, and **11** [one for the rhodium(I) complex and one for silver(I)].

[14] The Ohio State University Postdoctoral Fellow, 1970–1971.

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Isomorphous Heteropoly Complexes Containing Various Pairs of Paramagnetic Atoms. Exchange-Coupled Differing Spins with Absence of Long-Range Magnetic Interactions. A New Class of Paramagnetic Behavior. Theoretical Treatment. Novel Geometrical Isomerism

Sir:

In 1966 a large new structural category of heteropoly complexes was fully established:[1,2] the biheteroatom 11-heteropoly anions

$$[(Y^{y-})M^{m+}O_5X^{x+}O_4(W\text{ or }Mo)_{11}O_{30}]^{(12-m-x+y)-}$$

of structure[1,3] shown inFigure 1. That paper[1] also reported then-unexplained unique paramagnetic behavior, for $K_7[(H_2O)Co^{2+}O_5Co^{3+}O_4W_{11}O_{30}]\cdot 12H_2O$, for which the susceptibility changed only 13% between −143 and 23°.

Subsequently, others[4–9] reported many derivatives (various M's and X's) formulated according to this proven[1,2] structure. Only one of those new compounds contained two paramagnetic atoms: $[(H_2O)Ni^{2+}O_5Fe^{3+}O_4W_{11}O_{30}]^{7-}$, similar unexplained antiferromagnetic behavior being noted.[7] In 1970 the original structural interpretation was extended.[3]

The present paper shows that the biheteroatom 11-heteropoly complexes offer a clearly propitious area for study of paramagnetic interactions. *Via* suitable substitutional routes, salts of pure complexes may be made containing a very wide variety of pairs of paramagnetic heteroatoms. Subtle variations may be made by using various Y's or by substituting Mo's for W's. All the complexes are isomorphous, obviating a major obstacle to comparative interaction studies. Long-range magnetic order effects are neither expected nor found. Thus many paramagnetic interactions may be clearly and systematically studied, *e.g.*, for relative *J*'s, in exactly comparable circumstances.

Isomorphous compounds prepared,[10,11] fully analyzed,[10,11] and studied in the present work, some containing complexes which are geometrical isomers of a new and significant sort, were:[12] I, $K_7[(H_2O)Fe^{3+}O_5Co^{2+}O_4W_{11}O_{30}]\cdot 14H_2O$; II, $K_7[(H_2O)Co^{2+}O_5Fe^{3+}O_4W_{11}O_{30}]\cdot 13H_2O$; III, $K_6[(H_2O)Fe^{3+}O_5Co^{3+}O_4W_{11}O_{30}]\cdot 13H_2O$; IV, $K_7[(H_2O)Co^{2+}O_5Co^{3+}O_4W_{11}O_{30}]\cdot 12H_2O$; V, $(NH_4)_8[(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}]\cdot 13H_2O$; VI, $K_6[(H_2O)Co^{3+}O_5Fe^{3+}O_4W_{11}O_{30}]\cdot 18H_2O$. Ligand field spectra [10,11] confirm the coordination geometries,

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[1] L. C. W. Baker, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2329 (1966).

[2] L. C. W. Baker, *Proc. Int. Conf. Coord. Chem., 9th, 1966*, 421 (1966).

[3] L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).

[4] T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).

[5] S. A. Malik and T. J. R. Weakley, *Chem. Commun.*, 1094 (1967); *J. Chem. Soc. A*, 2647 (1968).

[6] R. Ripan and M. Puscasu, *Z. Anorg. Allg. Chem.*, **358**, 83 (1968).

[7] M. Puscasu, D.Sc. Dissertation, Academy of the Socialist Republic of Romania, Institute of Chemistry, Cluj Section, Romania, 1969.

[8] C. Tourné, *C. R. Acad. Sci., Ser. C*, **266**, 702 (1968).

[9] C. Tourné and G. Tourné, *ibid.*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).

[10] V. E. Simmons, Doctoral Dissertation, Boston University, 1963.

[11] S. H. Wasfi, Doctoral Dissertation, Georgetown University, 1971.

[12] In these compounds small differences in the numbers of the zeolytic waters of hydration do not affect the isomorphism, nor do small differences in numbers of simple cations, some of which are in the zeolytic channels.