The ^1H and ^{13}C NMR spectra of [8-^{13}C]-1 gave doublet patterns at the resonance positions for ^1H and ^{13}C in the ^1H–$^{13}C(8)$ unit, J = 209 Hz. A trio of peaks in the mass spectrum of 1 at m/z 135 (0.05), 136 (1.00), and 137 (0.02), along with the absence of extraneous peaks in the ^1H and ^{13}C NMR spectra, demonstrated that labeling was regiospecific and complete. The good yield of 1 from an available source of ^{13}C makes this procedure attractive for the synthesis of [8-^{13}C]adenine and related derivatives. The base can be used directly in feeding experiments or converted to ribonucleosides or deoxyribonucleosides for synthetic applications.

Experimental Section

[8-^{13}C]Adenine (1). Sodium [^{13}C]formate (1.0 g, 14.49 mmol, 99%) was converted to morpholinium formate according to the procedure of Sharma.[7] The low melting salt was then heated to 95 °C under nitrogen for 45 min, during which time moisture was observed to form on the walls of the flask. 4,5,6-Triaminopyrimidine sulfate hydrate (Aldrich) (3.5 g, 14.5 mmol) was dissolved in 10 mL of 1 N HCl with gentle heating and added to the flask. The resulting mixture was allowed to stir under nitrogen at 95 °C. The progress of the reaction was monitored by HPLC on a Waters ACCELL CM cation exchange column using 0.02 M ammonium formate, pH 4.5, as the eluting buffer. After 36 h the reaction was complete. The solution was allowed to cool to room temperature, neutralized with 6 N NaOH, and allowed to stand at 4 °C for 24 h. Crystals were collected on a glass frit, washed thoroughly with water, and dried over P_2O_5. The mother liquor was lyophilized. The residue was recrystallized from hot water and dried over P_2O_5. The combined crystallizations gave 1.2 g (61%) of a white solid; UV λ_{max} (H_2O) 261 nm (ϵ 1.32 × 10^4); EI-MS (relative intensity), m/z at 136 (M^+, 100), 135 (4.5), 109 (17.7), 54 (5.1), 53 (2.8); ^1H NMR (400 MHz, DMSO) δ 8.25 (1 H, d, J = 209 Hz, H8), 8.24 (1 H, s, NH), 7.89 (1 H, s, H2), 7.05 (2 H, br s, NH_2); ^{13}C NMR (DMSO) δ 140.9 (d, J = 209 Hz).

Anal. Calcd for $C_5H_7N_5O$ (adenine monohydrate): C, 39.6; H, 4.5; N, 45.4. Found: C, 39.3; H, 4.4; N, 45.0.

A separate reaction was interrupted after 12 h, and three UV-active components were separated by HPLC on an ACCELL CM cation exchange column upon elution with 20 mM ammonium formate, pH 4.5. Two of the materials, unreacted 5 and 1, were identified from their ^1H and ^{13}C NMR spectra. The third component, 5, was a white solid; EI-MS (relative intensity), m/z at 154 (M^+, 100) 125 (73), 124 (5), 98 (4), 97 (9), 71 (14), 70 (7); ^1H NMR (DMSO, 300 MHz) δ 9.22 (1 H, s, amide H), 8.20 (1 H, s, H6), 8.09 (1 H, d, J = 199 Hz, formamide), 7.70 (4 H, br s, amino H); ^{13}C NMR (^1H decoupled, DMSO) δ 161.54, 147.4, 143.3, 91.4. Formamide 5 was converted to 1 when heated at 95 °C in 1 N hydrochloric acid.

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Photodesulfurization of Indoline-2-thiones: A Facile Synthesis of Indoles

Takehiko Nishio

Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

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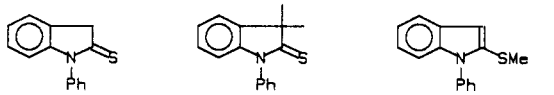
The photochemistry of thiones has been extensively studied over the past 2 decades.[1] However, relatively few reports have dealt with the photochemical properties of thioamides[2] and the major photochemical processes of the thioamides are largely limited to intra- or intermolecular cycloaddition to alkenes. Das et al. reported that on irradiation indoline-2-thiones reacted with methyl methacrylate to give a mixture of isomeric 2-substituted indoles.[2c] One of these isomers has been employed as a key intermediate in a synthesis of indole alkaloids. In continuation of our work on the photochemistry of cyclic conjugated nitrogen–thiocarbonyl systems,[2g] we have studied the photochemical behavior of the indoline-2-thiones 1.

Due to the ambident nature of the indoline-2-thiones 1, either thione 1 or thiol 1′ forms are possible. Thus UV and ^{13}C NMR spectra of 1-phenylindoline-2-thione (**1a**) were compared with those of the 3,3-dimethyl-1-phenylindoline-2-thione (**1m**) (thione form) and 2-(methylthio)-1-phenylindole (**6**) (thiol form). The UV spectrum of **1a** [λ_{max} (EtOH) 225 (ϵ 13400), 294 (7900), and 321 nm



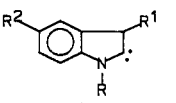
(1a) (1m) (6)

λ_{max}(EtOH) λ_{max}(EtOH) λ_{max}(EtOH)

225 nm (ε 13400), 294 (7900), 321 (12800)

226 nm (ε 14700), 294 (8400), 317 (13900)

219 nm (ε 29400), 260 sh (12500), 283 (16000), 290 (15900)



(7)

(12800)] is similar to that of 3,3-dimethyl-1-phenylindoline-2-thione (**1m**, thione form)[3] but different from that of 2-(methylthio)-1-phenylindole (**6**, thiol form).[3] Furthermore, the ^{13}C NMR spectrum of **1a** showed signals at δ 49.7 (t) and 202.5 (s), assignable to methylene at C-3 and thiocarbonyl carbon at C-2, respectively. Consequently, the indoline-2-thione **1a** is present preferentially in the thione form in the ground state.[4]

Irradiation of 1-phenylindoline-2-thione (**1a**) in benzene in a Pyrex vessel with a high-pressure mercury lamp under

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(3) The UV spectrum of **1m**: λ_{max} (EtOH) 226 (ϵ 14700), 294 (8400), and 317 nm (13900). The UV spectrum of **6**: λ_{max} (EtOH) 219 (ϵ 29400), 260 sh (12500), and 283 (16000), and 290 nm (15900).

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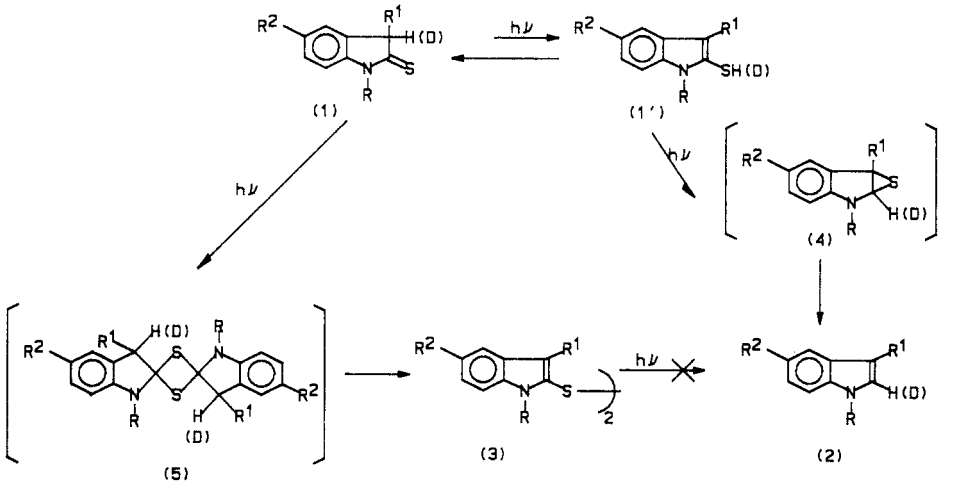
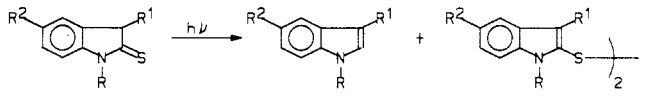
0022-3263/88/1953-1323$01.50/0

Scheme I



argon at room temperature gave 1-phenylindole (**2a**) and bis(1-phenylindol-2-yl) disulfide (**3a**), in 73% and 18%



R: H, Alkyl, Aryl
R^1: H, Alkyl, Aryl
R^2: H, Me

yields, respectively. The structure of the indole **2a** was confirmed by an independent synthesis from the reduction of 1-phenylindolin-2-one with LAH followed by dehydrogenation with Pd–C.[6] The structure of the disulfide **3a** was elucidated on the basis of spectroscopic properties and elemental analysis. The yields of the indole **2a** and disulfide **3a** reduced to 4% and 6%, respectively, when the indoline-2-thione **1a** was irradiated in the n,π^* region of the thioamide group. This suggests that the photoreaction of the indoline-2-thione **1a** proceeds from the upper excited state, as in the case of thiones.[1b]

Irradiation of **1a** in benzene under an oxygen atmosphere gave the disulfide **2a** as main product, and the yield of the indole **1a** was quite low (trace). Similarly, irradiation of the indoline-2-thiones **1b–i,k,l** gave the desulfurization products, indoles **2b–i,k,l**, in 17–80% yields, together with indolyl disulfides. Sulfur was isolated in 16% yield when 1-butylindoline-2-thione (**1f**) was photolyzed. On the other hand, 1-methylindoline-2-thione (**1j**) yielded only as intractable mixture on irradiation.

A reasonable mechanism for the formation of the indoles **2** and disulfides **3** is presented in Scheme I. In this postulated mechanism, an amino episulfide (**4**) is formed initially through the thiol tautomer, which may be present in equilibrium with the thione tautomer under irradiation. Then the amino episulfide **4** postulated as an intermediate loses sulfur to give the indole **2**. Photochemical-induced desulfurization of episulfide had been reported.[7] The intermediacy of **4** in the reaction could not be confirmed. However, when the 3-deuteriated indoline-2-thione **1b**-D (D content 44%), which was prepared by the reaction of the indoline-2-thione **1b** with acetic acid-d_4,[4a] was irradiated under the same conditions, the 2-deuteriated indole **2b**-D (D content 32%) was obtained.

The formation of the indoles **1** via carbene intermediates **7**[1d,5] seems improbable, in view of the ready addition of alcohols to carbene.[8] Irradiation of **1a** in alcoholic solvent such as methanol and 2-propanol also gave the indole **2a** and disulfide **3a**; no alcohol addition product was detected (Table I). In reducing solvents, hydrogen abstraction by carbene would also be expected.[9] However, such products were not isolated when irradiation of **1a** was carried out in cyclohexane. Furthermore, irradiation of the indoline-2-thiones **1** in the presence of alkene did not yield the products that were produced by the reaction of alkene with carbene **7** and gave only the 2-substituted indoles, which arise through [2 + 2] photocycloaddition.[2c,10] On the other hand, formation of the disulfides **3** can be explained in terms of the dimerization of **1** and subsequent reductive decomposition of the resulting dithietanes **5**. Photochemical dimerization of thiones to dithietanes and subsequent conversion of dithietanes into disulfides have been reported.[1d,11] Photochemical conversion of the disulfides **3** to indoles **2** was disproved because the disulfide **3a** did not give the indole **2a** upon irradiation. The photoreaction described here would provide a facile method for the synthesis of the N-substituted indoles, especially *N*-arylindoles.

Experimental Section

Melting and boiling points are uncorrected. Melting points were measured with a Yanaco micro melting point apparatus (MP-J3) and boiling points were measured with a Büchi Kugelrohr (KR-3) apparatus. UV spectra were recorded on a JASCO UVIDEC-505 photospectrometer and IR spectra were determined with a Hitachi 260-30 photospectrometer. ^1H and ^{13}C NMR spectra were run on a JEOL FX 100 spectrometer (100 MHz) using $CDCl_3$ as solvent. Mass spectra were measured with a Hitachi M-80 spectrometer. A HaLõs (Eikosha EHP-300 W) high-pressure mercury lamp was used as an irradiation source.

Materials. Indoline-2-thiones **1a–l** were prepared by the thiation of the corresponding indoline-2-ones with 2,4-bis(*p*-methoxyphenyl)-1,3-dithiadiphosphetane 2,4-disulfide (Lawesson's reagent).[12]

1-Phenylindoline-2-thione (1a): mp 100–101 °C; UV (EtOH) 225 (ϵ 13 400), 294 (7900), 321 nm (12 800); IR (KBr) 1610, 1590,

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(9) Reference 8, p 209.
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Table I. Yield of the Photoproducts 2 and 3

	R	R^1	R^2	solvent	irradn time (h)	yield (%)[a] 2	3	recovered 1
1a	Ph	H	H	benzene	15	73	18	5
				benzene[b]	15	trace	23	5
				benzene[c]	15	4	6	82
				MeOH	15	12	trace	10
				i-PrOH	15	31	22	27
				CH_3CN	15	47	16	28
				CH_2Cl_2	15	29	trace	trace
				cyclohexane	15	26	20	33
1b	Ph	Me	H	benzene	5	28	63	trace
				benzene	15	30	60	trace
1c	Ph	Et	H	benzene	15	31	38	trace
1d	Ph	Ph	H	benzene	15	17	70	trace
1e	*p*-tolyl	H	Me	benzene	15	80	trace	15
1f	Bu	H	H	benzene	15	77	trace	trace; S (16%)
1g	Bu	Me	H	benzene	15	66	trace	33
1h	Bu	Ph	H	benzene	15	56	35	8
1i	CH_2Ph	H	H	benzene	24	32	ND[d]	48
1j	Me	H	H	benzene	15	*e*	*e*	*e*
1k	Me	Ph	H	benzene	15	58	10	30
1l	H	H	H	benzene	15	35	ND	10

[a] Isolated yield. [b] Irradiation was carried out under an oxygen atmosphere. [c] Halogen lamp (λ >400 nm) was used. [d] Not detected. [e] Intractable mixture.

1500, 1460, 755, 700 cm^{-1}; ^1H NMR δ 4.27 (s, 2 H), 6.54–6.69 (m, 1 H), 7.10–7.69 (m, 8 H); ^{13}C NMR 49.7 (t), 110.5 (d), 123.9 (d), 124.3 (d), 127.5 (d), 127.8 (d), 129.0 (s), 129.1 (d), 129.8 (d), 133.6 (s), 147.8 (s), 202.5 ppm (s). Anal. Calcd for $C_{14}H_{11}NS$: C, 74.63; H, 4.92; N, 6.21. Found: C, 74.73; H, 5.06; N, 5.86.

3-Methyl-1-phenylindoline-2-thione (1b): mp 130–131 °C; UV (EtOH) 228 (ϵ 17900), 295 (9100), 321 nm (12300); IR (KBr) 1605, 1590, 1490, 755, 700 cm^{-1}; ^1H NMR δ 1.72 (d, 3 H, J = 7.3 Hz), 3.97 (q, 1 H, J = 7.3 Hz), 6.54–6.72 (m, 1 H), 7.08–7.69 (m, 8 H); ^{13}C NMR 19.7 (q), 53.0 (d), 110.4 (d), 123.6 (d), 124.2 (d), 127.5 (d), 127.8 (d), 128.5 (d), 129.0 (d), 135.0 (s), 136.7 (s), 146.3 (s), 208.7 ppm (s). Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.11; H, 5.50; N, 5.82.

3-Ethyl-1-phenylindoline-2-thione (1c): mp 80–81 °C; UV (EtOH) 229 (ϵ 18300), 295 (8800), 322 nm (13900); IR (KBr) 1610, 1590, 1495, 1445, 760, 700 cm^{-1}; ^1H NMR δ 0.84 (t, 3 H), 2.20–2.48 (m, 2 H), 4.01 (t, 1 H, J = 5.4 Hz), 6.54–6.72 (m, 1 H), 7.08–7.69 (m, 8 H); ^{13}C NMR 8.8 (q), 27.5 (t), 58.1 (d), 110.3 (d), 123.8 (d), 127.5 (d), 127.8 (d), 129.0 (d), 129.8 (d), 133.1 (s), 136.9 (s), 147.0 (s), 207.3 ppm (s). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.96; N, 5.52. Found: C, 75.77; H, 6.01; N, 5.48.

1,3-Diphenylindoline-2-thione (1d), oil. **1d** exists in a mixture of thione and thiol forms (ca. 1:4): IR (film) 2510, 1595, 1495, 1445, 760, 745, 695 cm^{-1}; ^1H NMR δ 3.27 (s, 0.8 H), 5.08 (s, 0.2 H), 6.91–7.80 (m, 14 H). Anal. Calcd for $C_{20}H_{15}NS$: C, 79.69; H, 5.01; N, 4.64. Found: C, 79.50; H, 4.66; N, 4.52.

5-Methyl-1-*p*-tolylindoline-2-thione (1e): mp 134–135 °C; IR (KBr) 1510, 1485, 805 cm^{-1}; ^1H NMR δ 2.34 (s, 3 H), 2.43 (s, 3 H), 4.22 (s, 2 H), 6.50 (d, 1 H, J = 8.3 Hz), 7.00 (d, 1 H, J = 8.3 Hz), 7.14–7.42 (m, 5 H); ^{13}C NMR 21.0 (q), 21.3 (q), 49.5 (t), 110.2 (d), 124.7 (d), 126.1 (d), 127.0 (d), 128.1 (s), 130.4 (d), 134.0 (s), 139.0 (s), 145.7 (s), 202.0 ppm (s). Anal. Calcd for $C_{16}H_{15}NS$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.71; H, 6.39; N, 5.82.

1-Butylindoline-2-thione (1f): mp ~30 °C: IR (KBr) 1605, 1455, 1438, 740, 705 cm^{-1}; ^1H NMR δ 0.98 (s, 3 H), 1.27–1.92 (m, 4 H), 4.06 (s, 2 H), 4.17 (t, 2 H), 6.92–7.41 (m, 4 H); ^{13}C NMR 13.8 (q), 20.3 (t), 28.3 (t), 44.3 (t), 49.2 (t), 109.7 (d), 127.8 (d), 129.3 (s), 146.0 (s), 200.4 ppm (s). Anal. Calcd for $C_{12}H_{15}NS$: C, 70.19; H, 7.36; N, 6.82. Found: C, 69.87; H, 7.31; N, 6.76.

1-Butyl-3-methylindoline-2-thione (1g): bp 140 °C (2 mmHg); IR (film) 1605, 1455, 740 cm^{-1}; ^1H NMR δ 0.97 (t, 3 H), 1.58 (d, 3 H, J = 7.8 Hz), 1.14–1.92 (m, 4 H), 3.75 (q, 1 H, J = 7.8 Hz), 4.18 (t, 2 H), 6.85–7.60 (m, 4 H); ^{13}C NMR 13.9 (q), 19.4 (q), 20.3 (t), 44.3 (t), 52.7 (d), 109.6 (d), 123.5 (d), 123.9 (d), 127.8 (d), 135.4 (s), 144.7 (s), 206.5 ppm (s). Anal. Calcd for $C_{13}H_{17}NS$: C, 71.18; H, 7.81; N, 6.38. Found: C, 70.96; H, 7.77; N, 6.28.

1-Butyl-3-phenylindoline-2-thione (1h): bp 190 °C (2 mmHg); IR (film) 1595, 1500, 1460, 745, 695 cm^{-1}; ^1H NMR δ 0.99 (t, 3 H), 1.29–1.97 (m, 4 H), 4.23 (dt, 2 H, J = 2.0, 7.3 Hz), 4.91 (s, 1 H), 6.99–7.47 (m, 9 H); ^{13}C NMR 13.9 (q), 20.4 (t), 28.4 (t), 44.6 (t), 63.9 (d), 109.6 (d), 124.3 (d), 124.9 (d), 127.5 (d), 128.3 (d), 128.7 (d), 139.0 (s), 145.1 (s), 158.0 (s), 203.9 ppm (s). Anal. Calcd for $C_{18}H_{19}NS$: C, 76.84; H, 6.81; N, 4.93. Found: C, 76.88; H, 6.80; N, 4.87.

1-Benzylindoline-2-thione (1i): mp 125–126 °C; IR (KBr) 1605, 1590, 1485, 1455, 1425, 745, 715, 685 cm^{-1}; ^1H NMR δ 4.18 (s, 2 H), 5.44 (s, 2 H), 6.80–6.95 (m, 1 H), 7.02–7.53 (m, 8 H); ^{13}C NMR 48.0 (t), 49.2 (t), 110.4 (d), 123.9 (d), 124.2 (d), 127.3 (d), 127.8 (d), 128.8 (d), 129.0 (s), 134.6 (s), 145.8 (s), 201.7 ppm (s). Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.60; H, 5.42; N, 5.57.

1-Methyl-3-phenylindoline-2-thione (1k): mp 93–94 °C; IR (KBr) 1605, 1595, 1490, 1465, 750, 720, 690 cm^{-1}; ^1H NMR δ 3.65 (s, 3 H), 4.92 (s, 1 H), 6.98–7.55 (m, 9 H); ^{13}C NMR 31.5 (q), 63.7 (d), 109.4 (d), 124.5 (d), 124.8 (d), 127.5 (d), 128.3 (d), 128.7 (d), 133.8 (s), 138.7 (s), 145.6 (s), 204.3 ppm (s). Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.25; H, 5.20; N, 5.83.

3,3-Dimethyl-1-phenylindoline-2-thione (1m): mp 105–106 °C; UV (EtOH) 226 (ϵ 14700), 294 (8400), 317 nm (13900); IR (KBr) 1610, 1590, 1450, 755, 695 cm^{-1}; ^1H NMR δ 1.56 (s, 6 H), 6.95–6.77 (m, 1 H), 7.09–7.69 (m, 8 H); ^{13}C NMR 28.5 (q), 55.2 (s), 110.5 (d), 122.8 (d), 124.2 (d), 127.5 (d), 127.6 (d), 129.0 (d), 139.6 (s), 140.0 (s), 144.8 (s), 213.5 ppm (s). Anal. Calcd for $C_{16}H_{15}NS$: C, 78.85; H, 5.96; N, 5.52. Found: C, 75.79; H, 5.94; N, 5.46.

Indoline-2-thiones 1j,l: their spectroscopic properties were in accord with those in the literature.[4a]

Preparation of 2-(Methylthio)-1-phenylindole (6). A solution of **1a** (225 mg) and CH_3I (~1 mL) in acetone (30 mL) in the presence of K_2CO_3 (165 mg) was stirred for 1 h at room temperature. A usual workup gave **6** (230 mg; 92%): bp 160 °C (2 mmHg); UV (EtOH) 219 (ϵ 29400), 260 sh (12500), 283 (16000), 290 nm (15900); IR (film) 1595, 1495, 1440, 755, 740, 695 cm^{-1}; ^1H NMR δ 2.29 (s, 3 H), 6.59 (s, 1 H), 7.08–7.19 (m, 3 H), 7.32–7.61 (m, 6 H); ^{13}C NMR 18.0 (q), 104.3 (d), 109.9 (d), 119.4 (d), 120.3 (s), 120.3 (d), 121.8 (d), 128.0 (d), 129.2 (d), 135.2 (s), 137.3 (s), 138.9 ppm (s). Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47; N, 5.85. Found: C, 75.59; H, 5.50; N, 5.84.

General Procedures for the Photochemical Reactions of the Indoline-2-thiones 1. A solution of the indoline-2-thione **1** (200 mg) in solvent (70 mL) in a Pyrex vessel under argon was irradiated with a high-pressure mercury lamp (300 W) for 5–24 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel (Wakogel C-300 or Merck Kieselgel 60; flash chromatography) column with benzene–hexane (1:4–4:1) as eluant to give the indoles **2** and the disulfides **3**, accompanied by recovered **1**.

1-Phenylindole (2a): bp 150 °C (2 mmHg) [lit.[13] bp 110 °C (0.5 mmHg)]; IR (film) 1595, 1495, 1450, 765, 740, 720, 695 cm^{-1}; ^1H NMR δ 6.61 (d, 1 H, J = 3.4 Hz), 7.08–7.70 (m, 10 H); ^{13}C NMR 103.5 (d), 120.3 (d), 121.0 (d), 122.2 (d), 124.1 (d), 126.2 (d), 127.7 (d), 129.2 (s), 129.4 (s), 135.7 (s), 139.6 ppm (s); MS, m/z 193 (M^+).

Bis(1-phenylindol-2-yl) disulfide (3a): mp 230–232 °C; IR (KBr) 1585, 1490, 1440, 740, 695 cm^{-1}; ^1H NMR δ 7.13–7.67 (m, 20 H); ^{13}C NMR 110.6 (d), 111.5 (d), 120.1 (d), 121.1 (d), 123.2 (s), 125.2 (d), 126.9 (d), 128.2 (d), 129.3 (d), 137.3 (s), 138.4 ppm (s). Anal. Calcd for $C_{28}H_{20}N_2S_2$: C, 74.96; H, 4.49; N, 6.24. Found: C, 75.16; H, 4.32; N, 5.98.

3-Methyl-1-phenylindole (2b): bp 150 °C (2 mmHg); IR (film) 1600, 1500, 1450, 770, 740, 695 cm^{-1}; ^1H NMR δ 2.36 (d, 3 H, J = 1.5 Hz), 7.01–7.68 (m, 10 H); ^{13}C NMR 9.6 (q), 110.3 (d), 112.7 (s), 119.1 (d), 119.7 (d), 122.2 (d), 123.9 (d), 125.3 (d), 125.8 (d), 129.4 (d), 129.7 (s), 135.9 (s), 139.9 ppm (s); MS, m/z 207 (M^+). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.75. Found: C, 86.77; H, 6.34; N, 6.87.

Bis(3-methyl-1-phenylindol-2-yl) disulfide (3b): mp 116–117 °C; IR (KBr) 1590, 1495, 1445, 740, 695 cm^{-1}; ^1H NMR δ 2.00 (s, 6 H), 6.89–7.30 (m, 18 H), 7.41–7.55 (m, 2 H); ^{13}C NMR 9.5 (q), 110.6 (d), 119.6 (d), 119.9 (d), 122.5 (d), 124.3 (d), 127.2 (d), 127.4 (s), 128.5 (d), 128.6 (d), 137.1 (s), 139.0 ppm (s); MS, m/z 476 (M^+), 238 (M^+ - 238, 100%). Anal. Calcd for $C_{30}H_{24}N_2S_2$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.93; H, 5.27; N, 5.81.

3-Ethyl-1-phenylindole (2c): bp 145 °C (2 mmHg); IR (film) 1595, 1500, 1455, 770, 740, 695 cm^{-1}; ^1H NMR δ 1.37 (t, 3 H), 2.83 (q, 2 H), 7.10–7.72 (m, 10 H); ^{13}C NMR 14.3 (q), 18.3 (t), 110.4 (d), 119.2 (d), 119.7 (d), 119.8 (s), 122.3 (d), 124.3 (d), 123.9 (d), 125.6 (d), 128.9 (d), 136.0 (s), 140.0 ppm (s); MS, m/z 221 (M^+). Anal. Calcd for $C_{16}H_{15}N$: C, 86.83; H, 6.83; N, 6.32. Found: C, 86.51; H, 6.76; N, 6.19.

Bis(3-ethyl-1-phenylindol-2-yl) disulfide (3c): mp 105–106 °C; IR (KBr) 1585, 1495, 1440, 750, 740, 695 cm^{-1}; ^1H NMR δ 1.06 (t, 3 H), 2.62 (q, 4 H), 6.84–7.31 (m, 16 H), 7.51–7.64 (m, 2 H); ^{13}C NMR 15.2 (q), 18.5 (t), 110.8 (d), 119.6 (d), 119.8 (d), 124.1 (d), 126.6 (d), 127.3 (d), 127.6 (s), 128.5 (d), 128.8 (d), 137.2 (s), 139.3 ppm (s); MS, m/z 504 (M^+), 252 (M^+ - 252, 100%). Anal. Calcd for $C_{32}H_{28}N_2S_2$: C, 76.17; H, 5.59; N, 5.55. Found: C, 76.32; H, 5.65; N, 5.49.

1,3-Diphenylindole (2d): mp 103–104 °C; IR (KBr) 1595, 1500, 1450, 765, 735, 695 cm^{-1}; ^1H NMR δ 7.02–7.75 (m, 14 H), 7.84–8.06 (m, 1 H); ^{13}C NMR 110.8 (d), 119.1 (s), 120.1 (d), 120.8 (d), 122.7 (d), 124.4 (d), 125.4 (d), 126.1 (d), 126.6 (d), 127.1 (d), 127.5 (d), 128.8 (d), 129.6 (d), 135.0 (s), 136.6 (s), 139.4 ppm (s). Anal. Calcd for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 88.87; H, 5.56; N, 5.12.

Bis(1,3-diphenylindol-2-yl) disulfide (3d): mp 192–194 °C; IR (KBr) 1595, 1495, 1440, 760, 750, 740, 695 cm^{-1}; ^1H NMR δ 6.90–7.39 (m, 26 H), 7.35–7.65 (m, 2 H); ^{13}C NMR 110.8 (d), 120.2 (d), 120.8 (d), 124.6 (d), 126.1 (s), 126.5 (d), 127.6 (d), 128.6 (d), 129.1 (d), 130.0 (d), 133.3 (s), 136.8 (s), 139.4 ppm (s). Anal. Calcd for $C_{40}H_{28}N_2S_2$: C, 79.98; H, 4.70; N, 4.66. Found: C, 79.85; H, 4.65; N, 4.56.

5-Methyl-1-*p*-tolylindole (2e): bp 140 °C (2 mmHg); IR (film) 1605, 1515, 1475, 820, 795, 760, 715 cm^{-1}; ^1H NMR δ 2.33 (s, 3 H), 2.43 (s, 3 H), 6.52 (d, 1 H, J = 3.9 Hz), 6.93–7.43 (m, 8 H); ^{13}C NMR 20.9 (q), 21.3 (q), 102.7 (d), 110.1 (d), 120.6 (d), 123.7 (d), 123.9 (d), 127.8 (d), 128.2 (s), 129.2 (s), 129.9 (s), 134.2 (s), 135.8 (s), 137.8 ppm (s); MS, m/z 221 (M^+). Anal. Calcd for $C_{16}H_{15}N$: C, 86.83; H, 6.83; N, 6.32. Found: C, 86.96; H, 6.63; N, 6.06.

1-Butylindole (2f): bp 125 °C (2 mmHg); IR (film) 1610, 1505, 1460, 760, 740, 715 cm^{-1}; ^1H NMR δ 0.91 (t, 3 H), 1.13–1.54 (m, 2 H), 1.64–1.94 (m, 2 H), 4.07 (t, 2 H, J = 6.8 Hz), 6.47 (d, 1 H, J = 3.4 Hz), 6.98–7.38 (m, 4 H), 7.56–7.67 (m, 1 H); ^{13}C NMR 13.7 (q), 20.1 (t), 32.3 (t), 46.0 (t), 100.7 (d), 109.3 (d), 119.1 (d), 120.8 (d), 121.2 (d), 127.6 (d), 128.5 (s), 135.9 ppm (s); MS, m/z 173 (M^+). Anal. Calcd for $C_{12}H_{15}N$: C, 83.18; H, 8.72; N, 8.08. Found: C, 82.92; H, 8.72; N, 8.03.

1-Butyl-3-methylindole (2g): bp 130 °C (2 mmHg); IR (film) 1605, 1465, 735 cm^{-1}; ^1H NMR δ 0.90 (t, 3 H), 1.12–1.49 (m, 2 H), 1.53–1.90 (m, 2 H), 2.31 (d, 3 H, J = 1.0 Hz), 4.08 (t, 2 H), 6.81 (d, 1 H, J = 1.0 Hz), 6.98–7.34 (m, 3 H), 7.45–7.60 (m, 1 H); ^{13}C NMR 9.6 (q), 13.7 (q), 20.2 (t), 32.5 (t), 45.7 (t), 109.1 (d), 109.9 (s), 118.3 (d), 118.9 (d), 121.2 (d), 125.4 (d), 128.6 (s), 136.3 ppm (s). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.14; N, 7.47. Found: C, 83.57; H, 9.23; N, 7.46.

1-Butyl-3-phenylindole (2h): bp 185 °C (2 mmHg); IR (film) 1600, 1540, 1460, 760, 735, 695 cm^{-1}; ^1H NMR δ 0.90 (t, 3 H), 1.14–1.52 (m, 2 H), 1.63–1.68 (m, 2 H), 4.06 (t, 2 H), 7.01–7.71 (m, 9 H), 7.83–8.02 (m, 1 H); ^{13}C NMR 13.7 (q), 20.2 (t), 32.2 (t), 46.1 (t), 109.7 (d), 116.5 (s), 119.7 (d), 119.9 (d), 121.7 (d), 125.5 (d), 126.2 (s), 127.2 (d), 128.6 (d), 135.7 (s), 136.7 ppm (s). Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.61. Found: 86.47; H, 7.69; N, 5.67.

Bis(1-butyl-3-phenylindol-2-yl) disulfide (3h): bp 200 °C (2 mmHg); IR (film) 1595, 1480, 1445, 760, 695 cm^{-1}; ^1H NMR δ 0.87 (t, 6 H), 1.12–1.81 (m, 8 H), 4.02 (t, 4 H), 6.77–7.61 (m, 18 H); ^{13}C NMR 13.7 (q), 20.3 (t), 31.9 (t), 43.4 (t), 110.1 (d), 120.0 (d), 120.5 (d), 124.1 (d), 124.4 (s), 126.0 (d), 126.3 (d), 127.4 (d), 127.6 (s), 129.8 (d), 133.4 (s), 133.7 ppm (s). Anal. Calcd for $C_{36}H_{36}N_2S_2$: C, 77.10; H, 6.47; N, 4.99. Found: C, 76.97; H, 6.48; N, 4.90.

1-Benzylindole (2i): bp 155 °C (2 mmHg); IR (film) 1605, 1505, 1455, 755, 735, 720, 695 cm^{-1}; ^1H NMR δ 5.23 (s, 2 H), 6.50–6.60 (m, 1 H), 6.77–7.34 (m, 9 H), 7.53–7.69 (m, 1 H); ^{13}C NMR 50.0 (t), 101.6 (d), 109.6 (d), 119.4 (d), 120.9 (d), 121.6 (d), 126.0 (d), 127.5 (d), 128.1 (d), 128.6 (d), 130.1 (s), 136.2 (s), 137.4 ppm (s). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.75. Found: C, 87.06; H, 6.06; N, 6.40.

1-Methyl-3-phenylindole (2k): bp 170 °C (2 mmHg); IR (film) 1600, 1545, 1480, 1465, 765, 695 cm^{-1}; ^1H NMR δ 3.59 (s, 3 H), 7.00–7.67 (m, 8 H), 7.85–8.02 (m, 1 H); ^{13}C NMR 32.6 (q), 109.5 (d), 116.5 (s), 119.8 (d), 121.9 (d), 125.6 (d), 126.0 (s), 126.5 (d), 127.2 (d), 128.7 (d), 135.6 (s), 137.4 ppm (s). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.75. Found: C, 86.74; H, 6.33; N, 6.62.

Bis(1-methyl-3-phenylindol-2-yl) disulfide (3k): mp 140–141 °C; IR (KBr) 1600, 1480, 1440, 745, 690 cm^{-1}; ^1H NMR δ 3.52 (s, 6 H), 6.65–7.50 (m, 18 H); ^{13}C NMR 29.7 (q), 110.0 (d), 120.1 (d), 120.2 (d), 124.1 (s), 124.1 (d), 126.0 (d), 127.4 (d), 127.8 (s), 129.6 (d), 133.3 (s), 138.4 ppm (s). Anal. Calcd for $C_{30}H_{24}N_2S_2$: C, 75.59; H, 5.07; N, 5.87. Found: C, 75.29; H, 5.08; N, 5.90.

Registry No. **1a**, 73425-20-4; **1b**, 112817-80-8; **1c**, 112817-81-9; **1d**, 112817-82-0; **1e**, 112817-83-1; **1f**, 112817-84-2; **1g**, 112817-85-3; **1h**, 112817-86-4; **1i**, 104501-75-9; **1j**, 13637-38-2; **1k**, 33693-09-3; **1l**, 496-30-0; **1m**, 112817-87-5; **2a**, 16096-33-6; **2b**, 112817-88-6; **2c**, 112817-89-7; **2d**, 20538-11-8; **2e**, 112817-90-0; **2f**, 22014-99-9; **2g**, 1914-00-7; **2h**, 112817-91-1; **2i**, 3377-71-7; **2k**, 30020-98-5; **2l**, 120-72-9; **3a**, 112817-92-2; **3b**, 112817-93-3; **3c**, 112817-94-4; **3d**, 112817-95-5; **3h**, 112817-96-6; 3k, 51206-75-8; **6**, 112817-97-7; 1-phenylindolin-2-one, 3335-98-6; 3-methyl-1-phenylindolin-2-one, 23210-22-2; 3-ethyl-1-phenylindolin-2-one, 112817-98-8; 1,3-diphenylindolin-2-one, 23210-25-5; 5-methyl-1-*p*-tolylindolin-2-one, 112817-99-9; 1-butylindolin-2-one, 28148-20-1; 1-butyl-3-methylindolin-2-one, 112818-00-5; 1-butyl-3-phenylindolin-2-one, 112818-01-6; 1-benzylindolin-2-one, 7135-32-2; 1-methyl-3-phenylindolin-2-one, 3335-97-5; 1*H*-indolin-2-one, 59-48-3; 1-methylindolin-2-one, 61-70-1.

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Carbonyl to Methylene Conversion: Selenium-Assisted Reduction of Aromatic Ketones with Carbon Monoxide and Water

Yutaka Nishiyama* and Sawako Hamanaka

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

Akiya Ogawa, Nobuaki Kambe, and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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There is increasing interest in the organic chemistry of selenium, and much effort is being devoted to the synthesis of new selenium compounds and to their use for a wide

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