The helianthate salt was converted to streptothricin F trihydrochloride[3] and the 67.88-MHz proton-noise decoupled ^{13}C NMR spectrum of the sample in 2% pyridine/D_2O obtained. Only the signals from the guanido and carbamate carbons showed spin couplings indicating the presence of ^{15}N, and none of the 18 observable singlets showed enhancement of ^{13}C content when normalized to the signal of the anomeric sugar carbon and compared with the natural abundance spectrum.

The natural abundance peak of the δ 160.38 signal was obscured by the superposition of a large triplet (J_{CN} = 20 Hz) and a small doublet (J_{CN} = 20 Hz).[8] This signal can now clearly be assigned to the guanido carbon of **1**.[3] Since **4a** was not 100% enriched in ^{13}C and ^{15}N, a triplet was observed for the 81% of **1a** containing a $^{15}N{=}^{13}C{-}^{15}N$ grouping ($J_{AB} \sim J_{BC}$) and a doublet was observed for the 10% of **1a** containing either a $^{15}N{=}^{13}C{-}^{14}N$ or a $^{14}N{=}^{13}C{-}^{15}N$ grouping.[9] A small doublet (J_{CN} = 26 Hz) flanked the carbamate signal at δ 155.44, indicating the specific—though much more distant—derivation of this moiety from arginine, too.[10]

Measurement of the guanido and carbamate signals in the ^{13}C NMR spectrum of **1a** indicated enrichments of 26% and 0.4%, respectively, when normalized to the signal of the lactam carbonyl and compared with the natural abundance spectrum.

We next synthesized DL-[*guanido*-^{13}C,2-^{15}N]arginine **4b**.[11] A portion of this material (11.15 mg as the hydrochloride, 52 μmol, 90 atom % ^{13}C, 98 atom % ^{15}N), mixed with 2.23 μCi of DL-[5-^{14}C]arginine, was fed to each of four 250-mL production broths. Pure helianthate (231 mg) was obtained in standard fashion. The 67.88-MHz ^{13}C NMR spectrum of pure streptothricin F trihydrochloride (**1b**) now revealed a new doublet (J_{CN} = 12.0 Hz)[12] flanking the guanido signal.

This doublet, showing a small upfield shift (1.05 Hz)[13] and measuring for a 2.9% enrichment, clearly demonstrated the formation of the new C–N bond predicted in Scheme II. Thus, all three guanido nitrogens of **1** are derived from arginine. Since the two labels in **4b** were separated by a potentially labile bond, this result along with that obtained from the incorporation of **4a** confirms the intact incorporation of arginine into **5** and gives strong support for the validity of the pathway outlined in Scheme II.

Recognizing that arginine is incorporated into **5** intact, the strategic inclusion of DL-[5-^{14}C]**4** in the L-**4a** feeding can now be used to show that only L-arginine is utilized in the biosynthesis of **1**. On the basis of the amount of antibiotic present at the end of the fermentation (218 mg),[14] 8.2% of the radioactivity fed had been incorporated. This would predict an 11.8% total enrichment of ^{13}C had both D- and L-arginine been utilized whereas utilization of only L-arginine would have yielded a 23.6% enrichment. The observed total enrichment was 26.4%.

Future work will examine further details of streptolidine and β-lysine biosynthesis by using additional $^{13}C/^{15}N$- as well as $^{13}C/^{2}H$-labeled precursors.

Acknowledgment. This work was supported by Public Health Service Research Grant GM 25996 from the National Institute of General Medical Sciences. The L-[*guanido*-^{13}C,$^{15}N_2$]arginine and potassium [^{15}N]phthalimide were provided by the Stable Isotopes Resource at the Los Alamos Scientific Laboratory, jointly supported by the U.S. Department of Energy and the NIH (RR-00962-02, Division of Research Resources). We are grateful to Dr. Donald Borders, Lederle Laboratories, Pearl River, NY, for generous gifts of streptothricin F and *Streptomyces* L-1689-23. Peter Demou of the Chemistry Department, Yale University, is thanked for obtaining the ^{13}C NMR spectra. The Bruker HX-270 NMR instrument facility at Yale University used in this work was supported by National Institutes of Health Grant RR 01077.

(8) These observed coupling constants are nearly identical with the J_{CN} = 21.3 Hz observed for **4a**; see ref 7b.

(9) This value is arrived at by multiplying the enrichments at each of the three positions of **4a**.

(10) See ref 7b. Also see: Hornemann, U.; Eggert, J. H. *J. Antibiot.* **1975**, *28*, 841-843 for previous labeling of carbamates by arginine.

(11) Arginine **4b** was synthesized from potassium [^{15}N]phthalimide and [^{13}C]urea by adapting the procedures of Murray and Williams, Kurtz, and Janus (Murray, A., III; Williams, D. L. "Organic Synthesis with Isotopes"; Interscience: New York, 1958; pp 1781-1785. Kurtz, A. C. *J. Biol. Chem.* **1949**, *180*, 1253-1267. Janus, J. W. *J. Chem. Soc.* **1955**, 3551-3552).

(12) The position of the carbon-nitrogen double bond in **1** is still not unequivocal. The position we use comes from the X-ray structure of streptolidine obtained by hydrolysis of **1**;[6] since many subtle factors influence the magnitude of ^{13}C-^{15}N spin couplings, our data do not necessarily indicate otherwise.

(13) Others have reported such shifts: see ref 7d,e, and references cited therein. Of the numerous compounds we have made, this is only the second time we have observed an isotope shift.

(14) Determined by bioassay with *Bacillus subtilis* ATCC 6633 grown on brain-heart infusion agar.

Optical Resolution of Metal Chelates by Use of Adsorption on a Colloidal Clay

Akihiko Yamagishi*

Department of Chemistry, Faculty of Science
Hokkaido University, Sapporo 060, Japan

Mitsuyuki Soma

National Instutute of Environmental Studies
Tsukuba, Ibaraki 305, Japan

Received March 10, 1981

We wish to report the utilization of a colloidal clay for the optical resolution of racemic metal chelates. This research was motivated by the following findings about the racemic adsorption of *d*- and *l*-iron(II) tris(1,10-phenanthroline) chelates, [Fe(phen)$_3$]$^{2+}$, on a clay surface. In 100 mL of distilled water, 87 mg of sodium montmorillonite (Na^+M^-) (Kunipia-G, Kunimine Ind. Co., Japan) was dispersed. The resultant solution contained 1.0×10^{-3} M cation-exchange site. When Na^+M^- was added to a $(+)_{510}$-iron(II) tris(1,10-phenanthroline) bis(antimony *d*-tartrate) [(+)[Fe(phen)$_3$]$^{2+}$·(+)L^{2-}], the red solution was instantly tinted with pale pink. The absorption spectrum was measured without any serious interference by scattering. Curve a in Figure 1 shows the dependence of the increase of the apparent extinction coefficient at 530 nm ($\Delta\epsilon_{530}$) on the ratio of Na^+M^- to the metal chelate. $\Delta\epsilon_{530}$ leveled off at about [Na^+M^-]/[(+)-[Fe(phen)$_3$]$^{2+}$·(+)-L^{2-}] = 2. The same results were obtained for a solution of $(-)_{510}$-iron(II) tris (1,10-phenanthroline) bis(antimony *l*-tartrate) [(-)-[Fe(phen)$_3$]$^{2+}$·(-)-L^{2-}]. In both cases, more than 90% of the Na^+M^- was consumed for the binding with the metal chelate at [Na^+M^-]/[metal chelate] = 2.[1] Thus, each metal chelate occupies two cation-exchange sites on a clay surface when it is adsorbed from a solution of a single enantiomer.

The results were different, however, when Na^+M^- was added to the racemized solution of (+)-[Fe(phen)$_3$]$^{2+}$·(+)-L^{2-}[$^1/_2$-(+)-[Fe(phen)$_3$]$^{2+}$ + $^1/_2$(-)-[Fe(phen)$_3$]$^{2+}$·(+)-L^{2-}. As shown in curve b in Figure 1, $\Delta\epsilon_{530}$ attained a maximum value at [Na^+M^-]/[$^1/_2$(+)-[Fe(phen)$_3$]$^{2+}$ + $^1/_2$(-)-[Fe(phen)$_3$]$^{2+}$·(+)-L^{2-}] = 1 and decreased gradually with further increase of Na^+M^-. The results imply that each metal chelate occupies one cation-exchange site when it is adsorbed from a racemic solution. These conclusions also hold when (+)-L^{2-} is replaced with $2ClO_4^-$ (Figure 1).[2]

From X-ray diffraction measurements of the wet precipitates of clay–metal chelate adducts, the basal spacing of a clay sheet was determined to be 17.9 and 14.8 Å for the 1:2 (+)-[Fe(phen)$_3$]$^{2+}$/M^- and 1:1 ($^1/_2$(+)-[Fe(phen)$_3$]$^{2+}$ + $^1/_2$(-)-[Fe(phen)$_3$]$^{2+}$)/M^- adducts, respectively.[3] The former value is close

(1) The free Na^+M^- was titrated against the acridine orange cation (details will be described in a later paper).

(2) So far the racemic adsorption has been observed for [Ni(phen)$_3$](ClO$_4$)$_2$, [Fe(phen)$_2$(CN)$_2$], and [Fe(byp)$_3$(CN)$_2$]. The results on these metal chelates will be published elsewhere.

(3) For the sake of charge neutrality, $^1/_2$ equiv of (+)-L^{2-} should be included in the 1:1 ($^1/_2$(+)-[Fe(phen)$_3$]$^{2+}$ + $^1/_2$(-)-[Fe(phen)$_3$]$^{2+}$)/M^- adduct.

0002-7863/81/1503-4640$01.25/0

Table I. Effects of Adsorption on Clay of a Solution Containing Two Kinds of Metal Chelates

run	solution I[a]	solution II[b]
1	(+)-$[Ni(phen)_3]^{2+}\cdot 2ClO_4^-$ (2.7×10^{-4} M) ($^1/_2$(+)-$[Fe(phen)_3]^{2+}$ + $^1/_2$(−)-$[Fe(phen)_3]^{2+}$)$\cdot 2ClO_4^-$ (2.2×10^{-4} M)	(+)-$[Ni(phen)_3]^{2+}$ (1.4×10^{-4} M) (+)-$[Fe(phen)_3]^{2+}$ (0.6×10^{-4} M)
2	(−)-$[Ni(phen)_3]^{2+}\cdot 2ClO_4^-$ (4.3×10^{-4} M) ($^1/_2$(+)-$[Fe(phen)_3]^{2+}$ + $^1/_2$(−)-$[Fe(phen)_3]^{2+}$)$\cdot 2ClO_4^-$ (2.2×10^{-4} M)	(−)-$[Ni(phen)_3]^{2+}$ (0.2×10^{-4} M) (−)-$[Fe(phen)_3]^{2+}$ (0.5×10^{-4} M)
3	(+)-$[Ni(phen)_3]^{2+}\cdot 2ClO_4^-$ (1.8×10^{-4} M) ($^1/_2$(+)-$[Fe(bpy)_3]^{2+}$ + $^1/_2$(−)-$[Fe(bpy)_3]^{2+}$)$\cdot 2ClO_4^-$ (2.1×10^{-4} M)	(+)-$[Ni(phen)_3]^{2+}$ (0.5×10^{-4} M) (+)-$[Fe(bpy)_3]^{2+}$ (0.8×10^{-4} M)
4	(−)-$[Ni(phen)_3]^{2+}\cdot 2ClO_4^-$ (0.5×10^{-4} M) ($^1/_2$(+)-$[Fe(bpy)_3]^{2+}$ + $^1/_2$(−)-$[Fe(bpy)_3]^{2+}$)$\cdot 2ClO_4^-$ (2.1×10^{-4} M)	(−)-$[Fe(bpy)_3]^{2+}$ (0.5×10^{-4} M) (+)-$[Fe(bpy)_3]^{2+}$ (0.1×10^{-4} M)
5	(+)-$[Ni(phen)_3]^{2+}\cdot 2ClO_4^-$ (1.8×10^{-4} M) ($^1/_2$(+)-$[Ru(phen)_3]^{2+}$ + ($^1/_2$(−)-$[Ru(phen)_3]^{2+}$)$\cdot 2ClO_4^-$ (1.9×10^{-4} M)	(+)-$[Ni(phen)_3]^{2+}$ (0.4×10^{-4} M) (+)-$[Ru(phen)_3]^{2+}$ (0.4×10^{-4} M) (−)-$[Ru(phen)_3]^{2+}$ (0.4×10^{-4} M)
6	(+)-$[Ni(phen)_3]^{2+}\cdot 2ClO_4^-$ (1.8×10^{-4} M) ($^1/_2$(+)-$[Co(en)_2$(L-palan)$]^{2+}$ + $^1/_2$(−)-$[Co(en)_2$(L-palan)$]^{2+}$)$\cdot 2I^-$ (2.0×10^{-4} M)[c]	(+)-$[Ni(phen)_3]^{2+}$ (0.2×10^{-4} M) (+)-$[Co(en)_2$(L-palan)$]^{2+}$ (0.8×10^{-4} M) (−)-$[Co(en)_2$(L-palan)$]^{2+}$ (0.8×10^{-4} M)

[a] An initial solution containing two kinds of metal chelates. [b] The same solution filtered through a membrane filter after $(2-3) \times 10^{-4}$ M Na^+M^- was added. [c] L-palan = L-phenylalanine; en = ethylenediamine.

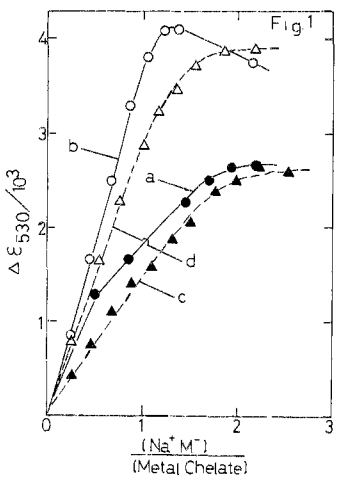


Figure 1. Dependence of the apparent extinction coefficient at 530 nm on the added amount of Na^+M^-. Initial concentration of the iron chelate is as follows: (a) $[(+)\text{-}[Fe(phen)_3]^{2+}\cdot(+)\text{-}L^{2-}] = 2.4 \times 10^{-5}$ M. (b) $[(^1/_2(+)\text{-}[Fe(phen)_3]^{2+} + ^1/_2(-)\text{-}[Fe(phen)_3]^{2+})\cdot(+)\text{-}L^{2-}] = 2.4 \times 10^{-5}$ M. (c) $[(+)\text{-}[Fe(phen)_3]^{2+}\cdot 2ClO_4^-] = 3.0 \times 10^{-5}$ M. (d) $[(^1/_2(+)\text{-}[Fe(phen)_3]^{2+} + ^1/_2(-)\text{-}[Fe(phen)_3]^{2+})\cdot 2ClO_4^-] = 3.0 \times 10^{-5}$ M.

to the spacing of the clay sheet without any metal chelate (18.8 Å).[4] From measurements of the decay rate of transient electric birefringence, the average size of a clay particle (r) was estimated;[5] r increased from 0.6×10^4 to 2.0×10^4 Å, when clay bound the metal chelates from both the racemic and the single enantiomeric solutions. These results suggest that the clay–metal chelate adduct in solution consists of several clay sheets with the metal chelates intercalated between them. Accordingly, the observed bathochromic changes in the spectra (Figure 1) are caused by interaction among the neighboring bound metal chelates between the sheets. The larger value of $\Delta\epsilon_{530}$ for a solution of the racemic mixture than for the single enantiomer may imply that the metal chelates in the former adduct are more closely packed than in the latter.

The results shown in Figure 1 caused us to suspect that the present metal chelate always adsorbs as a racemic mixture when the solution contains both the *d* and *l* enantiomers. This has been verified by the following experiments: 1.0×10^{-4} M Na^+M^- was added to a solution of 1.4×10^{-4} M $(+)\text{-}[Fe(phen)_3]^{2+}\cdot(+)\text{-}L^{2-}$ and 0.6×10^{-4} M $(-)\text{-}[Fe(phen)_3]^{2+}\cdot(+)\text{-}L^{2-}$. The clay–metal chelate adduct was filtered off throgh a membrane filter (Toyo TM-2), and the electronic and ORD spectra of the filtrate were measured. The filtrate contained 0.8×10^{-4} M $(+)\text{-}[Fe(phen)_3]^{2+}$ and 0.1×10^{-4} M $(-)\text{-}[Fe(phen)_3]^{2+}$. In other words, the ratio of $(+)\text{-}[Fe(phen)_3]^{2+}$ to $(-)\text{-}[Fe(phen)_3]^{2+}$ increased from 2.3 to 8 during the above procedures. This was apparently attained by

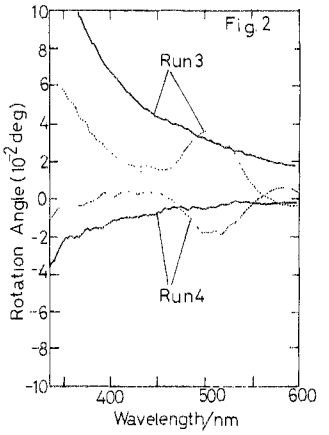


Figure 2. ORD spectra of runs 3 and 4 in Table I. The solid and dotted curves are for the solutions before and after filtering through a membrane filter, respectively.

the preferential adsorption as a racemic pair.

We have utilized the above facts in order to resolve the racemic mixture of one kind of metal chelate (M_I) at the expense of the enantiomer of another kind (M_{II}). It was expected that the *l* enantiomer of M_{II}, for example, was eliminated as a clay adduct with the *d* enantiomer of M_I. As a result, the *l* enantiomer of M_I becomes enriched in solution. The experimental results are tabulated in Table I. Figure 2 shows the ORD spectra of the filtrates when the resolution was successful. Among the results, racemic $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ (bpy = α,α'-bipyridyl) were resolved at the expense of the *d* or *l* enantiomer of $[Ni(phen)_3]^{2+}$. Thus the "pseudo" racemic pair is formed between the opposite enantiomers of $[Fe(phen)_3]^{2+}$ (or $[Fe(bpy)_3]^{2+}$) and $[Ni(phen)_3]^{2+}$. The resolution of racemic $[Ru(phen)_3]^{2+}$ and $[Co(en)_2$(L-palan)$]^{2+}$ (L-palan = L-phenylalanine) was unsuccessful. The reason for this may be that these metal chelates are too bulky or small to form a pseudo racemic pair with $[Ni(phen)_3]^{2+}$.[6] In other words, rigorous steric requirements are operative in forming the clay–racemic pair adducts.

The above examples are concerned with the configurational isomers of metal chelates. In certain cases, however, the unbalancing of asymmetric ligands induces the unbalancing of configurational isomers due to ligand stereoselectivity.[7] Under these circumstances, the enrichment of one of the configurational isomers of a metal chelate in solution eventually leads to enrichment of one of the optical isomers of an asymmetric ligand. As a consequence, clay is able to accumulate either one of optical isomers (L-amino acids, for example) after the occurrence of a slight excess of L-amino acids over D isomers.[8]

(4) The clay was in a moist state (Norrish K. *Discuss. Faraday Soc.* **1954**, *18*, 120.

(5) r was estimated by the equation derived by: Yamakawa, H. *Macromolecules* **1975**, *8*, 339

(6) The radii of $[Ni(phen)_3]^{2+}$, $[Ru(phen)_3]^{2+}$ and $[Co(en)_2\cdot$(L-palan)$]^{2+}$ are estimated to be 9, 11, and 6 Å, respectively.

(7) Buckingham, D. A.; Dekkers, J.; Sargeson, A. M.; Wein, M. *Inorg. Chem.* **1973**, *12*, 2019.

Acknowledgment. Thanks are due to Professor Jun-ichi Aihara of Shizuoka University for his valuable discussions and Mr. Haruo Inoue of Inoue Firebrick Ind. Co. (Sapporo) for presenting some of the clay samples.

(8) If the initial unbalancing of *d* and *l* ligands is $[d\text{-L}]/[l\text{-L}] = 1 + \alpha$ ($\alpha \ll 1$) and the ligand stereoselectivity is given by $[(+)\text{-M}(d\text{-L})]/[(-)\text{-M}(d\text{-L})] = 1 + \beta$ ($0 < \beta$), the resultant unbalancing of the configurational isomers is $[(+)\text{-M}(d\text{-L}) + (+)\text{-M}(l\text{-L})]/[(-)\text{-M}(d\text{-L}) + (-)\text{-M}(l\text{-L})] = 1 + \gamma$ with $\gamma = \alpha\beta(2 + \alpha + \beta)^{-1}$. If the racemic adsorption occurs between the different configurational isomers irrespective of the ligand asymmetry, the ratio of [*d*-L] to [*l*-L] remaining in solution becomes $(1 + \alpha)(1 + \beta)$. In other words, the *d*-L isomer is enriched by a factor of $1 + \beta$.

Diphenylselenium Bis(trifluoroacetate): A New Reagent for Biomimetic Oxidations of Amines and Amino Acids

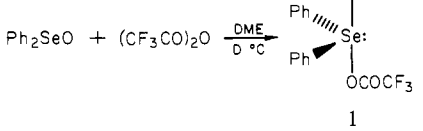
J. P. Marino* and Robert D. Larsen, Jr.

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received March 18, 1981

As part of an effort to develop mild and selective two electron oxidants for phenolic compounds,[1] we have been investigating the chemistry of diarylselenuranes[2] bearing heteroatoms. The classical role of selenium dioxide in organic synthesis has been expanded to include a number of organoselenium reagents of various oxidation states for selenium.[3] Balenovic was the first to report that diphenyl selenoxide is an effective oxidant for hydrazides, amines,[4] and catechols.[5] Recently, we have applied the selective oxidation of catechols by diphenyl selenoxide to phenolic coupling processes in the isoquinolines.[6] In this communication, we report a new selenium(IV) reagent, diphenylselenium bis(trifluoroacetate) (**1**), for the controlled oxidations of heterocyclic amines and α-amino acids.

Paetzold[7] first reported the preparation of selenurane **1** in 1973 from the reaction of diphenylselenium dibromide with silver trifluoroacetate. We have found a more convenient preparation of **1** from diphenyl selenoxide.[8,9] Addition of 1 equiv of trifluoroacetic anhydride to a solution of diphenyl selenoxide in dimethoxyethane (DME) provides reagent **1** in quantitative yield.[10]



1

By analogy to sulfuranes[11] and from spectral properties, the diphenylselenium bis(trifluoroacetate) is best represented as a neutral selenurane (**1**), possessing trigonal-bipyramid geometry as opposed to an ionic selenonium trifluoroacetate. Although compound **1** and related dioxyselenuranes have been known since 1973,[12] their use in oxidation chemistry has not been previously reported.[13]

In this report, we wish to focus on the oxidation of secondary and tertiary amines of substituted tetrahydropyridine systems. Initially, a representative series of 1-substituted 1,2,3,4-tetrahydroisoquinolines[14] (**2b–d**) were oxidized with reagent **1** at room temperature and in high yields to their 3,4-dihydroisoquinoline derivatives.[15] In the oxidations of **2b,c**, a small amount (10%) of the isoquinoline derivatives **4b** and papaverine (**4c**) was isolated.[16,17] Attempts at further oxidation of the 3,4-dihydro compounds **2a,b,d** with large excesses of **1** failed to yield the isoquinolines. However, when **2c** was reacted with 6 equiv of reagent **1** for 12 h at room temperature and then 12 h at reflux (DME), a 75% yield of papaveraldine,[18] **4** [$R_2 = (MeO)_2C_6H_3CO$], was obtained. Tetrahydroisoquinoline-3-carboxylic acid (**2e**)[19] and its methyl ester **2f** oxidized directly to isoquinoline systems with 3 equiv of selenurane **1** at room temperature. The reaction of the free amino acid **2e** proved to be complicated in that both aromatization to the isoquinoline acid (isolated as methyl ester **4e**, 40%) and oxidative decarboxylation to isoquinoline itself (26%) occurred. This latter process represents one of the mildest, nonaqueous oxidative decarboxylations of an α-amino acid. The amino ester **2f** was quantitatively oxidized to isoquinoline **4f**.

As a further test of the compatibility of reagent **1** with other nitrogen heterocycles, we examined the oxidation of the medicinally important 1,2,3,4-tetrahydrocarbolines **5** and **6**.[20] With 1.2 equiv of selenurane **1** (room temperature), **5** was oxidized to its 3,4-dihydro derivative[21] in 85% yield. Increasing the oxidant to 3 equiv produced the β-carbolines **7** and **8**[21] in yields of 61% and 70%, respectively. Undoubtedly, the indole ring influences

(1) (a) For a summary of sulfur cations in phenolic oxidation processes see: Marino, J. P. *Top. Sulfur Chem.* **1976**, *1*, 1. (b) Marino, J. P.; Samanen, J. M. *Tetrahedron Lett.* **1973**, 4553.

(2) The term selenurane has been used for tetravalent Se(IV) compounds by analogy to sulfurane (Martin, J. C., Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2339). There is, however, a possible ambiguity with derivatives of the uranyl ion (UO_2^{2+}) and the suffix for selenurane. There is currently under consideration by the IUPAC Commission on Nomenclature of Organic Chemistry a proposal to use the name λ^4-selane to denote tetravalent Se(IV) compounds (Smith, P. A. S., private communication).

(3) For a review of selenoxides as oxidizing agents, see: Reich, H. J. "Oxidations in Organic Reactions, Part C"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Chapter 1.

(4) Poje, M.; Balenovic, K. *Bull. Sci., Sect. A (Zagreb)* **1975**, *20*, 1. *Chem. Abstr.* **1975**, *83*, 43558u.

(5) (a) Perina, I.; Bregant, N.; Balenovic, K. *Bull. Sci., Sect. A (Zagreb)* **1973**, *18*, 3. *Chem. Abstr.* **1973**, *79*, 50966. (b) Balenovic, K.; Bregant, N.; Perina, I. *Synthesis* **1973**, 172.

(6) Marino, J. P.; Schwartz, A. *Tetrahedron Lett.* **1979**, 4553.

(7) Horn, V. V.; Patezold, R. *Z. Anorg. Allg. Chem.* **1973**, *398*, 186.

(8) Leicester, H. M., "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 238. Also commercially available from Eastman Chemicals.

(9) Cinquini, M.; Colonna, S.; Giovanni, R. *Chem. Ind. (London)* **1969**, 1737.

(10) General experimental procedure: Dried diphenyl selenoxide (vacuum desiccation, 10^{-1} torr, 90 °C, 24 h) is dissolved in dry DME (1 g per 40 mL) and an equimolar amount of trifluoroacetic anhydride (freshly distilled from phosphorus pentoxide) is added via a syringe. This solution is stirred at 25 °C for 15 min and then added dropwise to a DME solution of the amine over a one-half-hour period. The oxidation reactions are normally complete after 3-12 h. Selenurane **1** is a white hygroscopic solid that can be isolated and stored at 0 °C under an inert atmosphere. Data for **1**: mp 175–176 °C (lit.[7] mp 172-174 °C); ^{1}H NMR (60 MHz, $CDCl_3$) (Me_4Si) δ 7.65 (br s); ^{19}F NMR (100 MHz, $CDCl_3$) (CF_3CO_2D, external) δ 2.0 (s); IR ($CHCl_3$) 1730, 1716, 1215, 1150 cm^{-1}. Anal. Calcd for $C_{16}H_{10}F_6O_4Se$: C, 41.85; H, 2.20; F, 24.82. Found: C, 41.61; H, 2.20; F, 24.70.

(11) For structural and spectral characterization of oxysulfuranes, see: Martin, J. C.; Livant, P. *J. Am. Chem. Soc.* **1977**, *99*, 5761 and references cited therein.

(12) Paetzold, R.; Reichenbacher, M. *Org. Selenium Compd.: Their Chem. Biol.* **1973**, 305.

(13) Schwartz, Alan Ph.D. Thesis, University of Michigan, 1979.

(14) **2a**: Buck, J. S. *J. Am. Chem. Soc.* **1974**, *56*, 1769. **2b**: Spaeth, E.; Dengel, F. *Chem. Ber.* **1938**, *71*, 113. **2c**: Falck, J. R.; Miller, L. L.; Stermitz, F. R. *Tetrahedron* **1974**, *30*, 391. **2d**: Hershenson, F. M. *J. Org. Chem.* **1975**, *40*, 740.

(15) **3a**: Ban, Y.; Yonemitsu, O.; Terashima, M. *Chem. Pharm. Bull (Tokyo)* **1960**, *8*, 183, 194. **3b**: Bruderer, H.; Brossi, A. *Helv. Chim. Acta* **1965**, *48*, 1945. **3c**: Wehrli, P. A.; Schaer, B. *Synthesis* **1974**, 288. Data for **3d**: mp 178-179 °C; ^{1}H NMR (60 MHz, $CDCl_3$) (Me_4Si) δ 3.3 (m, 2 H), 4.0 (m, 2 H), 4.0 (m, 2 H, buried), 4.0 (s, 3 H), 4.1 (s, 3 H), 6.9 (s, 1 H), 7.9 (s, 1 H); MS *m/e* 235 (M^+), 191 (M^+ - 44), 176 (M - 59). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.26; H, 5.58; N, 5.96. Found: C, 60.98; H, 5.42; N, 5.58.

(16) Umezawa, B.; Hoshina, O.; Sawaki, S. *Chem. Pharm. Bull. (Tokyo)* **1969**, *17*, 1115.

(17) Rosenmund, K. W.; Nothnagel, M.; Riesenfeldt, H. *Chem. Ber.* **1927**, *60*, 392.

(18) Buck, J. S.; Haworth, R. D.; Perkin, W. H. *J. Chem. Soc.* **1924**, *125*, 2176.

(19) **2e**: Julian, P. L.; Karpel, W. J. *J. Am. Chem. Soc.* **1948**, *70*, 180. **2f**: Soxena, A.; Jain, P. C.; Anand, N. *Indian J. Chem.* **1975**, *13*, 230.

(20) **5**: Ho, B. T.; Walker, K. E. *Org. Synth.* **1971**, *51*, 136. **6**: Snyder, H. R.; Hansch, C. H.; Katz, L.; Parameter, S. M.; Spaeth, E. C. *J. Am. Chem. Soc.* **1948**, *70*, 219.

(21) O'Rell, D.D.; Lee, F. G. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *94*, 3205. **7**: Speitel, R.; Schlitter, *Helv. Chim. Acta* **1949**, *32*, 860. **8**: ref 20b.

0002-7863/81/1503-4642$01.25/0