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Control of Stereochemistry in Potassium Alkoxide Accelerated [1,3] Sigmatropic Rearrangements by the Use of a Crown Ether for the Apparent Destruction of Ion Pairs. Evidence for a Fragmentation Mechanism in a Vinylcyclobutane Rearrangement

M. Bhupathy[1] and Theodore Cohen*

Department of Chemistry, University of Pittsburgh Pittsburgh, Pennsylvania 15260

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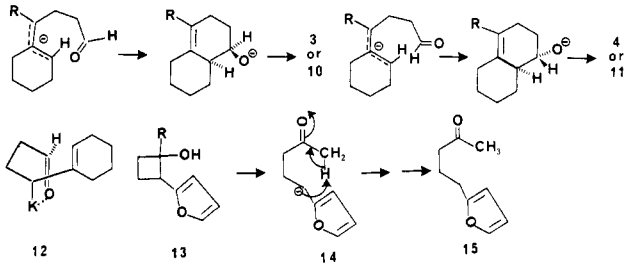
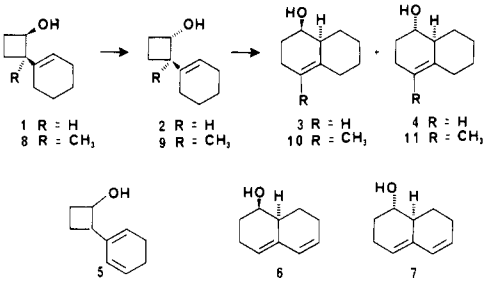
We wish to report that a striking reversal of the stereochemical course of a potassium alkoxide accelerated vinylcyclobutane rearrangement[2-5] can be induced by the use of complexing agents for potassium ion. This novel use of complexing agents has important mechanistic as well as synthetic implications.

When *trans*-2-(1-cyclohexenyl)cyclobutanol (**2**)[6] is treated with potassium hydride in refluxing THF for 2 h, it undergoes a ring expansion in 88% yield to a mixture of *cis*- and *trans*-octalinols[6b] (**3** and **4**, respectively) in a ratio of 70:30. This reaction thus favors

Scheme I



formation of the presumably less stable axial alcohol. When the same alcohol is treated with KH at 25 °C for 15 min in THF containing catalytic or equivalent quantities of 18-crown-6, it is converted in 98% yield to the same octalinols but this time the more stable trans (equatorial) alcohol is by far the major product: ratio of **3** to **4**, 10:90; the products are stable to the reaction conditions. Thus, the addition of a complexing agent for potassium ion not only greatly accelerates the rearrangement but reverses its stereochemical course, *causing the ratio of epimeric products to change by a factor of 21*. The *cis*-cyclobutanol **1** behaves in a similar fashion, but we have found that at lower temperatures (25 °C in the absence of crown ether and −23 °C in its presence) **1** epimerizes to **2**; we[5] and Gadwood[4] had noted similar epimerizations previously.



Earlier,[5] we had noted that the cis and trans isomers of 2-(1,3-cyclohexadien-2-yl)cyclobutanol (**5**) rearrange in KH–THF to yield the cis (axial) alcohol **6** and the trans (equatorial) alcohol **7** in ratios of 72:28 and 92:8, respectively, and we were puzzled by the nearly opposite results reported by Danheiser[3] that both **8** and **9** rearrange to a mixture consisting of a high ratio of **11** to **10**. It now appears very likely that the greatly different steric results of the rearrangement of **5** on the one hand and **8** and **9** on the other are due to the presence in the latter case of the complexing agent for potassium ion hexamethylphosphoric triamide (HMPT). We have now repeated the rearrangement of **8** and **9**[3,6,7] but in the absence of HMPT and we find that both isomers rearrange far more slowly, that the product mixture is richer in the less stable cis alcohol **10**, and that the (*Z*)-cyclobutanol **8**, like **1**, isomerizes to its epimer (**9**). After 4 days at 25 °C, **8** provides 63% of **9** and small amounts of **10** and **11**. **9**, which is stable under these conditions, gives 43% of **10** and 29% of **11** after being heated at reflux for 5.5 h in THF–KH. As expected, 18-crown-6 greatly accelerates both the epimerization and ring expansion, and it reverses the stereochemical outcome of the latter, leading to a 3:97 ratio of **10** to **11** from the (*E*)-cyclobutanol **9**, *a 47-fold change in product ratio* (the *Z* alcohol **8** also gives mainly **11**, presumably via **9**); the products do not epimerize under these conditions. The stereochemical outcome is similar with HMPT and crown ether but the latter has a greater accelerating effect.

It is extremely difficult to explain our stereochemical results by a concerted [1,3] rearrangement. On the other hand both the ring expansion and epimerizations are completely consistent with a fragmentation to an aldehyde allylic anion that can recombine to a 4- or a 6-member ring.[8,9] The sharply different results in the presence and absence of complexing agents for potassium ion strongly suggest that this ion plays a key role in determining the stereochemistry of the ring expansion reaction in the absence of a complexing agent. This role is readily rationalized when it is realized that the formation of the axial alcohols requires that the oxygen atom be pointing toward the allylic anion as the carbonyl group and anion approach each other (Scheme I). The attractive interaction between the two groups, to which we alluded earlier,[5] thus appears to be chelation with a potassium ion; **12** represents a reasonable structure for the intermediate in the absence of complexing agents, but the exact juxtaposition of the potassium and allylic ions is, of course, uncertain.[10] When the potassium ion is complexed instead with external agents, the two groups must approach each other with the oxygen atom pointing away from the allylic anion, a consequence of steric and charge repulsions;

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(6) (a) The cyclobutanols were prepared and characterized as in the previous report.[5] (b) All new compounds have been characterized by IR and NMR spectroscopy and by mass spectrometry, including the determination of their exact masses.
(7) Danheiser's assignment of stereochemistry to **8** and **9** was confirmed by the use of Eu(tfc)$_3$ chemical shift reagent. The changes in δ per mol of Eu were 7.23 and 2.79 respectively for the vinyl protons of the *Z* (**8**) and *E* (**9**) isomers.
(8) Gadwood and Lett[4] have also invoked such a fragmentation mechanism and have referenced literature precedents for ionic fragmentation of metal salts of homoallylic alcohols. A diradical cleavage is calculated to be far less favorable: Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3315, 3319.
(9) The formation of a ketone and an allylic anion has recently been suggested as the mechanism of fragmentation of the potassium salt of a doubly homoallylic anion: Snowden, R. L.; Muller, B. L.; Schulte-Elte, K. H. *Tetrahedron Lett.* **1982**, *23*, 335.
(10) The structure of an allyl anion with a potassium counterion is believed to be a contact ion pair: Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674.

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such an orientation leads to the equatorial alcohol (Scheme I). Such intermediates also neatly explain the isomerizations from *cis*- to *trans*-2-vinylcyclobutanols observed here as well as in related systems in our earlier report and in the example reported by Gadwood.[4] The same hypothesis readily explains why **13** (R = H) undergoes the [1,3] shift to a ring-expanded product whereas **13** (R = CH_3) undergoes ring opening to **15**;[5] the intermediate anion ketone **14** can easily undergo a 1,5-proton transfer to yield the enolate precursor of **15**. This may also be the explanation for the sharply reduced yields of ring-expansion product noted by Danheiser when an alkyl group was present on the carbinol carbon atom of the cyclobutanol.[3]

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Anion-Assisted Transfer of a Sterically Constrained Proton: Molecular Structure of $HMo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2^+ AlCl_4^-$

John M. Hanckel and Marcetta Y. Darensbourg*

Department of Chemistry, Texas A&M University College Station, Texas 77843

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The understanding of heterolytic activation of dihydrogen by transition-metal catalysts requires knowledge of M–H^+ as well as M–H^- bond reactivity. Two recent physical organometallic studies have provided fundamentally important thermodynamic and kinetic stability measurements of the deprotonation of structurally simple neutral metal carbonyl hydrides.[1,2] Jordan and Norton noted that "...knowledge of proton-transfer rates in straightforward cases should help identify less obvious proton-transfer mechanisms."[1] Accordingly reported herein is our study of $HMo(CO)_2(Ph_2P(CH_2)_2PPh_2)_2^+$ (**1H**$^+$),[3,4] which notes unusual and significant counterion influences on proton-transfer reaction rates and equilibrium positions.

Although tetrahydrofuran solutions of **1H**$^+$ BF_4^- were observed to be stable for several days at room temperature, the $AlCl_4^-$ salt deprotonated significantly in less than 24 h, producing *cis*-$Mo(CO)_2(DPPE)_2$ (*cis*-**1**). Since chloride is known to be readily displaced from $AlCl_4^-$ (and even $AlCl_3$) by THF[5] but BF_4^- is stable even in water, the role of chloride anion in the deprotonation of **1H**$^+$ was implicated. The following study was designed to define the system.

Reactions of **1H**$^+$ BF_4^- with a variety of different bases and base mixtures (eq 1) in CH_2Cl_2 were monitored to equilibrium by

$$HMo(CO)_2(DPPE)_2^+ BF_4^- + \text{base} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo(CO)_2(DPPE)_2 + \text{base}{\cdot}H^+ BF_4^- \quad (1)$$

FT-IR.[7] The data in Table I infer a qualitative and typical ordering of base strengths: $F^- \sim OAc^- > NEt_3 > NHEt_2 >$ py $> Cl^- > I^-$.

Table I. Deprotonation Reactions of $[HMo(CO)_2(DPPE)_2^+]$ BF_4^- (0.0040 M in CH_2Cl_2 Solution): Equilibrium Positions

base	equiv	% deprotonation at equilibrium (time)
pyridine	25	45 (5 d)
$NHEt_2$	25	75 (10 d)
NEt_3	25	100 (3 d)
PPN^+Cl^-	25	20 (4–6 h)
PPN^+OAc^-	10	100 (4–6 h)
PPN^+OAc^-	2	95 (18 h)
PPN^+I^-	25	10 (4–6 h)
PPN^+F^-	10	100 (1 h)
PPN^+I^-	2	95 (18 h)

Whereas the equilibrium data of Table I provided no surprises, the rates of reaching equilibrium did not correlate with thermodynamic base strengths. The rate of reaction 1 using pyridine as base showed a first-order dependence both on [**1H**$^+$] and on [py] (Table II). Addition of $PPN^+ Cl^-$ to the reaction of **1H**$^+$ and pyridine resulted in 100% deprotonation and a rate enhancement of ca. 10^2. As noted in Table II, the pseudo-first-order rate constants of chloride/pyridine mixtures were linearly dependent on [Cl^-] but *independent* of [py] or of the amine itself (i.e., NEt_3, entry 9). Thus the sole function of the amine is to serve as a thermodynamic trap for HCl.

Deprotonation rates in the presence of other anionic additives (Table II) vary in the order $F^- > Cl^- > OAc^- > I^-$. The reactivity order for the halides compares favorably with their order to thermodynamic base strengths. However pyridine and acetate are both stronger bases than Cl^- but in reaction 1 are kinetically less reactive. Consistent with this apparent dependence of kinetic reactivity on the size of the deprotonating agent 2,6-lutidene does not react with **1H**$^+$ BF_4^- over a period of days.

An equally impressive counterion effect was observed for the rate of proton exchange between **1** and ^{13}CO-labeled **1H**$^+$ (eq 2).[9]

$$\underset{^{13}\mathbf{1H}^+}{HMo(^{13}CO)_2(DPPE)_2^+ BF_4^-} + \underset{^{12}\mathbf{1}}{Mo(^{12}CO)_2(DPPE)_2} \overset{CH_2Cl_2}{\rightleftharpoons} \underset{^{12}\mathbf{1H}^+}{HMo(^{12}CO)_2(DPPE)_2^+ BF_4^-} + \underset{^{13}\mathbf{1}}{Mo(^{13}CO)_2(DPPE)_2} \quad (2)$$

In the absence of any additives reaction 2 failed to produce any exchange products within 24 h; however addition of 0.5 equiv of $PPN^+ Cl^-$ produced the expected statistical ratio of $^{13}\mathbf{1}/^{12}\mathbf{1}$ within 6 h. There was no intermolecular CO exchange within 24 h. Few examples of such slow rates of proton-exchange reactions have been reported. At least one example is provided in J.-M. Lehn's cryptand chemistry, but it is an example of a protonated site severely constrained both electronically and sterically in the interior of a large cryptand.[10]

The implication of steric constraints on deprotonation is substantiated by the molecular structure of $HMo(CO)_2(DPPE)_2^+$-$AlCl_4^-$ as determined by single-crystal X-ray diffraction analysis.[11]

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(6) Massey, A. G. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 99.
(7) Pertinent ν(CO) band positions in CH_2Cl_2: $HMo(CO)_2(DPPE)_2^+$, 1880 cm^{-1}; *cis*-$Mo(CO)_2(DPPE)_2$, 1851 s, 1781 s; *trans*-$Mo(CO)_2(DPPE)_2$, 1822 s.
(8) All kinetic studies were performed in CH_2Cl_2 and reactions were followed by observation of the 1880-cm^{-1} band of **1H**$^+$. Values of k_{obsd} were determined from pseudo-first-order plots of ln (Abs – Abs$_\infty$) vs. time. Abs$_\infty$ represents an equilibrium value for entries 1–4 (Table II). Reactions 5–13 resulted in 100% deprotonation.
(9) $Mo(^{13}CO)_2(DPPE)_2$ was prepared as described in ref 3. $HMo(^{13}CO)_2(DPPE)_2BF_4$ was prepared by reaction of $Mo(^{13}CO)_2(DPPE)_2$ with $HBF_4{\cdot}OEt_2$ in THF. ν(CO) IR band positions in CH_2Cl_2: *cis*-$Mo(^{13}CO)_2(DPPE)_2$, 1808 s, 1742 s; *trans*-$Mo(^{13}CO)_2(DPPE)_2$, 1782 s; *trans*-$HMo(^{13}CO)_2(DPPE)_2^+$, 1839 cm^{-1}.
(10) Smith, P. B.; Dye, J. L.; Cheney, J.; Lehn, J.-M. *J. Am. Chem. Soc.*, **1982**, *103*, 6044.
(11) Single crystals of **1H**$^+$ $AlCl_4^-$ were grown from THF/hexane and data collection carried out at 23 °C. The compound is in the monoclinic space group *Cc* with a = 16.897 (4) Å, b = 15.573 (5) Å, c = 23.501 (13) Å; β = 91.55 (3)°; Z = 4. R_W = 0.054 for 4675 reflections with $I > 3\sigma(I)$. Crystallographic analysis was carried out by Molecular Structure Corporation, College Station, TX. Details to be published separately.

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