Preparation and Reactivities of Novel (Diacetoxyiodo)arenes Bearing Heteroaromatics

Hideo Togo,*,† Takahiro Nabana,† and Kentaro Yamaguchi‡

Department of Chemistry, Faculty of Science, and Chemical Analysis Center, Chiba University, Yayoi-cho 1−33, Inage-ku, Chiba 263-8522 Japan

togo@scichem.s.chiba-u.ac.jp

Received August 4, 2000

Extensive study on hypervalent iodine compounds has been carried out, and their uses in organic synthesis have been gaining popularity.[1] (Diacetoxyiodo)benzene has been especially popular for oxidation of hydroquinones and sulfides, α-hydroxylation of ketones, and oxidative 1,2-rearrangement of ketones, in organic synthesis.[2] However, to our knowledge, the preparation and the reactivities of (diacetoxyiodo)arenes containing heteroaromatics instead of a phenyl group have so far not been studied, though the preparation of 3,5-dimethyl-4-[bis(trifluoroacetoxy)iodo]isoxazole and its reaction with aromatics[3a] and the reactions of other organotrivalent iodine compounds with heteroaromatics to form the corresponding trivalent iodine compounds containing heteroaromatics[3] are known. Thus, we planned to prepare (diacetoxyiodo)arenes by bonding heteroaromatics to the iodine atom and compare the reactivities with that of (diacetoxyiodo)benzene (**1**). Herein two types of (diacetoxyiodo)arenes, those containing π-excess heteroaromatics, such as thiophene, and π-deficient heteroaromatics, such as pyrrazole [i.e., 2-(diacetoxyiodo)thiophene (**2a**), 3-(diacetoxyiodo)thiophene (**2b**), *N*-tosyl-4-(diacetoxyiodo)pyrrazole (**2c**), and *N*-trifluoromethanesulfonyl-4-(diacetoxyiodo)pyrrazole (**2d**), Figure 1], were prepared using sodium perborate in acetic acid.[4] X-ray analysis of *N*-tosyl-4-(diacetoxyiodo)pyrrazole (**2c**) showed that the structure adopted the same T-shaped structure as that seen for (diacetoxyiodo)benzene.[5] The thermal stability of these novel trivalent iodine compounds was studied in $ClCD_2CD_2Cl$ in sealed tubes at about 120 °C by NMR. The results showed that compounds **2d**, **2b**, and **2a** decomposed cleanly after 3 h, 7 h, and 21 h, respectively, while 50% of the starting materials, compounds **1** and **2c**, remained after 21 h. The main decomposition products were the corresponding iodoheteroaromatics, formed through homolytic bond cleavage of the I−O bonds in compounds **2**. Then the reactivities for oxidation of hydroquinones, the oxidative 1,2-rearrangement of ethyl aryl ketones, iodination of aromatics, oxidation of diaryl sulfides, the Hofmann rearrangement of amides, and radical cyclization[2k] were examined, and the reactivities were compared with that of (diacetoxyiodo)benzene, as shown in Tables 1−6. In both oxidation of hydroquinones and oxidative 1,2-rearrangement of ethyl aryl ketones, compounds **2a**−**d** showed the same reactivities as (diacetoxyiodo)benzene with high yields. However, in the iodination of aromatics, compound **2d** gave poor results, though (diacetoxyiodo)benzene and compound **2c** showed good reactivity and compounds **2a** and **2b** showed moderate reactivity. Probably, this result comes from the facts that the ethyl acetate solution of compound **2d** is not homogeneous and that the oxidation potential of compound **2d** is high; in this case, the iodine was further oxidized via an acylhypoiodite species, which is the real iodination species of aromatics. As a result, iodination of the aromatics did not occur effectively when using **2d**. On the other hand, in the oxidation of diphenyl sulfide at 40 °C, compound **2d** gave diphenyl sulfone mainly, though other compounds, **1** and **2a**−**c**, gave diphenyl sulfoxide mainly. At room temperature (24 h), compound **2d** also gave diphenyl sulfoxide alone in 96% yield. Moreover, compounds **2a**, **2c**, and **2d** gave ditolyl sulfone in the oxidation of ditolyl sulfide, while compounds **1** and **2b** gave ditolyl sulfoxide mainly under the same conditions. In the Hofmann rearrangement of benzamide and cinnamyl amide, the corresponding carbamates were obtained in good yields with compounds **1**, **2a**, and **2b**. However, compound **2c** showed the moderate reactivity, and compound **2d** gave poor results, because the methanol solution of compound **2d** were not homogeneous again. In the radical cyclization of sulfonamides **14** via the corresponding sulfonamidyl radical, in the presence of iodine under the irradiation conditions with a tungsten lamp, compounds **1** and **2a**−**c** showed the same reactivities with high yields, though the ratio of compounds **a** and **b** depends on compounds **1** or **2**. Again the reactivity of compound **2d** decreased because of poor solubility of compound **2d**. In summary, compounds **2a**−**d** have the same reactivity as (diacetoxyiodo)benzene in the oxida-

† Department of Chemistry.

‡ Chemical Analysis Center.

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(5) Compound **2c**: bond lengthes (Å) I−O 2.18, 2.12, I−C 2.06; bond angles (deg) O−I−O 167.5, O−I−C 84.9, 82.7. Compound **1**: bond lengths (Å) I−O 2.14, 2.16, I−C 2.10; bond angles (deg) O−I−O 163.9, O−I−C 81.8, 82.1.

10.1021/jo001186n CCC: $19.00
Published on Web 11/01/2000

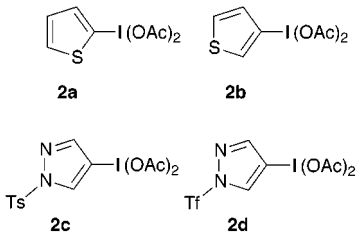
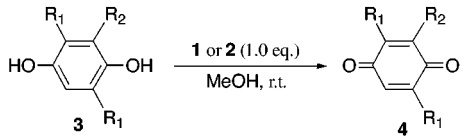


Figure 1. Novel (diacetoxyiodo)arenes bearing heteroaromatics.

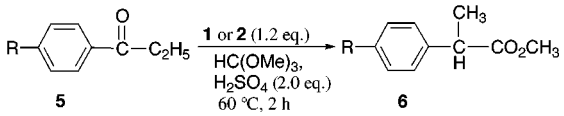
Table 1. Oxidation of Hydroquinones



1 or **2**	R_1	R_2	yield (%)
1	t-Bu	H	99
	Me	Me	92
2a	t-Bu	H	96
	Me	Me	97
2b	t-Bu	H	99
	Me	Me	79
2c	t-Bu	H	99
	Me	Me	89
2d	t-Bu	H	93
	Me	Me	99

[a] Reaction time was 70 min. for **3** (R_1 = Bu-t, R_2 = H). [b] Reaction time was 50 min. for **3** (R_1 = R_2 = Me).

Table 2. 1,2-Rearrangement of Alkyl Aryl Ketones



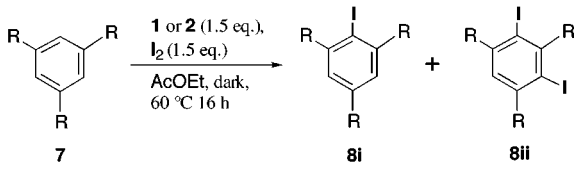
1 or **2**	R	yield (%)
1	Me	92
	H	87
	F	81
2a	Me	85
	H	79
	F	73
2b	Me	97
	H	94
	F	88
2c	Me	95
	H	91
	F	88
2d	Me	96
	H	90
	F	93

tion of hydroquinones, oxidative 1,2-rearrangement of ethyl aryl ketones, and radical cyclization, while compound **2d** has more powerful oxidizing ability toward sulfides, though the iodination of aromatics and the Hofmann rearrangement reaction with **2d** did not work because of poor solubility. Thus, these novel (diacetoxyiodo)arenes containing heteroromatics can be used as synthetic reagents in organic synthesis similarly to (diacetoxyiodo)benzene.

Experimental Section

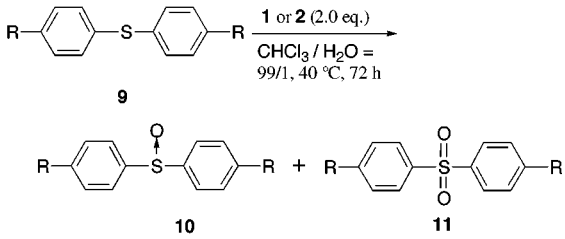
General. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers and ^{13}C NMR spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are expressed in ppm downfield from TMS in δ units. *J*-Values are given in hertz. In ^{13}C NMR spectra, p, s, t, and q means primary, secondary, tertiary, and quaternary. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. Wakogel C-200 and Silica Gel 50 (Merck) were used

Table 3. Iodination of 1,3,5-Trialkylbenzenes



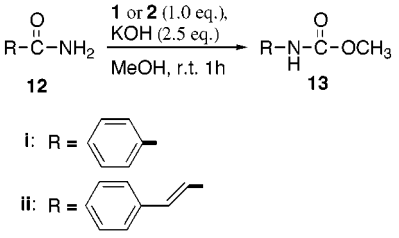
		yields (%)	
1 or **2**	R	**8i**	**8ii**
1	i-Pr	90	0
	Me	0	98
2a	i-Pr	50	0
	Me	73	21
2b	i-Pr	33	0
	Me	96	0
2c	i-Pr	80	0
	Me	74	21
2d	i-Pr	0	0
	Me	52	0

Table 4. Oxidation of Diaryl Sulfides



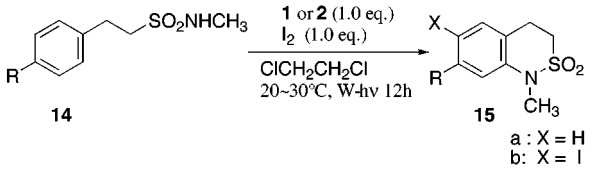
		yields (%)	
1 or **2**	R	**10**	**11**
1	H	93	0
	Me	95	4
2a	H	86	14
	Me	9	84
2b	H	82	0
	Me	55	37
2c	H	85	15
	Me	7	85
2d	H	26	74
	Me	0	95

Table 5. Hofmann Rearrangement



1 or **2**		yield (%)
1	**12i**	87
	12ii	80
2a	**12i**	87
	12ii	85
2b	**12i**	92
	12ii	98
2c	**12i**	82
	12ii	43
2d	**12i**	30
	12ii	0

Table 6. Radical Cyclization onto the Aromatic Ring



1 or **2**	R	yields (%) of **15** (**a**/**b**)
1	H	75 (19/66)
	CH_3	92 (0/92)
2a	H	87 (61/26)
	CH_3	95 (25/70)
2b	H	88 (42/46)
	CH_3	86 (0/86)
2c	H	94 (94/0)
	CH_3	91 (34/57)
2d	H	67 (67/0)
	CH_3	71 (59/12)

for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

General Procedure for the Preparation of Compounds 2. To the solution of iodoarene (10 mmol) in acetic acid (100 mL) was added sodium perborate tetrahydrate (100 mmol) over 0.5 h. Then the solution was heated at 50−60 °C for 8−24 h under argon atmosphere, until the starting iodoarene disappeared. After the reaction, the solvent was removed. Water was added to the residue, and the mixture was extracted with chloroform for three times (30 mL × 3). The combined organic layer was dried over Na_2SO_4. After the filtration, the solvent was removed, and the residue was recrystallized from chloroform and hexane.

2-(Diacetoxyiodo)thiophene 2a: mp 120−122 °C (decomp); IR (KBr) 3100, 1640, 1560, 1270, 1010, 710, and 500 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.01 (6H, S), 7.14 (1H, dd, J = 5.4 and 3.9 Hz), 7.64 (1H, dd, J = 5.4 and 1.2 Hz), 7.78 (1H, dd, J = 3.9 and 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 20.29 (p), 106.22 (q), 128.57 (t), 134.81 (t), 139.01 (t), 176.95 (q).

3-(Diacetoxyiodo)thiophene 2b: mp 168−178 °C (decomp); IR (KBr) 3100, 1640, 1590, 1290, 1010, 700, and 500 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.02 (6H, s), 7.52 (1H, dd, J = 5.2 and 1.3 Hz), 7.48 (1H, dd, J = 5.2 and 3.0 Hz), 8.05 (1H, dd, J = 3.0 and 1.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 20.29 (p), 106.42 (q), 128.14 (t), 133.58 (t), 133.58 (t), 176.53 (q). Elem. Anal. Found: C, 29.04; H, 2.85%. Calcd for $C_8H_9IO_4S$: C, 29.28; H, 2.76%.

N-**Tosyl-4-(diacetoxyiodo)pyrrazole 2c:** mp 183−193 °C (decomp); IR (KBr) 3050, 1640, 1590, 1270, 1160, 1050, 930, and 500 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.05 (6H, s), 2.46 (3H, s),7.40 (2H, d, J = 8.2 Hz), 7.97 (1H, s), 7.97 (2H, d, J = 8.2 Hz), 8.50 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 20.24 (p), 21.79 (p). 90.56 (q), 128.77 (t), 130.33 (t), 132.65 (q), 135.08 (t), 145.96 (t), 147.09 (q), 176.93 (q). Elem. Anal. Found: C, 35.59; H, 3.22; N, 5.90%. Calcd for $C_{14}H_{15}IN_2O_6S$: C, 36.06; H, 3.24; N, 6.01%.

N-**Trifluoromethanesulfonyl-4-(diacetoxyiodo)pyrrazole 2d:** mp 122−124 °C (decomp); IR (KBr) 3130, 1640, 1560, 1415, 1300, 1190, 1160, 1040, 730, and 500 cm^{-1};^1H NMR ($CDCl_3$) δ = 2.03 (6H, s), 8.06 (2H, s); ^{13}C NMR ($CDCl_3$) δ = 20.33 (p), 89.17 (q), 138.74 (t), 176.78 (q).

General Procedure for Oxidation of Hydroquinone. Hydroquinone (1 mmol) was added to (diacetoxyiodo)arene (1.3 mmol) in methanol (5 mL). The mixture was stirred for 2 h at room temperature under an argon atmosphere. Then, the reaction mixture was evaporated, and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 5/1) to give a pure quinone.

General Procedure for 1,2-Rearrangement of Alkyl Aryl Ketones. Sulfuric acid (2 mmol) was added dropwise to a solution of (diacetoxyiodo)arene (1.2 mmol) and propiophenone (1.0 mmol) in 3 mL of trimethyl orthoformate at 0 °C. The reaction mixture was stirred for 2 h at 60 °C under an argon atmosphere. Then the reaction mixture was poured into water and extracted with chloroform twice. The combined organic layer was dried over Na_2SO_4. After the filtration, the solvent was evaporated under reduced pressure, and the residue was purified by preparative TLC on silica gel.

General Procedure for Iodination. A mixture of aromatics (0.5 mmol), (diacetoxyiodo)arene (0.9 mmol), and iodine (0.9 mmol) in dry ethyl acetate (5 mL) was stirred for 5 h at 60 °C under dark conditions and an argon atmosphere. The resulting solution was quenched with aq Na_2SO_3, and the solution was extracted with chloroform twice. The extract was dried over Na_2SO_4 and evaporated under reduced pressure; the residual oil was purified by preparative TLC on silica gel using hexane.

General Procedure for Oxidation of Sulfide. Sulfide (1 mmol) was added to (diacetoxyiodo)arene (2.0 mmol), in chloroform (5 mL) containing 1% of water. The mixture was stirred for 72 h at 40 °C under an argon atmosphere. Then the reaction mixture was evaporated, and the residue was purified by preparative TLC on silica gel (eluent: hexane/ethyl acetate = 5/1) to give pure sulfoxide and sulfone.

General Procedure for the Hofmann Rearrangement. Amide (1 mmol) was added to the homogeneous solution of methanol (50 mL) and KOH (2.5 mmol), and subsequently (diacetoxyiodo)arene (1 mmol) was added to the solution. The mixture was stirred for 15 min at 0 °C and then for 1 h at room temperature under argon atmosphere. Then, the reaction mixture was evaporated, and the residue was treated with pTLC on silica gel (eluent: hexane: ethyl acetate = 3:1) to give carbamate ester.

General Procedure for the Radical Cyclization. (Diacetoxyiodo)arene (0.8 mmol) and iodine (0.5 mmol) were added to a solution of amide (0.5 mmol) in 1,2-dichloroethane (5 mL). The mixture was irradiated with a tungsten lamp (500 W) at 20−30 °C for 2 h under agon atmosphere. After the reaction, the mixture was poured into a saturated aqueous sodium sulfite solution and extracted with chloroform three times. The organic layer was dried over sodium sulfate. After removal of the solvent, the residue was treated with pTLC on silica gel (eluent: hexane: ethyl acetate:chloroform = 6:3:1) to give the cyclized product.

2,3,5-Trimethyl-1,4-benzoquinone: mp 28−29 °C (lit. mp 29 °C[6]) IR (KBr) 3060, 2880, 1650, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.01(3H, q, J = 1.1 Hz), 2.03 (3H, q, J = 1.1 Hz), 2.04 (3H, d, J = 1.7 Hz), 6.56 (1H, q, J = 1.7 Hz).

2,6-Di-*tert*-butyl-1,4-benzoquinone: mp 146−147 °C (lit. mp 150−151 °C[6]); IR (KBr) 2870, 1650, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.27 (18H, s), 6.48 (2H, s).

Methyl 2-phenylpropanoate: bp 65 °C/2.5 mmHg (lit. bp 104−105 °C/18 mmHg[2e]); IR (neat) 2980, 1740, 1600, 1495, 1455, 1210, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.50 (3H, d, J = 7.2 Hz, 3.66 (3H, s), 3.73 (1H, q, J = 7.2 Hz), 7.24−7.35 (5H, m).

Methyl 2-(4-fluorophenyl)propanoate: oil; IR (neat) 2980, 2960, 1740, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 1.48 (3H, d, J = 7.2 Hz), 3.66 (3H, s), 3.71 (1H, q, J = 7.2 Hz), 7.00 (2H, tt, J = 8.7 and 2.1 Hz), 7.26 (2H, ddt, J = 8.7, 5.3 and 2.1 Hz); HRMS (EI) found m/z 182.0740, calcd for $C_{10}H_{11}FO_2$ 182.0743.

Methyl 2-(4-Methylphenyl)propanoate: oil; IR (neat) 2955, 1740, 1515, 1460, 1205, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 1.48 (3H, d, J = 7.2 Hz), 2.33 (3H, s), 3.65 (3H, s), 3.69 (1H, q, J = 7.2 Hz), 7.13 (2H, d, J = 8.1 Hz), 7.19 (2H, d, J = 8.1 Hz); HRMS (EI) found m/z 178.0997, calcd for $C_{11}H_{14}O_2$ 178.0994.

1-Iodo-2,4,6-triisopropylbenzene: oil; bp = 115 °C/2.5 mmHg (lit. bp 173−175 °C/28 mmHg[7a]); IR (neat) 2950, 1565, 1460, and 740 cm^{-1};^1H NMR ($CDCl_3$) δ = 1.24 (12H, d, J = 6.8 Hz), 1.25 (6H, d, J = 7.0 Hz), 2.87 (1H, sept, J = 7.0 Hz), 3.39 (2H, sept, J = 7.0 Hz), 6.95 (2H, s); ^{13}C NMR ($CDCl_3$) δ = 23.43 (p), 23.98 (p), 33.88 (t,), 39.26 (t), 105.71 (q), 122.07, (t), 148.83 (q), 150.77 (q); MS (EI) Found: M^+ = 330. Calcd for $C_{15}H_{22}I$: M = 330.

Diiodomesitylene: mp 79.0−80.3 °C (lit. mp 82 °C [7b]); IR (KBr) 2975, 1440, 1375, and 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.42 (6H, s), 2.92 (3H, s), 7.00 (1H, s); MS (EI) Found: M^+ = 372. Calcd for $C_9H_{10}I_2$: M = 372.

Iodomesitylene: mp 30−31 °C (lit. mp 30.5−31 °C [7a]); IR (KBr) 2975, 1440, 1373, and 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.24 (3H, s), 2.42 (6H, s), 6.89 (2H, s); MS (EI) Found: M^+ = 246. Calcd for $C_9H_{11}I$: M = 246.

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Di(*p*-tolyl) sulfoxide: mp 91 °C (lit. mp 92 °C[8]); **di(*p*-tolyl) sulfone**: mp 156 °C (lit. mp 158 °C [8]); **diphenyl sulfoxide**: mp 70 °C (lit. mp 70 °C[8]); **diphenyl sulfone**: mp 126 °C (lit. mp 127 °C[8]).

Methyl *N*-phenylcarbamate: mp 44−45 °C (lit. mp 47−48 °C[9]); **methyl (*E*)-*N*-(2-phenylethenyl)carbamate:** mp 115−116 °C (lit. mp119 °C[9]).

***N*-Methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide:** mp 77.0−79.0 °C; IR (KBr) 2980, 2940, 1580, 1490, 1330, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.30 (3H, s), 3.33 (2H, t, J = 6.9 Hz), 3.44 (2H, t, J = 6.9 Hz), 6.96 (1H, dd, J = 8.0, 1.0 Hz), 7.05 (1H, t,d J = 7.6, 1.0 Hz), 7.16 (1H, dd, J = 7.6, 1.2 Hz), 7.27 (1H, m); ^{13}C NMR ($CDCl_3$) δ = 27.90 (s), 31.97(p), 45.55 (s), 117.47 (t), 122.82 (q), 123.14 (t), 127.88 (t), 129.30 (t), 141.14 (q); MS (EI) M^+ 197. Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.74; H, 5.52; N, 7.07.

***N*-Methyl-6-iodo-3,4-dihydro-2,1-benzothiazine 2,2-dioxide:** mp 139.0−141.0 °C; IR (KBr) 2940, 1590, 1560, 1320, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.26 (3H, s), 3.32 (2H, t, J = 7.1 Hz), 3.40 (2H, t, J = 7.1 Hz), 6.70 (1H, d, J = 8.8 Hz), 7.49 (1H, d, J = 2.0 Hz), 7.55 (1H, dd, J = 8.8, 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 27.51 (s), 31.74 (p), 45.27 (s), 86.24 (q), 119.16 (t), 125.03 (q), 136.73 (t), 137.89 (t), 141.06 (q); MS (EI) M^+ 323. Anal. Calcd for $C_9H_{10}INO_2S$: C, 33.45; H, 3.12; N, 4.33. Found: C, 33.55; H, 3.06; N, 4.27.

***N*-Methyl-6-iodo-7-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide:** mp 138.0−139.0 °C; IR (KBr) 3000, 2940, 1600, 1550, 1330, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.41 (3H, s), 3.27 (3H, s), 3.30 (2H, t, J = 6.8 Hz), 3.38 (2H, t, J = 6.8 Hz), 6.82 (1H, s), 7.57 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 26.95 (s), 27.89 (p), 31.86 (p), 45.31 (s), 93.21 (q), 118.45 (t), 122.07 (q), 139.06 (t), 141.07 (q), 141.31 (q); MS (EI) M^+ 337. Anal. Calcd for $C_{10}H_{12}INO_2S$: C, 35.62; H, 3.59; N, 4.15. Found: C, 35.67; H, 3.45; N, 3.99.

***N*-Methyl-7-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide:** mp 79.0−81.0 °C; IR (KBr) 3000, 2940, 1620, 1570, 1330, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.34 (3H, s), 3.29 (3H, s), 3.29−3.34 (2H, m), 3.40 (2H, t, J = 7.3 Hz), 6.77 (1H, s), 6.86 (1H, m), 7.04 (1H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 26.95 (s), 27.89 (p), 31.86 (p), 45.31 (s), 93.21 (q), 118.45 (t), 122.07 (q), 139.06 (t), 141.07 (q), 141.31 (q); HRMS (EI) m/z 211.0674, calcd for $C_{10}H_{13}NO_2S$ 211.0667.

Acknowledgment. Financial support from a Grant-in-Aid for Scientific Research (No. 08554031) from the Ministry of Education, Science, Culture of Japan, Futaba Electronics Memorial Foundation, and The Research Center of Taiho Phamaceutical Co. are gratefully acknowledged. We thank Ms. Ritsuko Hara for the measurements of MS(EI) and Dr. Hiroko Seki and Ms. Yukiko Hiramoto for elemental analysis in the Chemical Analysis Center of Chiba University.

Supporting Information Available: Copies of ^1H NMR spectra for compounds **2a**−**d**, **4**, **6**, **8**, **10**, **11**, **13**, and **15**, and X-ray data of compounds **1** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001186N

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