$\rightleftharpoons [Cl_2FeS_2MoS_2]^{2-}$ (**4**) + $FeCl_2$.[16] Reaction of well-authenticated **4**[16-18] with PhS^- affords $[(PhS)_2FeS_2MoS_2]^{2-}$[17] (**5**), also obtainable by other methods.[16-19] As yet we have found no routes to the vanadium analogues of binuclear **4** and **5** or to the molybdenum analogue of trinuclear **2**.

The foregoing structural and reactivity differences of $[MoS_4]^{2-}$ and $[VS_4]^{3-}$—notably the large difference in Fe–Cl bond lengths between **1** and **3** and the ready formation and stability of *tri*nuclear **1** and **2**—are particularly clear manifestations of the higher negative charge of $[VS_4]^{3-}$ and attendant enhanced affinity for binding of FeX_2 groups with either hard (X = Cl) or soft (X = SPh) ligands. Highly stable interactions of these sorts are not sustained by $[MoS_4]^{2-}$. This feature may permit synthesis of extended linear metal–sulfur arrays on the basis of repeating $[VS_4]^{3-}$ units, a matter under investigation. One further problem in group 5a thiometalate chemistry is the preparation of discrete Nb(V) and Ta(V) ions. We have been unable to repeat the reported synthesis of $[NbO_2S_2]^{3-}$.[20] However, syntheses of soluble salts of $[M_6S_{17}]^{4-}$ (M = Nb, Ta), ions with exceptional structures, have been developed.[21] This research and a more detailed account of Fe–V–S chemistry will be presented subsequently.

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Supplementary Material Available: X-ray structural data for $(NH_4)_3VS_4$ and $(Me_4N)_3[VFe_2S_4Cl_4]\cdot DMF$: positional and isotropic and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Nitroxyl-Mediated Electrooxidation of Amines to Nitriles and Carbonyl Compounds

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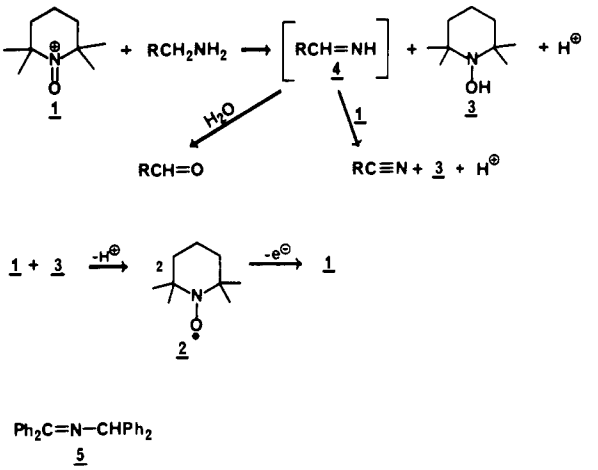
Oxidations employing an electrochemically regenerated reagent are finding increasing application in organic synthesis.[1] We have been interested in the oxidizing and other chemical properties of the nitrosonium ion **1**, which is easily generated by electrooxidation of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, **2**) at + 0.33 V (vs. Ag/Ag^+).[2] The oxidation of alcohols to aldehydes and ketones using catalytic amounts of **2** and controlled potential electrolysis has been reported, including the observation of a special selectivity for primary alcohols in the presence of secondary alcohols.[3,4] Here we report the reactions of amines under similar oxidation conditions, demonstrating efficient direct formation of aldehydes and ketones (in aqueous media) and a direct conversion to nitriles (in anhydrous acetonitrile).[5-7]

Scheme I



In the process (Scheme I), the nitrosonium ion **1** is expected to react with the amine, eliminating a proton and producing the hydroxylamine **3**.[8] Syn proportionation of **1** and **3** produces **2**, which is reoxidized electrochemically to complete a catalytic cycle. A weak base (2,6-lutidine is satisfactory) is used to avoid the inhibiting effect of high acid concentration. Imines (**4**) are the expected intermediates, which can react again with **1** to produce nitriles or can be hydrolyzed to carbonyl compounds; imines have not been detected.

Reactions are performed at 23 °C and are generally complete in a few hours using initial currents in the range 200–300 mA. The amount of catalyst at the start (0.2–0.4 mol equiv) is adjusted to provide complete conversion and reasonable rates, as the nitrosonium ion **1** slowly decomposes during the oxidation. The reactions proceed with about 90% Coulomb efficiency on the basis of starting amine. In the simplest procedure (A), the amine (1 mmol), 2,6-lutidine (8 mmol), and **2** (0.2 mmol; or the 4-hydroxy analogue[9]) were added to 25 mL of electrolyte solution[10] in a

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(2) Cation **1** is easily formed by oxidation of the readily available nitroxy **2** with (a) chlorine (Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Akad. Sci. USSR* **1965**, 1927–1936), (b) peracid (Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *Tetrahedron Lett.* **1975**, 2869–2872), and (c) electrooxidation (Sümmermann, W.; Deffner, U. *Tetrahedron* **1975**, *31*, 593–596).
(3) Electrocatalytic oxidation of alcohols and special selectivity were reported very recently: Semmelhack, M. F.; Chou, C. S.; Cortés, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492.
(4) The first observation of oxidation of alcohols with **1** (generated chemically) demonstrated simply that methyl, ethyl, and isopropyl alcohols could be converted into the corresponding carbonyl compounds: (a) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Akad. Sci. USSR* **1978**, 1874–1881. A combination of **2** and peracid is also reported to convert alcohols to aldehydes (and acids) and ketones: (b) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860–1862. (c) Ganem, B. *Ibid.* **1975**, *40*, 1998–1999.
(5) Highly electrophilic oxidizing agents of the sort that readily oxidize alcohols have not been generally successful in the conversion of amines to carbonyl compounds. For examples and discussion, see: (a) Rawalay, S. S.; Schechter, H. *J. Org. Chem.* **1967**, *32*, 3129. (b) Audette, R. J.; Quail, J. W.; Smith, P. J. *Tetrahedron Lett.* **1971**, 279. (c) Stephens, F. F.; Bower, J. D. *J. Chem. Soc.* **1949**, 2971. Nakagawa K.; Onoue, H. Sugita, *J. Chem. Pharm. Bull.* **1964**, *12*, 1135.
(6) Direct methods for converting amines to nitriles with electrophilic reagents are rare. For examples, see: (a) Kametani, T.; Takahashi, K.; Ohsawa, T.; Ihara, M. *Synthesis* **1977**, 245. (b) Schmidt, H.-J.; Schäfer, H. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 109. (c) Czarny, M. *Synth. Commun.* **1976**, *6*, 285. Recently, a direct electrochemical method employing nickel hydroxide electrodes in a basic medium has been reported for conversion of simple amines to nitriles. It is not useful for conversion of amines to aldehydes: (d) Fledhues, U.; Schäfer, H. J. *Synthesis* **1982**, 145–146.
(7) An indirect strategy for conversion of amines to ketones and aldehydes is based on a biological process and is not applicable for the formation of nitriles. The practical examples of the biomimetic scheme require several operations and fairly complex reagents in stoichiometric amounts but can give high efficiency. For a brief review of amine oxidation and leading references, see: Buckley, T. H.; Rappoport, H. *J. Am. Chem. Soc.* **1982**, *104*, 4446.
(8) Hydroxylamine **3** has not been detected in the amine oxidations, but it was characterized in the study of alcohol oxidations[3] and is a reasonable product from amines as well.

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Table I. Oxidation of Amines to Nitriles and Carbonyl Compounds

entry	amine	procedure (conditions)	products (yield)[a]
1	$Ph(CH_2)_3NH_2$	B	$Ph(CH_2)_2CN$ (66%)
2	$Ph(CH_2)_3NH_2$	B	$Ph(CH_2)_2CN$ (78%)[b,c]
3	$Ph(CH_2)_2NH_2$	B	$PhCH_2CN$ (55%)
4	$PhCH(CH_3)CH_2NH_2$	B	$PhCH(CH_3)CN$ (68%)
5	$CH_3(CH_2)_5NH_2$	B	$CH_3(CH_2)_4CN$ (77%)
6	$CH_3(CH_2)_7NH_2$	B	$CH_3(CH_2)_6CN$ (74%)
7	p-$MeOC_6H_4CH_2NH_2$	A[d,f]	p-OC_6H_4CN (91%)[b]
8	p-$MeOC_6H_4CH_2NH_2$	A[d]	p-OC_6H_4CN (85%)[b,c]
9	piperonylamine	A[d]	piperonylnitrile (85%)[b]
10	$PhCH_2NH_2$	A[d,f]	PhCN (77%) PhCHO (3%)
11	$PhCH_2NH_2$	A[d,e]	PhCN (76%) PhCHO (9%)
12	$PhCH_2NH_2$	A (25:1, CH_3CN/H_2O)	PhCN (13%) PhCHO (80%)
13	$PhCH_2NH_2$	A (12:1, CH_3CN/H_2O)	PhCN (3%) PhCHO (97%)
14	$PhCH_2NH_2$	A (4:1, CH_3CN/H_2O)	PhCN (0%) PhCHO (97%)
15	p-$MeOC_6H_4CH_2NH_2$	A (1:1, CH_3CN/H_2O)	p-$MeOC_6H_4CHO$ (84%)[b,c]
16	piperonylamine	A (1:1, CH_3CN/H_2O)	piperonal (84%)[b]
17	p-$NCC_6H_4CH_2NH_2$	A (1:1, CH_3CN/H_2O)	p-NCC_6H_4CHO (69%)[b]
18	cyclohexylamine	A (4:1, CH_3CN/H_2O)	cyclohexanone (93%)
19	cyclopentylamine	A[f] (4:1, CH_3CN/H_2O)	cyclopentanone (42%)
20	Ph_2CHNH_2	B[g] (1:1, CH_3CN/H_2O)	Ph_2CO (86%)[b]
21	$Ph(CH_2)_3NH_2$	B[g] (1:1, CH_3CN/H_2O)	$Ph(CH_2)_2CN$ (18%) $Ph(CH_2)_2CHO$ (69%)
22	$Ph(CH_2)_3NH_2$	A (1:1, CH_3CN/H_2O)	$Ph(CH_2)_2CN$ (8%) $Ph(CH_2)_2CHO$ (68%)
23	$PhCH_2NH(CH_3)$	B[d] (1:1, CH_3CN/H_2O)	PhCHO (89%)

[a] Unless otherwise noted, the yields are obtained by calibrated GLPC analysis on organic extracts after aqueous isolation procedures. [b] Isolated yield. [c] 10-mmol scale instead of 1.0 mmol. [d] 0.4 mol equiv of 2 instead of 0.2 mol equiv. [e] Excess calcium hydride was used as a water scavenger. [f] Instead of TEMPO (2), 4-hydroxy-TEMPO was used. [g] Slow addition with 0.2 mol equiv of 2 was used.

standard apparatus.[11] However, aliphatic amines gave higher efficiency when the concentration of **1** was kept high. An effective technique is slow addition of the amine over 3.5 h to 2 mol equiv of preformed **1** with constant electrolysis to continually regenerate **1** (procedure B). The side reactions of the amine and imine intermediate have not been elucidated in every case. Czarny mentions imine to enamine rearrangement as one pathway.[6c] We have isolated the Schiff base **5** as the major product from benzhydrylamine using procedure A.[12] Slow addition improved the situation in this case (Table I, entry 20).

For isolation of the nitrile products, the contents of the working electrode chamber were poured into 10% aqueous hydrochloric acid and extracted with ether. The ether solution was washed with an aqueous sodium bisulfite solution to remove aldehyde byproduct and dried over anhydrous magnesium sulfate. The yield of nitrile was measured either by quantitative GLPC analysis on the ether extract or by weighing the purified nitrile. The yields of aldehydes and ketones were determined in the same way, deleting the sodium bisulfite washing procedure. In cases where significant amounts of residual **2** complicated purification procedures, the ether extract was washed with a solution of sodium iodide in 10% aqueous hydrochloric acid. This treatment converts the nitroxyl **2** into the hydroxylamine **3**,[13] which is then removed as the ammonium salt. A final wash with sodium thiosulfate removes the iodine byproduct.

Table I summarizes the results obtained, indicating which procedure (A or B) gave optimum results. The first 11 entries are examples of nitrile synthesis, using both procedures, under anhydrous conditions. Standard procedures for minimizing water content were effective; small amounts (ca. 3–8%) of aldehydes were generally formed. Attempts to further reduce the aldehyde formation, such as addition of calcium hydride (entry 11), were not effective.

As the concentration of water was increased (entries 10–14), the proportion of aldehyde in the product increased smoothly. In three preliminary tests, ketones were formed successfully (entries 18–20). Although aliphatic aldehydes slowly decompose in the electrolysis medium, reasonable yields were obtained with the simple procedure (A; entry 22). The secondary benzylic amine (entry 23) also gave excellent conversion to aldehyde.

Further studies are under way to answer other selectivity questions, such as functional group compatibility and the steric effect on the rates of oxidation.

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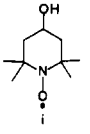
(9) The 4-hydroxy derivative i has significantly lower R_f on silica gel



i

chromatography than typical aldehydes, ketones, and nitriles, facilitating removal of the residual reagent. It does not otherwise interfere, although the secondary hydroxyl group will be oxidized over extended periods under these conditions.

(10) For conversion of amines to nitriles, the electrolyte was a 0.5 M solution of anhydrous lithium perchlorate in anhydrous acetonitrile. For conversion of amines to aldehydes and ketones, the electrolyte was a 0.5 M solution of lithium perchlorate in mixtures of water and acetonitrile (see Table I); the most effective mixtures were 4:1 CH_3CN/H_2O (v:v) up to 1:1 CH_3CN/H_2O.

(11) The electrolysis was carried out in a standard "H" cell. A platinum gauze electrode was held at +0.33 V (vs. Ag/Ag^+) until the high initial current (ca. 300 mA) decayed to a low const. value (ca. 10 mA). Freshly distilled acetonitrile (from calcium hydride) was used in all amine to nitrile reactions. Reagent grade acetonitrile was used for oxidation to carbonyl compounds. Oxidations were performed on a PAR 173 Potentiostat equipped with Model 179 Digital Coulometer. Substrates were used as received or distilled as necessary. Ethylene bromide (1 mL) was used as depolarizer in the counter chamber.

(12) Compound **5** precipitated from the electrolysis medium. It was collected by filtration, washed with 4:1 CH_3CN/H_2O, and dried (64% yield): mp 158.5–160.5° C; ^1H NMR ($CDCl_3$) δ 7.8–7.6, 7.5–7.0 (m, 20 H, aryl H), 5.56 (s, 1 H, CH); mass spectral M_r 347. Hydrolysis in 10% aqueous hydrochloric acid/acetone (1:1) at 25 °C for 2 h produced benzophenone and benzhydrylamine.

Registry No. 1, 45842-10-2; **2**, 2564-83-2; $Ph(CH_2)_2NH_2$, 64-04-0; $PhCH(CH_3)CH_2NH_2$, 60-15-1; $CH_3(CH_2)_5NH_2$, 111-26-2; $CH_3(CH_2)_7NH_2$, 111-86-4; p-$MeOC_6H_4CH_2NH_2$, 2393-23-9; $PhCH_2NH_2$, 100-46-9; p-$NCC_6H_4CH_2NH_2$, 10406-25-4; Ph_2CHNH_2, 91-00-9; $Ph(CH_2)_3NH_2$, 2038-57-5; $PhCH_2NH(CH_3)$, 103-67-3; $Ph(CH_2)_2CN$, 645-59-0; $PhCH_2CN$, 140-29-4; $PhCH(CH_3)CN$, 1823-91-2; $CH_3(CH_2)_4CN$, 628-73-9; $CH_3(CH_2)_6CN$, 124-12-9; p-$MeOC_6H_4CN$, 874-90-8; PhCN, 100-47-0; PhCHO, 100-52-7; p-$MeOC_6H_4CHO$, 123-11-5; p-NCC_6H_4CHO, 105-07-7; Ph_2CO, 119-61-9; $Ph(CH_2)_2CHO$, 104-53-0; piperonylamine, 2620-50-0; cyclohexylamine, 108-91-8; cyclopentylamine, 1003-03-8; piperonylnitrile, 4421-09-4; piperonal, 120-57-0; cyclohexanone, 108-94-3; cyclopentanone, 120-92-3; 4-hydroxy-TEMPO, 2226-96-2; 2,6-lutidine, 108-48-5.

Solubilization in Surfactant Media: Use of an Isomerizable Solute Probe To Determine Microheterogeneity in Microemulsions

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There is considerable interest in reactions in organized media, particularly due to opportunities to control reactivity in a useful way.[2] Modification of reactivity has been proposed to occur via orientation effects,[3] solubilization of reagents not mutually soluble in homogeneous solvents,[4] or charge effects at, or near, surfactant head groups[5] or to be due to differential solubility of solutes in different regions within an organized assembly.[6] Vital to understanding reaction control within surfactant assemblies are questions concerning solubilization. One approach is the use of probe molecules to study solubilization sites and microenvironments present within micelles, vesicles, and microemulsions. Although these studies often provide useful information, different probes can give conflicting results since a given medium can provide different sites or the sites could be modified substantially by the probe.[4,7,8]

We previously reported studies of donor–acceptor substituted azobenzenes whose absorption spectra and reactivity are strongly affected by polarity in homogeneous solvents.[9-11] The absorption spectrum of the trans isomer of p-nitro-p'-(diethylamino)azobenzene (**1t**) is strongly red shifted with increase in solvent polarity.[11] This correlates quantitatively with solvent polarity parameters developed by Kosower, Reichardt and Dimroth, and Taft and co-workers.[12] Similarly, $\Delta G^{\ddagger}$ for thermal cis–trans isomerization of **1c** ($\Delta G_{ct}^{\ddagger}$) can be independently correlated with solvent polarity as indicated by the same indices;[11] the decrease in $\Delta G_{ct}^{\ddagger}$ with increase in polarity suggests that there is development of considerable charge separation as **1c** approaches the isomerization transition state. We report here a comparison of the solubilization behavior of the trans isomer **1t** as studied by its absorption spectrum and the cis isomer **1c** as indicated by $\Delta G_{ct}^{\ddagger}$ in microemulsion solutions contrasted with these processes in homogeneous solvents. The results are particularly interesting in that they suggest that the cis and trans isomers can occupy different solubilization sites in surfactant solutions, and from the observations one can infer the degree of "homogeneity" of solubilization sites that are available to the azobenzene dye **1**.

The rate of isomerization for **1c** was studied as previously indicated;[11,13] the absorption of **1t** measured in homogeneous and

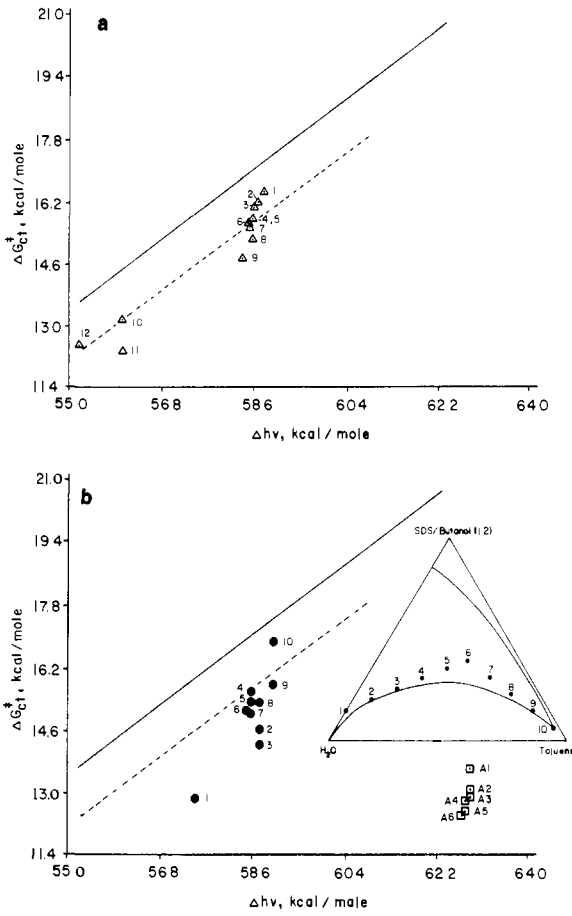

Figure 1. (a) $\Delta G_{ct}^{\ddagger}$ vs. $\Delta h\nu$ for homogenous solvents. Solid line indicates "best fit" for data in aprotic solvents.[11] Triangles indicate data for protic solvents: (1) *tert*-butyl alcohol, (2) 1-heptanol, (3) 1-hexanol, (4) 1-pentanol, (5) 1-butanol, (6) 2-propanol, (7) 1-propanol, (8) ethanol, (9) methanol, (10) ethylene glycol, (11) 50% MeOH/50% H_2O, (12) glycerol; line with unit slope drawn for reference. (b) $\Delta G_{ct}^{\ddagger}$ vs. $\Delta h\nu$ for μE solutions. Solid circles are for μE with composition as indicated by phase diagram (wt %); squares are for AOT-reversed micelles at constant ω (see Table I for $[H_2O]$).

Table I. k_{ct} in AOT/Heptane/Water Reversed Micelles[a]

constant [AOT] = 0.07 M		constant $\omega = 2$		
ω	k_{ct}, s^{-1}	soln[b]	$[H_2O]$, M	$10^3 k_{ct}$, s^{-1}
0	5.59	A1	0.04	0.549
1.6	4.08×10^2	A2	0.08	1.24
4.0	4.4×10^3	A3	0.12	2.14
7.9	2.0×10^4	A4	0.16	2.73
		A5	0.20	3.33
		A6	0.24	4.07

[a] Reversed Micelle solutions prepared by adding 1t, H_2O, and AOT (in quantities to yield desired concentrations) to 10-mL volumetric flasks. The solutions were then diluted with heptane and sonicated (bath) for several minutes. [b] Data for points in Figure 1b.

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