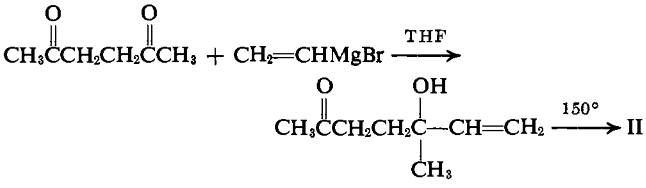
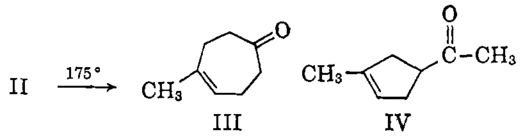
restrictions of such electron reorganizations, we have investigated the thermal behavior of an example of this type, 2,5-dimethyl-2-vinyl-2,3-dihydrofuran (II). II was prepared by treatment of 2,5-hexanedione with 1 equiv of vinylmagnesium bromide in tetrahydrofuran followed by cyclodehydration of the monoaddition product. The latter process occurred smoothly at 150° on a glpc column of SE-30 on Gas-Chrom P. The structure of II, purified by glpc recycling, follows unequivocally from its spectral properties. The mass spectrum shows a parent ion peak of m/e 124. The infrared spectrum reveals vinylic hydrogen absorptions at 3100, 985, 975, 945, and 920 cm^{-1}, a very intense double bond stretching band at 1680 cm^{-1}, typical of vinyl ethers, and a weak band at 1645 cm^{-1} due to the side-chain double bond. Strong bands associated with carbon–oxygen stretching vibrations are found at 1185 and 1270 cm^{-1}. The nmr spectrum (in CDCl$_3$) shows a typical ABX pattern for the three protons of the vinyl side chain with δ values of 6.02, 5.18, and 5.00 ppm, and $J_t = 17$, $J_c = 10$, and $J_{gem} = 2$ cps. The olefinic hydrogen at C-4 appears as a complex multiplet of area 1 at $\delta = 4.40$ ppm. A broad signal of area two showing complex splitting at $\delta = 2.49$ ppm is assigned to the C-3 methylene protons while a three-proton signal at $\delta = 1.77$ ppm, broadened by fine splitting, is that of the allylic methyl hydrogens at C-5. The proton signal of the 2-methyl group appears as a singlet of area 3 at $\delta = 1.40$ ppm.



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 + CH_2{=}CHMgBr \xrightarrow{THF} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{CH_3}{\overset{OH}{C}}{-}CH{=}CH_2 \xrightarrow{150^\circ} II}$$

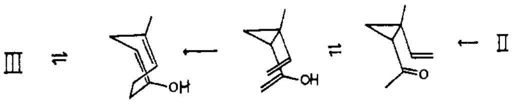
When II is heated, neat or in n-decane, at 175° for 24 hr, it rearranges in nearly quantitative yield to a single product, 4-methyl-4-cycloheptenone (III). The structure of III is based on the following evidence. Its mass spectrum shows a parent ion peak of m/e 124 and, significantly, no peak of m/e 43 indicative of an acetyl fragment anticipated for the "normal" Claisen rearrangement product 1-methyl-4-acetylcyclopentene (IV). The infrared spectrum of III reveals a strong carbonyl band at 1705 cm^{-1} and weak double bond absorption at 1670 cm^{-1}. The nonconjugated nature of the double bond and the carbonyl function is confirmed by the ultraviolet spectrum, λ_{max}^{EtOH} 280 mμ (ϵ 27); $\lambda_{max}^{cyclohexane}$ 282 mμ (ϵ 22). The nmr spectrum (in benzene) shows signals at $\delta = 5.46$ ppm, area 1, broad multiplet with fine splitting (C=CH); $\delta = 1.65$ ppm, area 3, complex multiplet with fine splitting (C=CCH$_3$); and two groups of four protons each, centered at $\delta \sim 2.5$ and $\sim$2.0 ppm, assigned to the α-methylene protons and the allylic methylene protons, respectively. The location of the double bond at the 4 position and the assignment of the two groups of methylene protons are supported by the nmr spectrum of III-d_4, prepared by base-catalyzed deuterium exchange. In the spectrum of III-d_4 the multiplet at $\delta = 2.5$ ppm has disappeared and the signals of the four allylic methylene protons show a much simplified pattern at $\delta = 1.9$ ppm. Finally, catalytic reduction of III with 1 equiv of hydrogen yields 4-methylcycloheptanone, identical in all respects with an authentic sample.[4]



The unidirectional and heretofore unobserved rearrangement of II to III has important mechanistic and synthetic implications. It appears that the geometric restraint imposed on the bisallylic system, I, by methylene bridging of the third (c) and sixth (f) atoms provides a barrier of such magnitude to the usually facile Claisen rearrangement that another, energetically less demanding, route is traversed.[5] Two possible sequences are suggested: (A) rearrangement of the dihydrofuran system to cis-1-acetyl-2-vinylcyclopropane followed by enolization toward the methyl group and rapid thermal reorganization of the very labile cis-divinylcyclopropane system;[8] (B) isomerization of II to the exo-methylene derivative with subsequent rearrangement of the new (and less constrained) allyl vinyl ether system. Experiments designed to distinguish these possibilities and to explore the generality of the rearrangement are in progress.

A.

B.



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[4] Synthesized by the method of C. Djerassi, *et al.*, *J. Am. Chem. Soc.*, **85**, 949 (1963).

[5] Formally, II may be viewed as a tetraalkylated allyl vinyl ether with c,c,e,f substitution of the bisallylic system I. Closely analogous acyclic systems[6] and allylic aryl ethers,[7] differentiable from II only by the absence of geometric restraint imposed by the methylene bridge, invariably show the characteristic of a facile, concerted, thermal reorganization with ultimate bonding of the a and f atoms through a six-atom transition state. To our knowledge, there is no case on record in which the alternative four-atom complex (leading to bonding of the c and f atoms) is preferred when the geometry of the system permits the achievement of both.

[6] L. Stein and G. W. Murphy, *J. Am. Chem. Soc.*, **74**, 1041 (1952); A. W. Burgstahler, *ibid.*, **82**, 4681 (1960); Y. Pocker, *Proc. Chem. Soc.*, 141 (1961); H. M. Frey and B. M. Pope, *J. Chem. Soc., Sec. B*, 209 (1966).

[7] Reviews by D. S. Tarbell, *Org. Reactions*, **2**, 1 (1944), and S. J. Rhoads in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 11.

[8] E. Vogel, *Angew. Chem.*, **72**, 21 (1960); E. Vogel, K. H. Ott, and K. Gajek, *Ann.*, **644**, 172 (1961); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[9] National Science Foundation Summer Fellow, 1966.

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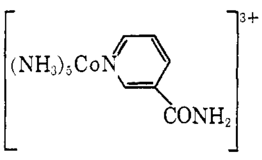
Electron Transfer by Remote Attack in Substituted Pyridine Bridging Ligands

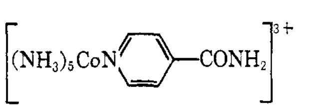
Sir:

Electron transfer by remote attack at a bridging group has been suggested as a pathway for the reduction of certain pentaamminecobalt(III) complexes.[1] Proof of this mechanism has rested upon the report that hydrolysis accompanies the reduction of (methyl fumarato)pentaamminecobalt(III) by chromous ion. However, a reinvestigation[2] has failed to reproduce these results. Although secondary evidence, such as the rate law and rate comparisons, still suggests remote attack, confirmation is necessary.[3] In this communication we present the results of experiments for two systems in which remote attack is clearly a major pathway for cobalt reduction.

Pentaamminecobalt(III) complexes of nicotinamide and isonicotinamide were prepared in N,N-dimethylformamide and were isolated as perchlorate salts. The evidence to be described shows that the nicotinamide- and isonicotinamidepentaamminecobalt(III) ions have the structures I and II, respectively. Treatment of the nicotinamidepentaammine with $NOClO_4$ (which is capable of oxidizing amides to carboxylic acids) in trimethyl phosphate yields a cobalt complex having a visible spectrum almost identical with that of the starting material but having a titratable proton with a pK of *ca.* 2.4 (the pK of nicotinic acid is 2.1). Thus the amide group in the complex is left free to undergo its characteristic reaction without disturbing the cobalt bond. It should further be noted that the nicotinamide (ϵ 62.4 at 476 mμ) and the isonicotinamide (ϵ 64.6 at 474 mμ) complexes have visible spectra almost identical with that of pyridinepentaammine (ϵ 63.8 at 474 mμ).[7]



I



II

Reactions of the pentaammine complexes with Cr^{2+} were studied at acid concentrations of 0.05 M and greater. Perchlorate salts were used exclusively except where noted otherwise. Both the nicotinamide- and the isonicotinamidepentaamminecobalt(III) ions react in acid solution with an equimolar amount of Cr^{2+} to produce the equivalent amounts of Co^{2+} and NH_4^+. The fate of the sixth ligand and of the substitution inert chromium(III) ion is the point of interest and will be described separately for each complex.

When the nicotinamide complex is reduced in the presence of a large excess of Cr^{2+} and the absorbance followed at a wavelength near a chromium(III) peak, an increase in absorbance is observed, which is followed by a slower and less pronounced decrease in absorbance. Data obtained from these changes were analyzed[8] and were found to conform to the scheme of two consecutive first-order reactions. The spectra obtained after the absorbance changes have stopped indicate that $Cr(H_2O)_6^{3+}$ is the final chromium product. The first reaction can be attributed to the reduction of cobalt(III) and the formation of a chromium(III) nicotinamide complex, and the second reaction to the aquation of the chromic ion. The chromic complex in a reaction mixture could be separated from other ions and free nicotinamide by ion-exchange chromatography at 0°. The complex is retained on the column even after the $Cr(H_2O)_6^{3+}$ has been eluted.

Aquation of the chromic complex obeys a first-order rate law with $k = 5 \times 10^{-5}$ sec^{-1} at 25° in 0.9 M H^+. The spectrum of the complex shows maxima at 410 mμ (ϵ 21.7) and 585 mμ (ϵ 20.8). Repeated infrared spectra of the complex in D_2O (acidified with DCl) show that peaks at 1618 and 1452 cm^{-1} for a fresh solution are gradually replaced by peaks at 1665 and 1427 cm^{-1}. The time scale of this change is the same as that observed for the aquation of the chromic complex, and the final spectrum is identical with that of nicotinamide in acidic D_2O.

Infrared studies of urea complexes[9] have shown that coordination of the nitrogen by Pt or Pd causes the stretching frequency of C=O to increase and that of the C–N to decrease, whereas coordination of the oxygen, as with the chromic and ferric complexes, produces the opposite effect to the extent that the vibrations become coupled significantly. Although the shifts of the nicotinamide vibration frequencies in the chromic complex are perhaps not as dramatic as those observed for urea, they are clearly in the direction indicating a chromium–oxygen bond. The visible spectrum of the chromic complex, having maxima at slightly longer wavelengths than those of $Cr(H_2O)_6^{3+}$ (408 and 575 mμ), is consistent with coordination by a weakly basic oxygen. The affinity of the complex for the ion-exchange column implies that it is more highly charged than $Cr(H_2O)_6^{3+}$. All lines of evidence support the conclusion that the chromic nicotinamide complex has the structure III.

A comparison of the spectrum of the chromic complex with the spectrum obtained from the Cr^{2+} reaction mixture indicates that 0.70 mole of chromic complex is produced for every mole of cobalt(III) reduced; the rest of the chromium(III) appears as $Cr(H_2O)_6^{3+}$ resulting from an outer sphere reduction by chromous. Thus it has been demonstrated that the major path for reduction of the nicotinamidepentaammine is by attack at the amide group which is then retained in the coordination sphere of the chromium(III).

Reduction of the isonicotinamidepentaammine complex proceeds at a rate over 300 times that of the nicotinamidepentaammine. Its reaction with $<10^{-3}$ M Cr^{2+} and >0.1 M H^+ produces a chromic complex having ion-exchange, spectral, and aquation properties very similar to the chromic complex described above. Its infrared spectrum in D_2O shows peaks at 1639 and 1452 cm^{-1} which are replaced later by peaks at 1664 and 1428 cm^{-1}. The final spectrum is that of isonicotinamide in acidic D_2O. Reasoning for the chromic

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[1] (a) R. T. M. Fraser, D. K. Sebera, and H. Taube, *J. Am. Chem. Soc.*, **81**, 2906 (1959); (b) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

[2] J. Hurst and H. Taube, private communication, to be submitted for publication.

[3] Since the earlier claims were made remote attack has been demonstrated for the bridging ligands NO_2^-,[4] CN^-,[4,5] and SCN^-;[6] however, confirmation for more extended bond systems is required.

[4] J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

[5] J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).

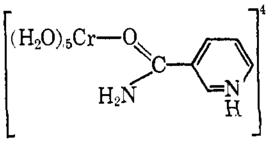
[6] A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

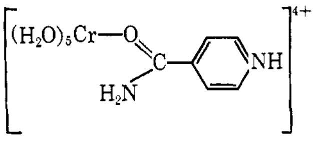
[7] ϵ values previously reported for the pyridinepentaamminecobalt(III) ion are 64.0 at 475 mμ by E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965), and 46 at 480 mμ by R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

[8] The rate data were fitted to an equation for consecutive first-order reactions by using a least-squares optimization program written in ALGOL 60. Computer time was made available by the Stanford Computation Center.

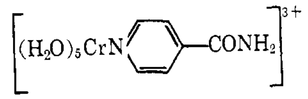
[9] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1574 (1957).

isonicotinamide complex as was done for the nicotinamide complex we conclude that the complex has structure IV. Preliminary estimates indicate that this chromic complex of isonicotinamide constitutes at least 90% of the chromium(III) product under these conditions.


III


IV

If, however, the isonicotinamidepentaammine is reduced in the presence of $>10^{-3}$ M Cr^{2+} and <0.1 M H^+, a different chromic product appears. This complex may also be isolated by ion-exchange chromatography, although with more difficulty than before because it is retained on the column only slightly more strongly than $Cr(H_2O)_6{}^{3+}$. Its absorption maxima are at 400 mμ (ε 18.2) and 558 mμ (ε 18.7). Its aquation rate is very slow, $k = 4.3 \times 10^{-5}$ sec^{-1} at 70° (for chromic complex III k would be 7×10^{-3} sec^{-1} at 70°). The infrared spectrum of the chromic complex has peaks at 1660 and 1435 cm^{-1}, very close to those of the free ligand indicating that the amide group is not coordinated. Visible bands for this complex appear at shorter wavelengths than for $Cr(H_2O)_6{}^{3+}$, implying coordination by a ligand higher in the spectrochemical series than H_2O. The ion-exchange behavior indicates that it probably has the same charge as $Cr(H_2O)_6{}^{3+}$. These observations support the assignment of structure V to this last chromic complex. The characterization of this isomer strengthens by contrast the arguments made for the assignment of structure IV (and III).


V

Despite the complexities in the product distributions the reduction of the isonicotinamidepentaammine can be described by a single term rate law, $d(Co^{III})/dt = -k(Co^{III})(Cr^{2+})$; it is furthermore found that complex IV does not react with Cr^{2+} at low (H^+) to form complex V.

These kinetic data in conjunction with the other observations cited imply that the rate-determining step leads to a metastable complex which can react to form either IV or V. In view of the Cr^{2+} and H^+ dependence, it is reasonable to supposet hat the metastable chromic complex is closely related to IV and can itself undergo attack by Cr^{2+} at the remote pyridinyl nitrogen (after loss of its proton) to produce complex V. Work in progress should settle this point and yield information about the metastable complex.

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[10] National Institutes of Health Predoctoral Fellow, 1964–1966.

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The Temperature Dependence of Fluorine and Carbon-13 Hyperfine Interactions of Hexakis(trifluoromethyl)benzene Anion

Sir:

We have observed the effect of temperature on ^{19}F and both ^{13}C hyperfine splittings of the hexakis(trifluoromethyl)benzene anion (I).

The variations with temperature of the ^{19}F and ^{14}N hyperfine splittings in bis(trifluoromethyl) nitroxide (II) were described recently by Scheidler and Bolton,[1] who found that a^F increased and a^N decreased linearly as the temperature was lowered. These temperature effects were explained by assuming that configurations leading to increased conjugation between nitrogen and fluorine are favored at lower temperatures.[1]

I was produced by reducing the fluorocarbon with potassium in tetrahydrofuran *in vacuo*.[2] Sample concentrations were about 10^{-3} M. The esr spectra of I were measured on a Varian V-4502 spectrometer operating at about 9.3 Gcps with a field modulation of 100 kcps. Constant temperatures were obtained by passing cold nitrogen through a quartz dewar running the length of the rectangular cavity. The temperature was monitored using a copper-constantan thermocouple located alongside the sample tube outside the cavity, but well within the dewar. During the course of an experiment there was no discernible change in temperature. The potentiometer could be read to ±1°. The field was determined from the frequency of a proton resonance probe inserted between one face of the magnet and the side of the cavity and was monitored with a Hewlett-Packard 5245L frequency counter. During the course of these experiments the probe and sample tube were kept at fixed positions in the magnetic field.

The esr spectrum of I consists of 19 lines with a binomial intensity distribution due to 18 equivalent fluorine nuclei. Each line has four satellites, each of which is 0.033 times as intense as the main line.[3] The ^{19}F splittings were determined by setting the field at the center of a line and simultaneously measuring the proton resonance frequency. The coupling constants were calculated from the difference in frequency between two lines. The ^{13}C splittings were determined from calibrated spectra presented on a chart recorder. Overlap of the ^{13}C satellites was compensated for with the aid of the calculated spectra of Lebedev, *et al.*[4] The estimated uncertainty in determination of ^{13}C coupling constants ranges from ±0.005 gauss at room temperature to ±0.020 gauss at 207°K, when the overlap of the satellites was the largest.

Table I gives the values of the coupling constants at several temperatures. A least-squares treatment of the data gives the following equations for the linear variation of the coupling constants with temperature.

$$a^F = 7.827 - 0.00100T \qquad (1)$$

$$a^{C_1} = 4.110 + 0.00205T \qquad (2)$$

$$a^{C_2} = 5.338 + 0.00162T \qquad (3)$$

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[1] P. J. Scheidler and J. R. Bolton, *J. Am. Chem. Soc.*, **88**, 371 (1966).

[2] D. E. Paul., D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

[3] M. T. Jones, *J. Chem. Phys.*, **42**, 4054 (1965).

[4] Y. S. Lebedev, D. M. Chernikova, N. N. Tikhomirova, and V. V. Voevodskii, "Atlas of Electron Spin Resonance Spectra," Consultants Bureau, New York, N. Y., 1963.