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Photolysis, Thermal Decomposition, and Oxidation of Naphtho[1,8-*de*]-1,2,3-thiadiazine. Efficient Synthesis of Naphtho[1,8-*bc*]thiete and the Corresponding Sulfoxide and Sulfone

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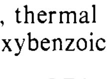
Abstract: Naphtho[1,8-*bc*]thiete (7) was prepared quantitatively by irradiation of acetone, acetonitrile, benzene, and methanol solutions of naphtho[1,8-*de*]-1,2,3-thiadiazine (4). Irradiation of a carbon disulfide solution, on the other hand, gave naphtho[1,8-*de*]-2,4-dihydro-1,3-dithiin-2-thione (9) (22%) in addition to 7 (52%). Thermal decomposition of 4 in di(ethylene glycol) diethyl ether at 155 °C also yielded mainly 7, while decomposition in carbon disulfide gave 9 (50%) and naphtho[1,8-*cd*]-1,2-dithiole (10) (11%). On irradiation or heating in carbon disulfide, 7 undergoes homolytic carbon-sulfur bond cleavage of the four-membered ring to yield 9 as the final product in a low yield. Oxidation of 4 with an equivalent of *m*-chloroperoxybenzoic acid gave 71% of naphtho[1,8-*bc*]thiete 1-oxide (16) and 4% of naphtho[1,8-*bc*]thiete 1,1-dioxide (17), while oxidation with 3 M amounts of *m*-chloroperoxybenzoic acid gave only 17 in 93% yield.

Single-atom peribridged naphthalenes (**1**) are compounds of current interest for a number of reasons, including the expected distortion of the bond lengths and angles of the naphthalene ring and possibly enhanced tendency of the four-membered ring to undergo ring opening reactions. The first synthesis of this type of compound was done in 1965 by Hoffmann and Sieber in the case of Z = SO_2 in **1**.[1] Although, since that time, many attempts to synthesize **1** were unsuccessful,[2,3] recently the syntheses of the sulfur-bridged analogue of **1** by photolysis of naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide,[4] carbon-bridged analogue by photolysis of (8-bromo-1-naphthyl)diazomethane,[5] and of the silicon-bridged analogue by reaction of 1,8-dilithionaphthalene with dialkyldichlorosilane[6] have been reported.

As to synthetic approach to **1**, extrusion of nitrogen, by photolysis or thermolysis, from compounds having the general formula of **2** seemed to be an excellent strategy. However, this is successful only in the case of Z = SO_2 in **2**.[1] In the case of Z = CR_2 or Z = NR, the diradical intermediate **3** encounters an insurmountable energy barrier to 1,4-cyclization yielding **1** and either undergoes a 1,6-hydrogen transfer or instead reacts with solvent or added olefin when R in CR_2 or NR is methyl.[3] We synthesized a new compound naphtho[1,8-*de*]-1,2,3-thiadiazine (**4**) (Z = S in **2**) and investigated its photolysis, thermal decomposition, and oxidation with *m*-chloroperoxybenzoic acid.



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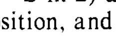

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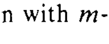

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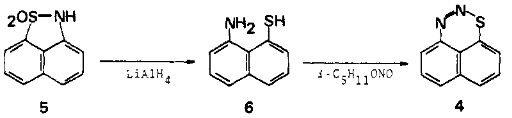
Results and Discussion

Synthesis of Naphtho[1,8-*de*]-1,2,3-thiadiazine (4). Diazotization of 1-amino-8-naphthalenethiol (**6**) is a promising route to **4** in the light of diazotization of sodium 1-aminonaphthalene-8-sulfinate producing naphtho[1,8-*de*]-1,2,3-thiadiazine 1,1-dioxide (Z = SO_2 in **2**).[1] Compound **6** had been prepared as its hexachlorostannate by reduction of 1-nitro-8-naphthalenesulfonyl chloride,[7] but it was more conveniently obtained by reduction of **5** with lithium aluminum hydride in 87–97% yield as yellowish orange crystals sensitive to air oxidation. Diazotization of **6** with isopentyl nitrite gave the expected azo compound **4** in 44% yield. Pure **4** decomposes at its melting point 149 °C with the evolution of nitrogen. The UV spectrum of **4** has maxima at 450 (ϵ 1.2 × 10^2), 352 (4.0 × 10^3), 336 (5.3 × 10^3), 326 (5.3 × 10^3), and 321 nm (5.4 × 10^3).



5 **6** **4**

Photolysis of 4. All the photolyses were conducted at ambient temperature by dissolving 1 mmol of **4** in 120 mL of a solvent (8.3 × 10^{-4} M) and irradiating with a 120-W high pressure mercury discharge lamp in a Pyrex apparatus. Acetone, acetonitrile, benzene, and methanol solutions of **4** were irradiated. The photolytic reaction proceeded surprisingly quickly in all the solvents. After 5 min of irradiation, the red solution of **4** turned pale yellow with evolution of nitrogen, although irradiation was usually continued for 15–20 min. Evaporation of the solvent and purification by chromatography yielded naphtho[1,8-*bc*]thiete (**7**) quantitatively. The identity of **7** was confirmed by comparison of its properties with those reported.[4] Compound **7** appears to be the result of 1,4-cyclization of the diradical intermediate **8** formed by loss of nitrogen, although the formation of **8** may be a two-step process via $\cdot SC_{10}H_6N_2\cdot$. Any products arising from reaction of **8** with solvent molecules were not detected. This fact, along with extremely short irradiation time and easy preparation of the precursor compound, makes the reaction a very useful synthetic method for obtaining **7**.

In contrast to the foregoing results, irradiation of a carbon disulfide solution of **4** for 15 min yielded 22% of naphtho[1,8-*de*]-2,4-dihydro-1,3-dithiin-2-thione (**9**) in addition to 52% of **7**. Prolonged irradiation (50 min) also yielded **9** and **7** in a similar ratio (23 and 52% yields, respectively). The structure of **9** was determined by spectroscopic and elemental analyses. Furthermore, **9** was converted to the known compound naphtho[1,8-*cd*]-1,2-dithiole (**10**) by alkaline hydrolysis and air oxidation of resulting 1,8-naphthalenedithiol.[8]

Compound **7** does not react with carbon disulfide in the dark at room temperature, but, on irradiation in carbon disulfide for 30 min, it was converted to **9** in 4.3% yield with 91% recovery. We must therefore conclude that (a) **9**, produced on irradiation of **4**, mostly arises from reaction of carbon disulfide with the diradical **8** formed from **4**, and (b) the thiete **7**, on irradiation, undergoes homolytic carbon-sulfur bond cleavage to give the same diradical **8**, which may be responsible for the formation of a minor part of **9**.[9] Relief of the strain of the

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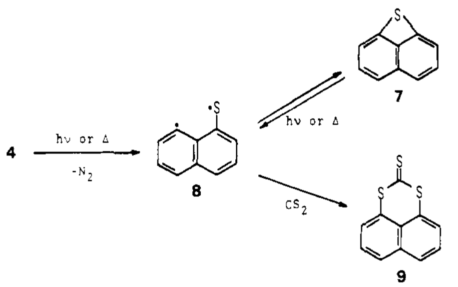

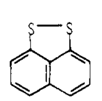
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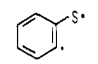
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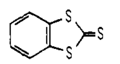
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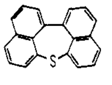
four-membered ring must be responsible for the ready cleavage of the sulfur-carbon bond. An analogy to the present trapping reaction with carbon disulfide is found in the decomposition of 1,2,3-benzothiadiazole.[10] The intermediate diradical **11**[12] can be effectively trapped with carbon disulfide to give 1,3-benzodithiol-2-thione (**12**).

Our next aim was to capture **8** with olefins. However, photolysis of **4** in the presence of a large excess of 2-norbornene or ethyl vinyl ether resulted in the formation **7** quantitatively; products arising from **8** and olefin were not detected at all.

Thermal Decomposition of 4. A di(ethylene glycol) diethyl ether solution of **4** was heated at 155 °C for 2 h under nitrogen. The major product was the thiete **7** (30%) with 12% recovery of the azo compound. Three minor products were also isolated, for one of which the tentative structure **13** was assigned from mass spectral analysis.

Thermolysis of **4** in carbon disulfide was also examined. The reaction at 150–155 °C for 2 h in an autoclave gave the 1,2-dithiole **10** (11%), unexpectedly, in addition to the expected thione **9** (50%), the thiete **7** not being formed at all. When **7** alone was heated in carbon disulfide at 125 °C for 2 h, 8.5% of **9** and a considerable amount of polymeric products were obtained with 5% recovery of **7**. Therefore, **7** is labile under these pyrolytic conditions and is assumed to undergo ring opening reaction of the four-membered ring, as observed with photolysis, to give the diradical **8**; a minor part of **9** produced by decomposition of **4** accordingly must come from the initial product **7**. A plausible mechanism for the formation of **10** involves reaction of **8** with carbon disulfide and loss of carbon monosulfide from the resulting diradical **14**.[12] If this is the case, however, **10** should be also formed in the photolysis of **4** in carbon disulfide.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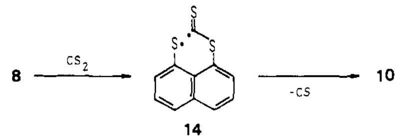
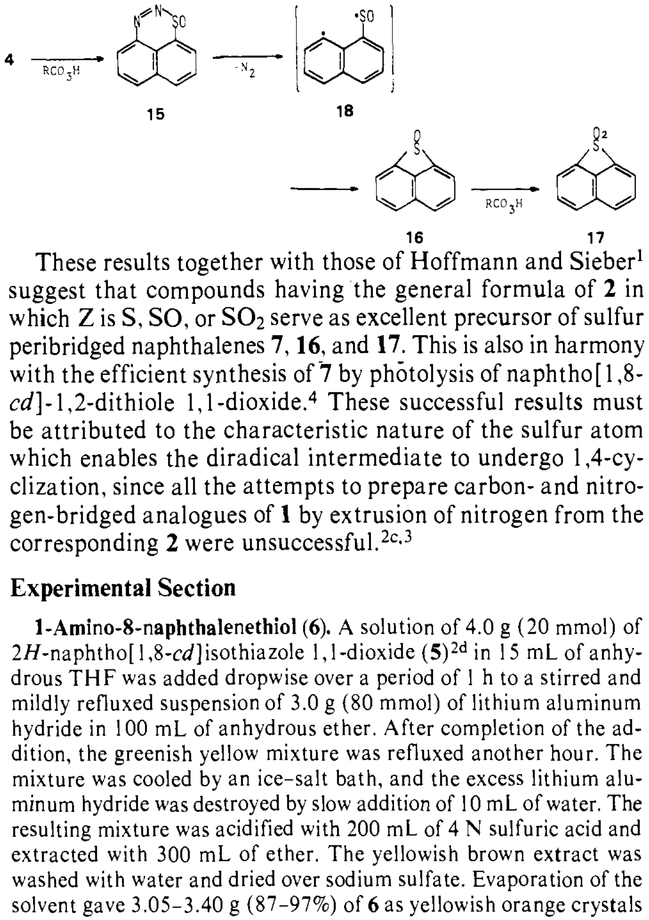


Oxidation of 4 with *m*-Chloroperoxybenzoic Acid. In the light of the foregoing results, both the photolysis and thermolysis of naphtho[1,8-*de*]-1,2,3-thiadiazine 1-oxide (**15**) would be expected to give naphtho[1,8-*bc*]thiete 1-oxide (**16**). Thus, oxidation of **4** with *m*-chloroperoxybenzoic acid was examined with expectation of obtaining **15**. The oxidation of **4** with an equivalent of *m*-chloroperoxybenzoic acid proceeded smoothly at room temperature with unexpected evolution of nitrogen gas. Workup of the mixture with chromatography gave 71% of **16**, 4% of naphtho[1,8-*bc*]thiete 1,1-dioxide (**17**), tion with 3 M amounts of *m*-chloroperoxybenzoic acid gave only **17** in 93% yield. The results suggest that the expected initial product **15** is thermally very unstable and immediately decomposes, with evolution of nitrogen, to give **16**, which is further oxidized to **17**. The formation of **17** by further oxidation of **15** to naphtho[1,8-*de*]-1,2,3-thiadiazine 1,1-dioxide (Z = SO_2 in **2**) followed by loss of nitrogen from the latter is less likely, because this dioxide is known to be fairly stable thermally.[1] In any case, the reaction provides an efficient synthetic method of **16** and **17** depending upon the molar ratio of the oxidizing reagent to the substrate.

The formation of **16** from **4** is expected via the diradical intermediate **18**. However, attempted trapping of **18** with carbon disulfide was unsuccessful. The oxidation in a mixture of carbon disulfide and methylene chloride yielded 71% of **16**, 4% of **17**, and 20% of the starting material.



These results together with those of Hoffmann and Sieber[1] suggest that compounds having the general formula of **2** in which Z is S, SO, or SO_2 serve as excellent precursor of sulfur peribridged naphthalenes **7**, **16**, and **17**. This is also in harmony with the efficient synthesis of **7** by photolysis of naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide.[4] These successful results must be attributed to the characteristic nature of the sulfur atom which enables the diradical intermediate to undergo 1,4-cyclization, since all the attempts to prepare carbon- and nitrogen-bridged analogues of **1** by extrusion of nitrogen from the corresponding **2** were unsuccessful.[2c,3]

Experimental Section

1-Amino-8-naphthalenethiol (6). A solution of 4.0 g (20 mmol) of 2*H*-naphtho[1,8-*cd*]isothiazole 1,1-dioxide (**5**)[2d] in 15 mL of anhydrous THF was added dropwise over a period of 1 h to a stirred and mildly refluxed suspension of 3.0 g (80 mmol) of lithium aluminum hydride in 100 mL of anhydrous ether. After completion of the addition, the greenish yellow mixture was refluxed another hour. The mixture was cooled by an ice-salt bath, and the excess lithium aluminum hydride was destroyed by slow addition of 10 mL of water. The resulting mixture was acidified with 200 mL of 4 N sulfuric acid and extracted with 300 mL of ether. The yellowish brown extract was washed with water and dried over sodium sulfate. Evaporation of the solvent gave 3.05–3.40 g (87–97%) of **6** as yellowish orange crystals melting at 75–76 °C. The compound is sensitive to air, turns blue to black on standing and, therefore, was used immediately.

Anal. Calcd for $C_{10}H_9NS$: C, 68.58; H, 5.18; N, 8.00. Found: C, 68.98; H, 4.72; N, 7.78.

Ir (KBr) 3430, 3320, 1610, 1552, 1448, 1332, 812, 802, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.0 (broad s with fine structure, 2 H, variable), 6.7 (m, 1 H), and 7.0–8.0 (m 5 H).

Naphtho[1,8-*de*]-1,2,3-thiadiazine (4). A solution of 1.17 g (10 mmol) of isopentyl nitrite in 30 mL of 1,2-dichloroethane was added dropwise at room temperature over a period of 2 h to a stirred solution of 1.52 g (8.7 mmol) of **6** and a catalytic amount of trichloroacetic acid (ca. 5 mg) in 60 mL of 1,2-dichloroethane. The mixture was stirred for another 1.5 h. The resulting deeply colored mixture was evaporated to leave a dark solid, which was chromatographed on silica gel (150 g) with benzene as eluent. The first 200 mL was discarded; rechromatography of this fraction with hexane as eluent gave a small amount of naphtho[1,8-*bc*]thiete (**7**), which must be formed by decomposition of **4** during workup. The next fraction (ca. 400 mL) was collected and evaporated to give 0.84 g of brownish red crystals, which was sublimed at 90 °C/0.5 mmHg to give 0.72 g (44.5%) of **4** as red crystals melting at 144–148 °C (dec). Crystallization from cyclohexane raised the mp to 149 °C (dec). Further elution of the column gave deeply colored solid scarcely soluble in organic solvents.

Addition of a 1,2-dichloroethane solution of **6** to a stirred mixture of isopentyl nitrite and trichloroacetic acid in 1,2-dichloroethane gave **4** in a decreased yield (33%).

Anal. Calcd for $C_{10}H_6N_2S$: C, 64.51; H, 3.25; N, 15.05. Found: C, 64.25; H, 3.21; N, 15.32.

Ir (KBr) 1608, 1580, 1552, 1452, 1412, 1375, 1350, 1184, 1068, 1020, 941, 810, 799, and 750 cm^{-1}; UV (hexane) 269 (ϵ 6.7 × 10^3), 278 (6.7 × 10^3), 289 (5.5 × 10^3), 321 (5.4 × 10^3), 326 (5.3 × 10^3), 336 (4.5 × 10^3), 352 (4.0 × 10^3), 450 (1.2 × 10^3), 474 (sh) (1.0 × 10^3), 506 (sh) (4.7 × 10^2), and 516 nm (sh) (3.1 × 10^2); ^{1}H NMR ($CDCl_3$) 6.62 (d/d, 1 H) and 7.0–7.9 (complex m, 5 H).

Photolysis of 4 in Acetone, Acetonitrile, Benzene, and Methanol. A solution of 186 mg (1 mmol) of **4** in 120 mL of a solvent was irradiated with a 120-W high pressure mercury discharge lamp and a Pyrex apparatus. After irradiation for 5 min, the red solution turned pale yellow with evolution of nitrogen, although irradiation was usually continued for 15–20 min. The photolysis mixture was evaporated to leave a yellow oil which solidified on standing. It was purified by silica gel chromatography with hexane as eluent to give a quantitative yield of naphtho[1,8-*bc*]thiete (**7**) as near-white crystals; compound purified by sublimation melted at 40–41 °C (lit.[4] mp 40–42 °C). Properties of the material agreed with those reported[4] in all respects.

Photolysis of 4 in Carbon Disulfide. A solution of 186 mg (1 mmol) of **4** in 120 mL of carbon disulfide was irradiated for 15 min under nitrogen. A small amount of insoluble product was filtered off and the yellowish brown filtrate was evaporated onto 0.5 g of silica gel. The residue was placed at the head of a silica gel column (40 g). Exhaustive elution of the column with hexane gave three principal fractions. The first fraction, on removal of the solvent, gave 82.4 mg (52.1%) of **7**, mp 38–40°C. The second fraction gave 6 mg of a brown solid. The last of these gave 52.0 mg (22.2%) of naphtho[1,8-*de*]-2,4-dihydro-1,3-dithiin-2-thione (**9**), which was recrystallized from cyclohexane in orange needles, mp 199–201 °C. Ir (KBr) 1560, 1504, 1375, 1216, 1038, 945, 810, and 760 cm^{-1}. Anal. Calcd for $C_{11}H_6S_3$: C, 56.42; H, 2.58; S, 41.00. Found: C, 56.41; H, 2.55; S, 40.67.

Irradiation of 186 mg of **4** in 120 mL of carbon disulfide for 50 min gave 82.4 mg (52.1%) of **7**, 10.3 mg of the brown solid, and 54.7 mg (23.4%) of **9**.

Conversion of 9 to Naphtho[1,8-*cd*]-1,2-dithiole (10). A mixture of 75 mg (0.32 mmol) of **9** and 100 mg of potassium hydroxide in 10 mL of methoxyethanol was heated under reflux for 3 h. The red mixture was poured into 20 mL of ice water, acidified with 0.5 mL of concentrated hydrochloric acid, and extracted with 100 mL of ether. The ether extract was washed with water, dried, and evaporated. The residue was chromatographed on silica gel (30 g) with hexane as eluent. The first fraction gave 28 mg (46%) of **10**, mp 120.5–121 °C (from hexane), red prisms (lit. mp 116,[8] 120–121 °C[13]). Further elution of the column gave 35 mg of unidentified yellow crystals.

Photolysis of 7 in Carbon Disulfide. A solution of 158 mg (1 mmol) of **7** in 120 mL of carbon disulfide was irradiated with a 120-W high pressure mercury discharge lamp for 0.5 h under nitrogen. A small amount of insoluble product was filtered off and the yellow filtrate was evaporated to give a crystalline solid, which was chromatographed on silica gel (40 g). Elution with hexane gave 144 mg (91%) of the starting material, mp 38–40 °C, and 10 mg (4.3%) of **9**, mp 199.5–202 °C (from cyclohexane).

Photolysis of 4 in the Presence of 2-Norbornene or Ethyl Vinyl Ether. A mixture of 186 mg (1 mmol) of **4**, 25 mL of 2-norbornene, and 95 mL of methylene chloride was irradiated for 15 min. The pale yellow mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel. Elution with hexane gave 158 mg (100%) of **7** as white crystals, mp 38–40 °C.

Similarly, irradiation of a mixture of 186 mg of **4**, 50 mL of ethyl vinyl ether, and 70 mL of methylene chloride for 15 min yielded **7** quantitatively.

Thermal Decomposition of 4 in Di(ethylene Glycol) Diethyl Ether. A solution of 372 mg (2 mmol) of **4** in 20 mL of anhydrous di(ethylene glycol) diethyl ether was heated at 155 °C for 2 h under nitrogen. The resulting polymeric insoluble product (64 mg) was filtered off and the red filtrate was dissolved in 200 mL of ether and washed 15 times with 100-mL portions of water, dried, and evaporated. The red oily residue (207 mg) was chromatographed on silica gel (50 g). Elution with hexane gave five distinct fractions. The first fraction gave 46 mg (12.4%) of the starting material. The next fraction gave 96.5 mg (30.5%) of yellow crystals, which was further purified by sublimation to give 91 mg of **7** as pale yellow crystals melting at 40–41 °C. The third fraction gave 5.4 mg of yellow crystals. Material purified by preparative TLC melted at 170–174 °C. Ir (KBr) 3050, 1608, 1575, 1505, 1382, 1305, 1202, 805, and 740 cm^{-1}; MS *m/e* 284 (100%, M$^+$, $C_{20}H_{12}S$), 280 (48), 252 (26), 149 (84), and 140 (67). Tentative structure **13** was assigned for this compound. The fourth and last fractions were less than 5 mg and not further examined.

Thermal Decomposition of 4 in Carbon Disulfide. A solution of 372 mg of **4** in 30 mL of carbon disulfide was heated in an autoclave at 150–155 °C for 2 h. The resulting mixture was evaporated to give a brown crystalline solid, which was subjected to a silica gel chromatography. Elution with hexane afforded 43 mg (11.3%) of **10**, mp 120.5–121 °C (from hexane), and 232 mg (49.6%) of **9**, mp 199–201 °C (from cyclohexane). **7** was not obtained.

Reaction of 7 with Carbon Disulfide. A solution of 158 mg of **7** in 30 mL of carbon disulfide was heated at 125 °C for 2 h in an autoclave. The mixture was evaporated and chromatographed on silica gel (40 g). Elution with hexane gave 8 mg (5%) of **7** and then 20 mg (8.5%) of **9**. Further elution of the column with methylene chloride and then with ether did not give any products.

Oxidation of 4 with *m*-Chloroperoxybenzoic Acid. A solution of 173 mg (1 mmol) of *m*-chloroperoxybenzoic acid in 20 mL of methylene chloride was added dropwise over a period of 15 min to a stirred solution of 186 mg (1 mmol) of **4** in 20 mL of methylene chloride. Immediately evolution of nitrogen was observed. The mixture was stirred for 1 h and washed with sodium bicarbonate solution and then with water and dried. Evaporation of the solvent left a brown crystalline residue, which was subjected to a silica gel chromatography (40 g). Elution with benzene gave 27 mg (14.5%) of the starting material and then 8 mg (4.2%) of naphtho[1,8-*bc*]thiete 1,1-dioxide (**17**), mp 185–186 °C (from methanol); a specimen prepared by oxidation of **7** with *m*-chloroperoxybenzoic acid[4] melted at 184–186 °C (lit. mp 184,[1] 183–184 °C[4]). No depression of the mixture melting point was observed. Further elution of the column with methylene chloride gave 124 mg (71%) of naphtho[1,8-bc]thiete 1-oxide (**16**), mp 103–104.5 °C (dec) (from hexane) (lit.[4] mp 105–106 °C). Properties of this compound agreed in all respects with those reported.[4]

Oxidation of 186 mg (1 mmol) of **4** with 518 mg (3 mmol) of *m*-chloroperoxybenzoic acid in methylene chloride gave 177 mg (93%) of **17**, mp 185–187 °C (from methanol) with similar treatment as above.

Oxidation of 186 mg (1 mmol) of **4** with 173 mg (1 mmol) of *m*-chloroperoxybenzoic acid in a mixture of 10 mL of carbon disulfide and 20 mL of methylene chloride gave 37 mg (19.9%) of the starting material, 8 mg (4.2%) of **17**, and 124 mg (71%) of **16**.

References and Notes

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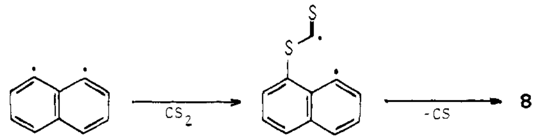
(9) The intervention of **8** as intermediate was also suggested in the reaction of 1,8-dehydronaphthalene with carbon disulfide, which yielded **7** and **9**, in addition to some other products, in a similar ratio as obseved with the present reaction (unpublished results by S. Dan of our laboratory). In this case, 1,8-dehydronaphthalene reacts with carbon disulfide to give the diradical **19**, which loses carbon monosulfide, as might be expected from results with radicals ($Ar{-}S{-}\dot{C}{=}S$),[12] to afford **8**.



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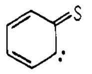
(11) In this case, the intermediate may be the thio-keto carbene **20** rather than



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the diradical **11**. In our case, thio-keto carbene intermediate can be a priori ruled out because of structural demands.

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Addition of Complexed Amino Radicals to Conjugated Alkenes[1]

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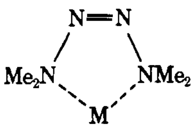
Abstract: Dimethylamino radicals, complexed by zinc chloride, added to styrene, α- and β-methylstyrenes, and indene to give the corresponding bis(dimethylamino) adducts in fair to good yields. The radicals were generated by the thermal (60 °C) decomposition of the tetramethyl-2-tetrazene:zinc chloride complex. The addition of the two dimethylamino groups is shown to be a stepwise process, rather than concerted, as suggested previously by us. The relative rates of addition of the zinc chloride complexed amino radicals to substituted α-methylstyrenes were well correlated by the Hammett equation with a ρ value of -0.98 ± 0.04. In contrast, the ρ value for the addition of uncomplexed radicals was found to be $+0.69 \pm 0.03$. The addition of dimethylamino radicals coordinated by $ZnBr_2$, $HgCl_2$, and $CdCl_2$ to α-methylstyrene was also observed, but no addition was obtained with $ZnSO_4$, $Zn(OAc)_2$, $Zn(C_6H_5)_2$, or $Zn(C_6F_5)_2$.

Tetramethyl-2-tetrazene (TMT) forms 1:1 complexes with a variety of Lewis acids, such as zinc halides, zinc alkyls and aryls,[3] mercuric, aluminum, and cadmium halides,[4] and aluminum alkyls.[5] The structure of these complexes was assumed to be the cis structure **1**. This structure was shown to be incorrect by the single crystal X-ray structure determination of bis(perfluorophenyl)tetramethyltetrazenezinc(II), **2**.[6]



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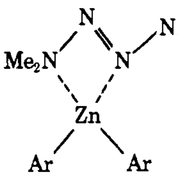
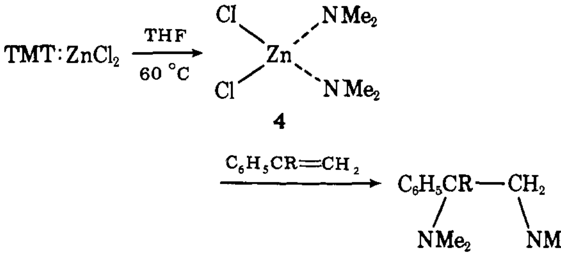


2, Ar = C_6F_5

The TMT:$ZnCl_2$ complex was shown to lose nitrogen at low temperatures.[3] We showed that, when this complex was decomposed in the presence of styrene or α-methylstyrene, 30–40% yields of the diamino adducts, **3**, were obtained.[7] This initial study was carried out before the correct structure of the complex was known. As a consequence of this, we assumed that the complex decomposed to the biradical intermediate, **4**, which was then captured by the olefin.



(1)

3, R = H, Me

The purpose of this paper is to show that this initial assumption was incorrect, to suggest a more correct mechanism for the addition, and to discuss the reactivity of the zinc chloride complexed amino radical and to contrast it with the reactivity of the neutral, uncomplexed radical.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237 spectrophotometer; NMR spectra were recorded on Varian A60D and XL100 instruments (chemical shifts reported in this paper are in ppm at 60 MHz); the mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6D spectrometer. GLPC was carried out on a Varian Aerograph 1520 instrument, equipped with both thermal conductivity and flame ionization detectors and a Disc integrator. HPLC analyses were carried out on a Waters ALC-201 instrument using a 13 ft × 0.25 in. i.d. column packed with Porasil A. Benzene, containing 5% methanol, was the eluting solvent with a flow rate of 3 mL per min. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Materials. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere. It was then stored over 4-Å molecular sieves under a nitrogen atmosphere.

Anhydrous zinc chloride was prepared from the hydrate by fusion in a crucible until water evolution ceased. This material was then cooled in a dry nitrogen atmosphere, broken up into a powder, and stored as a saturated solution in dry THF under nitrogen in a glove box. Anhydrous zinc bromide was prepared in an analogous manner.

Cadmium chloride was dried over P_2O_5 in a vacuum desiccator for 1 week. Reagent grade mercuric chloride was used without treatment.

Bis(perfluorophenyl)tetramethyltetrazenezinc(II) was prepared by the method of Noltes and van den Hurk.[3] The Grignard reagent, prepared from pentafluorobromobenzene, was treated with anhydrous $ZnCl_2$ to give bis(pentafluorophenyl)zinc, which, when treated with TMT, gave almost quantitative yields of the complex. The compound crystallized from pentane is well defined: white needles, mp 144–146 °C (lit.[3] 136–137 °C); NMR spectrum (benzene-d_6) 2.41 ppm (s). Anal. Calcd for $C_{16}H_{12}F_{10}N_4Zn$: C, 37.27; H, 2.35; N, 10.87. Found: C, 36.94; H, 2.34; N, 10.81.

Diphenyl(tetramethyltetrazene)zinc(II) was prepared in the same manner as the fluorinated analogue. This material, although formed in high yield from diphenylzinc and TMT, was more difficult to purify, mp 70–77 °C (lit.[3] 73–75 °C).

Dichloro(tetramethyltetrazene)zinc(*II*) was best prepared by adding TMT to a saturated solution of anhydrous zinc chloride in ether. Crystals of this complex formed immediately. These could be dried under nitrogen, but always retained a trace of ether. This ether could be removed by repeated washing with dry pentane. The crystals

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