Pergamon

Tetrahedron, Vol. 53, No. 36, pp. 12159-12166, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00549-8

A New Synthesis of Isoselenoureas by Imidoylation of Amines with Selenium and Isocyanides

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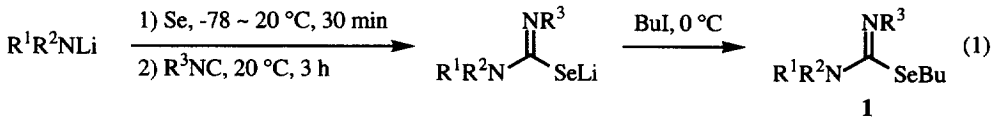
Abstract: Lithium amides prepared from secondary amines reacted with selenium and isocyanides to yield lithium selenocarbamimidates which were trapped with butyl iodide to give the corresponding isoselenoureas in good to high yields. © 1997 Elsevier Science Ltd.

Isoselenoureas (**1**) and their onium salts have been used as potent reagents for selective introduction of organoselenium moieties into organic molecules such as sugars,[1] guanosines,[2] and spin labels.[3] They have also attracted much attention as useful materials since they show unique pharmacological activity,[4] radioprotectivity,[5] and conductivity.[6] Here we report a convenient one-pot procedure for the synthesis of isoselenoureas (**1**) from amines, selenium, isocyanides, and butyl iodide (eq 1).



(1)

1

A typical example is as follows. Lithium piperidide prepared from piperidine and BuLi in THF / HMPA was allowed to react with selenium at -78 °C, and the reaction mixture was warmed up to 20 °C and stirred for 30 min. To the mixture was added 2,6-xylyl isocyanide (XyNC), and the stirring was continued for 3 h. Addition of butyl iodide at 0 °C followed by usual workup gave the corresponding isoselenourea (**1a**) in 67% yield. Table 1 lists several examples of this reaction performed using different secondary amines and isocyanides. This reaction has wide generality and can be applied to various substrates having aliphatic and aromatic substituents. Reaction of morpholine and 1-methylpiperazine gave the corresponding isoselenoureas

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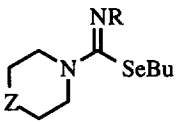
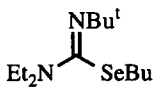
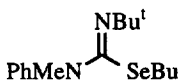
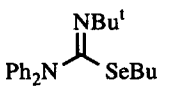
obtained in higher yields (compare runs 1 and 2, 3 and 4, and 5 and 6). The reaction of diethylamine gave **1g** in moderate to good yields (runs 3 and 5). When *t*-BuNC was used instead of XyNC, desired products were in a moderate yield (run 7), but diisopropylamine did not afford the corresponding isoselenourea even when *t*-BuNC was used probably due to the steric hindrance. Reactions of aromatic amines such as *N*-methylaniline and diphenylamine also proceeded well to yield isoselenoureas (**1h** and **1i**) in high yields (runs 8, 9). Under similar conditions, primary amines such as butylamine and aniline gave complex mixtures of products, and the corresponding isoselenoureas were not obtained.

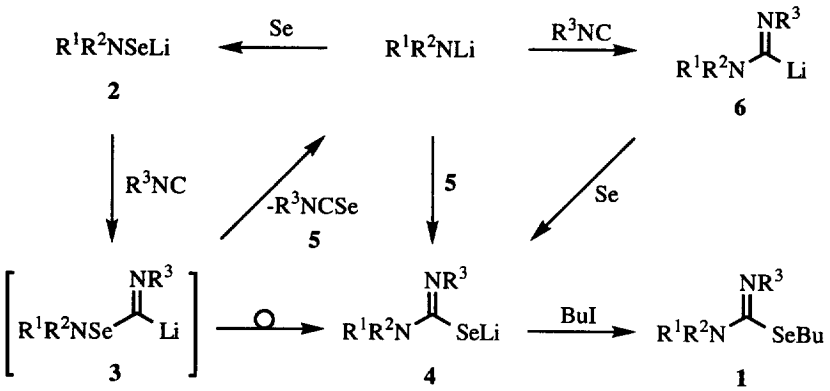
Table 1. Synthesis of Isoselenoureas (**1**)

run	R^1R^2NH	R^3NC[a]	isoselenourea[a]	isolated yield (%)
				
1	$Z = CH_2$	XyNC	$Z = CH_2$, R = Xy (**1a**)	67
2		*t*-BuNC	$Z = CH_2$, R = *t*-Bu (**1b**)	86
3	Z = O	XyNC	Z = O, R = Xy (**1c**)	60
4		*t*-BuNC	Z = O, R = *t*-Bu (**1d**)	83
5	Z = NMe	XyNC	Z = NMe, R = Xy (**1e**)	34
6		*t*-BuNC	Z = NMe, R = *t*-Bu (**1f**)	76
7	Et_2NH	*t*-BuNC	 (**1g**)	48
8	PhMeNH	*t*-BuNC	 (**1h**)	79
9	Ph_2NH	*t*-BuNC	 (**1i**)	74

Conditions: R^1R^2NH (2.0 mmol), BuLi (2.2 mmol), THF (25 mL), HMPA (6.0 mmol), -78 °C, 30 min; Se (2.4 mmol), -78 ~ 20 °C, 30 min; R^3NC (2.2 mmol), 20 °C, 3 h; BuI (4.0 mmol), 0 °C, 30 min.
a) Xy = 2,6-xylyl.

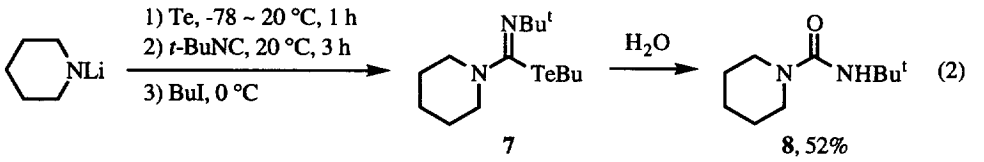
In Scheme 1, we postulate plausible pathways of the present imidoylation. Reaction of lithium amides with selenium affords selenolates (**2**), which then react with isocyanides to give lithium selenocarbamimidates (**4**) probably *via* formal rearrangement of **3**. Isoselenoureas (**1**) are formed by trapping of **4** with butyl iodide. It is still a question whether the rearrangement proceeds intermolecularly or intramolecularly with or without elimination of isoselenocyanates (**5**), respectively. However, the intermolecular pathway is supported by the

following evidence; (i) isocyanides react with selenium in the presence of amines to give the corresponding isoselenocyanates[7] and (ii) primary or secondary amines react with isoselenocyanates at their central carbon to afford the corresponding selenoureas.[7,8] An alternative pathway *via* generation of imidoyllithium (**6**) by the direct reaction of lithium amides with isocyanides followed by subsequent trapping with selenium can not be ruled out. This pathway is similar to that proposed by us for the tellurocarbamate synthesis.[9]



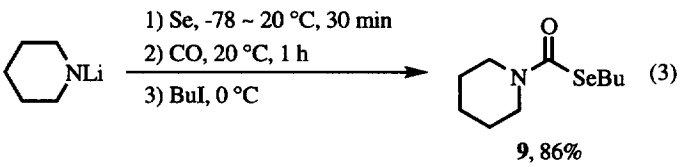
Scheme 1. Plausible Reaction Pathways

We then examined imidoylation by using other chalcogen elements. When we used sulfur in place of selenium, no desired isothiourea was obtained. However, when tellurium was used in the absence of HMPA, a urea derivative (**8**) was isolated in 52% yield after usual workup probably *via* hydrolysis of **7** (eq 2).[10]



(2)

In addition, when we tested carbonylation of piperidine by the use of atmospheric pressure of carbon monoxide instead of isocyanide in a similar manner, piperidine was smoothly carbonylated to give the corresponding selenocarbamate (**9**) in 86% yield (eq 3).[11]



(3)

As for the synthesis of isoselenoureas, there have been known the following two types of reactions: (i) alkylation of selenoureas with alkyl halides,[1c,1d,1f,2,3,4e,8o,12] and (ii) reaction of selenocyanates with amines.[13] The former requires preparation of the corresponding selenoureas carrying desired substituents. As for the

latter procedure, only one example *via* intramolecular reaction has been reported, and this method can not be applied to the synthesis of isoselenoureas having substituents on their imino nitrogen. Our method described herein might be synthetically useful since the products are obtained in good yields by a convenient one-pot procedure from easily available substrates, and the reaction has wide generality.

EXPERIMENTAL SECTION

General Comments

THF was distilled from sodium benzophenone ketyl. HMPA was fractionally distilled and dried over calcium hydride. BuLi (1.6 M hexane solution), S, Se, Te and *t*-BuNC were used as purchased. BuI was distilled from P_2O_5. Amines were obtained from commercial sources, and were used after purification by distillation from calcium hydride or recrystallization. 2,6-Xylyl isocyanide (XyNC) was synthesized according to the literature,[14] and purified by recrystallization.

A melting point was determined on a Yanagimoto Micro Melting Point apparatus. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz and 68 MHz, respectively) or a JEOL JNM-ALICE-400 (400 MHz and 100 MHz, respectively) spectrometer using Me_4Si as an internal standard. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. Purification of products was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent or by column chromatography using Fuji-Davison silica gel WB-300 (100-250 mesh) or by preparative TLC with Wakogel B-5F silica gel (325 mesh). Mass spectra (EI) were taken on a SHIMADZU GCMC-QP2000 operating in the electron impact mode (70 eV) equipped with CBP1-M25-025 column. Mass spectra (CI) were obtained on a JEOL JMS-DX303 in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Elemental analyses were performed on a Perkin Elmer 240C apparatus.

Synthesis of Isoselenoureas. A General Procedure

To a THF (25 mL) / HMPA (1 mL, 6 mmol) solution of an amine (2.0 mmol) was added BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol) at -78 °C under nitrogen. After 30 min, finely ground selenium powder (190 mg, 2.4 mmol) was added, and the mixture was warmed to 20 °C. A homogeneous solution was obtained within 30 min. Then an isocyanide (2.2 mmol) was added to the solution and stirring was continued for 3 h. To the solution was added BuI (736 mg, 4.0 mmol) at 0 °C and the stirring was continued for 30 min. Aqueous saturated NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give a yellow residue. Purification by silica gel column chromatography, recycling preparative HPLC or preparative TLC afforded the corresponding isoselenourea (**1**).

2-Butyl-3-(2,6-dimethylphenyl)-1-piperidinoisoselenourea (1a)

Purified by silica gel column chromatography (hexane/ether = 1/1) (67% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, J = 7.4 Hz, 3 H), 1.30 (sext, J = 7.4 Hz, 2 H), 1.57 (quint, J = 7.4 Hz, 2 H), 1.67 (brs, 6 H), 2.07 (s, 6 H), 2.68 (t, J = 7.4 Hz, 2 H), 3.54 (brs, 4 H), 6.86 (dd, J = 8.3, 6.8 Hz, 1 H), 6.97 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 18.5, 23.0, 25.2, 25.9, 27.0, 32.9, 50.7, 122.3, 127.6, 128.3, 148.6, 153.8; IR (NaCl) 2933, 2855, 1614, 1587, 1223, 1172, 1120, 1089, 1005, 761 cm^{-1}; MS (CI), m/z (%)

= 84 (5), 215 (100), 243 (6), 257 (3), 353 (M^++1, 28). Anal. Calcd for $C_{18}H_{28}N_2Se$: C, 61.53; H, 8.03; N, 7.97. Found: C, 61.46; H, 8.16; N, 7.81.

2-Butyl-3-*tert*-butyl-1-piperidinoisoselenourea (1b)

Purified by silica gel column chromatography (hexane/ether = 1/1) (86% yield). Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.4 Hz, 3 H), 1.31 (s, 9 H), 1.40 (sext, J = 7.4 Hz, 2 H), 1.53 (brs, 6 H), 1.68 (quint, J = 7.4 Hz, 2 H), 2.77 (t, J = 7.4 Hz, 2 H), 3.18 (brs, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.2, 25.3, 26.1, 27.8, 30.7, 33.1, 50.9, 54.2, 148.4; IR (NaCl) 2963, 2931, 2856, 1612, 1357, 1230, 1171, 1114, 999, 892 cm^{-1}; MS (CI), m/z (%) = 111 (15), 167 (100), 220 (2), 305 (M^++1, 21). Anal. Calcd for $C_{14}H_{28}N_2Se$: C, 55.43; H, 9.30; N, 9.23. Found: C, 55.17; H, 9.20; N, 9.05.

2-Butyl-3-(2,6-dimethylphenyl)-1-morpholinoisoselenourea (1c)

Purified by silica gel column chromatography (hexane/ether = 1/1) followed by PTLC (hexane/ether = 1/1) (60% yield). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 7.4 Hz, 3 H), 1.30 (sext, J = 7.4 Hz, 2 H), 1.56 (quint, J = 7.4 Hz, 2 H), 2.07 (s, 6 H), 2.67 (t, J = 7.4 Hz, 2 H), 3.60 (t, J = 4.6 Hz, 4 H), 3.77 (t, J = 4.6 Hz, 4 H), 6.88 (t, J = 7.5 Hz, 1 H), 6.99 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 18.4, 22.9, 27.0, 32.8, 49.9, 66.6, 122.2, 127.3, 127.6, 147.6, 153.1; IR (NaCl) 2959, 2929, 2852, 1614, 1587, 1265, 1185, 1151, 1119, 1021, 763 cm^{-1}; MS (EI), m/e (%) = 86 (32), 105 (5), 131 (6), 217 (100), 297 (1), 354 (M^+, 13). HRMS (EI) Calcd for $C_{17}H_{26}N_2OSe$: 354.1210. Found: 354.1197.

2-Butyl-3-*tert*-butyl-1-morpholinoisoselenourea (1d)

Purified by silica gel column chromatography (hexane/ether = 1/1) (83% yield). Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3 H), 1.31 (s, 9 H), 1.41 (sext, J = 7.3 Hz, 2 H), 1.69 (quint, J = 7.3 Hz, 2 H), 2.77 (t, J = 7.3 Hz, 2 H), 3.23 (t, J = 4.5 Hz, 4 H), 3.66 (t, J = 4.5 Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.1, 28.0, 30.6, 33.1, 50.4, 54.4, 67.0, 147.0; IR (NaCl) 2963, 2928, 2850, 1617, 1358, 1260, 1154, 1120, 1014 cm^{-1}; MS (CI), m/z (%) = 113 (31), 169 (100), 251 (4), 307 (M^++1, 45). Anal. Calcd for $C_{13}H_{26}N_2OSe$: C, 51.14; H, 8.58; N, 9.18. Found: C, 51.01; H, 8.65; N, 9.08.

2-Butyl-3-(2,6-dimethylphenyl)-1-(4-methylpiperazino)isoselenourea (1e)

Purified by recycling preparative HPLC (34% yield). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 7.4 Hz, 3 H), 1.30 (sext, J = 7.4 Hz, 2 H), 1.55 (quint, J = 7.4 Hz, 2 H), 2.07 (s, 6 H), 2.34 (s, 3 H), 2.49 (brs, 4 H), 2.67 (t, J = 7.4 Hz, 2 H), 3.62 (brs, 4 H), 6.86 (t, J = 7.3 Hz, 1 H), 6.98 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 18.4, 22.9, 26.9, 32.8, 46.0, 49.1, 54.8, 122.1, 127.2, 127.7, 147.8, 152.8; IR (NaCl) 2958, 2934, 2872, 2845, 2791, 1613, 1587, 1462, 1362, 1288, 1224, 1175, 1131, 1004, 762 cm^{-1}; MS (EI), m/e (%) = 99 (29), 105 (3), 131 (4), 230 (100), 310 (4), 367 (M^+, 10). HRMS (EI) Calcd for $C_{18}H_{29}N_3Se$: 367.1526. Found: 367.1509.

2-Butyl-3-*tert*-butyl-1-(4-methylpiperazino)isoselenourea (1f)

Purified by silica gel column chromatography (ether) (76% yield). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3 H), 1.31 (s, 9 H), 1.41 (sext, J = 7.3 Hz, 2 H), 1.68 (quint, J = 7.3 Hz, 2 H), 2.29 (s, 3 H), 2.39 (brs, 4 H), 2.76 (t, J = 7.3 Hz, 2 H), 3.27 (brs, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6,

23.1, 27.8, 30.6, 33.0, 46.0, 49.3, 54.2, 55.2, 146.3; IR (NaCl) 2964, 2931, 2842, 2789, 1616, 1456, 1359, 1286, 1229, 1172, 1131, 1005, 900 cm^{-1}; MS (EI), m/e (%) = 99 (4), 126 (100), 182 (41), 262 (3), 320 (M^+, 1). HRMS (EI) Calcd for $C_{14}H_{30}N_3Se$: 320.1604. Found: 320.1595.

2-Butyl-3-*tert*-butyl-1,1-diethylisoselenourea (1g)

Purified by silica gel column chromatography (hexane/ether = 5/1) (48% yield). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3 H), 1.04 (t, J = 7.0 Hz, 6 H), 1.31 (s, 9 H), 1.39 (sext, J = 7.4 Hz, 2 H), 1.67 (quint, J = 7.4 Hz, 2 H), 2.75 (t, J = 7.4 Hz, 2 H), 3.28 (q, J = 7.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 13.6, 23.2, 28.0, 30.7, 33.1, 44.0, 54.2, 144.3; IR (NaCl) 2964, 2930, 2871, 1613, 1460, 1378, 1357, 1236, 1207, 1079, 899 cm^{-1}; MS (CI), m/z (%) = 99 (21), 155 (100), 293 (M^++1, 35). Anal. Calcd for $C_{13}H_{28}N_2Se$: C, 53.59; H, 9.69; N, 9.62. Found: C, 53.51; H, 9.73; N, 9.57.

2-Butyl-3-*tert*-butyl-1-methyl-1-phenylisoselenourea (1h)

Purified by silica gel column chromatography (hexane/ether = 1/1) followed by recycling preparative HPLC (79% yield). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, J = 7.3 Hz, 3 H), 1.27 (sext, J = 7.3 Hz, 2 H), 1.38 (s, 9 H), 1.48 (quint, J = 7.3 Hz, 2 H), 2.49 (brs, 2 H), 3.17 (s, 3 H), 7.00 (t, J = 7.2 Hz, 1 H), 7.08 (d, J = 7.2 Hz, 2 H), 7.26 (t, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 23.0, 27.7, 30.3, 32.5, 40.9, 55.3, 121.9, 128.1, 145.8, 146.8; IR (NaCl) 2964, 2928, 1615, 1593, 1493, 1232, 1202, 1107, 698 cm^{-1}; MS (CI), m/z (%) = 133 (9), 189 (100), 327 (M^++1, 43). HRMS (CI) Calcd for $C_{16}H_{27}N_2Se$: 327.1340. Found: 327.1338.

2-Butyl-3-*tert*-butyl-1,1-diphenylisoselenourea (1i)

Purified by silica gel column chromatography (hexane/ether = 5/1) followed by recycling preparative HPLC (74% yield). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, J = 7.2 Hz, 3 H), 1.29 (brs, 11 H), 1.53 (brs, 2 H), 2.70 (brs, 2 H), 7.04 (t, J = 7.8 Hz, 2 H), 7.13 (d, J = 7.8 Hz, 4 H), 7.25 (t, J = 7.8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 23.1, 28.1, 29.5, 32.1, 56.1, 122.8, 123.0, 128.3, 145.1, 145.8; IR (NaCl) 2964, 2928, 1615, 1591, 1492, 1288, 1218, 1202, 751, 694 cm^{-1}; MS (CI), m/z (%) = 195 (22), 251 (100), 389 (M^++1, 32). HRMS (CI) Calcd for $C_{21}H_{29}N_2Se$: 389.1496. Found: 389.1494.

***N*-*tert*-Butyl-*N'*-piperidinourea (8)**

The typical procedure for the synthesis of **1** was followed, by employing tellurium instead of selenium in the absence of HMPA. Purified by silica gel column chromatography (ether) (52% yield). White solid; mp 141 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.35 (s, 9 H), 1.56 (brs, 6 H), 3.26 (brs, 4 H), 4.29 (brs, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.4, 24.6, 28.5, 43.9, 49.5, 156.2; IR (KBr) 3368, 2938, 2852, 2362, 1624, 1530, 1393, 1273, 1216 cm^{-1}; MS (EI), m/e (%) = 57 (21), 84 (100), 112 (74), 127 (24), 169 (27), 184 (M^+, 64). Anal. Calcd for $C_{10}H_{20}N_2O$: C, 65.18; H, 10.94; N, 15.20. Found: C, 65.03; H, 11.06; N, 15.14.

***Se*-Butyl piperidine-1-selenocarbamate (9)**

The typical procedure for the synthesis of **1** was followed, by employing atmospheric pressure of carbon monoxide instead of an isocyanide. Purified by recycling preparative HPLC (86% yield). Yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3 H), 1.41 (sext, J = 7.4 Hz, 2 H), 1.59 (brs, 6 H), 1.69

(quint, J = 7.4 Hz, 2 H), 2.93 (t, J = 7.4 Hz, 2 H), 3.34 (brs, 2 H), 3.58 (brs, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.6, 23.2, 24.7, 25.6, 26.6, 33.0, 45.1, 47.8, 163.6; IR (NaCl) 2936, 2857, 1653, 1405, 1245, 1203, 1130, 1118, 998 cm^{-1}; MS (EI), m/e (%) = 41 (8), 56 (3), 69 (26), 84 (1), 112 (100), 249 (M^+, 11). HRMS (EI) Calcd for $C_{10}H_{19}NOSe$: 249.0632. Found: 249.0629.

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University.

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(*Received* 10 *March* 1997; *accepted* 18 *April* 1997)