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References and Notes

(1) A preliminary account of portions of this work has appeared: F. E. Stary, D. E. Emge, and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 5671 (1974).
(2) P. D. Bartlett and M. Lahav, *Isr. J. Chem.*, **10**, 101 (1972).
(3) P. D. Bartlett and P. Gunther, *J. Am. Chem. Soc.*, **88**, 3288 (1966).
(4) P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4799 (1967).
(5) P. G. Thompson, *J. Am. Chem. Soc.*, **89**, 4316 (1967).
(6) L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc.*, **89**, 4313 (1967).
(7) N. A. Milas and S. M. Djokic, *J. Am. Chem. Soc.*, **84**, 3098 (1962).
(8) J. A. Howard and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1056 (1968).
(9) T. Mill and R. S. Stringham, *J. Am. Chem. Soc.*, **90**, 1062 (1968).
(10) G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.*, **No. 77**, 15 (1968).
(11) M. C. Whiting, A. J. N. Bolt, and J. H. Parish, *Adv. Chem. Ser.*, **No. 77**, 4 (1968).
(12) J. E. Batterbee and P. S. Bailey, *J. Org. Chem.*, **32**, 3899 (1967).
(13) J. D. Austin and L. Spialter, "Oxidation of Organic Compounds", *Adv. Chem. Ser.*, **No. 77**, 26 (1968).
(14) R. E. Erickson, R. T. Hansen, and J. Harkins, *J. Am. Chem. Soc.*, **90**, 6777 (1968).
(15) C. C. Price and A. L. Tumolo, *J. Am. Chem. Soc.*, **86**, 4691 (1964).
(16) P. S. Bailey, D. A. Mitchard, and A.-I. Y. Khashab, *J. Org. Chem.*, **33**, 2675 (1968).
(17) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).
(18) P. S. Bailey, T. P. Carter, Jr., and L. M. Southwick, *J. Org. Chem.*, **37**, 2997 (1972).
(19) H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).
(20) R. E. Erickson, D. Bakalik, C. Richards, M. Scanlon, and G. Huddleston, *J. Org. Chem.*, **31**, 461 (1966).
(21) P. S. Bailey, A. M. Reader, P. Kolsaker, H. M. White, and J. C. Barborak, *J. Org. Chem.*, **30**, 3042 (1965).
(22) T. M. Hellman and G. A. Mamilton, *J. Am. Chem. Soc.*, **96**, 1530 (1974).
(23) G. Czapski and B. H. J. Bielski, *J. Phys. Chem.*, **67**, 2180 (1963).
(24) T. V. Yagodovskoya, N. P. Klimushina, L. I. Nekrasov, and Yu. A. Pentin, *Russ. J. Phys. Chem.*, **41**, 369 (1967).
(25) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **90**, 537 (1968).
(26) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **90**, 4161 (1968).
(27) E. Wasserman, R. W. Murray, M. L. Kaplan, and W. A. Yager, *J. Am. Chem. Soc.*, **90**, 4160 (1968).
(28) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **91**, 5358 (1969).
(29) R. W. Murray, J. W.-P. Lin, and M. L. Kaplan, *Ann. N.Y. Acad. Sci.*, **171**, 121 (1970).
(30) R. W. Murray, W. C. Lumma, Jr., and J. W.-P. Lin, *J. Am. Chem. Soc.*, **92**, 3205 (1970).
(31) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p. 83.
(32) D. Swern, A. H. Clements, and T. M. Luong, *Anal. Chem.*, **41**, 412 (1969).
(33) We are indebted to Professor P. D. Bartlett for this suggestion.
(34) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 1425 (1954).
(35) E. Koch, *Tetrahedron*, **26**, 3503 (1970).
(36) S. W. Benson and R. Shaw in "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970, p 126.
(37) R. Criegee and G. Schröder, *Chem. Ber.*, **93** 689 (1960).
(38) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Am. Chem. Soc.*, **88**, 4098 (1966).
(39) L. E. Schniepp, H. H. Geller, and R. W. Van Korff, *J. Am. Chem. Soc.*, **69**, 672 (1947).
(40) E. Briner, *Adv. Chem. Ser.*, **No. 21**, 184 (1959).
(41) C. R. Dick and R. F. Hanna, *J. Org. Chem.*, **29**, 1218 (1964).
(42) H. K. Reimschuessel and G. A. Mountford, *J. Colloid Interface Sci.*, **25**, 558 (1967).
(43) G. A. Cook, A. D. Kiffer, C. V. Klumpp, A. H. Malik, and L. A. Spence, *Adv. Chem. Ser.*, **No. 21**, 44 (1959).
(44) P. S. Bailey and A. M. Reader, *Chem. Ind. (London)*, 1063 (1961).
(45) P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, 1400 (1964).
(46) A. M. Reader, P. S. Bailey, and H. M. White, *J. Org. Chem.*, **30**, 784 (1965).
(47) A. A. Syrov and V. K. Tsyskovskii, *Zh. Org. Khim.*, **6**, 1392 (1970).
(48) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **89**, 2429 (1967).
(49) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(50) A. I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd ed, Longmans, Green and Co., New York, N.Y., 1956, p 694.
(51) NMR chemical shift values given are δ values relative to internal Me_4Si.
(52) E. Whittaker and G. Robinson, "The Calculus of Observation", 4th ed, Blackie and Sons, Ltd., London, 1958, Chapter IX.
(53) F. B. Zienty, *J. Am. Chem. Soc.*, **68**, 1385 (1946).
(54) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 417 (1953).
(55) F. W. Schwab and E. Wichers, *J. Res. Natl. Bur. Stand.*, **34**, 333 (1945).
(56) The benzoic acid proton absorption is very weak since most of the acid precipitates out under the conditions used.
(57) 1,3-Diphenylisobenzofuran is converted to *o*-dibenzoylbenzene upon exposure to light. All operations using this acceptor particularly the recrystallization must be carried out with the exclusion of light.
(58) H. H. Wasserman, J. R. Scheffer, and J. L. Cooper, *J. Am. Chem. Soc.*, **94**, 4991 (1972).

Oxidation of Primary Amines Bound to Bis(2,2′-bipyridine)ruthenium(II)

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Abstract: In the net sense, chemical and electrochemical oxidations of the ions $[Ru(bpy)_2(NH_2CH_2R)_2]^{2+}$ (NH_2CH_2R = allylamine, benzylamine, and *n*-butylamine) occur by dehydrogenation at the amine ligands giving the corresponding bis(nitrile) complexes, $[Ru(bpy)_2(N{\equiv}CR)_2]^{2+}$. The reactions appear to proceed by initial oxidation of Ru(II) to Ru(III), followed by a series of stepwise dehydrogenation reactions which occur via imine intermediates.

Net reactions involving the oxidative dehydrogenation of chelated amines to imines have been reported for macrocyclic amines,[1,2] and for ethylenediamine and related diamines.[3-7] For chelated amines, dehydrogenation stops at the imine stage; further oxidation gives hydroxodiimines[8] or net decomposition, rather than nitriles.[7]

There are two examples of the oxidation of monodentate primary amines to nitriles or cyanides. McWhinnie et al.[9] have reported the isolation of Ru(III) products containing the cyanide ion following the aerial oxidation of $[Ru(NH_2CH_3)_6]^{2+}$, and Diamond, Tom, and Taube[10] have shown that benzylamine bound to pentaammineruthenium(II) can be oxidized to benzonitrile.

Previous work has shown that oxidation of ligands bound to bis(2,2′-bipyridine)ruthenium(II) can be facile, and quantitative.[7,11] The reactions appear to proceed via initial oxidation of Ru(II) to Ru(III), followed by a series of rapid steps in which the net reactions involve the oxidation of a coordinated ligand.

Experimental Section

Electronic spectra were recorded on a Bausch and Lomb 210UV spectrophotometer. ^1H NMR spectra were measured on a Jeol C-60-HL spectrometer using acetone-d_6 solutions of PF_6^- salts

(Me_4Si internal reference). Ir spectra were recorded on a Perkin-Elmer 421 grating spectrophotometer using KBr disks (ca. 5 mg of complex/200 mg of KBr).

Benzylamine (Eastman), benzonitrile (MCB), allylamine (Eastman), acrylonitrile (Aldrich), *n*-butylamine (Fisher), and *n*-butyronitrile (Aldrich) were used without purification. For spectral measurements, acetonitrile (MCB, spectrograde) was used without purification and water was deionized and distilled from alkaline $KMnO_4$ before use. The complex $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ was prepared as described previously,[12] and recrystallized (as the anhydrous compound) by Soxhlet extraction from methylene chloride before use. $[Ru(bpy)_2CO_3]\cdot 2H_2O$ was also prepared as described previously.[13]

Electrochemical measurements were made in acetonitrile solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte, or in 1.0 M HCl, vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C, and are uncorrected for junction potentials. All potentials reported are reduction potentials vs. the SSCE. Potential control for electrochemical experiments was obtained with a Princeton Applied Research Model 173 potentiostat/galvanostat. The waveform generator for voltammetric experiments was a Princeton Applied Research Model 175 universal programmer. Voltammograms and slow scan cyclic voltammograms were recorded on a Hewlett-Packard Model 7004B x-y recorder. Fast scan cyclic voltammograms were obtained from photographs of the trace of a Tektronix Model 564B storage oscilloscope. Values of *n*, where *n* is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were carried out at platinum electrodes in solutions deaerated with a stream of dry, prepurified nitrogen.

Elemental analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tenn.

Preparation of Complexes. $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2](PF_6)_2$. $[Ru(bpy)_2Cl_2]$ (0.46 g) was suspended in 50% aqueous MeOH (40 ml). Allylamine (5 ml) was added and the mixture kept at steam-bath temperature under N_2 for 2 h. Methanol and allylamine were evaporated off, the solution was cooled, and solid NH_4PF_6 was added slowly with stirring. The product was filtered, washed with ice-cold water and dried in vacuo, yield 0.68 g, 90%. Recrystallization was achieved by dissolution of the product in a minimum volume of CH_2Cl_2 (ca. 200 ml), filtering, and precipitating by the addition of ligroine (bp 30–60°). The red precipitate was filtered, washed with ligroine, and dried in vacuo. Anal. Calcd for $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2](PF_6)$: C, 38.2; H, 3.70; N, 10.3. Found: C, 38.0; H, 3.58; N, 10.2.

$[Ru(bpy)_2(NH_2CH_2C_6H_5)_2](ClO_4)_2$. $[Ru(bpy)_2Cl_2]$ (0.41 g) was suspended in 50% aqueous MeOH (40 ml). Benzylamine (5 ml) was added and the solution heated on a steam bath under an atmosphere of N_2 for 2 h. Methanol was evaporated off, the solution cooled, and then extracted three times with 25-ml portions of ether to remove excess benzylamine. The remaining aqueous solution was filtered, and the product precipitated by the slow addition of a filtered, saturated solution of $LiClO_4$. The red precipitate was collected, and the solid washed with ice-cold water, 2-propanol, and ether, and then dried in vacuo, yield, 0.65 g, 92%. Anal. Calcd for $[Ru(bpy)_2(NH_2CH_2C_6H_5)_2](ClO_4)_2$: C, 49.4; H, 4.15; N, 10.2. Found: C, 49.3; H, 4.09; N, 10.2.

$[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)_2](PF_6)_2$. $[RuB_2Cl_2]$ (0.45 g) was suspended in 50% aqueous MeOH (40 ml), *n*-butylamine (5 ml) was added, and the mixture heated on a steam bath under an N_2 atmosphere 2 h. The methanol and *n*-butylamine were evaporated off, and the last traces of the amine were removed by extraction with ether. The product was precipitated by the slow addition of solid NH_4PF_6 to a stirred solution of the complex. The solid was collected by filtration, washed with ice-cold water, and dried in vacuo. The product was recrystallized by adding a filtered CH_2Cl_2 solution to pentane, yield 0.50 g, 63%. Anal. Calcd for $[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)_2](PF_6)_2$: C, 39.6; H, 4.51; N, 9.9. Found: C, 39.5; H, 4.52; N, 9.7.

$[Ru(bpy)_2(N{\equiv}CR)_2](PF_6)_2$ (R is $-CH{=}CH_2$ (Acrylonitrile) and $-C_3H_7$ (*n*-Butyronitrile)). $[Ru(bpy)_2(CO_3)]\cdot 2H_2O$ (0.40 g) was suspended in acetone (15 ml) and concentrated HPF_6 (ca. 0.2 ml) added. The solution was stirred for 10 min, and anhydrous Na_2CO_3 (ca. 1 g) added. After stirring for a further 10 min the solution was filtered, the required nitrile (5 ml) added, and the mixture stirred for 2 h. The products were precipitated by adding the reaction mixtures dropwise to large volumes (300 ml) of ether, yields 0.57 g (90%) for acrylonitrile and 0.53 g (80%) for *n*-butyronitrile. Recrystallization was achieved in both cases from acetone–ether. Anal. Calcd for $[Ru(bpy)_2(N{\equiv}CCH{=}CH_2)_2](PF_6)_2$: C, 38.6; H, 2.74; N, 10.4. Found: C, 38.7; H, 2.75; N, 10.3. Calcd for $[Ru(bpy)_2(N{\equiv}CCH_2CH_2CH_3)_2](PF_6)_2$: C, 40.0; H, 3.59; N, 10.0. Found: C, 39.8; H, 3.52; N, 9.8.

$[Ru(bpy)_2(N{\equiv}CC_6H_5)_2](PF_6)_2$. The benzonitrile salt was prepared in a manner analogous to that given for the bis(benzylamine) complex, except that the complex was precipitated by the addition of NH_4PF_6 after excess benzonitrile had been removed by ether extraction. The salt was recrystallized by dissolution in CH_2Cl_2, filtering the solution, and precipitating by the addition of ligroine (bp 30–60°). The product was obtained in 71% yield. Anal. Calcd for $[Ru(bpy)_2(N{\equiv}CC_6H_5)_2](PF_6)_2$: C, 44.9; H, 2.88; N, 9.2. Found: C, 44.9; H, 2.87; N, 8.9.

Electrochemical Preparations. $[Ru(bpy)_2(N{\equiv}CC_6H_5)_2](PF_6)_2$. The salt $[Ru(bpy)_2(NH_2CH_2C_6H_5)_2](ClO_4)_2$ (120 mg) was dissolved in 1 M HCl (120 ml). The solution was electrolyzed exhaustively at 0.80 V until the current had fallen to 1% of its initial value (n = 7.9). The resulting solution was filtered and solid NH_4PF_6 added with stirring. The yellow precipitate which appeared was filtered, washed with ice-cold water, and dried in vacuo, yield 0.105 g, 87%. Recrystallization was achieved by adding ligroine (bp 30–60°) dropwise to a solution of the complex in CH_2Cl_2. Anal. Calcd for $[Ru(bpy)_2(N{\equiv}CC_6H_5)_2](PF_6)_2$: C, 44.9; H, 2.88; N, 9.2. Found: C, 44.8, H, 3.00; N, 9.2.

$[Ru(bpy)_2(NH_2CH_2C_6H_5)(N{\equiv}CC_6H_5)](PF_6)_2$. The salt $[Ru(bpy)_2(NH_2CH_2C_6H_5)_2](ClO_4)_2$ (113 mg) was dissolved in 1 M HCl (80 ml). The solution was electrolyzed exhaustively at 0.70 V until the current had fallen to 1% of its initial value (n = 3.9). The solution was filtered and solid NH_4PF_6 added slowly with stirring. The resultant precipitate was filtered, washed with ice-cold water, 2-propanol, and ether, and then air dried, yield 0.10 g, 88%. The salt was recrystallized from acetone–ether. Anal. Calcd for $[Ru(bpy)_2(NH_2CH_2C_6H_5)(N{\equiv}CC_6H_5)](PF_6)_2$: C, 44.7; H, 3.31; N, 9.2. Found: C, 44.7; H, 3.32; N, 9.2.

$[Ru(bpy)_2(NH_2CH_2R)(N{\equiv}CR)](PF_6)_2$ (R is $-CH{=}CH_2$ and $-C_3H_7$). The respective salts $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2](PF_6)_2$ and $[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)_2](PF_6)_2$ (100 mg) were dissolved in acetonitrile (30 ml; 0.1 M TBAH) and electrolyzed exhaustively at 1.10 V until the current decreased to 1% of its initial value (n = 3.8 and 3.9, respectively). The products were precipitated by filtering the solutions dropwise into stirred excesses of ether (250 ml). Recrystallization of the allylamine–(acrylonitrile) complex was achieved from CH_2Cl_2–ligroine (30–60°) (yield 0.08 g, 80%), and the *n*-butylamine–(*n*-butyronitrile) complex from acetone–ether (yield 0.03 g, 30%). Anal. Calcd for $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)(N{\equiv}CCH{=}CH_2)](PF_6)_2$: C, 38.4; H, 3.22; N, 10.3. Found: C, 38.0; H, 3.16; N, 10.2. Calcd for $[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)(N{\equiv}CCH_2CH_2CH_3)](PF_6)_2$: C, 39.8; H, 4.05; N, 9.9. Found: C, 39.5; H, 3.86; N, 10.0.

Results and Discussion

Electrochemical Oxidative Dehydrogenation of Bound Primary Amines. From cyclic voltammetric studies, the complexes $[Ru(bpy)_2(NH_2CH_2R)_2]^{2+}$ (R is -Ph, $-CH{=}CH_2$, $-CH_2CH_2CH_3$) undergo electrochemically reversible, one-electron oxidations in acetonitrile with $E_{1/2}$ = 1.03–1.04 V (Table I).[14] The electrochemical oxidations clearly involve reversible Ru(III)/Ru(II) couples; they are one-electron processes, and the $E_{1/2}$ values fall in the range found for the $[Ru(bpy)_2(NH_3)_2]^{3+/2+}$ ($E_{1/2}$ = 0.92 V) and related diamine couples.[7] However, exhaustive electrolysis on the diffusion plateaus of the oxidation waves indicated that n (the number of electrons passed per mole of complex) is greater than one, and is dependent (within certain limits) on the potential used for the electrolysis. At poten-

Table I. $E_{1/2}$ Values for Amine-Nitrile Complexes of Bis(2,2′-bipyridine)ruthenium(II) in Acetonitrile[a]

Complex	$E_{1/2}$, V (V vs. SSCE)
$[Ru(bpy)_2(NH_2CH_2Ph)_2]^{3+/2+}$	1.04
$[Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{3+/2+}$	1.29
$[Ru(bipy)_2(N{\equiv}CPh)_2]^{3+/2+}$	1.52
$[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2]^{3+/2+}$	1.04
$[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)(N{\equiv}CCH{=}CH_2)]^{3+/2+}$	1.26[b]
$[Ru(bpy)_2(N{\equiv}CCH{=}CH_2)_2]^{3+/2+}$	1.53
$[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)_2]^{3+/2+}$	1.03
$[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)(N{\equiv}CCH_2CH_2CH_3)]^{3+/2+}$	1.24
$[Ru(bpy)_2(N{\equiv}CCH_2CH_2CH_3)_2]^{3+/2+}$	1.48

[a] At a Pt-bead electrode in 0.1 M TBAH-acetonitrile at 25 ± 2°. [b] Reversible only at scan speeds equal to or greater than 500 mV/s.

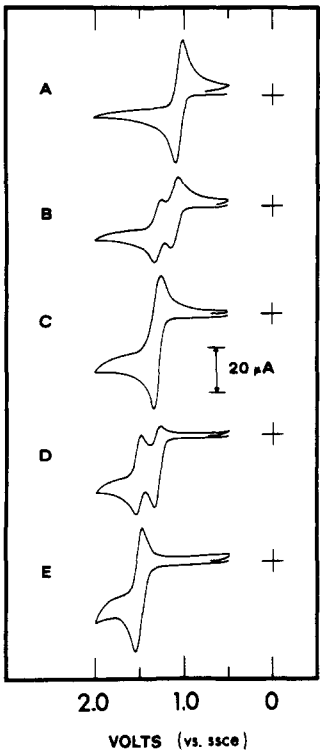


Figure 1. Cyclic voltammograms in acetonitrile of: (A) $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$, (B) solution A following two-electron oxidation, (C) solution A following four-electron oxidation (giving $([Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+}$), (D) six-electron oxidation of A, and (E) eight-electron oxidation of A (giving $[Ru(bpy)_2(N{\equiv}CPh)_2]^{2+}$). (Scan rate 200 mV/s at a Pt-bead electrode vs. the saturated sodium chloride calomel electrode at 25 ± 2°.)

tials sufficiently high on the diffusion plateau, reproducible n values of ~8.0 were obtained.

For the bis(benzylamine) complex, $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$, the electrolytic oxidation was monitored in detail using cyclic voltammetry (Figure 1). Cyclic voltammograms were obtained following controlled potential electrolyses at a series of potentials. Figure 1A shows a cyclic voltammogram for the reversible $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{3+/2+}$ couple. Figure 1B shows the cyclic voltammogram following electrolysis at 1.15 V until n = 2.0; there are two waves, one attributable to unreacted $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$. The waves have roughly equal peak currents, indicating that there are in solution equal amounts of the starting complex, and a four-electron

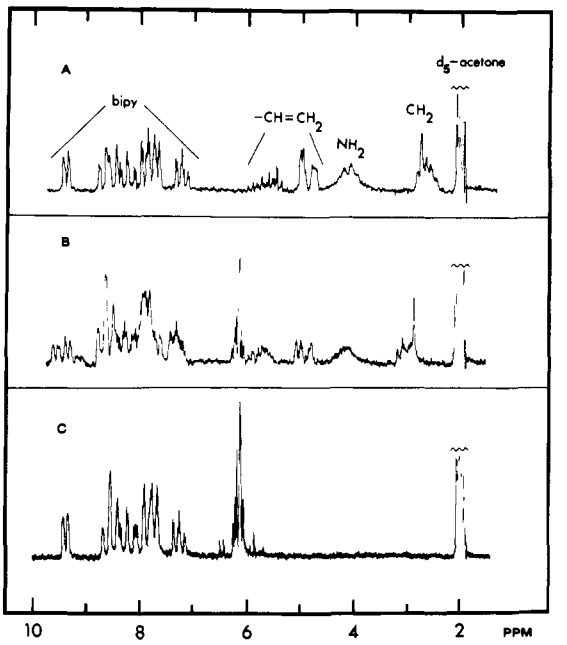


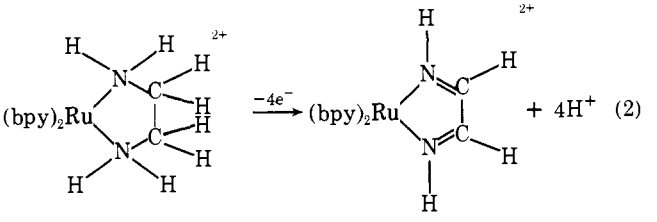
Figure 2. The 60-MHz ^1H NMR spectra in acetone d_6 of (A) $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2]^{2+}$, (B) four-electron oxidation product of A, and (C) eight-electron oxidation product of A ($[Ru(bpy)_2(N{\equiv}CCH{=}CH_2)_2]^{2+}$).

oxidation product with $E_{1/2}$ = 1.29 V. After complete electrolysis at 1.15 V (n = 4.0), only the four-electron oxidation product remains in solution (Figure 1C).

There are two, equally interesting, possibilities for the identity of this four-electron oxidation product. Firstly, both amine ligands might oxidize by two electrons to give the bis(monoimine) complex, $[Ru(bpy)_2(NH{=}CHPh)_2]^{2+}$ (eq 1).

$$[Ru(bpy)_2(NH_2CH_2R)_2]^{2+} \xrightarrow{-4e^-} [Ru(bpy)_2(NH{=}CHR)_2]^{2+} + 4H^+ \quad (1)$$

Reaction 1 is a likely possibility since the related four-electron oxidations of chelated diamines bound to bis(2,2′-bipyridine)ruthenium(II) have been well characterized[7] (e.g., eq 2). The second possibility is that oxidation is localized at



only one of the amine ligands, and the product is the amine-nitrile complex (eq 3).

$$[Ru(bpy)_2(NH_2CH_2R)_2]^{2+} \xrightarrow{-4e} [Ru(bpy)_2(NH_2CH_2R)(N{\equiv}CR)]^{2+} + 4H^+ \quad (3)$$

Predicted elemental analyses for the two possibilities are, of course, the same. However, the ^1H NMR spectrum of the complex allows a distinction to be made between them.

The effect of the four-electron oxidation on the ^1H NMR spectrum of $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2]^{2+}$ is shown in Figure 2. The spectrum of the bis(allylamine) complex (2A) has a typically broad and complicated region due to the 2,2′-bipyridine protons (δ 7.1–9.6 ppm, relative to Me_4Si). The $-CH{=}CH_2$ proton resonances appear at high-

er field (δ 4.7–6.1 ppm), and the $-NH_2$ and $>CH_2$ resonances are centered at δ 4.2 and 2.8 ppm, respectively.

The four-electron oxidation product has the spectrum shown in Figure 2B. An integrated spectrum indicates that the $-NH_2$ and $>CH_2$ regions are reduced to half their intensity relative to the bpy region when compared with 2A. The changes in the ^1H NMR spectra require that the four-electron oxidation product be $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)(N{\equiv}CCH{=}CH_2)]^{2+}$ and not $[Ru(bpy)_2(NH{=}CHCH{=}CH_2)_2]^{2+}$. In the latter case the imine protons would be expected to appear at lower field. Furthermore, the new resonance in the $-CH{=}CH_2$ region in 2B (δ 6.2 ppm) is an obvious characteristic of the acrylonitrile ligand, since for the bis(acrylonitrile) complex (Figure 2C) this peak constitutes the entire $-CH{=}CH_2$ resonance.

The ^1H NMR spectral changes upon oxidation for the benzylamine complex are analogous to the changes shown in Figure 2. The ^1H NMR experiment clearly shows that the four-electron oxidation product is the amine-nitrile complex, and, consequently, that the four-electron oxidation of $[Ru(bpy)_2(NH_2CH_2R)_2]^{2+}$ is described satisfactorily by eq 3.

It is worth noting that the $[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)(N{\equiv}CCH{=}CH_2)]^{3+/2+}$ couple is reversible only at scan rates of > 500 mV/s. This indicates that at slower scan rates further ligand oxidation is competitive with recapture of Ru(III) at the electrode.

A further oxidation process occurs past the n = 4.0 stage. Continued electrolysis on the diffusion plateau of the $E_{1/2}$ = 1.29 V wave (at 1.35 V) gave rise to a further oxidation. If the electrolysis is stopped at n = 2.0 (n_{total} = 6.0 based on $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$ as the starting complex) there are two reversible waves in the cyclic voltammogram (Figure 1D), with equal peak currents. The wave at $E_{1/2}$ = 1.29 V is clearly unreacted $[Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+}$, and the wave at $E_{1/2}$ = 1.52 V corresponds to an n = 4.0 (n_{total} = 8.0) oxidation product. Exhaustive electrolysis on the diffusion plateau of the $E_{1/2}$ = 1.29 V wave gave n_{total} = 8.0, and the complex with $E_{1/2}$ = 1.52 V as the sole product (Figure 1E). Spectral, electrochemical, and chemical isolation studies have shown that the eight-electron product is the totally oxidized, bis(nitrile) complex, $[Ru(bpy)_2(N{\equiv}CPh)_2]^{2+}$ (eq 4).

$$[Ru(bpy)_2(NH_2CH_2R)(N{\equiv}CR)]^{2+} \xrightarrow{-4e^-} [Ru(bpy)_2(N{\equiv}CR)_2]^{2+} + 4H^+ \quad (4)$$

The ^1H NMR spectrum of the bis(acrylonitrile) complex in acetone-d_6 is shown Figure 2C.

As shown by cyclic voltammetry (Figure 1E and Table I), the bis(nitrile) complexes undergo reversible one-electron oxidations at relatively high reduction potentials. It is expected that the ruthenium(III) nitrile complexes, $[Ru(bpy)_2(N{\equiv}CR)_2]^{3+}$, should undergo rapid hydrolysis at the nitrile group to give the corresponding amides,[10,15] but these reactions have not yet been investigated.

Infrared Spectra. Infrared spectra are also informative as to the nature of the four- and eight-electron oxidation products. The four-electron products of $[Ru(bpy)_2(allylamine)_2]^{2+}$ and $[Ru(bpy)_2(benzylamine)_2]^{2+}$ have bands at 2238 and 2235 cm^{-1}, respectively, indicating the presence of nitrile ligands. Both $[Ru(bpy)_2(acrylonitrile)_2]^{2+}$ and $[Ru(bpy)_2(benzonitrile)_2]^{2+}$ have $\nu_{C{\equiv}N}$ bands at 2235 cm^{-1}.

For coordinated organonitriles where little back-bonding is expected, such as in Rh(III),[16] Ru(III),[17] and Co(III)[18] complexes, the $\nu_{C{\equiv}N}$ band is found to be 50–70 cm^{-1} higher than for the uncoordinated nitrile. In the case of $[Ru(NH_3)_5(N{\equiv}CR)]^{2+}$, $\nu_{C{\equiv}N}$ was found to decrease (0–50 cm^{-1}) from the free ligand value. The decrease has been attributed to the strong back-bonding donor ability of the $(NH_3)_5Ru^{2+}$ moiety.[17] In the nitrilebis(2,2′-bipyridine) complexes of Ru(II), $\nu_{C{\equiv}N}$ increases slightly compared to the free ligand (*n*-butyronitrile, 2271 vs. 2253 cm^{-1}; acrylonitrile, 2238 vs. 2234 cm^{-1}), or is unchanged (benzonitrile, $\nu_{C{\equiv}N}$ 2235 cm^{-1} in both cases). The increases in $\nu_{C{\equiv}N}$ are small compared with related Ru(III), Rh(III), and Co(III) cases, which is reasonable and probably means that π-back-bonding in the $Ru(bpy)_2^{2+}$ complexes is present, but to a lesser extent than in $(NH_3)_5Ru^{2+}$ type complexes. The conclusion is expected, given the strongly back-bonding acceptor nature of the 2,2′-bipyridine ligands.

Table II. Electronic Spectral Data for the Amine-Nitrile Complexes of Bis(2,2′-bipyridine)ruthenium(II) in Acetonitrile

Complex	λ_{max}, nm(ϵ)[a]
$[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$	491 (9 200) 348 (7 400) 297 (54 100) 248 (17 500)
$[Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+}$	449 (10 000) 291 (61 100) 235 (29 100)
$[Ru(bpy)_2(N{\equiv}CPh)_2]^{2+}$	414 (9 500) 286 (57 400) 228 (38 500)
$[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)_2]^{2+}$	492 (8 800) 349 (7 100) 296 (56 600) 248 (17 300)
$[Ru(bpy)_2(NH_2CH_2CH{=}CH_2)(N{\equiv}CCH{=}CH_2)]^{2+}$	446 (8 300) 290 (57 500) 246 (22 700)
$[Ru(bpy)_2(N{\equiv}CCH{=}CH_2)_2]^{2+}$	416 (9 300) 286 (58 000) 256 (17 900) 247 (17 900)
$[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)_2]^{2+}$	496 (8 700) 352 (7 300) 297 (56 800) 248 (17 800)
$[Ru(bpy)_2(NH_2CH_2CH_2CH_2CH_3)(N{\equiv}CCH_2CH_2CH_3)]^{2+}$	450 (7 500) 287 (53 100) 242 (17 600)
$[Ru(bpy)_2(N{\equiv}CCH_2CH_2CH_3)_2]^{2+}$	427 (8 500) 287 (55 300) 246 (17 400)

[a] λ values are ±2 nm; ϵ values are ±5%.

Electronic Spectra and Reduction Potentials. Electronic spectra (Table II) and Ru(III)/Ru(II) reduction potentials (Table I) also reflect the effects of back-bonding, but at the metal rather than at the nitrile ligand. The spectra of the bis(amine) complexes are similar to the spectrum of $[Ru(bpy)_2(NH_3)_2]^{2+}$, having two maxima in the visible region (ca. 490 and 345 nm) which have previously been assigned to $d\pi(Ru(II)) \rightarrow \pi^*(bpy)$ MLCT transitions.[19] There are also two maxima in the ultraviolet region (ca. 290 and 245 nm) which have been assigned as $\pi \rightarrow \pi^*(bpy)$ transitions for $[Ru(bpy)_2(NH_3)_2]^{2+}$.[19] Upon the replacement of an amine ligand by a nitrile group, only one $d\pi(Ru(II)) \rightarrow \pi^*(bpy)$ MLCT absorption band is found in the visible region and that band is at higher energy (450 nm). Both observations are consistent with an increase in back-bonding leading to a relative stabilization of the $d\pi$ orbitals.[7,19] This trend continues for the bis(nitrile) complexes where λ_{max}

for the single $d\pi(Ru(II)) \rightarrow \pi^*(bpy)$ band is between 414 and 427 nm (Table II). The positions of the absorbance maxima and $\nu_{C\equiv N}$ stretching frequencies for the bis(nitrile) complexes are consistent with the qualitative order of back-bonding: benzonitrile > acrylonitrile > *n*-butyronitrile.

The conclusions concerning the stabilization of $d\pi(Ru)$ levels by back-bonding are borne out by $E_{1/2}$ values for the series of Ru(III)/Ru(II) couples given in Table I. From a variety of evidence, metal → ligand back-bonding is relatively unimportant in complexes of Ru(III).[20] The effect of replacing saturated amine ligands by back-bonding ligands is to stabilize the $d\pi$ levels of Ru(II) which stabilizes the Ru(II) state. In the bis(bipyridine) complexes, the Ru(II) state is already strongly stabilized by back-bonding to the 2,2′-bipyridine ligands. However, Ru(III)/Ru(II) redox potentials remain sensitive to changes in the ligands at the fifth and sixth coordination sites.[21] This can be seen clearly in the data in Table I where the redox potentials fall into three classes: bis(amines), 1.03–1.04 V amine-nitriles, 1.24–1.29 V; bis(nitriles), 1.48–1.52 V. Changes in reduction potentials follow directly from the number of back-bonding ligands in the fifth and sixth coordination positions.

Solutions of the bis(amine) complexes in acetonitrile were found to be stable over many hours in the dark. However, in normal laboratory lighting, a clean reaction occurred which exhibited well-defined isosbestic points when monitored in the uv-visible spectral region. The photochemical reactions are apparently light-induced substitutions to give amine-acetonitrile complexes. The products had spectra which were very similar to the amine-nitrile complexes (Table II). The amine-nitrile and bis(nitrile) complexes were more stable in solution, but prolonged exposure to light caused substitution of acetonitrile into the coordination sphere. Because of the light sensitivity, much of the work reported here, including the electrochemical and spectral studies, was carried out on solutions which were protected from the light.

Oxidation by Ce(IV). Mechanism of Oxidative Dehydrogenation. The bis(amine) complexes are oxidized rapidly and quantitatively by Ce(IV) in acetonitrile. Spectrophotometric experiments have shown that upon addition of 4 mol of Ce(IV) per mole of $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$, the resulting product is the amine-nitrile complex (eq 5).

$$[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+} + 4Ce(IV) \rightarrow [Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+} + 4H^+ + 4Ce(III) \quad (5)$$

When 8 mol of Ce(IV) are added, the bis(nitrile) complex is the product (eq 6).

$$[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+} + 8Ce(IV) \rightarrow [Ru(bpy)_2(N{\equiv}CPh)_2]^{2+} + 8H^+ + 8Ce(III) \quad (6)$$

The Ce(IV) oxidations were followed stepwise by spectrophotometric titrations using a fast mixing device. The titrations were followed in two stages: 0–4 mol of added Ce(IV)/mole of complex, and 4–8 mol of added Ce(IV). In neither stage were isosbestic points observed. If clean mixtures of $[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+}$ and $[Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+}$ (0–4 mol of Ce(IV) added) or of $[Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+}$ and $[Ru(bpy)_2(N{\equiv}CPh)_2]^{2+}$ (4–8 mol of Ce(IV)) had been present in the solutions, isosbestic points would be expected. The absence of isosbestic points indicates the existence of intermediates in the titrations. Since the overall reactions are quantitative, the most reasonable intermediates are two-electron oxidation products containing bound imine groups: $[Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{2+}$ and $[Ru(bpy)_2(NH{=}CHPh)(N{\equiv}CPh)]^{2+}$. This conclusion is reasonable in light of evidence obtained recently for imine intermediates in the oxidation of amines bound to $(NH_3)_5Ru(II)$[10] and in the oxidation of coordinated diamines to α,α'-diimines.[7]

Preliminary stopped-flow kinetic studies of the oxidation reaction revealed, by direct observation of the Ru(III) species, that the Ru(II) → Ru(III) oxidation step occurs very rapidly[22] so that the ligand dehydrogenation is necessarily a subsequent process. Detailed kinetic data are not available for the dehydrogenation reactions, so that proposal of a detailed mechanism is not possible. However, assuming the intermediacy of the imine species, a series of *net* reactions can be written for the oxidation process. For example, on removal of one electron per mole of complex:

$$2[Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+} \xrightarrow{-2e^-} 2[Ru(bpy)_2(NH_2CH_2Ph)_2]^{3+} \quad (7)$$

$$2[Ru(bpy)_2(NH_2CH_2Ph)_2]^{3+} \rightarrow [Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{2+} + [Ru(bpy)_2(NH_2CH_2Ph)_2]^{2+} + 2H^+ \quad (8)$$

The two-electron oxidation of the ligand by the one-electron oxidant (Ru(III)) requires a *net* disproportionation of the type given in eq 8; furthermore, there is direct evidence for a *net* reaction of this type in the metal-assisted oxidation of $Ru(bpy)_2(2\text{-aminomethylpyridine})^{2+}$.[7] Upon removal of a second electron, a similar sequence of *net* reactions can be written:

$$2[Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{2+} \xrightarrow{-2e} 2[Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{3+} \quad (9)$$

$$2[Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{3+} \rightarrow [Ru(bpy)_2(NH_2CH_2Ph)(N{\equiv}CPh)]^{2+} + [Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{2+} + 2H^+ \quad (10)$$

Oxidation up to the eight-electron stage (the bis(nitrile) complex) can be represented by a related series of net reactions.

It should be noted that the Ru(III) imine complex is also accessible by reactions such as that given in eq 11:

$$[Ru(bpy)_2(NH_2CH_2Ph)_2]^{3+} + [Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{2+} \rightarrow [Ru(bpy)_2NH_2CH_2Ph)_2]^{2+} + [Ru(bpy)_2(NH_2CH_2Ph)(NH{=}CHPh)]^{3+} \quad (11)$$

Such reactions are known to be rapid in related systems.[23] We emphasize again that detailed mechanistic information is not yet available for the individual steps and that following oxidation of Ru(II) to Ru(III) a series of interrelated reactions occurs.

In the electrochemical experiments there was no evidence for either of the imine intermediates (Figure 1). This is reasonable since electrochemical oxidation processes (eq 7 and 9) are far slower than Ce(IV) oxidations, and reactions like eq 11 allow for the conversion of the imine intermediates into the amine-nitrile and bis(nitrile) products before their concentrations become appreciable.

The ligand oxidation reactions are much more rapid in acidic aqueous solution than in acetonitrile. Cyclic voltammograms of the amine complexes in 1.0 M HCl were completely irreversible at scan rates up to 50 V/s, indicating that ligand oxidation is more rapid than recapture of Ru(III) at the electrode. Electrolysis to $n = 4.0$ at potentials more anodic than E_p for the irreversible Ru(II) → Ru(III) step, gave a mixture of 0-, 4-, and 8-electron products for R = $-CH_2CH_2CH_3$ and $-CH{=}CH_2$, and the

amine–nitrile complex was obtained cleanly only for benzylamine.

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References and Notes

(1) N. F. Curtis, *Chem. Commun.*, 881 (1966); *Coord. Chem. Rev.*, **3**, 3 (1968).
(2) J. C. Dabrowlak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 5502 (1972); V. L. Goedken and D. H. Busch, *ibid.*, **94**, 7355 (1972).
(3) H. Elsbernd and J. K Beattie, *J. Chem. Soc. A*, 2598 (1970).
(4) B. C. Lane, J. E. Lester, and F. Basolo, *Chem. Commun.*, 1618 (1971).
(5) D. F. Mahoney and J. K. Beattie, *Inorg. Chem.*, **12**, 2561 (1973).
(6) V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).
(7) G. M. Brown, T. R. Weaver, F. R. Keene, and T. J. Meyer, *Inorg. Chem.*, **15**, 190 (1976).
(8) H. L. Chum and P. Krumholz, *Inorg. Chem.*, **13**, 514, 519 (1974).
(9) W. R. McWhinnie, J. D. Miller, J. B. Watts, and D. Y. Wadden, *Chem. Commun.*, 629 (1971); *Inorg. Chim. Acta*, **7**, 461 (1973).
(10) S. E. Diamond, G. M. Tom, and H. Taube, *J. Amer. Chem. Soc.*, **97**, 2661 (1975).
(11) G. M. Brown, R. W. Callahan, and T. J. Meyer, *Inorg. Chem.*, **14**, 1915 (1975).
(12) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).
(13) S. A. Adeyemi, Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1973.
(14) Electrochemical reversibility was determined, when possible, by plots of log $(i_l - i)/i$ vs. E using stirred-solution voltammetry data. In cases where subsequent ligand reactions were too rapid, reversibility was determined using cyclic voltammetry using the ratio of anodic to cathodic peak currents (i_c/i_a), ΔE_p = 60–65 mV and the sweep rate independence of ΔE_p as criteria. The slightly greater value of ΔE_p than the theoretical value of 59 mV can be attributed to uncompensated solution resistance.
(15) A. W. Zanella and P. C. Ford, *Inorg. Chem.*, **14**, 42 (1975).
(16) R. D. Foust and P. C. Ford, *Inorg. Chem.*, **11**, 899 (1972).
(17) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).
(18) D. Pinnell, G. B. Wright, and R. B. Jordan, *J. Am. Chem. Soc.*, **94**, 6104 (1972); F. R. Keene and J. MacB. Harrowfield, unpublished data, Australian National University, Canberra, 1973.
(19) G. M. Bryant, J. E. Fergusson, and H. J. K. Powell, *Aust. J. Chem.*, **24**, 257 (1971).
(20) H. Taube, *Surv. Prog. Chem.*, **6**, 1 (1973).
(21) G. M. Brown, Ph.D. Dissertation, University of North Carolina, Chapel Hill, N.C., 1974.
(22) E. M. Gupton and F. R. Keene, unpublished data, University of North Carolina, Chapel Hill, 1974.
(23) J. C. Solenburger, Ph.D. Dissertation, Washington University, St. Louis, Mo., 1969; M. Chan and A. C. Wahl, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., 1974, Abstract INOR 97.

Electrostatic Facilitation of General Acid Catalyzed α-Oxonium Ion Formation in a Lysozyme-Like Environment: Synthesis of the Models

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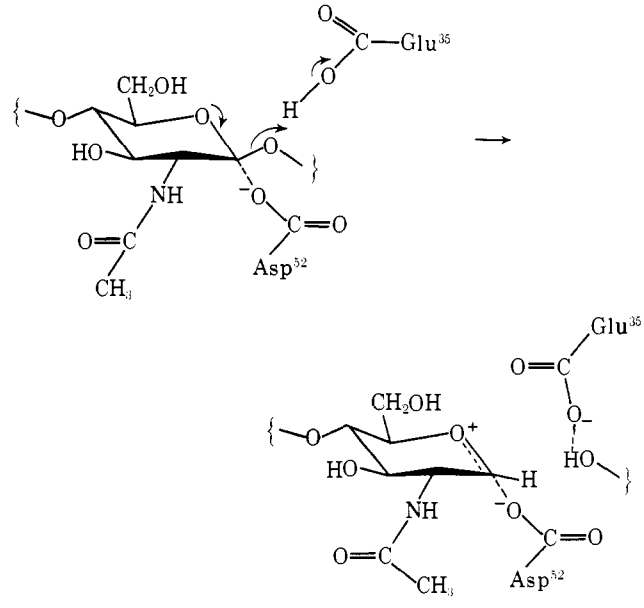
Abstract: The syntheses and structural correlations of *exo*-2,5-dimethyl-*endo*-2-(1-methoxyvinyl)bicyclo[2.2.1]heptyl-*endo*-5-carboxylic acid (**1**) and a reference compound, *exo*-2-methyl-*endo*-2-(1-methoxyvinyl)bicyclo[2.2.1]heptyl-*exo*-5-carboxylic acid (**2**) are described, and arguments are presented which suggest that the effect of ionization of the *endo*-carboxylic acid group on the hydrolysis of **1** should be a reasonable model for the effect of aspartic acid-52 of lysozyme on saccharide hydrolysis by the enzyme.

Crystallographic results have suggested several catalytic features which are believed to be of importance in the mechanism of action of hen lysozyme.[1] For example, "general acid catalysis" of saccharide substrates by glutamic acid-35 (Glu^{35}) of the enzyme has been postulated, and the reasonableness of such a mechanism has been amply verified in model studies.[2] Substrate distortion was implicated in the catalytic mechanism of the enzyme from the crystallographic results, and model studies have shown that this feature may indeed lead to substantial rate enhancements in acetal and ketal hydrolyses.[3-7] One aspect of lysozyme catalysis, however, which has not been satisfactorily reproduced with models is a postulated rate enhancement due to stabilization of the developing carbonium ion intermediate in the saccharide cleavage reaction by a second ionized carboxyl group, identified as aspartic acid-52 (Asp_{52}) from the crystallographic work (Scheme I). Despite a large number of attempts, no case of such a rate acceleration has been found which is at the same time kinetically unambiguous.

In previous work examining this question using both acetal[2] and vinyl ether[8,9] hydrolyses to generate the appropriate α-oxocarbonium ion, the rigid template to which the carboxylate ion and the proionic carbon have been attached, is a small, planar (or nearly planar) ring system, usually a benzene ring. Aromatic systems are generally excellent for

Scheme I



this purpose because a wide variety of substitution products are synthetically accessible,[10] aromatic chromophores ren-