mm, 4-mm diameter) packed with LiChrosorb RP-18 (10 μm) and a variable wavelength UV detector. Isocratic elution (1 cm^3 min^{-1}) with mixtures of acetonitrile and acetic acid buffer (pH 4.4) was employed throughout, the detection wavelength being generally 260 nm. The retention times observed are given in Table V.

Calculation of the Rate Constants. The first-order rate constants, k_1, for the disappearance of the starting materials were calculated from eq 6, where $[S(total)]_0$ is the initial substrate

$$\ln\frac{[S(total)]_0}{[S(total)]_t} = k_1 t \quad (6)$$

concentration and $[S(total)]_t$ the concentration at the moment t. The first-order rate constants, k_2, for the disappearance of the first accumulated intermediate, **2**, in the hydrolysis of 9-(β-D-ribofuranosyl)purine and its 2′,3′-*O*-isopropylidene derivative were obtained by least-squares fitting by eq 7. Here $[B]_t$ denotes the

$$\frac{[B]_t}{[B]_T} = \frac{e^{-k_1 t} - e^{-k_2 t}}{e^{-k_1 T} - e^{-k_2 T}} \quad (7)$$

concentration of **2** at the moment t, and $[B]_T$ is the maximum concentration reached at time t = T. The first-order rate constants, k_2, for the cleavage of the $^{14}C8$ atom from 9-(β-D-ribofuranosyl)[8-^{14}C]purine were obtained by least-squares fitting by eq 8, where $[H^{14}COO^-]$ stands for the concentration of the formate

$$[H^{14}COO^-] = [S(total)]_0\left(1 - \frac{k_2}{k_2 - k_1}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}\right) \quad (8)$$

ion released at the moment t. First-order rate constants, k_3, for the formation of 4,5-diaminopyrimidine and the release of D-ribose from 9-([1′-^{14}C]β-D-ribofuranosyl)purine were calculated by least-squares fitting by eq 9. [P] stands for the concentration of 4,5-diaminopyrimidine or D-ribose formed at the moment t.

$$[P] = [S(total)]_0\left(1 - \frac{k_2 k_3}{(k_2 - k_1)(k_3 - k_1)}e^{-k_1 t} - \frac{k_1 k_3}{(k_1 - k_2)(k_3 - k_2)}e^{-k_2 t} - \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)}e^{-k_3 t}\right) \quad (9)$$

First-order rate constants for the formation of purine and 4,5-diaminopyrimidine from 4-amino-5-formamidopyrimidine were obtained by multiplying the rate constant for the disappearance of the starting material by the appropriate mole fractions of the products at infinite time.

Acknowledgment. The financial aid from the Academy of Finland, Council for the Natural Sciences, is gratefully acknowledged.

Oxidation of *N,N′*-Dialkyl-1,2-bishydroxylamines

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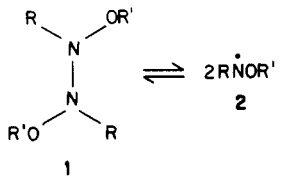
Oxidation of *N,N′*-dialkyl-1,2-bishydroxylamines $RNHOCH_2CH_2ONHR$ gives products that are a function of oxidant. For R = *i*-Pr (**5**) and *m*-chloroperbenzoic acid the products are diisopropyl azo dioxide, $HOCH_2CH_2ONHCH(CH_3)_2$, and ethylene glycol. Product ratios indicate independent oxidation of the two hydroxylamine functions. Na_2WO_4/H_2O_2 in D_2O gives the azo dioxide, ethylene glycol, and acetone oxime. Oxidation with bromine and 1,4-diazabicyclo[2.2.2]octane or *tert*-butyl hypochlorite and triethylamine gives product ratios that are consistent with two pathways to the bis oxime **7**: one that appears to give **7** directly and a second that goes through the monohydroxylamine monooxime **15**. It is proposed that the former reaction proceeds through the 1,4,2,3-dioxadiazine ring, which is oxidized quickly to products. Reaction products from the bishydroxylamine with R = CH_3 are similar to those with R = *i*-Pr.

Dialkoxyhydrazines **1** are a little known class of generally labile molecules.[1] The *N,N′*-dialkyl derivatives have not been seen, but their existence has been inferred from kinetic and product studies of hydroxylamine free radicals **2**.[2] Kaba and Ingold have identified four pathways for



1 **2**

bimolecular self-reaction of **2** involving production of (a) nitrogen and the alcohol (R = H), (b) the azo compound and alcohol (R = Ph), (c) the azo compound, aldehyde, and alcohol (R = CHR_2, Russell fragmentation), and (d) the hydroxylamine and oxime (R′ = CH_2Ph, disproportionation). Thus the *N,N′*-dialkyl-*N,N′*-dialkoxyhydrazines have the interesting property that they exist partly or largely as the hydroxylamine free radical but decompose to give products which generally retain the N–N bond.

One way of forcing the equilibrium toward the hydrazine form is to connect the two hydroxylamine radicals, i.e., to synthesize a cyclic dialkoxyhydrazine. A particularly interesting member of this class would be the six-membered dioxadiazine **3**.[3] If it were to decompose with retention of the N–N bond, an azo compound and the 1,4-dioxygen diradical **4** would be formed. Diradical **4** is the intermediate in dioxetane chemiluminescence.[4,5] On the other

(1) Dixon, D. K. W.; Weiss, R. H.; Nelson, W. N. *Tetrahedron Lett.* **1983**, *24*, 4393–4396, and references therein.
(2) Kaba, R. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7375–7380.
(3) We recently synthesized the first 1,4,2,3-dioxadiazines, the dicarbomethoxy and dicarbethoxy derivatives of **3**.[1] Dialkoxyhydrazines bearing electron-withdrawing groups can be isolated, see references in ref. 1.
(4) (a) Adam, W.; Zinner, K. In "Chemical and Biological Generation of Excited States"; Adam, W., Cilento, G., Eds.; Academic Press: New York, 1982; pp 153–189. (b) Adam, W.; Cilento, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 529–542.
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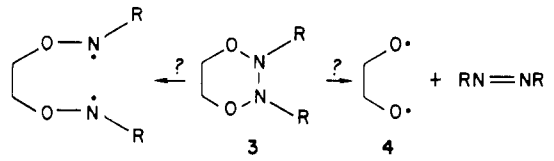
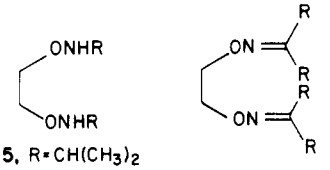
hand, homolysis of the N–N bond would lead to a 1,6-diradical, which could fragment to an olefin and the nitroso compound.[6]



3 4

The most promising route to **3** involves oxidation of the corresponding bishydroxylamine. In this paper we report an investigation of the oxidation of two *N,N'*-dialkyl-1,2-bishydroxylamines **5** and **6**. The products are a function of oxidant. In some cases it appears that the dioxadiazine ring system is indeed formed but that oxidation to other products is faster than unimolecular decomposition.



5, R = $CH(CH_3)_2$
6, R = CH_3

7, R = CH_3
8, R = H

The bishydroxylamines **5** and **6** were synthesized by reduction of the corresponding bisoximes which were in turn made from 1,2-bis(aminooxy)ethane and acetone or formaldehyde. Reduction of **7** with $NaBH_3CN$ (ref 7) gave **5** smoothly in 82% yield. Treatment of **8** with $NaBH_3CN$ gave a number of products. Reduction of **8** with borane–pyridine complex,[8] however, gave **6** as the main product in 23% yield.

The first oxidants chosen were Ag_2O and Ag_2CO_3/Celite. With **5**, both of these gave only unchanged starting material, the former even after 24 h at reflux in benzene. The reason for this stability is unclear. Kaba and Ingold have reported that Ag_2O oxidation of *N*-isopropyl-*O*-methylhydroxylamine (degassed benzene, 24 h, 20 °C) gives 20 mol % methanol and 10 mol % *O*-methylacetoxime.[2] *O,N*-Dimethylhydroxylamine under the same conditions gave methanol as the only major organic product. In our hands, *O,N*-dimethylhydroxylamine oxidized with Ag_2O, although the product mixture was more complicated, perhaps due to the presence of oxygen. Bishydroxylamine **5** was also unreactive toward PbO_2.

Other reagents did result in the oxidation of the bishydroxylamines, however. Treatment of **5** with 1 equiv of *m*-chloroperbenzoic acid (MCPBA) in $CDCl_3$ for 24 h gave mixture whose NMR spectrum (360 MHz) was consistent with ~52% starting material, 27% azo dioxide **9** (ref 9) [δ 1.37 (d, J = 9 Hz, 6 H), 5.33 (sept, J = 9 Hz, 2 H)], 16% ethylene glycol (**10**) (δ 3.75, s), and 32% monoalcohol monohydroxylamine **11** [δ 1.18 (s, 3 H), 3.87 (m, 2 H), 3.92 (m, 2 H), the other half of the methyl doublet and the methine septet are presumably under starting material]. The products indicate oxidation of **5** to **12**, which decomposes to nitrosopropane and **11** (Scheme I). Oxidation of **11** gives ethylene glycol and a second molecule of nitrosopropane, which dimerizes to the azo dioxide.

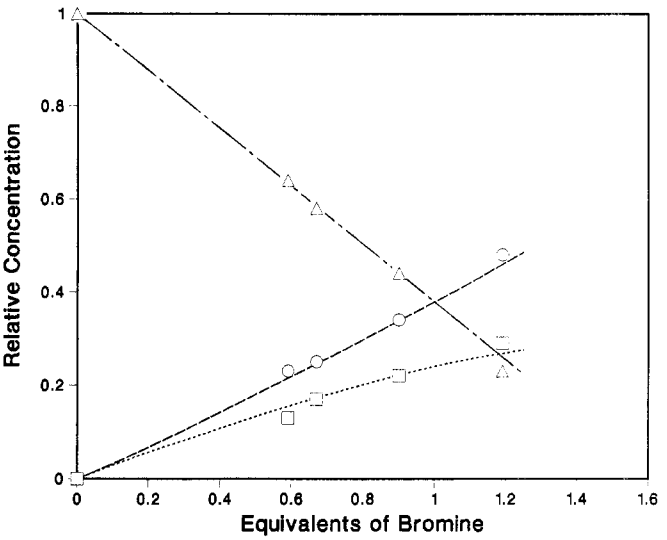
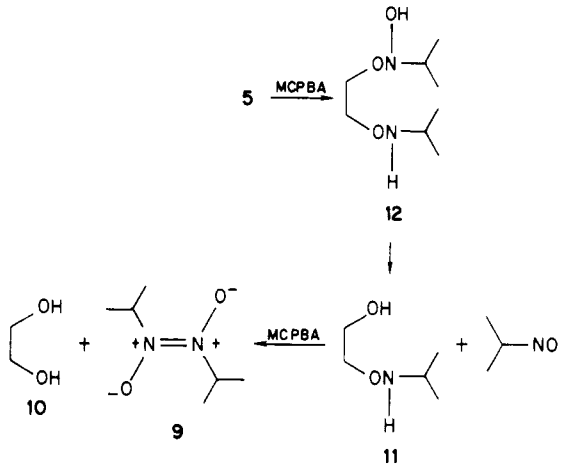


Figure 1. Relative concentrations of bishydroxylamine **5** (△), monohydroxylamine monoxime **15** (□), and bisoxime **7** (○) as a function of added bromine (4 equiv of 1,4-diazabicyclo[2.2.2]octane, Me_2SO-d_6, ^1H NMR). The open points are experimental. The lines are calculated for the relative rate constants k_1 = 1.0, k_2 = 0.5, k_3 = 1.3.

Scheme I



Oxidation of **5** with Na_2WO_4/H_2O_2 in D_2O gave ethylene glycol, azo dioxide **9**, and acetone oxime (**13**) in 80%, 45%, and 30% yields, respectively. A small amount of 1,2-bis(aminooxy)ethane (**14**) (1%, estimated by GC) probably came from hydrolysis of the bisoxime **7**. An unknown compound was also detected (~15% yield, ^1H NMR showed a doublet at δ 1.50). The formation of ethylene glycol and the azo dioxide **9** is similar to the oxidation of **5** with MCPBA. In aqueous solution, the nitroso compound rearranges to give acetone oxime. Oxidation of **6** with Na_2WO_4/H_2O_2 gave ethylene glycol as the only identified product.

Oxidation of **5** with nickel peroxide in CH_2Cl_2 for 20 h led to recovery of starting material, presumably due to steric hindrance of the isopropyl groups. Bishydroxylamine **6** did react with nickel peroxide, however, to give a complex mixture of products. The ^1H NMR of the mixture contained, in addition to other signals, a singlet at 2.95 ppm appropriate for an N–CH_3 group (integration of signal ~20% that of total methyl region). It is unlikely that this belongs to the dioxadiazine, because heating the mixture at 45 °C for 6.5 h did not decrease the intensity of the signal. Attempts to isolate the compound by extraction or column chromatography led to loss of the sin-

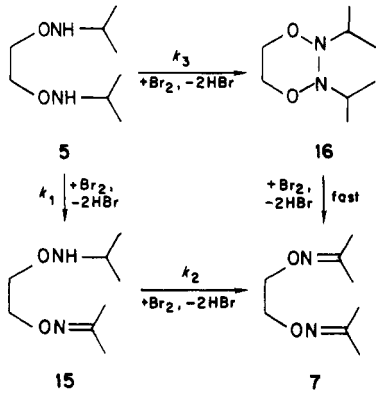
(6) Hydroxylamine free radicals of the form RNOR' do not cleave to R'· and RNO. For leading references, see: Negoita, N.; Baican, R.; Balaban, A. T. *Tetrahedron Lett.* **1973**, 1877–1878. Woynar, H.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 3813–3815.
(7) Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897–2904.
(8) Kawase, M.; Kikugawa, Y. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 643–645.
(9) Taylor, K. G.; Chi, M.-S.; Clark, M. S. *J. Org. Chem.* **1976**, *41*, 1131–1135.

Table I. Oxidation of Bishydroxylamines 5 and 6

starting material	reagent (equiv)	conditions[b]	products[c] (% yield)
5	Ag_2O (6.7)	benzene, 2 d, RT	NR
	Ag_2CO_3/Celite (2.1)	benzene, 16 h, RT	NR
	PbO_2 (2.1)	benzene, 16 h, RT	NR
	$Pb(OAc)_4$ (2.0)	benzene, 16 h, RT	7 (100%)
	MCPBA (1.0)	$CDCl_3$, 24 h, RT	5 (52%), 9 (27%), 10 (16%), 11 (32%)
	NiO_x (3.0)	CH_2Cl_2, 20 h, RT	NR
	DEAD (1.0)	$CHCl_3$, 48 h, RT	a
	Na_2WO_4 (0.44), H_2O_2 (1.6)	D_2O, 1 h, RT	9 (80%), 10 (45%), 13 (30%), 14 (1%)
	t-BuOCl (1.0), Et_3N (1.0)	$CDCl_3$, 5 min, 0 °C → RT	5 (54%), 7 (35%), 15 (11%)
	t-BuOCl (2.0), Et_3N (2.0)	$CDCl_3$, 5 min, 0 °C → RT	7 (100%)
	Br_2 (1.0), Na_2CO_3 (1.0)	D_2O, 5 min, RT	5 (31%), 7 (66%), 15 (3%)
6	Na_2WO_4 (0.44), H_2O_2 (2.6)	D_2O, 1 h, RT	10
	NiO_x (3.0)	CH_2Cl_2, 23 h, RT	a
	t-BuOCl (1.0), Et_3N (1.0)	$CDCl_3$, 5 min, 0 °C → RT	6, 8
	t-BuOCl (2.0), Et_3N (2.0)	$CDCl_3$, 5 min, 0 °C → RT	8 (100%)

[a] Products not identified, see text. [b] RT = room temperature. [c] NR = no reaction.

Scheme II



glet. Oxidation of **5** with diethyl azodicarboxylate (DEAD) also lead slowly to a complex mixture of products.

Bisoximes were formed when **5** and **6** were treated with halogen reagents or $Pb(OAc)_4$ (Table I). The oxidation of **5** with bromine was investigated in detail. Figure 1 shows the relative concentration of monohydroxylamine monooxime **15** and bisoxime **7** as a function of added Br_2. It can be seen that the amount of bisoxime **7** is always greater than that of the monooxime **15**. This observation is inconsistent with a simple **5** → **15** → **7** pathway and argues that there is another route from **5** to **7** that does not go through **15**. A mechanism that explains the products is shown in Scheme II. Bromination of one of the nitrogens could be followed by ring closure to give **16**. Reaction of **16** with a second molecule of Br_2 and loss of HBr would give the bisoxime. The experimental product ratios are consistent with k_1, k_2, and k_3 having similar magnitudes. If one assumes that $k_2 = 0.5k_1$ because the two ends of **5** oxidize separately in the pathway through **15**, then $k_3 = 1.3k_1$ gives a good fit to the experimental data, as shown in Figure 1.[10] Further support for this mechanism was obtained by oxidizing mixtures of **5**, **7**, and **15** made by mixing various amounts of the three compounds together. The product ratios were consistent with those found for the oxidation of bishydroxylamine **5** alone, indicating that neither **7** nor **15** acts as a catalyst for the oxidation of **5**.

The above observations indicate that the oxidants can be divided into three groups: those that do not effect oxidation (Ag_2O, Ag_2CO_3/Celite and PbO_2); those that initially hydroxylate the bishydroxylamine resulting in cleavage to alcohols and nitroso compounds (MCPBA and Na_2WO_4/H_2O_2); and those that effect closure to the dioxadiazine but oxidize the ring system to the bisoxime ($Pb(OAc)_4$, t-BuOCl/Et_3N, and Br_2/base). It therefore appears that oxidation of the dioxadiazine is faster than either homolysis of the N–O bonds to give the dioxygen diradical (**4**) and the azo compound or homolysis of the N–N bond and fragmentation of the 1,6-bishydroxylamine diradical to ethylene and two molecules of nitrosoalkane.

Experimental Section

General Methods. ^{13}C NMR spectra were taken on a JEOL FX-100 spectrometer. ^1H NMR spectra were taken on the FX-100, Perkin-Elmer R-24B 60-MHz, or Bruker WH-360 spectrometers. ^1H and ^{13}C NMR spectra are reported in parts per million (δ) relative to Me_4Si (δ 0.00). Infrared spectra were taken on a Perkin-Elmer 283B spectrophotometer. Mass spectra were obtained on a Finnigan 3200 GC/MS using a 4 ft × $^1/_4$ in. 3% SE-30 on Gaschrome Q column. Gas chromatography (GC) was done on a Perkin-Elmer Sigma 3B gas chromatograph using a 3% OV-1 on 100/120 mesh Chromosorb W column at 100 °C. Preparative GC was done on a 9 ft × $^1/_4$ in. 10% OV-17 on 40/50-mesh Anakrom ABS column at 130 °C.

Boiling points (bp) are uncorrected. Preparative TLC plates (silica gel G, 1000 μm) were purchased from Analtech. 1,2-Bis(aminooxy)ethane (**14**) was prepared by hydrazinolysis of 1,2-bis(phthalimidooxy)ethane.[11,12] Silver carbonate on Celite[13] and nickel peroxide[14] were prepared according to literature procedures. Silver(I) oxide was purchased from Allied Chemical; *tert*-butyl hypochlorite (Frinton) was purified by vacuum distillation. Sodium cyanoborohydride, borane–pyridine complex and DEAD were purchased from Aldrich.

***N,N'*-Diisopropyl-1,2-bis(aminooxy)ethane (5).** To a stirred solution of **7** (8.67 g, 50.3 mmol), $NaBH_3CN$ (12.7 g, 0.201 mol), and bromocresol green solution (1 mL) in MeOH (100 mL) was added 2 N HCl/MeOH dropwise at room temperature to maintain the yellow color of the indicator. The yellow color remained constant after 5 h of adding 2 N HCl/MeOH (75 mL). The mixture was stirred an additional 12 h at room temperature. Additional 2 N HCl/MeOH (10 mL) was added and the mixture was stirred 4 h more. The solvent was removed under reduced pressure and the residue was dissolved in H_2O (20 mL). The pH was raised >9 with 6 N KOH. The solution was extracted with CH_2Cl_2 (4 × 30 mL). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was vacuum distilled to give 7.27 g of **5** as a colorless liquid (82% yield).

(10) The kinetics simulation program is based on the DVOGER routine from the IMSL Scientific Library. International Mathematical and Statistical Libraries, Inc., GNB Bldg., 7500 Bellaire Blvd. Houston, TX 77036.

(11) Bauer, L.; Suresh, K. S. *J. Org. Chem.* **1963**, *28*, 1604–1608.
(12) Dixon, D. W.; Weiss, R. H. *J. Org. Chem.*, in press.
(13) McKillop, A.; Young, D. W. *Synthesis* **1979**, 401–422.
(14) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597–1601.

An analytically pure sample was obtained by preparative GC: bp 108–110 °C (45 mm); IR ($CHCl_3$) 3260, 2975, 1385, 1264, 1077, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 12 H), 3.17 (m, 2 H), 3.82 (s, 4 H), 5.35 (br s, 2 H, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 71.8, 50.5, 19.0; mass spectrum, m/e (relative intensity) 176 (0.30, M^+), 161 (16), 104 (28), 102 (77), 76 (6.7), 75 (11), 72 (46), 60 (29), 59 (6.9), 58 (100), 56 (21). Anal. Calcd for $C_8H_{20}N_2O_2$: C, 54.52; H, 11.44; N, 15.89. Found: C, 54.20; H, 11.53; N, 15.51.

***N,N'*-Dimethyl-1,2-bis(aminooxy)ethane (6).** To a stirred solution of 8 (4.47 g, 38.5 mmol) and borane–pyridine complex (25.9 mL, 0.257 mol) in EtOH (100 mL) maintained at less than 5 °C was added 20% ethanolic HCl (210 mL) dropwise over a 1.5-h period under N_2. After addition was complete, the mixture was stirred for 24 h at room temperature. The mixture was made basic with neat Na_2CO_3 and then filtered. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a liquid residue that was vacuum distilled to give 1.49 g of a colorless liquid. ^1H NMR showed the liquid to be a mixture of 6 (23% yield) and other unidentified products. Compound 6 was isolated by preparative GC: bp 80–84 °C (50 mm); IR ($CHCl_3$) 3290, 2960, 1470, 1073, 964 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70 (s, 6 H), 3.82 (s, 4 H), 5.56 (br s, 2 H, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 71.7, 39.2; mass spectrum, m/e (relative intensity) 120 (0.17, M^+), 90 (6.7), 89 (6.6), 75 (4.6), 74 (100), 73 (2.6), 72 (3.6), 62 (2.7), 61 (3.2), 60 (10), 58 (4.6). Anal. Calcd for $C_4H_{12}N_2O_2$: C, 39.99; H, 10.07; N, 23.31. Found: C, 39.84; H, 10.45; N, 23.52.

Acetone *O,O'*-1,2-Ethanediylbisoxime (7). Acetone (8.28 mL, 0.112 mol) was added dropwise to a stirred solution of 1,2-bis(aminooxy)ethane (5.16 g, 56.0 mmol) in H_2O (100 mL) at room temperature. The mixture was stirred for 7 h. The mixture was extracted with CH_2Cl_2 (5 × 100 mL). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a crude yellow liquid. Vacuum distillation gave 8.83 g of 7 as a colorless liquid (92% yield): bp 99–100 °C (35 mm); IR ($CHCl_3$) 2990, 1650, 1371, 1076, 946 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (s, 12 H), 4.17 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 154.9, 71.7, 21.8, 15.6; mass spectrum, m/e (relative intensity) 173 (0.99, $M^+ + H$), 172 (0.17, M^+), 117 (4.8), 116 (81), 100 (15), 74 (3.4), 73 (5.5), 70 (16), 57 (9.0), 56 (100), 55 (2.5), 54 (3.5).

Formaldehyde *O,O'*-1,2-Ethanediylbisoxime (8). Aqueous formaldehyde (37%, 7.6 mL, 94 mmol) was added dropwise to a stirred solution of 1,2-bis(aminooxy)ethane (4.33 g, 47.0 mmol) in CH_2Cl_2 (40 mL) at room temperature. The reaction was mildly exothermic. After stirring for 10 min, H_2O (15 mL) was added. The layers were separated and the aqueous layer was saturated with NaCl and extracted with CH_2Cl_2 (5 × 25 mL). The combined extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give 4.5 g of 8 as a colorless liquid (82% yield): IR ($CHCl_3$) 2940, 1617, 1356, 1061, 957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.28 (s, 4 H), 6.71 (AB quartet, J_{AB} = 8 Hz, ν_{AB} = 36 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 137.6, 72.2; mass spectrum, m/e (relative intensity) 117 (0.55, $M^+ + H$), 116 (0.18, M^+), 91 (9.1), 89 (4.5), 88 (100), 72 (28), 71 (29), 70 (3.0), 61 (63), 59 (4.3), 58 (84).

Acetone *O*-[2-[(*N*-Isopropylamino)oxy]ethyl]oxime (15). To a stirred solution of 7 (1.16 g, 6.74 mmol), $NaBH_3CN$ (565 mg, 8.99 mmol), and bromocresol green solution (few drops) in MeOH (20 mL) was added 2 N HCl/MeOH at room temperature to maintain the yellow color of the indicator. After 3 h of addition, the yellow color remained constant and the mixture was allowed to stir for 24 h. The solvent was removed under reduced pressure to give a residue that was dissolved in H_2O (10 mL). The pH was raised to >9 with 6 N KOH and the basic solution was extracted with $CHCl_3$ (5 × 30 mL). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give 968 mg of a colorless liquid that contained the desired monohydroxylamine monooxime 15 (33% yield) along with 5 and 7. Compound 15 was isolated by preparative TLC (silica gel, 1:2 cyclohexane/ethyl acetate). An analytically pure sample was obtained by preparative GC: IR ($CHCl_3$) 3260, 2980, 1650, 1373, 1078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, J = 7 Hz, 6 H), 1.36 (s, 6 H), 3.17 (sept, J = 7 Hz, 1 H), 3.37 (m, 2 H), 4.15 (m, 2 H), 5.27 (br s, 1 H, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 154.9, 73.1, 71.5, 51.5, 21.8, 20.0; mass spectrum, m/e (relative intensity) 174 (M^+, 0.09), 159 (2.2) 118 (2.4), 100 (18), 74 (8.0), 73 (12), 70 (23), 59 (3.1), 58 (18), 57 (7.9), 56 (100), 54 (4.8). Anal. Calcd for $C_8H_{18}N_2O_2$: C, 55.15; H, 10.41; N, 16.08. Found: C, 55.25; H, 10.62; N, 15.86.

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Registry No. 5, 92670-17-2; 6, 92670-18-3; 7, 92670-19-4; 8, 91523-97-6; 9, 92670-22-9; 10, 107-21-1; 11, 92670-21-8; 12, 92670-20-7; 13, 127-06-0; 14, 5627-11-2; 15, 92670-23-0; 16, 92670-24-1; MCPBA, 937-14-4; DEAD, 1972-28-7; Na_2WO_4, 13472-45-2; H_2O_2, 7722-84-1; Br_2, 7726-95-6; *t*-BuOCl, 507-40-4; Et_3N, 121-44-8; Ag_2O, 20667-12-3; Ag_2CO_3, 534-16-7; PbO_2, 1309-60-0; $Pb(OAc)_4$, 546-67-8; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; nickel oxide, 11099-02-8; acetone, 67-64-1; formaldehyde, 50-00-0.

Novel Electrocatalytic Procedure for the Oxidation of Alcohols, Aldehydes, Cyclic Ketones, and C–H Bonds Adjacent to Olefinic or Aromatic Groups

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A novel electrocatalytic procedure is described for the oxidation of primary and secondary alcohols, cyclic ketones, and C–H bonds adjacent to aromatic or olefinic groups. The procedure involves the use of the Ru^{IV} oxidant $[Ru(trpy)(bpy)(O)]^{2+}$ (trpy is 2,2',2''-terpyridine; bpy is 2,2'-bipyridine) in water at pH 6.8 or in dimethyl sulfone–water mixtures and is based on an electrochemical "shuttle" mechanism in which the Ru^{IV} complex is regenerated by electrochemical oxidation of $[Ru^{II}(trpy)(bpy)(H_2O)]^{2+}$.

Introduction

In principle, the use of electrolytic techniques for carrying out organic redox reactions has many appealing features.[1] In practice, complications can arise from high overvoltages and an absence of selectivity. Both reactivity characteristics have their origins in the intrinsic properties of the electrode–solution interface. An alternate approach involves the use of homogeneous or surface-attached catalysts where the redox chemistry occurs at the catalyst and the role of the electrode is to provide a source of oxidizing or reducing equivalents at a controlled potential. An obvious advantage of this approach is that the reactivity

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