Alkylation and Oxidation of 6,7-Dihydro-6-methyl-5*H*-dibenzo-[*b*,*g*][1,5]thiazocine. Selective Oxidation of the Sulfide Moiety by Transannular Participation of the Amino Group

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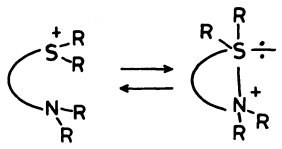
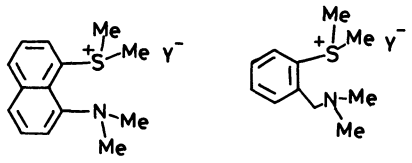
6,7-Dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine (**7**) was prepared by cyclization of the corresponding amino alcohol using thionyl chloride in acetonitrile. Methylation of **7** gave *N*,*N*-dimethyl derivative (**8**) as the sole product. Treatment of **7** with various oxidizing reagents, however, afforded the corresponding sulfoxide (**9**) and/or *N*-oxide (**13**), and sulfone (**14**) depending on the kind of reagent. Oxidation of **7** with sodium periodate furnished *N*-oxide (**13**) in 72% yield as a major product along with sulfoxide (**9**) in 12% yield, while **9** was obtained as a major product (76%) by oxidation with sodium hypochlorite together with a small amount of methoxysulfonium derivative (**15**) in aqueous methanol. The acceleration in oxidation of **7** compared with diphenyl sulfide as well as production of **15** is ascribed to the transannular participation of the amino group with the chlorosulfonio group or intermediacy of a sulfurane. In addition, structural features of **9** and **15** have been investigated by means of ^{1}H NMR and evidence for the transannular interaction between the two heteroatoms is presented.

Previously, one of us reported that the selectivity of alkylation of compounds containing both sulfur and nitrogen atoms is dependent upon the structure of the compounds and also the properties of reagents.[1] During the investigation, we invoked the presence of equilibrium between the sulfonioamine (**1**) and the ammoniosulfurane (**2**) or the formation of the latter (Eq. 1). No positive evidence for Eq. 1, however, could be obtained by ^{1}H NMR and UV spectroscopy even for **3** and **4**, where the two heteroatoms are designed to come closely. This was ascribed to the congestion among methyl groups.[1a]



(1)

1 **2**



3 **4**

On the other hand, Young and Hsieh proposed that a sulfurane intermediate with S–N bonding was required to account for the kinetic behavior in oxidation of methionine.[2] Moreover, Musker *et al.* also invoked such a sulfurane intermediate in the iodine oxidation of 5-methyl-1-thia-5-azacyclooctane on the basis of their kinetic investigation.[3]

In this paper, we wish to describe selective methylation and oxidation of 6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine (**7**) in which frontal congestion between the two heteroatoms can be got around. The corresponding ammonium salt (**8**) was obtained exclusively in the methylation and the oxidation took place predominantly on the sulfur where transannular participation of the amino group is proposed.

Results and Discussion

6,7-Dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine (**7**) and its ammonium salt (**8**) were prepared by a suitable modification of the procedure developed by Mehta and his coworkers[4] as illustrated in path A and the sulfoxide (**9**) in path B by Tanaka *et al.*[5] (Scheme 1). These contain the sulfide, the sulfoxide, and the amino groups, which are susceptible to electrophilic reactions.

Methylation of the Title Compound (7). Methylation of **7** with various reagents (MeI, MeI/HgI_2, $Me_3O^+BF_4^-$, MeI/$AgBF_4$, and FSO_3Me) gave the ammonium salt (**8**) as the sole product, which was identified on the basis of spectral comparisons with an authentic sample.[4] The spectral data and the reaction conditions are summarized in Table 1. The results are, on the whole, independent of the method of methylation and are contrary to those obtained for other substrates, where selective methylation took place on the amino and the sulfide groups according to the kind of reagent.[1] The observed spectra result from two kinds of conformer (BC and TB) in every case as reported by Mehta and coworkers.[4,6] Furthermore, reaction of the ammonium sulfide (**10**) with Meerwein's reagent ($Me_3O^+BF_4^-$) does not proceed, whereas *o*-(methylthio)benzylammonium salt (**12**) is smoothly converted into the corresponding sulfonium salt (**4**) under the same conditions (Scheme 2).[1a] The results indicate that the reactivity at the

sulfide function in **7** is extremely decreased due to the delocalization of a lone-pair electrons over two benzene rings.

Oxidation of the Title Compound (7). Due to relatively small difference between the oxidation potentials of sulfide and amine, considerable difficulty was expected for selective oxidation of the title compound (**7**), *i.e.*, oxidation potential in cyclic voltammetry is +1.81 V ($Ag/AgNO_3$) for diphenyl sulfide and +1.92 V ($Ag/AgNO_3$) for *N*,*N*-dibenzylmethylamine.[7] The results of oxidation of **7** with some reagents are illustrated in Scheme 3.

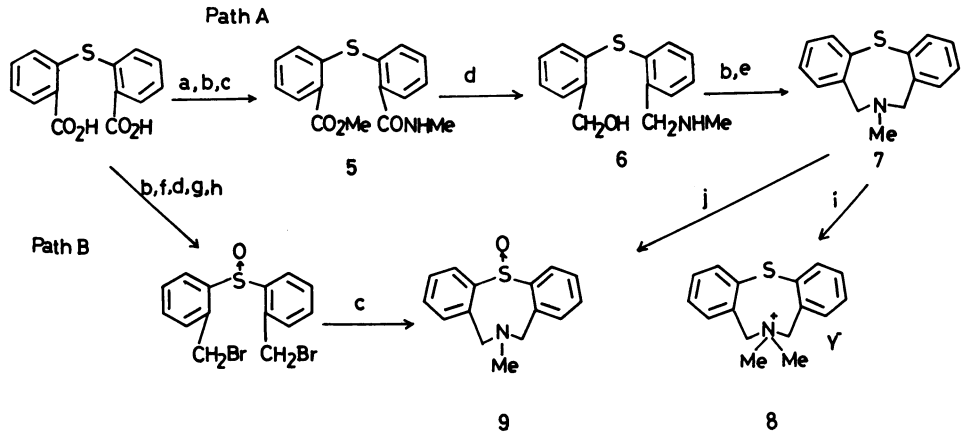
The reactive position clearly depends on the kind of oxidizing reagent. Oxidation of **7** with sodium periodate afforded a mixture of sulfoxide (**9**: 12%) and *N*-oxide (**13**: 72%), the latter is very polar with a low R_f value on silica gel and is an extremely hygroscopic compound. In the oxidation of **7** with hydrogen peroxide in refluxing acetic acid, sulfoxide (**9**) was not obtained but sulfone (**14**) was a sole product. Reaction of **7** with aqueous sodium hypochlorite at −78 °C in methanol solution afforded sulfoxide (**9**) in 76% yield. It is noteworthy that the oxidation at room temperature furnished methoxysulfonium derivative (**15a**) in a very small amount besides the major product (**9**: 47%). The structure of **9** was confirmed by an alternative synthesis developed by Tanaka *et al.* as shown in path B of Scheme 1.[5a] Structural assignment to **13** and **14** is based upon the spectral data and their chemical behavior in comparison with **9**.

It is noteworthy that the amino sulfide (**7**) was oxidized to **9** accompanied with a small amount of methoxysulfonium derivative (**15a**) smoothly with aqueous hypochlorite in methanol under the same conditions where diphenyl sulfide was inert. The structure of **15a** was assigned as methoxyammoniosulfurane on the basis of spectral analogy to that of **15b** obtained by methylation of **9**.[8a,c] Both the acceleration in oxidation of **7** and the formation of **15a** are understandable in terms of the intermediacy of ammoniochlorosulfurane such as **16a**. A similar chloride (**16b**) was obtained by treatment of **9** with thionyl chloride in benzene solution as a stable species in quantitative yield, and **16b** was converted to **16c** as relatively nonhygroscopic crystals by exchange of the counter anion using ammonium hexafluorophosphate.[8a] The S-chloro derivaives (**16b,c**) were easily hydrolyzed to give protonated amino sulfoxide which was converted back to **9** by neutralization.

It is therefore reasonable to consider that the S-chloro intermediate (**16a**) may react with water or methanol competitively to produce the final products in the aqueous methanol solution. The acceleration of the oxidation of 1,5-thiazocine with iodine has been ascribed to the presence of an analogous sulfurane, but such an intermediate has not been

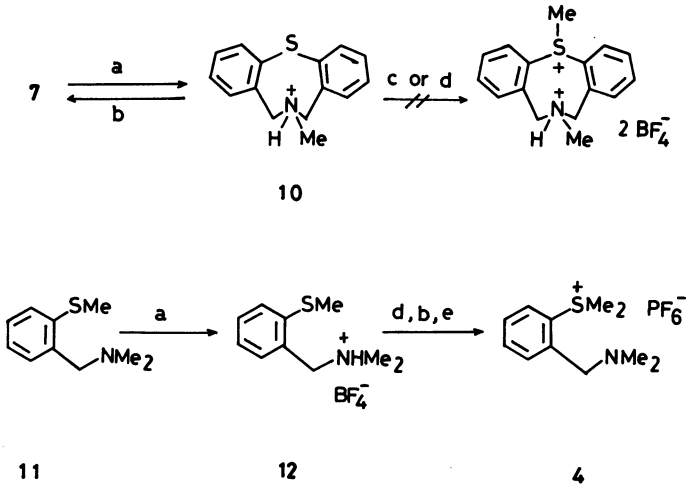
Table 1. Methylation of amino sulfide (**7**) with various reagents to afford dimethylammonium salt (**8**)

Reagent	Reaction conditions: Solvent	Temp °C	Reaction time/h	Yield %	Counter anion	Solvent	^{1}H NMR (δ): BC conformer N-Me(6H)	BC conformer CH_2(4H)	TB conformer N-Me(6H)	TB conformer CH_2(4H)	Aromatic
MeI/$AgBF_4$	CH_3CN	r.t.	4	50	BF_4^-	CD_3CN	2.58(s) 3.55(s)	4.43 and 5.60 (ABq, J=13 Hz)	3.00(s)	4.10 and 4.70 (ABq, J=14 Hz)	7.00—7.98 (m, 8H)
Me_3OBF_4	CH_2Cl_2	r.t.	4	90	BF_4^-	CD_3CN	2.58(s) 3.55(s)	4.43 and 5.60 (ABq, J=13 Hz)	3.00(s)	4.10 and 4.70 (ABq, J=14 Hz)	7.00—7.98 (m, 8H)
MeI	CH_3CN	r.t.	24	63	I^-	CD_3CN	2.73(s) 3.73(s)	4.68 and 5.77 (ABq, J=13 Hz)	3.16(s)	4.36 and 4.81 (ABq, J=14 Hz)	7.07—8.00 (m, 8H)
FSO_3Me	CH_3NO_2	r.t.	3	—	FSO_3^-	CD_3CN	2.60(s) 3.60(s)	4.46 and 5.63 (ABq, J=13 Hz)	3.02(s)	4.11 and 4.70 (ABq, J=14 Hz)	7.10—7.90 (m, 8H)
MeI/HgI_2	CH_3CN	82	5	22	HgI_3^-	DMSO-d_6	2.64(s) 3.67(s)	4.63 and 5.70 (ABq, J=13 Hz)	3.08(s)	4.37 and 4.70 (ABq, J=14 Hz)	7.20—7.90 (m, 8H)



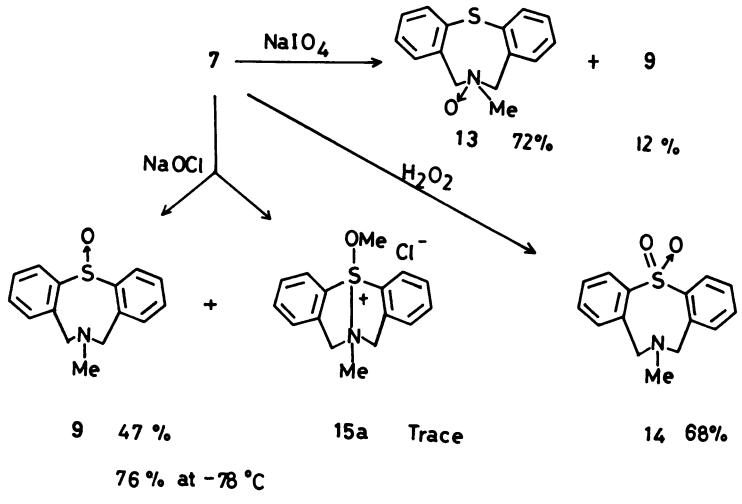
a), Reagents and conditions: (a) H_2SO_4, aq MeOH; (b) $SOCl_2$; (c) $MeNH_2$; (d) $LiAlH_4$; (e) KOH, MeOH; (f) MeOH; (g) PBr_3; (h) H_2O_2; (i) Methylating reagents (Y=I^-, BF_4^-, SO_3F^-, and HgI_3^-); (j) NaOCl, aq MeOH.

Scheme 1.[a)]

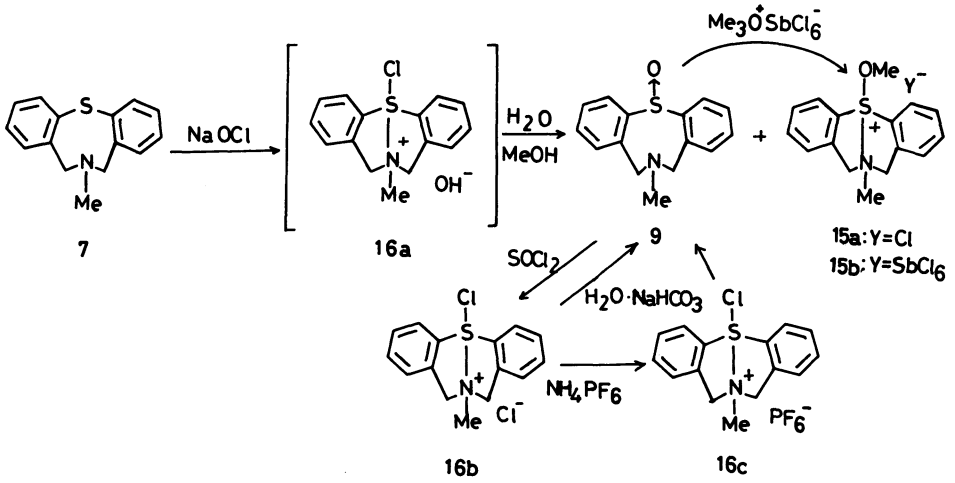


a), (a) HBF_4; (b) $NaHCO_3$; (c) $Me_3O^+BF_4^-$; (d) MeI/$AgBF_4$; (e) KPF_6/NH_4Cl.

Scheme 2.[a)]



Scheme 3.



Scheme 4.

isolated so far.[3]

Structural Considerations of **9** *and* **15**. There are some structural problems of **9** concerning the conformation of eight-membered ring and the relative stereochemistry around the sulfur atom. From theoretical and experimental investigations on conformational properties of 1,4-cyclooctadiene systems, it was concluded that the boat-chair (BC) conformer is significantly more stable than the twist-boat (TB) and boat-boat (BB) conformers,[9] but the TB conformer is of considerable importance in the heteroatom containing systems.[10] In the present system, sulfoxide (**9**) does not show any temperature dependence in ^{1}H NMR spectrum from −75 to 110 °C which indicates that only a single conformer is present for **9**, while both conformers exist for amino sulfide (**7**) and also for dimethylammonio sulfide (**8**) as reported by Tanaka *et al.* and Mehta *et al.*, respectively.[4,5] In the ^{1}H NMR spectrum of **9**, benzyl protons appear as a broad singlet at δ 3.88 in $CDCl_3$ solution but as a distinct AB quartet (J=15 Hz) at δ 3.18, 3.42 in benzene-d_6 solution. The proton-decoupled carbon spectrum features only eight lines, which reveals the presence of a single conformer for **9**. This spectral feature of **9** in solution is consistent with TB or BB conformer according to the criticism for such a conformer which was investigated in detail by Ollis *et al.*[10a] and Renaud *et al.*[10b] However the relative stereochemistry at the sulfur atom could not be completely determined by such a spectral consideration.

The unambiguous structure of **9** and **15b** in the solid state was determined by X-ray analysis on a single crystal (Fig. 1).[8a,c] The sulfur has distorted trigonal bipyramidal configuration and O, S, and N atoms are colinear with the angle of 179.5 and 175.0 ° for **9** and **15b**, respectively. The N···S distances are 2.593 and 2.207 Å for **9** and **15b** respectively and are very much shorter than the sum of van der Waals radii (3.35 Å) and longer than that of covalent radii (1.74 Å). It is concluded that there is a weak but definite attractive interaction between the electron-deficient sulfur and the donating amino group, which is strong enough to keep **9** and **15** in the unfavorable distorted BB conformation with TBP

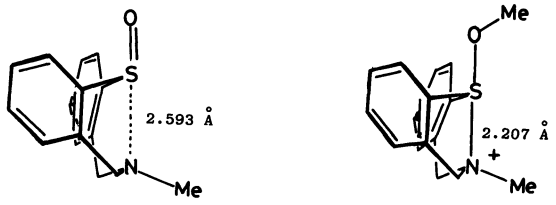
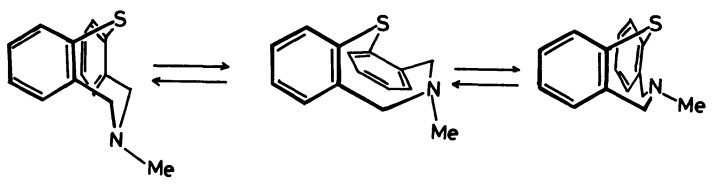


Fig. 1. Structure of **9** and **15**.



configuration at the sulfur. This is maintained also in solution as was exemplified by ^{1}H NMR study.[8,11,12]

In conclusion, the present investigation offers strong evidence for the formation of ammoniosulfuranes as intermediates in the oxidation of the sulfur of **7**, methionine, and 5-methyl-1-thia-5-azacyclooctane.[2,3]

Experimental

All the melting points are uncorrected. IR spectra were obtained with a Hitachi 215 grating IR spectrophotometer. ^{1}H NMR measurements were carried out on a Varian T-60 instrument and a Hitachi R-90H FT instrument, using tetramethylsilane as the internal reference. Mass spectra were measured with Hitachi RMU-6L spectrometer.

2-(Methoxycarbonyl)phenyl 2-(Methylcarbamoyl)phenyl Sulfide (5). Treatment of 2-(methoxycarbonyl)phenyl 2-carboxyphenyl sulfide (1.98 g, 6.88 mmol), which was prepared according to the literature,[4] with excess thionyl chloride (10 ml) gave a yellowish oil under refluxing for *ca.* 2 h. To a solution of the oil in 30 ml of ether was added an aqueous methylamine solution (in excess). The reaction mixture was poured into water after stirring for 2 h and extracted with dichloromethane. The organic layers were dried ($MgSO_4$) and concentrated to yield 1.41 g (68%) of the amide ester (**5**), mp 125—126 °C (hexane–dichloromethane); ν_{max} (KBr) 3260, 1705, and 1630 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ=2.78 (d, J=5 Hz, 3H), 3.92 (s, 3H), 6.70—7.62 (m, 7H), and 7.63—8.08 (m, 2H).

Found: C, 63.70; H, 4.94; N, 4.78%. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65%.

2-(Hydroxymethyl)phenyl 2-(Methylaminomethyl)phenyl Sulfide (6). To a solution of 2.23 g (7.41 mmol) of **5** in benzene (20 ml) was added phosphorus pentachloride (1.55 g, 7.43 mmol) and the mixture was heated at reflux for 1 h. After removal of benzene, the residue was dissolved in THF (30 ml) and added to a suspension of lithium aluminium hydride (1.6 g, 41 mmol) in the same solvent (20 ml). The mixture was stirred at 0 °C for 30 min and at room temperature for 35 h before the excess hydride was carefully decomposed with water. The solution was filtered and the filtrate was concentrated to yield 1.61 g (84%) of amino alcohol (**6**) as a colorless oil; ^{1}H NMR (CCl_4) δ=2.17 (s, 3H), 3.64 (s, 2H), 3.72 (s, 2H), 4.52 (s, 2H), and 6.65—7.80 (m, 8H). The product was crystallized as a hydrochloride; mp 221—223 °C (lit,[4] mp 216—219 °C); ν_{max} (KBr) 3360, 2920, 2760, and 1035 cm^{-1}; ^{1}H NMR (CD_3OD) δ=2.85 (s, 3H), 4.33 (s, 2H), 4.70 (s, 2H), 4.76 (s, 2H), and 6.90—7.74 (m, 8H).

*6,7-Dihydro-6-methyl-5*H*-dibenzo[*b,g*][1,5]thiazocine (7).* To a solution of amino alcohol (**6**) (1.0 g, 3.86 mmol) in 100 ml of benzene was added 10 ml of thionyl chloride and the mixture was heated at reflux for 2.5 h. After concentration of the reaction mixture, the residue was dissolved in 50 ml of ethanol and treated with potassium hydroxide (2.2 g) in 50 ml of the same solvent for 1 h at reflux temperature. Workup in the ordinary manner gave 0.77 g (83%) of a yellow oil. A pure sample of **7** was isolated by preparative TLC (silica gel; benzene–ethyl acetate (1:1)). Recrystallization from petroleum ether afforded a colorless solid of **7**, mp 65—66 °C (lit,[5] mp 68—69 °C); ν_{max} (KBr) 2875 cm^{-1}; ^{1}H NMR ($CDCl_3$, at 35 °C) δ=2.11 (s, 3H), 3.31—5.07 (br s, 4H), 6.90—7.30 (m, 6H), and 7.41—7.72 (m, 2H); ^{1}H NMR (CD_3OD, at −49.5 °C) δ=1.92 (s, Me for BC form), 2.23 (s, Me for TB form), 3.84 and 5.02 (ABq, J=14 Hz, CH_2 for BC form), 3.67 (br s, CH_2 for TB form), 7.08—7.49 (m, 6H), and 7.60—7.84 (m, 2H). BC/TB=2/1 at 49.1 °C.

*6,7-Dihydro-6,6-dimethyl-5*H*-dibenzo[*b,g*][1,5]thiazocinium Salt (8).* To a solution of amino sulfide (**7**) (50 mg, 0.21 mmol) in acetonitrile (1 ml) was added 40 mg (0.28 mmol) of methyl iodide dissolved in the same solvent (1.5 ml). The mixture was stirred at room temperature for 24 h. After evaporation of the solvent, a yellow solid (40 mg, 63%) of **8a** was obtained. By using different solvents and methylating reagents under the same procedure, the other salts (**8b—e**) were obtained. The ^{1}H NMR spectral data and reaction conditions are collected in Table 1.

Oxidation of Amino Sulfide (7) with Sodium Periodate.

*6,7-Dihydro-6-methyl-5*H*-dibenzo[*b,g*][1,5]thiazocine 6-Oxide (13).* A solution of **7** (224 mg, 0.93 mmol) in methanol (25 ml) was treated with sodium periodate (248 mg, 1.16 mmol) in water (5 ml) for 10 d. After ordinary workup, 219 mg of yellow residue was obtained. Thin layer chromatography of the residue on silica gel (ethyl acetate) gave 13.5 mg (12%) of **9** and 82.5 mg (72%) of **13** as a colorless solid. Recrystallization of **13** from dichloromethane–hexane afforded a pure sample, mp 175—177 °C (hygroscopic); ν_{max} (KBr) 905 cm^{-1}; ^{1}H NMR ($CDCl_3$) BC/TB=1/2.8, for BC form: δ=2.80 (s, 3H), 3.79 and 5.74 (ABq, J=14 Hz, 4H), and 7.00—8.00 (m, 8H); for TB form: 3.20 (s, 3H), 4.46 and 4.93 (ABq, J=16 Hz, 4H), and 7.00—8.00 (m, 8H); Mass (m/z) 257 (M^+), 241 (M^+-16), and 211 (M^+-46).

Found: C, 66.82; H, 6.15; N, 5.11%. Calcd for $C_{15}H_{15}NSO+0.7H_2O$: C, 66.77; H, 6.08; N, 5.19%.

Oxidation of Amino Sulfide (7) with Hydrogen Peroxide.

*6,7-Dihydro-6-methyl-5*H*-dibenzo[*b,g*][1,5]thiazocine 12,12-Dioxide (14).* A mixture of **7** (209 mg, 0.87 mmol) and 30% hydrogen peroxide (2.5 ml) in acetic acid (5 ml) was heated at reflux for 1.5 h. After ordinary workup and recrystallization from hexane–dichloromethane, 159.6 mg (68%) of **14** was obtained as a colorless solid; mp 170—174 °C: ν_{max} (KBr) 1305 and 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.97 (s, 3H), 3.95 and 5.62 (ABq, J=15 Hz, 4H), 7.06—7.71 (m, 6H), and 7.87—8.28 (m, 2H).

Found: C, 65.68; H, 5.52; N, 4.97%. Calcd for $C_{15}H_{15}NSO_2$: C, 65.91; H, 5.53; N, 5.12%.

*Oxidation of Amino Sulfide (7) with Sodium Hypochlorite. 6,7-Dihydro-6-methyl-5*H*-dibenzo[*b,g*][1,5]thiazocine 12-Oxide (9).* To a solution of **7** (352 mg, 1.46 mmol) in 7 ml of methanol was added 10% aqueous sodium hypochlorite (2.72 g, 3.65 mmol) at −78 °C. The mixture was stirred for 1 h at the same temperature before the mixture was poured onto ice and extracted with dichloromethane. The organic layers were washed with water, dried, and evaporated to yield yellow solids. Recrystallization of the solids from benzene–hexane gave **9** (284 mg, 76%) as colorless crystals, mp 113—115 °C; ν_{max} (KBr) 1065 and 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.56 (s,

3H), 3.88 (s, 4H), 6.98—7.67 (m, 6H), and 8.08—8.35 (m, 2H); ^{1}H NMR (C_6D_6) δ=2.02 (s, 3H), 3.18 and 3.42 (ABq, J= 15 Hz, 4H), 6.58—7.32 (m, 6H), and 8.50—8.67 (m, 2H); ^{13}C NMR (CD_3CN) δ=41.9 (q), 58.6 (t), 125.3 (d), 127.3 (d), 129.4 (d), 130.4 (d), 140.2 (s), and 145.8 (s); Mass (*m/z*) 257 (M^+), 241 (M^+ −16), 226 (M^+ −31), and 197 (M^+−60).

Found: C, 69.82; H, 5.91; N, 5.50%. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.88; N, 5.44%.

Oxidation of **7** with sodium hypochlorite at room temperature for 15.5 h afforded sulfoxide (**9**) (47%) as a major product together with a small amount of methoxysulfonium salt (**15a**). The latter was isolated in 4% yield by evaporation of the filtrate followed by trituration of the residue twice with benzene. The structure was assigned by spectral comparison with an analogous sample (**15b**) obtained by methylation of **9** as described below.

*6,7-Dihydro-6-methyl-12-methoxy-5*H*-dibenzo*[b,g]*[1,5]-thiazocinium Hexachlorantimonate (15b).* A mixture of sulfoxide (**9**) (512 mg, 1.99 mmol) and trimethyloxonium hexachloroantimonate (787 mg, 1.99 mmol) in dichloromethane (10 ml) was stirred at room temperature for 15 h under argon atmosphere. The mixture was filtered and the filtrate was concentrated to furnish 588 mg (49%) of **15b**. A pure sample of the salt (**15b**) was obtained by recrystallization from acetonitrile–ether: mp 148—151 °C: ν_{max} (KBr) 1445 and 993 cm^{-1}, ^{1}H NMR (CD_3CN) δ=2.77 (s, 3H), 3.92 (s, 3H), 4.25 (s, 4H), 7.35—7.80 (m, 6H), and 7.92—8.15 (m, 2H).

Found: C, 31.82; H, 2.98; N, 2.30%. Calcd for $C_{16}H_{18}NSOSbCl_6$: C, 31.67; H, 2.99; N, 2.31%.

*12-Chloro-6,7-dihydro-6-methyl-5*H*-dibenzo*[b,g]*[1,5]thiazocinium Chloride (16b).* To a solution of **9** (639 mg, 2.49 mmol) in dry benzene (14 ml) was added dropwise a solution of thionyl chloride (1 ml) in the same solvent (2 ml) under nitrogen atmosphere. The mixture was stirred at room temperature for 2.5 h and filtered. The yellowish solids were washed with dry benzene and ether successively before drying under an inert gas. There was obtained a colorless hygroscopic chloride (**16b**, 739 mg, 95%). ^{1}H NMR ($CDCl_3$) δ=3.13 (s, 3H), 4.70 (s, 4H), 7.22—8.02 (m, 6H), and 8.23—8.63 (m, 2H).

*12-Chloro-6,7-dihydro-6-methyl-5*H*-dibenzo*[b,g]*[1,5]thiazocinium Hexafluorophosphate (16c).* To a stirred suspension of **16b** in anhydrous dichloromethane (10 ml) prepared from **9** (517 mg, 2.01 mmol) was added ammonium hexafluorophosphate (1.31 g, 8.04 mmol). The mixture was stirred at room temperature for 17 h prior to filtration. The filtrate was diluted with dry ether to afford 288 mg (34%) of **16c** as a colorless solid: mp 145—155 °C (dec); ν_{max} 1470 and 820 cm^{-1}; ^{1}H NMR (CD_3CN) δ=3.13 (s, 3H), 4.59 and 4.72 (ABq, J=15.6 Hz, 4H), 7.30—8.05 (m, 6H), and 8.27—8.65 (m, 2H).

Found: C, 42.82; H, 3.62; N, 3.59; Cl, 8.65%. Calcd for $C_{15}H_{15}NSClPF_6$: C, 42.72; H, 3.58; N, 3.32; Cl, 8.41%.

Hydrolysis of **16b** or **16c**, followed by neutralization with sodium hydrogencarbonate, reverted back to amino sulfoxide (**7**) in quntitative yield.

N,N-*Dimethyl-2-(methylthio)benzylamine (11).* To a stirred suspension of lithium aluminium hydride (2.93 g, 75 mmol) in anhydrous tetrahydrofuran (100 ml) was added dropwise a solution of *N,N*-dimethyl-2-(methylthio)-benzamide[13] (4.88 g, 25 mmol) in the same solvent (50 ml). The mixture was stirred at 0 °C for 1 h and at room temperature for 6 d before the excess hydride was carefully decomposed with water. Workup in the predescribed manner gave 3.72 g (**11**, 82%) of a colorless oil:[1a] ν_{max} (neat) 1465 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.22 (s, 6H), 2.40 (s, 3H), 3.45 (s, 2H), and 6.87—7.40 (m, 4H); Mass (*m/z*) 181 (M^+) and 166 (M^+−15).

Dimethyl[2-(dimethylaminomethyl)phenyl]sulfonium Hexafluorophosphate (4). Treatment of **11** (1.03 g, 5.70 mmol) with 42% aqueous tetrafluoroboric acid (1.9 ml, 9.3 mmol) in acetonitrile (25 ml) gave 1.03 g (71%) of *N,N*-dimethyl-2-(methylthio)benzylammonium salt (**12**) as colorless crystals, mp 122—125 °C: ν_{max} (KBr) 1443 and 1068 cm^{-1}; ^{1}H NMR (CD_3CN) δ=2.54 (s, 3H), 2.84 (s, 6H), 4.38 (s, 2H), and 7.23—7.67 (m, 4H).

Treatment of **12** (1.03 g, 4.05 mmol) with methyl iodide (1.73 g, 12 mmol) and silver tetrafluoroborate (2.34 g, 12 mmol) in acetonitrile (10 ml) afforded 2.77 g of the sulfonium salt as yellow crystals: ^{1}H NMR (CD_3CN) δ=2.98 (d, J=5 Hz, 6H), 3.25 (s, 6H), 4.70 (d, J=5 Hz, 2H), 7.77—8.12 (m, 3H), and 8.12—8.50 (m, 1H).

The salt was neutralized with aqueous sodium hydrogen carbonate to give a colorless precipitate. The mixture was treated with an aqueous solution (10 ml) of potassium hexafluorophospate (10 g) and ammonium chloride (2 g) at room temperature for 1 h. After the usual workup, 742 mg (57%) of **4** was obtained as a colorless oil: ^{1}H NMR ($CDCl_3$) δ=2.23 (s, 6H), 3.10 (s, 6H), 3.63 (s, 2H), 7.27—7.82 (m, 3H), and 7.84—8.20 (m, 1H).

Found: C, 38.95; H, 5.52; N, 4.31%. Calcd for $C_{11}H_{18}NSPF_6$: C, 38.71; H, 5.32; N, 4.10%.

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