TLC analysis indicated the presence of the desired epoxy alcohol **4b**.

A dry, $N_2$-purged flask was charged with 5 mL of benzene, 0.675 mL of tetramethylpiperidine (4 mmol), cooled to 0 °C, and charged with 2.5 mL of *n*-BuLi (4 mmol, 1.6 M solution in hexane). After stirring for 30 min at 0 °C, 4 mL of diethyl aluminum chloride (4 mmol, 1 M solution in hexane) was added to the flask via syringe, and stirring was continued for an additional 30 min. The benzene solution of **4b** was added to the cold reaction mixture via syringe, and stirring was continued for 4 h. The reaction was quenched with 2.5 mL of saturated $NH_4Cl$, and the organic phase dried ($Na_2SO_4$), concentrated, and flash chromatographed with ether to give a colorless oil. In addition to the desired olefinic diol, NMR analysis showed the presence of residual tetramethylpiperidine: NMR ($CDCl_3$) $\delta$ 4.9 (d, 2), 4.25 (t, 1, $J$ = 6 Hz), 3.78 (t, 2, $^1J$ = 6 Hz), 1.5–2.0 (singlet superimposed on a multiplet, 5). This enediol **14** was added to a flask containing 25 mL of MeOH, ca. 20 mg of $PtO_2$, and a stirring bar. The mixture was placed under 1 atm of $H_2$, vigorously stirred for 1 h, and then filtered and concentrated to give a colorless oil. This oil was taken up in 20 mL of ether and stirred over 0.5 mL of saturated $CuSO_4$ to remove residual tetramethylpiperidine. After drying ($Na_2SO_4$) and concentration of the organic phase, the oily product was purified by preparative GLC to give a colorless oil which was 98% pure by analytical GLC. This product and authentic (*S*)-(−)-4-methyl-1,3-pentanediol[20] had identical capillary GLC retention times as demonstrated by conjection: $[\alpha]^{22}_D$ +6.67° (*c* 1.29, $CHCl_3$) [lit.[20] $[\alpha]^{27}_D$ −6.9° (*c* 2.84, $CHCl_3$)]; IR ($CCl_4$) $\nu_{max}$ 3610, 3360, 1380, 1345, 1050 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.80 (t, 2, $J$ = 6 Hz), 3.52 (t, 1, $^1J$ = 6Hz), 2.5 (br s, 2), 2.65 (m,3), 0.92 (d, 6).

**4-Amino-3(*R*)-hydroxybutyric Acid (17).** A 100-mL round-bottomed flask with a Teflon-coated stir bar was charged with 639 mg of $NaIO_4$, 1 mL of $H_2O$, and 6 $\mu$L of $CCl_4$. Stirring was initiated, and 100 mg of crude **1b** (1.1 mmol) was added. After several minutes 15 mg of $RuCl_3 \cdot (H_2O)_n$ was added and stirring was continued for 2 h. The heterogenous mixture was filtered and the aqueous and organic phases partitioned. The aqueous phase was extracted several times with THF and the organic phases were combined. The organic extracts were treated with excess concentrated $NH_4OH$ and warmed on a steam bath for 24 h. The reaction mixture was then concentrated to give ca. 86 mg of a tan solid (66%): $[\alpha]^{25}_D$ −9.76° (*c* 1.67, $H_2O$) (lit.[12] $[\alpha]^{25}_D$ −20.7° (*c* 1.83, $H_2O$)]; $^1H$ NMR ($D_2O$) $\delta$ 4.5–4.0 (1, m), 3.15 (2, m), 2.45 (2, d); mp 212 °C dec (lit.[12] mp 216–217 °C dec).

This solid was recrystallized 4 times from ethanol–water to give a white crystalline solid: $[\alpha]^{25}_D$ −20.11° (*c* 1.0, $H_2O$). About 20 mg of purified **17** was dissolved in 1 mL of concentrated $H_2SO_4$, warmed on a steamed bath for ca. 10 min, and diluted with 10 mL of water. After continued warming on a stream bath for 2 h the reaction was treated with lead carbonate, filtered, and concentrated. Treatment with EtOH gave a white crystalline solid with spectral characteristics identical with authentic GABOB: $[\alpha]^{25}_D$ 0.00° (*c* 1.0, $H_2O$). In addition $^1H$ NMR analysis showed evidence of vinylic protons which we believe to correspond to the vinylic protons of **18** ($\delta$ 6.96 m, 6.16 d).

**Acknowledgment.** We are grateful to the National Institutes of Health (GM28384) and Eli Lilly and Company for support of this work.

**Registry No.** **1a**, 627-27-0; (+)-(*R*)-**1b**, 76282-48-9; (*Z*)-**2a**, 928-96-1; (+)-(3*R*,4*S*)-**2b**, 91603-21-3; (*E*)-**3a**, 928-97-2; (+)-(3*R*,4*R*)-**3b**, 91603-22-4; **4a**, 763-89-3; (*R*)-**4b**, 91523-66-9; (*Z*)-**5a**, 51446-29-8; (+)-(*Z*)-**5b**, 91523-67-0; (*E*)-**6a**, 1594-24-7; (+)-(*E*)-**6b**, 91523-68-1; **7a**, 74126-47-9; (+)-**7b**, 91523-69-2; (−)-**8**, 75809-18-6; (−)-(*R*)-**9**, 91523-70-5; (−)-(*S*)-**11**, 41035-07-8; (+)-(3*R*,4*R*)-**12**, 91603-23-5; (−)-(*R*)-**13**, 13471-42-6; (*R*)-**14**, 91523-71-6; (+)-(*R*)-**15**, 16451-48-2; (*R*)-**17**, 7013-07-2; **18**, 91523-72-7; TBHP, 75-91-2; Ti(*i*-PrO)$_4$, 546-68-9; 1,4-hexanediol, 16432-53-4; L-(+)-diethyl tartarate, 87-91-2.

(20) We thank Prof. Büchi for a generous sample of (*S*)-(−)-4-methyl-1,3-pentanediol: Büchi, G.; Crombie, L.; Godin, P. J.; Kaltenbram, J. S.; Siddalingaiah, K. S.; Whiting, D. A. *J. Chem. Soc.* **1961**, 2843.

(21) The configuration of the chiral center bearing the ethyl group was not determined. While one might assume it should be *R* based on epoxide opening with inversion, literature precedent reveals that this type of opening can proceed with retention: Coxon, J. M.; Hartshorn, M. P.; Swallow, W. H. *Aust. J. Chem.* **1973**, *26*, 2521. We thank Dr. Edward Mihelich of Eli Lilly for bringing these points to our attention. Dr. Mihelich also has unpublished results similar to those of Coxon, et al.

# Electroorganic Chemistry. 81. Anodic Oxidation of Sulfonamides and Amidophosphates

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Oxidation peak potentials of sulfonamides and amidophosphates were measured in acetonitrile and compared with the corresponding amides and carbamates. The results showed that the order of easiness of oxidation was amides > carbamates > amidophosphates > sulfonamides. Furthermore, the reaction of silyl enol ethers or trimethyl phosphite with anodically α-methoxylated sulfonamides or amidophosphates has clearly shown that the α-methoxylated compounds are useful starting materials in organic synthesis. For example, optically active L-tryptophan was synthesized from α-methoxylated *N*-(*p*-tolylsulfonyl)-L-proline ester.

We have already reported that the anodic oxidation of cyclic (**1**, R,R′ = −$(CH_2)_n$−) and acyclic (**1**, R,R′ = higher alkyl groups) amides **1a** and carbamates **1b** in methanol is a convenient method to introduce a methoxyl group to the position α to the nitrogen atom of **1a** and **1b** and also suggested that the initiation step of the oxidation involves

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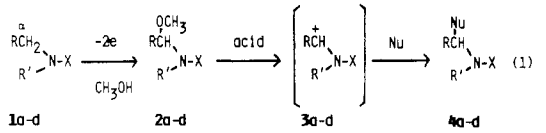
**Table I. Oxidation Potentials of 1a–d[a]**

| substrate | concn, mmol/L | $E_p$ V vs. SCE |
|---|---|---|
| 5 | 4.6 | 2.08 |
| 6 | 3.6 | 2.13 |
| 7 | 4.3 | 2.38 |
| 8 | 4.4 | 2.52 |
| 9 | 4.1 | 2.27 |
| 10 | 3.6 | 2.36 |
| 11 | 4.6 | 2.13 |
| 12 | 3.1 | 2.30 |

[a] Solvent, $CH_3CN$, platinum electrodes; supporting electrolyte, $LiClO_4$ (0.1 M); sweep time, 100 mV/s.

electron transfers from lone pair electrons of the nitrogen atom of **1b** to the anode.[1]




a ; X = -COR″
b ; X = -$CO_2$R″
c ; X = -$SO_2$R″
d ; X = -PO(OR″)$_2$

In connection with this study, we have been interested in the anodic oxidation of sulfonamides **1c** and amidophosphates **1d** from the following standpoints.

(1) The comparison of oxidation potentials of **1a–d** may provide us with some information about the effect of X on the process of electron transfer from the lone pair electrons of nitrogen atoms to the anode.

(2) It has been found by us[2] and other workers[3] that the α-methoxylated amides **2a** and carbamates **2b** are versatile intermediates in organic synthesis, since the methoxyl groups of **2a** and **2b** can be substituted by a variety of nucleophiles (Nu) in the presence of acid to afford **4a** and **4b**. Thus, if the anodic α-methoxylation of **1c** and **1d** is possible, and the α-methoxylated products **2c** and **2d** possess similar reactivities to **2a** and **2b**, **2c** and **2d** may also exhibit a variety of types of reactions useful in organic synthesis.

(3) Cyclophosphamide, a widely used antitumor agent, has been reported to be hydroxylated in vivo at the position α to the nitrogen atom.[4] The anodic α-methoxylation of **1d** is a similar reaction to this metabolic hydroxylation.

(4) The sulfonyl group of sulfonamides may be removed by electrochemical reduction[5] under milder conditions than elimination of the acyl group from amides.

This report describes the anodic oxidation of **2c** and **2d** and the utilization of the methoxylated products to some organic syntheses.

**Oxidation Potentials of Sulfonamides 1c and Amidophosphates 1d.** The anodic oxidation of amides **1a** and carbamates **1b** has been rather extensively studied, whereas except for the simplest sulfonamide, *N,N*-dimethylmethanesulfonamide,[6] the behaviors of **1c** and **1d** under conditions of anodic oxidation were not known. Thus, the oxidation peak potentials of **5–12** were measured in acetonitrile containing 0.1 M lithium perchlorate.

Oxidation waves have been observed in all of these compounds, suggesting that the electron transfer from lone

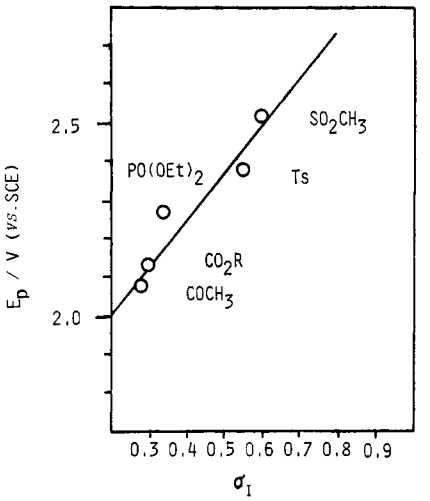
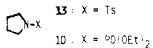
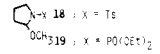
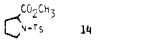
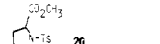
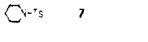
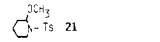
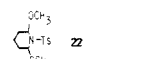
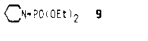
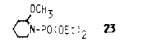
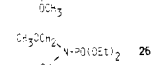
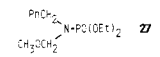
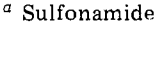
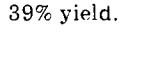



**Figure 1.** Relationship of oxidation peak potentials ($E_p$) with substituent constants ($\sigma_I$).

**Table II. α-Methoxylation of Sulfonamides 1c and Amidophosphates 1d**

| substrate | | passed electricity, F/mol | oxidation product | yield, % |
|---|---|---|---|---|
|  13 ; X = Ts<br>10 ; X = PO(OEt)$_2$ | | 3.5<br>5.0 |  18 ; X = Ts<br>19 ; X = PO(OEt)$_2$ | 78<br>50 |
|  14 | | 5.8 |  20 | 98 |
|  7 | | 4.0 |  21 | 27[a] |
| | | |  22 | 20[a] |
| | | 9.3 | **22** | 94 |
|  9 | | 5.0 |  23 | 64 |
|  15 | | 7.5 |  24 | 62 |
| ($n$-Bu)$_2$N-Ts | 16 | 4.0 |  25 | 77 |
| (CH$_3$)$_2$N-PO(OEt)$_2$ | 12 | 8.0 |  26 | 72 |
|  17 | | 10.5 |  27 | 55 |

[a] Sulfonamide 7 was recovered in 39% yield.

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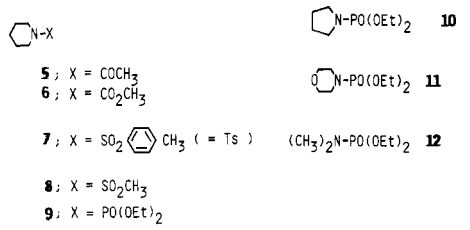
(6) Ross, S. D.; Finkelstein, M.; Rudd, E. J. *J. Org. Chem.* **1972**, *37*, 2387.




pair electrons of the nitrogen atom of **1c** and **1d** to the anode took place at the initiation step. The results are shown in Table I.

The relationship between the peak potentials of N-substituted piperidines **5–9** and the Hammett's substituent constants ($\sigma_I$)[7] of the substituent X depicted in Figure 1 implies that the inductive effect of X plays an important role in the process of the electron transfers from the substrates to anode.

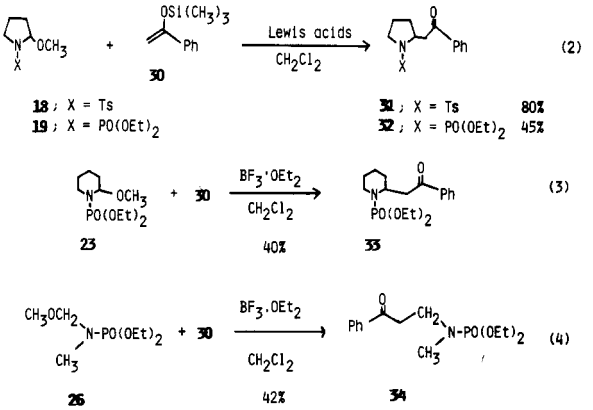
**Anodic Oxidation of Sulfonamides and Amidophosphates in Methanol.** Although the oxidative peak potentials suggest that **1c** and **1d** are less oxidizable than **1a** and **1b**, the preparative anodic oxidation of **1c** and **1d** in methanol containing tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte gave $\alpha$-methoxylated products **2c** and **2d** in satisfactory yields except the anodic oxidation of **7** (Table II). Under these conditions, the anode potential seems to be high enough for the oxidation of **1c** and **1d**.

In the anodic oxidation of **7**, further oxidation of the $\alpha$-methoxylated product **21** to give $\alpha,\alpha'$-dimethoxylated product **22** was faster than the oxidation of the starting material **7**. At the stage when 9.3 F/mol of electricity was passed, **22** was isolated in 94% yield.

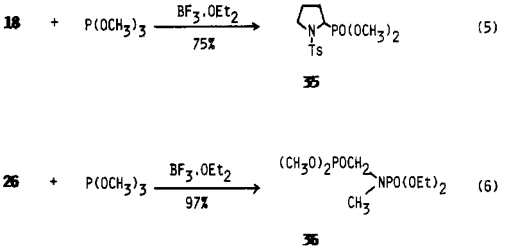
The $\alpha$-methoxylation of **1d** is interesting, since the pattern of reaction is similar to metabolic C-4-hydroxylation of cyclophosphamide.[4] The similarity between the electrochemical and metabolic oxidation of some amides has been suggested by our previous report.[11] The $\alpha$-methoxylation of unsymmetrically *N*,*N*-dialkylated sulfonamides (**14** and **15**) and amidophosphate **17** took place predominatly at the less substituted site. This regioselectivity is similar to that observed in the anodic $\alpha$-methoxylation of **1b**,[1] and a variety of explanations[1,12] have already been carried out for this selectivity, though they are not conclusive.

**Utilization of $\alpha$-Methoxylated Sulfonamides and Amidophosphates.** Treatment of **2c** and **2d** with Lewis acids ($BF_3OEt_2$ or $TiCl_4$) forms cationic intermediates **3c** and **3d** which can be trapped with nucleophiles such as silyl enol ether **30** and trimethyl phosphite. For example, treatment of **18** with Lewis acids in $CH_2Cl_2$ followed by the reaction with **30** afforded **31** in 80% yield. Similarly, **19** gave **32** in 45% yield (eq 2).

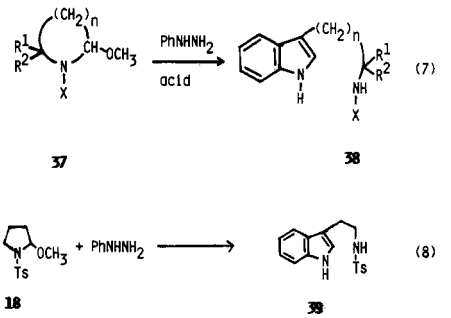
Other examples are shown in eq 3 and 4.



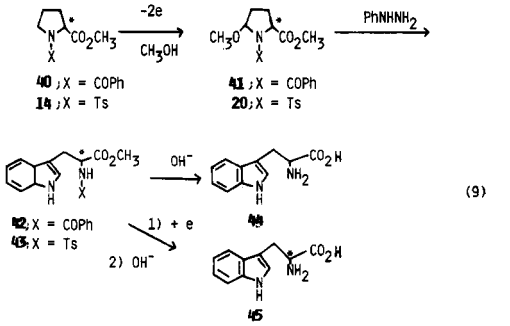

Also, the reaction of **18** or **26** with trimethyl phosphite gave the corresponding phosphonates **35** and **36** (eq 5 and 6).




We have preliminarily reported[13] that heating of **37** together with phenylhydrazine in the presence of Brønstead acids or Lewis acids yields **38**. Although this reaction was mainly investigated about $\alpha$-methoxylated amides (**37**, X = COPh) or lactams (**37**, $R^1$, $R^2$ = O, X = H), sulfonamide **18** also exhibited similar behavior. Namely, heating a solution of **18** and phenylhydrazine in xylene in the presence of anhydrous $ZnCl_2$ gave tryptamine derivative **39** in 63% yield. The advantage of sulfonamides over




amides was clearly shown by the synthesis of optically active tryptophan **45** starting from L-proline derivative **14**. Thus, tryptophan derivatives **42** and **43** were synthesized by the reaction of phenylhydrazine with **41** and **20** in satisfactory yields (74 and 71%), respectively.




(7) The Hammett's substituent constant ($\sigma_I$): $COCH_3$ (0.28),[8] $CO_2R$ (0.30),[8] $PO(OEt)_2$ (0.34),[9] $SO_2C_6H_4CH_3$(-*p*) (0.55),[10] $SO_2CH_3$ (0.60).[8]

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However, removal of the benzoyl group from **42** retaining the optical activity was impossible. The acid-catalyzed hydrolysis of **42** resulted in the decomposition of indol skeleton, while the alkaline hydrolysis of **42** yielded racemic tryptophan **44** in 70% yield. On the other hand, the electroreductive elimination of the tosyl group from **43** followed by the hydrolysis of the ester group gave **45** with 95% optical purity.

## Experimental Section

Proton nuclear magnetic resonance spectra were measured on Varian Associates EM-360 or EM-390 spectrometer with chemical shifts given in parts per million ($\delta$) downfield from tetramethylsilane as an internal standard. Infrared spectra were recorded on Hitachi 215 or 260-10 spectrometer. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University.

**Materials.** Amide **5**,[14] carbamate **6**,[1] sulfonamides **7**,[15] **8**,[16] **13**,[17] **15**,[18] **16**,[19] and **30**[20] were prepared according to the reported methods.

Sulfonamide **14** was synthesized as follows. L-Proline (5 g, 43.4 mmol) was added in methanol (25 mL), and dry hydrogen chloride was passed into the solution until the solid was dissolved. After methanol was evaporated in vacuo from the reaction mixture, methylene chloride (100 mL) and triethylamine (5.26 g, 52 mmol) were added into the residue and then pulvelized potassium carbonate (12 g, 87 mmol) was added. The solution was mechanically stirred, and 4-methylbenzenesulfonyl chloride (12 g, 63 mmol) was added in parts, and the solution was stirred for two days at room temperature. The reaction mixture was poured on water and extracted with $CH_2Cl_2$ (2 × 40 mL). The combined extracts were washed with 0.5 N HCl and aqueous $NaHCO_3$, successively, and dried on $MgSO_4$. After filtration, the solvent was evaporated to give a residue which was chromatographed on silica gel to afford **14** in 91% yield: mp 73.5–75 °C (from ether); IR (KBr) 2980, 2955, 2925, 1760, 1604, 1441, 1350, 1342, 1158, 1095, 1060, 1012, 890, 833, 788, 718 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.60–2.20 (m, 4 H), 2.26 (s, 3 H), 3.20–3.63 (m, 2 H), 3.73 (s, 3 H), 4.13–4.43 (m, 1 H), 7.35 (d, $J$ = 8.0 Hz, 2 H), 7.78 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.11; H, 6.05; N, 4.94; S, 11.32. Found: C, 55.40; H, 5.95; N, 5.04; S, 11.04.

Amidophosphates **9**, **10**, **11**, **12**, and **17** were prepared as follows. Into a cooled solution of amine (60 mmol) in water (30 mL) containing NaOH (2.4 g, 60 mmol) was added dropwise diethyl chlorophosphonate (10.4 g, 63 mmol).[21] The solution was stirred at room temperature for 1 h, added into brine (30 mL), and extracted with $CH_2Cl_2$. The extract was dried on $MgSO_4$, and the solvent was evaporated to yield a residue which was distilled to isolate amidophosphates.

**Diethyl 1-piperididophosphate (9)**: 81% yield; bp 91–92 °C (2 mm); IR (neat) 2975, 2940, 2850, 1440, 1380, 1340, 1250, 1165, 1130, 960, 780 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.27 (t, $J$ = 7.0 Hz, 6 H), 1.20–1.80 (m, 6 H), 2.80–3.30 (m, 4 H), 3.83 and 3.97 (d q, $J$ = 7.0 Hz, 4 H). Anal. Calcd for $C_9H_{20}NO_3P$: C, 48.86; H, 9.11; N, 6.33; P, 14.00. Found: C, 48.98; H, 9.38; N, 6.34; P, 13.81.

**Diethyl 1-pyrrolididophosphate (10)**: 86% yield; bp 94–95 °C (2 mm); IR (neat) 2980, 2880, 1445, 1395, 1260, 1100, 1060, 1030, 960, 790 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.27 (t, $J$ = 7.0 Hz, 6 H), 1.67–2.10 (m, 4 H), 2.90–3.30 (m, 4 H), 3.85 and 4.00 (d q, $J$ = 7.0 Hz, 4 H). Anal. Calcd for $C_8H_{18}NO_3P$: C, 46.37; H, 8.76; N, 6.76; P, 14.95. Found: C, 46.30; H, 8.99; N, 6.87; P, 14.89.

**Diethyl 4-morpholidophosphate (11)**: 81% yield; bp 108–110 °C (2 mm); IR (neat) 2980, 2910, 2860, 1450, 1400, 1370, 1300, 1260, 1170, 1140, 1120, 1060, 1030, 970 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 2.85–3.23 (m, 4 H), 3.35–3.67 (m, 4 H), 3.87 and 4.00 (d q, $J$ = 7.0 Hz, 4 H). Anal. Calcd for $C_8H_{18}NO_4P$: C, 43.05; H, 8.13; N, 6.28; P, 13.88. Found: C, 42.80; H, 8.38; N, 6.37; P, 13.59.

**Diethyl dimethylamidophosphate (12)**: 80% yield; bp 91 °C (18 mm); IR (neat) 2995, 2948, 2910, 2820, 1485, 1465, 1395, 1310, 1255, 1170, 1100, 1060, 1030, 1000, 965, 790 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.27 (t, $J$ = 7.0 Hz, 6 H), 2.53 (s, 3 H), 2.70 (s, 3 H), 3.83 and 3.97 (d q, $J$ = 7.0 Hz, 4 H). Anal. Calcd for $C_6H_{16}NO_3P$: C, 39.78; H, 8.90; N, 7.73; P, 17.10. Found: C, 39.58; H, 9.01; N, 7.67; P, 16.83.

**Diethyl *N*-benzyl-*N*-methylamidophosphate (17)**: 84% yield; bp 132–134 °C (2 mm); IR (neat) 2980, 2905, 1500, 1480, 1455, 1390, 1370, 1350, 1255, 1220, 1160, 1100, 1060, 1030, 960, 800, 710 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.27 (t, $J$ = 7.0 Hz, 6 H), 2.37 and 2.55 (2 s, 3 H), 3.93 and 4.03 (d q, $J$ = 7.0 Hz, 4 H), 4.05 and 4.20 (2 s, 2 H), 7.25 (s, 5 H). Anal. Calcd for $C_{12}H_{20}NO_3P$: C, 56.02; H, 7.84; N, 5.44; P, 12.04. Found: C, 56.21; H, 8.03; N, 5.47; P, 12.19.

**General Procedure of Anodic Oxidation.** Anodic $\alpha$-methoxylation of sulfonamides and amidophosphates were carried out under similar conditions to that of carbamates.[1] A general procedure is exemplified by the $\alpha$-methoxylation of diethyl 1-piperididophosphate (**9**). Into a cell equipped with carbon rod anode and cathode (8 mm $\phi$) were added a solution of **9** (3.0 g, 13.6 mmol) and $Et_4NOTs$ (2.0 g, 6.64 mmol) in methanol (40 mL). After 5 F/mol of electricity was passed at a constant current (0.2 A) through the solution which was cooled with ice water, the solvent was removed in vacuo without heating. The anodic oxidation was followed by checking the consumption of the starting material with TLC or GLC. Brine (40 mL) was added to the residue, and the organic portion was extracted with $CH_2Cl_2$. After the extract was dried over $MgSO_4$ and the solvent was removed in vacuo, the residue was chromatographed on silica gel (the eluent, AcOEt) to afford **diethyl 1-(2-methoxypiperidido)phosphate (23)** in 64% yield: IR (neat) 2980, 2945, 1445, 1395, 1260, 1130, 1090, 1055, 1030, 960 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 1.20–2.00 (m, 6 H), 2.70–3.47 (m, 2 H), 3.20 (s, 3 H), 3.60–4.23 (m, 4 H), 4.53–4.80 (m, 1 H). Anal. Calcd for $C_{10}H_{22}NO_4P$: C, 47.81; H, 8.83; N, 5.58; P, 12.33. Found: C, 48.09; H, 9.10; N, 5.54; P, 12.47.

**Diethyl 1-(2-methoxypyrrolidido)phosphate (19)**: 50% yield at 5.0 F/mol of electricity; IR (neat) 2950, 1440, 1260, 1220, 1170, 1020, 960, 800 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.32 (t, $J$ = 7.0 Hz, 6 H), 1.53–2.20 (m, 4 H), 2.90–3.35 (m, 2 H), 3.27 (s, 3 H), 3.75–4.35 (m, 4 H), 4.75–5.00 (br, 1 H). Anal. Calcd for $C_9H_{20}NO_4P$: C, 45.57; H, 8.50; N, 5.90; P, 13.06. Found: C, 45.61; H, 8.79; N, 6.01; P, 12.09.

**Diethyl *N*-methyl-*N*-(methoxymethyl)amidophosphate (26)**: 55% yield at 8.0 F/mol of electricity; IR (neat) 2990, 2940, 2905, 1450, 1395, 1350, 1250, 1165, 1020, 960, 910, 820, 800, 720 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 2.53 and 2.77 (2 s, 3 H), 3.25 (s, 3 H), 3.90 and 4.05 (d q, $J$ = 7.0 Hz, 4 H), 4.25 and 4.45 (2 s, 2 H). Anal. Calcd for $C_7H_{18}NO_4P$: C, 39.81; H, 8.59; N, 6.63; P, 14.67. Found: C, 39.52; H, 8.79; N, 6.47; P, 14.79.

**Diethyl *N*-benzyl-*N*-(methoxymethyl)amidophosphate (27)**: 55% yield at 10.5 F/mol of electricity; IR (neat) 2980, 2940, 1500, 1450, 1390, 1370, 1260, 1160, 1050, 1030, 960, 820, 730, 700 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 3.23 (s, 3 H), 3.65–4.47 (m, 8 H), 7.25 (s, 5 H). Anal. Calcd for $C_{13}H_{22}NO_4P$: C, 54.35; H, 7.72; N, 4.88; P, 10.78. Found: C, 54.39; H, 7.60; N, 5.04; P, 10.54.

**1-[(4-Methylphenyl)sulfonyl]-2-methoxypyrrolidine (18)**: 79% yield at 3.5 F/mol of electricity; IR (neat) 2950, 1600, 1448, 1345, 1204, 1165, 1100, 1080, 1045, 1005, 820, 713 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.85–2.07 (m, 4 H), 2.42 (s, 3 H), 2.77–3.57 (m, 2 H), 3.33 (s, 3 H), 4.97 (d, $J$ = 5.0 Hz, 1 H), 7.20 (d, $J$ = 8.0 Hz, 2 H), 7.63 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49; S, 12.56. Found: C, 56.55; H, 6.68; N, 5.41; S, 12.48.

**1-[(4-Methylphenyl)sulfonyl]-2-(methoxycarbonyl)-5-methoxypyrrolidine (20)**: 98% yield at 5.8 F/mol of electricity; a mixture of stereoisomers; IR (KBr) 3015, 2965, 2925, 1770, 1353, 1170, 1000, 676 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.05–1.56 (m, 0.4 H), 1.63–2.40 (m, 3.6 H), 2.44 (s, 3 H), 3.25 and 3.41 (2 s, 3 H), 3.72 (s, 3 H), 4.03–4.32 (m, 1 H), 5.13 (d, $J$ = 4.5 Hz, 0.6 H), 5.29 (s,

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0.4 H), 7.17–7.45 (m, 2 H), 7.65–7.97 (m, 2 H). Anal. Calcd for $C_{14}H_{19}NO_5S$: C, 53.66; H, 6.11; N, 4.47; S, 10.23. Found: C, 53.42; H, 6.39; N, 4.47; S, 10.29.

**1-[(4-Methylphenyl)sulfonyl]-2-methoxypiperidine (21)**: 27% yield at 4.0 F/mol of electricity; IR (neat) 2920, 1590, 1435, 1320, 1145, 1070, 915, 800, 740 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.99–2.03 (m, 6 H), 2.41 (s, 3 H), 2.70–3.80 (m, 2 H), 3.23 (s, 3 H), 4.96–5.16 (br, 1 H), 7.22 (d, $J$ = 8.0 Hz, 2 H), 7.67 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; S, 11.90. Found: C, 58.09; H, 7.19; N, 5.27; S, 11.76.

**1-[(4-Methylphenyl)sulfonyl]-2,6-dimethoxypiperidine (22)**: 94% yield at 9.3 F/mol of electricity; IR (KBr) 2940, 1594, 1440, 1410, 1330, 1280, 1200, 1160, 1090, 1040, 920, 820, 768 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.67–2.27 (m, 6 H), 2.43 (s, 1 H), 3.36 (s, 6 H), 4.80–5.04 (br s, 2 H), 7.23 (d, $J$ = 8.0 Hz, 2 H), 7.60 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{14}H_{21}NO_4S$: C, 56.17; H, 7.07; N, 4.68; S, 10.71. Found: C, 56.45; H, 7.23; N, 4.86; S, 10.61.

**1-[(4-Methylphenyl)sulfonyl]-2-methoxy-6-methylpiperidine (24)**: 62% yield at 7.5 F/mol of electricity; IR (KBr) 2950, 1595, 1440, 1404, 1360, 1328, 1304, 1164, 1100, 1050, 967, 930, 818 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.70–2.23 (m, 6 H), 1.35 (d, $J$ = 6.0 Hz, 3 H), 2.45 (s, 3 H), 3.33 (s, 3 H), 3.56–4.15 (m, 1 H), 5.03–5.24 (m, 1 H), 7.23 (d, $J$ = 8.0 Hz, 2 H), 7.77 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.34; H, 7.47; N, 4.94; S, 11.31. Found: C, 59.08; H, 7.28; N, 4.70; S, 11.42.

**1-[(4-Methylphenyl)sulfonyl]-*N*-butyl-*N*-(1-methoxybutyl)amine (25)**: 78% yield at 4.0 F/mol of electricity; IR (neat) 2920, 2855, 1590, 1440, 1330, 1244, 1150, 970, 898, 808 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.60–1.90 (m, 14 H), 2.43 (s, 3 H), 3.19 (s, 3 H), 2.77–3.30 (m, 2 H), 4.60–4.97 (m, 1 H), 7.15 (d, $J$ = 8.0 Hz, 2 H), 7.60 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{16}H_{27}NO_3S$: C, 61.31; H, 8.68; N, 4.47; S, 10.23. Found: C, 61.53; H, 8.86; N, 4.68; S, 10.42.

**Acid-Catalyzed Reaction of $\alpha$-Methoxylated Sulfonamide 18 and Amidophosphates 19, 23, and 26 with Silyl Enol Ether 30. General.** A solution of **23** (1.0 g, 3.98 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise into a solution of $BF_3{\cdot}OEt_2$ (1.3 mL, 10.57 mmol) in $CH_2Cl_2$ (20 mL) at −78 °C under nitrogen atmosphere. After the solution was stirred at the temperature for 10 min, a solution of **30** (1.5 g, 7.80 mmol) in $CH_2Cl_2$ (5 mL) was added and stirred for 6 h. After the reaction mixture was further stirred at room temperature for 14 h, the solution was poured into water and extracted with $CH_2Cl_2$. The extract was dried on $MgSO_4$, which was then filtered off. The solvent was evaporated in vacuo to give a residue which was column chromatographed on silica gel (AcOEt:hexane 2:1) to isolate **33**: 40% yield; IR (neat) 2980, 2940, 2860, 1680, 1600, 1580, 1450, 1390, 1370, 1295, 1250, 1170, 1060, 1030, 960, 790, 750, 690 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.25 and 1.30 (2 t, $J$ = 7.0 Hz, 6 H), 1.25–1.95 (m, 6 H), 2.90–4.50 (m, 3 H), 3.33 (d, $J$ = 7.5 Hz, 2 H), 3.67–4.40 (m, 4 H), 7.20–7.70 (m, 3 H), 7.80–8.20 (m, 2 H). Anal. Calcd for $C_{17}H_{26}NO_4P$: C, 60.17; H, 7.72; N, 4.13; P, 9.13. Found: C, 60.13; H, 7.87; N, 4.11; P, 8.95.

**32**: 45% yield; IR (neat) 2990, 1680, 1600, 1580, 1450, 1395, 1370, 1260, 1220, 1160, 1120, 1100, 1050, 1030, 960, 800, 760, 690 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 1.55–2.30 (m, 4 H), 2.65–3.90 (m, 5 H), 4.02 and 4.13 (d q, $J$ = 7.0 Hz, 4 H), 7.20–7.75 (m, 3 H), 7.90–8.25 (m, 2 H). Anal. Calcd for $C_{16}H_{24}NO_4P$: C, 59.07; H, 7.44; N, 4.31; P, 9.52. Found: C, 59.21; H, 7.63; N, 4.32; P, 9.25.

**34**: 42% yield; IR (neat) 2970, 2940, 2905, 1670, 1595, 1580, 1445, 1380, 1320, 1240, 1020, 960, 780, 740, 680 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 2.63 and 2.80 (2 s, 3 H), 3.00–3.80 (m, 4 H), 3.95 and 4.05 (d q, $J$ = 7.0 Hz, 4 H), 7.20–7.65 (m, 3 H), 7.75–8.10 (m, 2 H). Anal. Calcd for $C_{14}H_{22}NO_4P$: C, 56.18; H, 7.41; N, 4.68; P, 10.35. Found: C, 56.31; H, 7.52; N, 4.89; P, 10.05.

The reaction of **18** with **30** was carried out with $TiCl_4$ (1 equiv) as Lewis acid.

**31**: 80% yield; mp 105 °C (from AcOEt); IR (KBr) 1680, 1595, 1448, 1408, 1373, 1342, 1320, 1302, 1218, 1195, 1155, 1092, 1045, 1000, 980, 960, 810, 752, 685, 660 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.33–2.07 (m, 4 H), 2.47 (s, 3 H), 2.77–4.47 (m, 5 H), 7.33–8.34 (m, 9 H). Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08; S, 9.33. Found: C, 66.30; H, 6.14; N, 4.03; S, 9.39.

**Acid-Catalyzed Reaction of $\alpha$-Methoxylated Sulfonamide 18 and Amidophosphate 26 with Trimethyl Phosphite. General.** Into a solution of **18** (0.255 g, 1 mmol) and trimethyl phosphite (0.24 mL, 2 mmol) in $CH_2Cl_2$ (5 mL) was added $BF_3{\cdot}OEt_2$ (2 mmol) at −20 °C, and the solution was stirred at room temperature overnight. Brine (3 mL) was added to the solution, and the organic layer was separated. The aqueous layer was extracted three times with $CH_2Cl_2$, and the combined organic layer was dried on $MgSO_4$. Product **35** was isolated by PLC (silica gel, AcOEt): 0.250 g (0.75 mmol); 75% yield; mp 118–119.5 °C (from ether); IR (KBr) 2995, 2960, 2890, 2860, 1598, 1495, 1447, 1350, 1310, 1265, 1190, 1158, 1090, 1040, 995, 830, 812, 775, 760, 717, 708 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.85–2.17 (m, 4 H), 2.32 (s, 3 H), 3.31 (t, $J$ = 6.0 Hz, 2 H), 3.59, 3.66, 3.76, and 3.83 (4 s, 6 H), 4.05 (m, 1 H), 7.19 (t, $J$ = 8.0 Hz, 2 H), 7.62 (d, $J$ = 8.0 Hz, 2 H). Anal. Calcd for $C_{13}H_{20}NO_5PS$: C, 46.84; H, 6.05; N, 4.20; P, 9.29. Found: C, 46.57; H, 6.09; N, 4.26; P, 8.99.

**36**: bp 150–170 °C (0.45 mm); 97% yield; IR (neat) 2980, 2960, 2915, 2858, 1480, 1465, 1447, 1393, 1370, 1333, 1308, 1250, 1185, 1168, 1132, 1100, 1055, 1025, 968, 877, 800, 715 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.30 (t, $J$ = 7.0 Hz, 6 H), 2.65 and 2.81 (2 s, 3 H), 3.27 and 3.43 (2 d, $J$ = 9.0 Hz, 2 H), 3.67 (s, 3 H), 3.85 (s, 3 H), 3.96 and 4.07 (d q, $J$ = 7.0 Hz, 4 H). Anal. Calcd for $C_8H_{21}NO_6P_2$: C, 33.23; H, 7.32; N, 4.84; P, 21.42. Found: C, 32.95; H, 7.40; N, 4.78; P, 21.68.

**Synthesis of *N*-[(4-Methylphenyl)sulfonyl]tryptamine (39).** A solution of **18** (0.42 g, 2 mmol) in xylene (5 mL) was added into a solution of phenylhydrazine (0.24 g, 2.2 mmol) and zinc chloride (0.35 g, 2.4 mmol) in xylene (10 mL), which was in advance heated at 70–80 °C. The mixture was refluxed under nitrogen atmosphere for 1.5 h, cooled, and diluted with ethyl acetate (10 mL). The solution was added into aqueous $NaHCO_3$ (20 mL) and extracted with ethyl acetate (15 mL × 3). The combined extract was dried on $MgSO_4$, which was then filtered off.

The desired product **39** was isolated by column chromatography (silica gel, AcOEt:hexane (1:1): mp 115.9–116.8 °C (from methanol); 63% yield; IR (KBr) 3415, 3295, 3050, 2908, 1605, 1430, 1320, 1178, 822, 750 $cm^{-1}$; NMR ($CDCl_3$ + $Me_2SO$-$d_6$) $\delta$ 2.38 (s, 3 H), 2.72–3.02 (m, 2 H), 3.02–3.34 (m, 2 H), 6.47 (t, $J$ = 6.0 Hz, 1 H), 6.89–7.56 (m, 7 H), 7.72 (d, $J$ = 8.0 Hz, 2 H), 9.82 (br, 1 H). Anal. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.95; H, 5.77; N, 8.91; S, 10.20. Found: C, 64.96; H, 5.70; N, 9.01; S, 10.33.

**Preparation of 1-Benzoyl-2-(methoxycarbonyl)pyrrolidine (40).** L-Proline (5.75 g, 50 mmol) was added in methanol (25 mL), and dry hydrogen chloride was passed into the suspension to yield a clear solution saturated with the gas. After the solution was stirred at room temperature for 4 h, it was neutralized by adding a solution of potassium hydroxide in methanol. Potassium chloride was removed by filtration and methanol was evaporated in vacuo to give a residue. Benzoyl chloride (7.7 g, 54.8 mmol) was added to the solution of the residue and triethylamine (11 g, 0.11 mol) in $CH_2Cl_2$, and the mixture was stirred overnight. The solution was poured into water and the organic portion was extracted with $CH_2Cl_2$. The combined organic layers were washed with aqueous potassium hydroxide, diluted sulfuric acid, and aqueous sodium bicarbonate, successively, and dried with anhydrous magnesium sulfate. The solvent was removed in vacuo to give a solid, which was recrystalized from methanol to yield **40** (10.845 g, 46.5 mmol, 93% yield): mp 89–90 °C (from ether); IR (KBr) 2980, 2950, 2880, 1745, 1568, 1450, 1420, 1200, 1180, 800 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.70–2.56 (m, 4 H), 3.37–4.00 (m, 2 H), 3.81 (s, 3 H), 4.27–4.56 and 4.56–4.87 (m, 1 H), 7.30–7.76 (m, 5 H). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 67.09; H, 6.41; N, 5.76.

**Synthesis of 1-Benzoyl-2-methoxy-5-(methoxycarbonyl)-pyrrolidine (41).** 1-Benzoyl-2-(methoxycarbonyl)pyrrolidine (**40**) was anodically oxidized according to similar procedures to those described before to give a mixture of stereoisomers; 94% yield at 3.0 F/mol of electricity. They are separable by column chromatography (silica gel, AcOEt:hexane 1:1), though a mixture can be used for the preparation of indole derivative **41**: the less polar isomer; IR (neat) 2990, 2950, 2830, 1738, 1638, 1445, 1393, 1200, 1079, 742 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.74–2.70 (m, 4 H), 3.73 (s, 3 H), 2.98 and 3.40 (s and br, 3 H), 4.51 (d, $J$ = 9.0 Hz, 1 H), 4.83 (br s, 1 H), 7.22–7.73 (m, 5 H). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.31. Found: C, 63.90; H, 6.43; N, 5.24.

The polar isomer: IR (neat) 3050, 2948, 2825, 1742, 1637, 1388, 1200, 1080, 725, 700 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.51–2.51 (m, 4 H), 3.16 and 3.46 (2 s, 3 H), 3.68 (s, 3 H), 4.44 (t, $J$ = 8.5 Hz, 1 H), 5.02

(br, 1 H), 7.20-7.66 (m, 5 H). Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.59; H, 6.53; N, 5.29.

**Synthesis of *N*-Benzoyltryptophan Methyl Ester (42).** This compound was synthesized by procedures similar to the preparation of **39** from **18**: 74% yield; mp 110.8-112.5 °C (from AcOEt:hexane); IR (KBr) 3360, 1730, 1635, 1512, 1302, 1240, 1015, 732 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 3.35 (d, $J$ = 6.0 Hz, 2 H), 3.59 (s, 3 H), 5.04 (m, 1 H), 6.67-7.78 (m, 11 H), 8.90 (br, 1 H). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.73; H, 5.57; N, 8.55.

**Synthesis of *N*-[(4-Methylphenyl)sulfonyl]tryptophan Methyl Ester (43).** This compound was also prepared as follows. A solution of **20** (0.626 g, 2 mmol) and phenylhydrazine hydrogen chloride (0.3 g, 2.1 mmol) in glacial acetic acid (10 mL) was heated at 100 °C for 4 h under nitrogen atmosphere. After the solution was colled, brine (20 mL) was added, and the organic portion was extracted with $CH_2Cl_2$ (20 mL × 3). The extract was washed with brine and aqueous $NaHCO_3$ (20 mL). The organic layer was dried on $MgSO_4$, which was then filtered off. After the solvent was removed in vacuo, the residue was column chromatographed on silica gel (AcOEt:hexane 1:1) to afford **43** (0.54 g): 73% yield; mp 128.5-130.0 °C (from methanol); IR (KBr) 3404, 3290, 3055, 2950, 1742, 1350, 1168, 1100, 747, 680 $cm^{-1}$; NMR ($CDCl_3$ + $Me_2SO$-$d_6$) $\delta$ 2.36 (s, 3 H), 3.14 (d, $J$ = 8.0 Hz, 2 H), 3.46 (s, 3 H), 4.00-4.30 (m, 1 H), 6.77-7.23 (m, 5 H), 7.27-7.67 (m, 4 H), 9.9 (br, 1 H). Anal. Calcd for $C_{19}H_{20}N_2O_4S$: C, 61.27; H, 5.41; N, 7.52; S, 8.61. Found: C, 61.41; H, 5.38; N, 7.63; S, 8.43.

**Transformation of *N*-Benzoyltryptophan Methyl Ester (42) to Tryptophan.** Acid-catalyzed hydrolysis of **42** resulted in the formation of many unidentified products. On the other hand, the hydrolysis of **42** under alkaline conditions gave tryptophan **44**. A solution of **42** (3 g, 9.3 mmol) in 50% aqueous KOH (15 mL) was refluxed for 12 h. After the solution was cooled, the precipitate was filtered off and the solid was washed with water. The combined aqueous solution was acidified to pH 6 with concentrated HCl. After 1 h, the precipitate was filtered, washed with 30% aqueous EtOH (3 mL), EtOH (5 mL), and $CH_2Cl_2$ (20 mL), successively. The crude tryptophan was again dissolved in water (5 mL) containing a small amount of NaOH (0.5 g), and ethanol (10 mL) was added into the solution to precipitate a white solid, which was filtered off. The filtrate was warmed to 70 °C and acidified to pH 6 with acetic acid. Tryptophan was isolated as a plate crystal by cooling the above solution; 1.32 g (6.47 mmol), 70% yield. The IR spectrum of tryptophan was identical with that of DL-tryptophan **44**.

**Synthesis of L-Tryptophan 45 from 43.**[5] A solution of **43** (1.89 g, 5 mmol) and $Me_4NCl$ (1.1 g, 10 mmol) in methanol (25 mL) was placed in a cathodic side of a divided cell equipped with a platinum anode and a lead cathode, and a solution of $Me_4NCl$ (0.5 g, 4.56 mmol) in methanol (25 mL) was placed in the anodic side. A constant current (0.3 A, 4 A/$dm^2$) was passed through the cell for 1.5 h, and then further electricity (0.15 A, 50 min) was passed. During the electrolysis, a methanolic solution saturated with HCl (0.4 mL) was gradually added into the catholyte.

After the reduction, the catholyte was neutralized, and the solvent was evaporated in vacuo to afford a residue. The residue was then dissolved in water, and 2 N sodium hydroxide was added to make the solution alkaline (pH 10). Amino ester was extracted with $CH_2Cl_2$ (20 mL × 4) and dried on $MgSO_4$. The drying agent was filtered off and the evaporation of solvent gave a residue which was dissolved in 33% EtOH-water (15 mL) containing NaOH (0.27 g). The solution was stirred at room temperature overnight. Then, the solution was neutralized with 20% HCl to yield a precipitate, which was isolated by filtration and washed with EtOH (1 mL × 5). The IR spectra of this precipitate was identical with that of authentic tryptophan. The optical rotation of this precipitate was 95% of that of authentic tryptophan; 52% yield.

**Oxidation Potentials.** Oxidation peak potentials were measured at room temperature by using an H-type cell, potentiostat H-type cell, potentiostat HA-104, and Function Generator HB-107A (Hokuto Denko Ltd.). Oxidation was carried out in dry acetonitrile containing 0.1 M $LiClO_4$ as a supporting electrolyte at platinum electrode using on aqueous saturated calomel reference electrode. The scan rate was 100 mV/s. The concentration of substrates and the values of peak potentials were shown in Table I.

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# Photoelectron Spectra of Dioxabicyclo[*n*.2.1]alkanes

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The He(I) photoelectron (PE) spectra of 7-bromo-2,3-dioxabicyclo[2.2.1]heptane (**1a**), 8-bromo-6,7-dioxabicyclo[3.2.1]octane (**2a**), 9-bromo-7,8-dioxabicyclo[4.2.1]nonane (**3a**), 10-bromo-8,9-dioxabicyclo[5.2.1]decane (**4a**), and the corresponding unsubstituted bicyclic peroxides **2b-4b** have been recorded. The assignment of the PE spectra of **1-4** is made empirically and on the basis of model calculations (MINDO/3 and MNDO) for **1b-4b** and ab initio for **1b** and **2b**. For **2** we find that one $\sigma$-level is placed between $\pi_-$ and $n_-$. A comment is made on the relationship between the split of the bands assigned to $\pi_-$ and $n_-$ and the C-O-O-C torsional angle $\theta$.

Recently the He(I) photoelectron (PE) spectra of a number of cyclic and bicyclic peroxides have been reported.[1-5] For the bands which were assigned as due to ionization events from $a_2(\pi_-)$ and $b_2(n_-)$, a correlation with

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