Chemistry of 8-Substituted 1-Naphthylmethylenes and 2-Substituted Benzylidenes. A Simple Entry to 1*H*-Cyclobuta[*de*]naphthalenes

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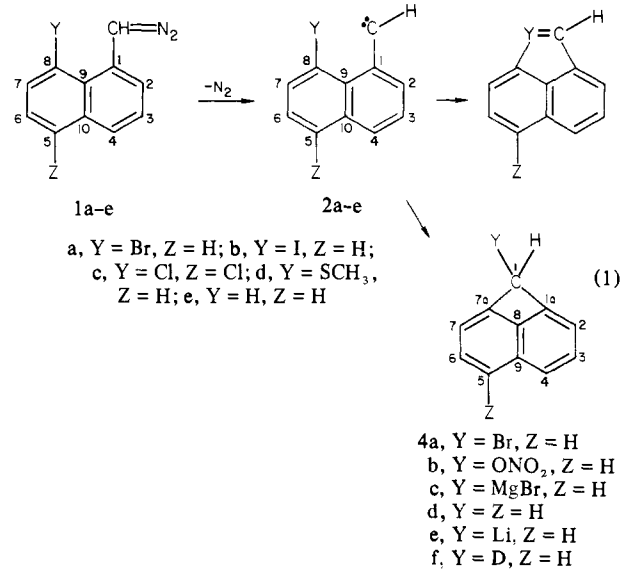
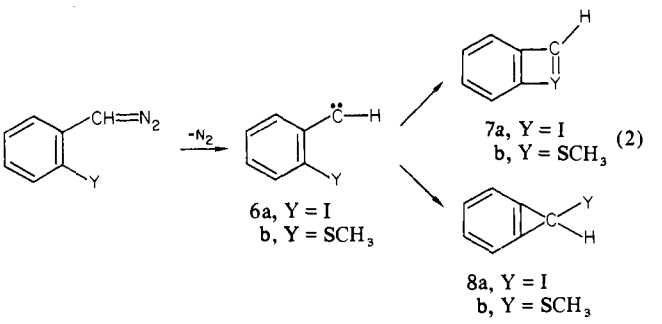
Abstract: Study has been made of neighboring heteroatom interaction in thermolysis and photolysis of proximally substituted aryldiazomethanes. Thus, (8-bromo-1-naphthyl)- (**1a**), (8-iodo-1-naphthyl)- (**1b**), and (5,8-dichloro-1-naphthyl)diazomethane (**1c**) isomerize at 132 °C to 9-bromo- (**18a**), 9-iodo- (**18b**), and 6,9-dichloro-3*H*-benz[*e*]indazoles (**18c**). Indazoles **18a** and **18b** are reduced by lithium aluminum hydride to 3*H*-benz[*e*]indazole (**21**), identical with that from decomposition of *N*-(1-methyl-2-naphthyl)-*N*-nitrosoacetamide (**19**). 1-Naphthyldiazomethane (**1e**) does not isomerize however to **21**; in benzene at −78 °C, **1e** converts to *trans*-bis(1-naphthyl)ethylene (**22b**), 1-naphthalazine (**26**), and 7-(1-naphthyl)cycloheptatriene (**24**) which rearranges to 1-(1-naphthyl)cycloheptatriene (**25**) when heated. Irradiation of **1a** in ethyl ether results in *trans*-bis-(8-bromo-1-naphthyl)ethylene (**22c**) and 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**4a**), the first aryne bridged in its peri positions by a single carbon atom moiety. Aqueous silver nitrate converts **4a** to 1*H*-cyclobuta[*de*]naphthyl nitrate (**4b**) and 1-naphthaldehyde (**28**, presumably by ring opening of 1-hydroxy-1*H*-cyclobuta[*de*]naphthalene (**27**)). Reaction of **4a** with magnesium and hydrolysis of the resulting Grignard reagent yield 1*H*-cyclobuta[*de*] naphthalene (**4d**), a hydrocarbon acid which undergoes deuterium exchange at C-1 considerably slower than do acenaphthene (**29**) and diphenylmethane (**30**). Thermolysis and photolysis of [8-(methylthio)-1-naphthyl]diazomethane (**1d**) to give 2-methyl-2*H*-naphtho[1,2-*cd*]thiophene (**33**) are of note in that methylthio participation in 8-(methylthio)-1-naphthylidene (**2d**) and thia-Stevens rearrangement appear to be involved. (*o*-Iodophenyl)diazomethane (**5a**) thermolyzes to *trans*-bis(*o*-iodophenyl)ethylene and *o*-iodobenzalazine (**36**); products of reaction of the iodine moiety with the carbenic center in *o*-iodobenzylidene (**6a**) were not found. Thermolysis however of (*o*-(methylthio)phenyl)diazomethane (**5b**) results in intramolecular C−H insertion to yield 4,5-dihydro[*b*]thiophene (**37**) along with *trans*-bis[*o*-(methylthio)phenyl]ethylene (**38**) and *o*-(methylthio)benzalazine (**39**). Intermolecular carbenic interception does occur in photolysis of **5b** in that 2-(2-ethoxy-1-propyl)thioanisole (**40**) is formed along with **38** and **39**. The mechanisms of the various participation processes in the above substituted 1-naphthylidenes and benzylidenes are discussed.

Single carbenes coordinate with and/or insert across heteroatomic moieties such as iodine, bromine, and thioalkyl groups.[1-3] The reactivities of such substituents have been related to their nonbonded electrons, d orbitals, sizes, and steric requirements.[1] A study is now reported of varied decomposition reactions of 8-substituted 1-naphthyldiazomethanes (**1**, eq 1) and *ortho*-substituted phenyldiazomethanes (**5**, eq 2). Among the research objectives are (1) generation of halonium[2] and sulfonium[3] heterocycles **3** and **7** (Y = X and SCH_3) derivable from **2** and **6** and (2) synthesis of strained derivatives **4**[4] and **8**.[5] The compounds investigated are 8-bromo-1-naphthyldiazomethane (**1a**), (8-iodo-1-naphthyl)diazomethane (**1b**), (5,8-dichloro-1-naphthyl)-diazomethane (**1c**), [8-(methylthio)-1-naphthyl]diazomethane (**1d**), (*o*-iodophenyl)diazomethane (**5a**), and [*o*-(methylthio)-phenyl]diazomethane (**5b**). To define the 1-naphthylmethylene system more completely, decomposition of 1-naphthyldiazomethane (**1e**) in liquid phase has also been studied.



(1)



(2)

Synthesis of 1 and 5. Diazomethanes **1** and **5** were prepared or generated in situ from salts of *p*-tosylhydrazones of substituted 1-naphthaldehydes and benzaldehydes. The synthetic methodology is summarized as follows.

(1) (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971, pp 407-456. (b) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. "The Chemistry of Diazonium and Diazo Groups", Part 2; Patai, S., Ed.; Wiley: New York, 1978; pp 949-956.

(2) (a) Pirkle, W. H.; Koser, G. F. *Tetrahedron Lett.* **1968**, 3959. (b) Pirkle, W. H.; Koser, G. F. *J. Am. Chem. Soc.* **1968**, *90*, 3598. (c) Sheppard, W. A.; Webster, O. W. *Ibid.* **1973**, *95*, 2697.

(3) (a) Ando, W. *Acc. Chem. Res.* **1977**, *10*, 181. (b) Ando, W. "The Chemistry of Diazonium and Diazo Groups", Part 1; Patai, S., Ed.; Wiley: New York, 1978; pp 445-458. (c) Gillespie, R. J.; Murray-Rust, J.; Murray-Rust, P.; Porter, A. E. A. *J. Chem. Soc., Chem. Commun.* **1978**, 83.

(4) (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (b) After initial synthesis of **4a** had been communicated:[4a] Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, *190* reported preparation of 1*H*-cyclobuta[*de*]naphthalene (**4c**) in ~40% yields by flash vacuum pyrolysis (10^{-1}-10^{-4} torr) of 1- and 2-naphthyldiazomethanes at 500-600 °C as generated in situ from sodium salts of 1- and 2-naphthaldehyde *p*-tosylhydrazones. (c) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, 2715 have prepared **4c** by thermolysis (525-650 °C) of [methoxy(1- or 2-naphthyl)methyl]trimethylsilanes.

(5) (a) Halton, B. *Chem. Rev.* **1972**, *73*, 113. (b) Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.

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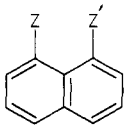
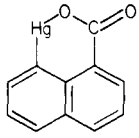
8-Bromo-1-naphthaldehyde (**13**) was obtained from 1,8-naphthalic acid (**9**) by (1) reaction with mercuric acetate and decarboxylation in hot acetic acid to give anhydro-8-(hydroxymercuri)-1-naphthoic acid (**10**, 97%), (2) synthesis of 8-bromo-

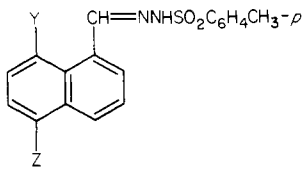


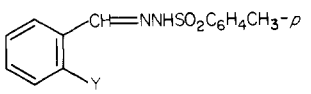


10

9, Z = Z' = CO_2H
11, Z = Br, Z' = CO_2H
12, Z = Br, Z' = CH_2OH
13, Z = Br, Z' = CH=O
14, Z = CH_3S, Z' = CH=O

1-naphthoic acid (**11**, 64%) from **10** and aqueous sodium hypobromite and its conversion by thionyl chloride and then lithium aluminum hydride to 8-bromo-1-naphthylmethanol (**12**, >88%), and (3) oxidation of **12** (85%) with N-chlorosuccinimide/dimethyl sulfide/triethylamine[6,7] or with aqueous sodium hypochlorite in the presence of benzyltrimethylammonium chloride.[8] Displacement of **13** by cuprous methylmercaptide in hexamethylphosphoric triamide/pyridine at 160 °C gave 8-(methylthio)-1-naphthaldehyde (**14**, 72%). Extensions of the procedures for **13** led to 8-iodo-1-naphthoic acid, 8-iodo-1-naphthaldehyde, 5,8-dichloro-1-naphthoic acid, and 5,8-dichloro-1-naphthaldehyde. In chlorination of **10** in acetic acid 5,8-dichloro-1-naphthoic acid rather than 8-chloro-1-naphthoic acid is the principal product and was converted to 5,8-dichloro-1-naphthaldehyde since chlorine at the 5-position does not interfere with the research objectives. Oxidation of *o*-iodobenzyl alcohol with ceric ammonium nitrate in acetic acid yielded *o*-iodobenzaldehyde. *o*-(Methylthio)benzaldehyde was obtained (94%) from *o*-(methylthio)benzyl alcohol, *N*-chlorosuccinimide, and dimethyl sulfide upon addition of triethylamine.[7] *p*-Tosylhydrazones **15a–e** and **16a–b** were prepared from their corresponding aldehydes by reaction with *p*-tosylhydrazine in methanolic or ethanolic hydrogen chloride and converted by various procedures to their sodium salts and thence to **1** and **5**.



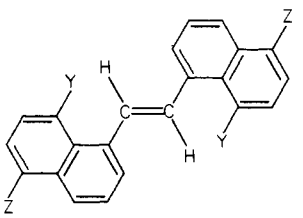


16a, Y = I
b, Y = SCH_3

15a, Y = Br, Z = H
b, Y = I, Z = H
c, Y = Cl, Z = Cl
d, Y = SCH_3, Z = H
e, Y = H, Z = H

Thermolysis of 1a–c,e. The thermal behavior of **1a,b** is surprising in that there is little loss of nitrogen and heterocyclic products result (eq 3). Thus **1a** and **1b** (and the sodium salts of **15a** and **15b**) decompose in refluxing chlorobenzene (~132 °C) to give 9-bromo-3*H*-benz[*e*]indazole (**18a**, 50%) and 9-iodo-3*H*-benz[*e*]indazole (**18b**, 52%), respectively. Similarly, the sodium salt of **15c**, presumably via **1c**, thermolyzes to 6,9-dichloro-3*H*-benz[*e*]indazole (**18c**, 45%); *trans*-bis(5,8-dichloro-1-naphthyl)ethylene (**22a**, 15%) is also obtained from this system. Products of types **3** and **4** were not detected however in any experiment.[4]

Formation of indazoles **18a–c** may be rationalized by sterically assisted electrophilic attack by terminal diazo nitrogen at C-2 in



22a, Y = Cl, Z = Cl
b, Y = H, Z = H
c, Y = Br, Z = H

1a–c to give **17a–c** (eq 3) followed by tautomerization. Although vinyldiazomethanes may isomerize to pyrazoles,[9] analogous cyclizations of aryldiazomethanes to indazoles have not been previously reported. Indazoles **18a** and **18b** are assigned from their spectra, analyses, and reduction by lithium aluminum hydride to 3*H*-benz[*e*]indazole (**21**, 97%), identical with that obtained by thermal decomposition of *N*-(1-methyl-2-naphthyl)-*N*-nitrosoacetamide (**19**, eq 4).[10] The structure of **18c** is derived from its chemical and physical properties and its origins and by comparison to **18a** and **18b**. Ethylene **22a**, an expected product of thermolysis of **1c**, is presumably formed by reaction of **2** (Y = Z = Cl) with **1c** with expulsion of nitrogen.

Attempts to isomerize **1e** to indazole **21** at temperatures up to 180 °C were unsuccessful. These results therefore imply that steric factors in cyclization of **1a–c** to **18a–c** are important. The peri-halo substituents in **1a–c** thus force the diazomethyl group out of coplanarity with the aromatic system and facilitate electrophilic attack from above or below the aromatic plane. Hydrogen at C-8 does not seriously sterically encumber **1e**. Thermolysis of **1e** in refluxing benzene apparently results then in loss of nitrogen and formation of 1-naphthylmethylene (**2e**)[4b,c] in that 7-(1-naphthyl)cycloheptatriene (**24**, 25%) and *trans*-bis(1-naphthyl)ethylene (**22b**, 42%) are produced along with 1-naphthalazine (**26**, 22%, eq 5). Cycloheptatriene **24** presumably originates from isomerization of norcaradiene **23** derived from addition of carbene **2e** to benzene. During preparative GLC, **24** isomerizes to 1-(1-naphthyl)cycloheptatriene (**25**), possibly via two consecutive thermally allowed migrations of hydrogen.[11]

Photolysis of 1a. The photochemical behavior of **1a** and the sodium salt of **15a** is spectacularly different from their thermal chemistry. Thus, irradiation (450-W mercury lamp through Pyrex) of **1a** or the sodium salt of **15a** in ethyl ether results in loss of nitrogen to yield 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**4a**, eq 1, >44%) along with *trans*-bis(8-bromo-1-naphthyl)-ethylene (**22c**, 10%). Strained bromide **4a** is the first example of a naphthalene derivative bridged in its peri positions by a single carbon atom moiety.[4a,12] The mechanism of formation of **4a** is not clear. Logical singlet possibilities for **2a** involve (1) formation of **3** (Y = Br, Z ; H; eq 1) and subsequent rearrangement, (2)

(6) An adaptation of the method of: Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, *94*, 7586.

(7) It has not yet been possible to develop efficient methods for reducing **11**, 8-iodo-1-naphthoic acid, and *o*-(methylthio)benzoic acid and their various acid derivatives to the corresponding aldehydes.

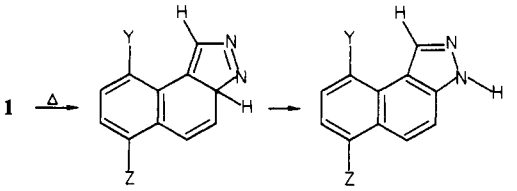
(8) (a) An extension of the method of: Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, 1641. (b) The contribution of F. E. Friedli in developing synthesis of **13** is acknowledged.

(9) (a) Adamson, D. W.; Kenner, J. *J. Chem. Soc.* **1935**, 286. (b) Hurd, C. D.; Lui, S. C. *J. Am. Chem. Soc.* **1935**, *57*, 2656.

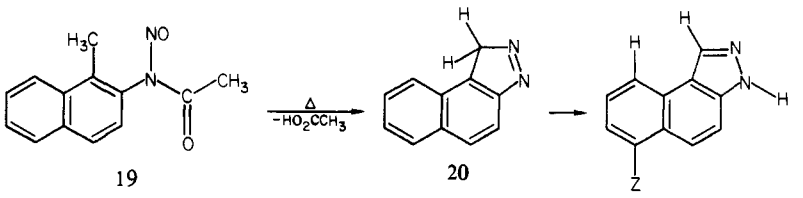
(10) (a) Huisgen, R.; Nakaten, H. *Justus Liebigs Ann. Chem.* **1954**, *84*, 586 report that thermolysis of **19** yields **20**. The product actually isolated is now reassigned as **21**. (b) In the thermolyses of **1a–c**, **17a–c** were not detected.

(11) (a) If **25** is formed by sigmatropic rearrangement processes, two suprafacial hydrogen migrations are required. (b) An alternate mechanism is ionization of **24** at elevated temperatures during GC and conversion to **25** under conditions of equilibrium control.

(12) (a) Efforts to effect preparative Wolff ring contractions of 2-diazoacenaphthenones to 1,8-naphthyleneketenes have been unsuccessful: Reid, W.; Lowasser, H. *Justus Liebigs Ann. Chem.* **1967**, *703*, 96. DeJongh, D. C.; Van Fossen, R. Y. *Tetrahedron* **1972**, *28*, 3603. Chang, S.-J.; Ravi Shankar, B. K.; Shechter, H. *J. Org. Chem.* **1982**, *47*, 4226. (b) Chapman, O. *Chem. Eng. News* **1978**, September 18, 17, has reported that photolysis of 2-diazoacenaphthenone in argon matrix at 8 K gives spectral evidence for 1,8-naphthyleneketene. (c) Attempts to prepare 1,1-dimethylcyclobuta[*de*]-naphthalene by irradiation of 1-isopropylidenaminonaphtho[1,8-*de*]triazine have failed: Burgess, E. M.; Carithers, R.; McCullagh, L. *J. Am. Chem. Soc.* **1968**, *90*, 1924. (d) Recently irradiation of 8-hydroxy-1-naphthylgyoxylic acid lactone in matrix at −195 °C has been found to result in extrusion of carbon dioxide and formation of 1*H*-cyclobuta[*de*]naphthalen-1-one,[12b] a ketone prepared previously in this laboratory from **4a**.



(3)

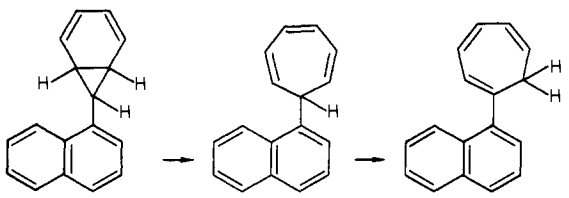


19 20 21, Z = H

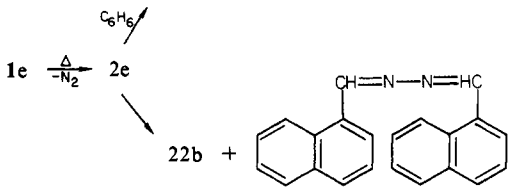
(4)

a, Y = Br, Z = H; b, Y = I, Z = H; c, Y = Cl, Z = Cl

direct insertion into the carbon–bromine bond at C-8, and (3) aromatic penetration at C-8 and nucleophilic displacement on (or



23 24 25



(5)

26

rearrangement of) bromine.[13] Whatever the mechanism, what is impressive about the overall result is that, in spite of the distance between C-1 and C-8, **2a** has the ability to adjust and form a classic strained structure such as **4a**.[14,15]

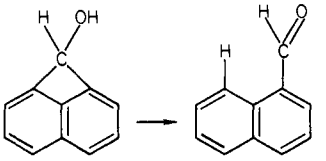
Bromide **4a** is a well-behaved white crystalline solid (mp 102–104 °C) which has been prepared in 6–9-g quantities in a single experiment. Its structure is indicated from its analysis, mass spectrum, origin, and its unique NMR absorptions. The ^{13}C NMR spectrum of **4a** is particularly revealing in that a seven-line absorption is exhibited, one for the alicyclic and six for the aromatic carbons, interpretable only in terms of a symmetrical peri-substituted naphthalene. The structure of **4a** is confirmed upon its conversion by silver nitrate at 60 °C in aqueous dioxane to 1-naphthaldehyde (**28**, 26%) along with 1-(1*H*-cyclobuta[*de*]-naphthyl) nitrate (**4c**). Aldehyde **28** presumably results from generation and ring opening of 1-hydroxy-1*H*-cyclobuta[*de*]-naphthalene (**27**, eq 6). As has been published,[16] X-ray analysis

Table I. Ultraviolet Absorption Maxima of **4a**, **4d**, and Naphthalene ($C_{10}H_8$)

compd	λ_{max}^{EtOH}, nm (ε)			
4a	320 (570)	307 (730)	284 (4650)	225 (67 000)
4b	312 (341)	302 (512)	272 (4650)	224 (69 500)
$C_{10}H_8$[a]	312 (255)	298 (324)	276 (5550)	221 (115 000)

[a] Naphthalene.

reveals that in the solid-state **4a** is essentially planar, its peri-bridged moiety has typical four-membered ring angles and di-



27 28

(6)

mensions, its forward sections are relatively compressed, and major strain relief comes from bond lengthening and angle widening of its rear end. Presumably the strain in **27** is relieved upon ionization of its hydroxyl group, ring opening and protonation at C-8 to give **28**.

Reaction of **4a** with magnesium in ethyl ether and hydrolysis of the Grignard reagent **4c** formed results in 1*H*-cyclobuta[*de*]-naphthalene (**4d**, >60%), a colorless distillable liquid which can be gas chromatographed at temperatures of ~150 °C without serious loss. Hydrocarbon **4d** is assigned from its combustion analysis and its spectral and chemical properties. Consistent with the expectation that the ring systems are essentially planar are (1) the 90-MHz ^1H NMR spectra in carbon disulfide at 20–25 °C and at −110 °C reveal that the protons at C-1 do not give an A–B pattern but rather a sharp singlet broadened only by long range coupling to the aromatic hydrogens and (2) the proton-coupled ^{13}C NMR spectrum shows the C-1 signal to be a triplet, indicating coupling to magnetically equivalent protons. Indeed, recent X-ray analysis[17] shows crystalline **4d** at −80 °C to be flat and its structural features closely resemble those of **4a**.[16] Further, the UV absorption spectra of **4a** and **4d** are similar to that of naphthalene (Table I). The slight shifts to longer wavelengths and the significant decreases in the extinction coefficients of the E_1 bands do reveal that the π-electron systems of **4a** and **4d** are

(13) An alternate mechanistic possibility is intramolecular bromine atom abstraction by the carbenic center in **2a** as a triplet, spin inversion in the diradical intermediate, and then radical pairing to give **4a**.

(14) The interatomic distance between the hydrogen atoms at the C_1 and C_8 positions in naphthalene is 2.40 Å: Cruickshank, D. W. *Acta Crystallogr.* **1957**, *10*, 504.

(15) (a) Synthesis of arenes bridged in peri positions by single atom moieties other than those containing carbon are described in the following references. (b) Hoffman, R. W.; Seiber, W. *Justus Liebigs Ann. Chem.* **1967**, *703*, 96. (c) Meinwald, J.; Knapp, S. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (d) Yang, L. S.; Shechter, H. *J. Chem. Soc., Chem. Commun.* **1976**, 775.

(16) Gessner, M.; Card, P.; Shechter, H.; Christoph, G. *J. Am. Chem. Soc.* **1977**, *99*, 2371.

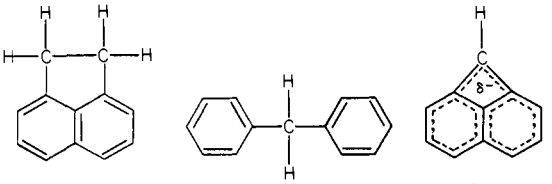
(17) Private communication: Gessner, M.; Christoph, G., Chemistry Department, The Ohio State University, Columbus, OH.

perturbed. The ^{13}C–H coupling constant of 143 Hz for C-1 in **4d** is also indicative of the (strained) four-membered ring moiety in the bridged hydrocarbon.

The carbanionic character of Grignard reagent **4c** is of interest with respect to the ability of the 1*H*-cyclobuta[*de*] naphthalene system to delocalize negative charge at C-1. The NMR spectrum of **4c** in tetrahydrofuran at 20–25 °C exhibits a singlet at δ 3.95 which corresponds to a 2.81 ppm upfield shift for the proton at C-1 as compared to that for **4c**.[4a] The hydrogens at C-2 and C-7 now resonate at δ 6.65, a net upfield shift of 0.53 ppm, whereas those at C-3 and C-4 are shifted ~0.4 ppm upfield. These observations are thus possibly indicative of slight ionic character of the carbon–magnesium bond in **4c** with some charge delocalization into the naphthalene nucleus.[18]

The acidity of **4d** at C-1 was then probed. Base-catalyzed deuterium exchange for the apical protons in **4d** to give 1-deuterio-1*H*-cyclobuta[*de*]naphthalene (**4f**) occurs only in the presence of very strong bases. Neither potassium *tert*-butoxide in *tert*-butyl alcohol-*d* nor sodium dimsylate in dimethyl-d_6 sulfoxide effects significant deprotonation of **4d** at ambient temperatures. Heating **4d** at 75 °C in sodium dimsylate/dimethyl-d_6 sulfoxide for 20 h results in only 32% mono exchange at C-1 in 20 h. Deprotonation of **4d** occurs efficiently, however, with *tert*-butyllithium at 20–25 °C to yield 1-(1*H*-cyclobuta[*de*]-naphthyl)lithium (**4e**). Thus, addition of *tert*-butyllithium to **4d** in tetrahydrofuran followed by deuterium oxide give **4f** containing 47% deuterium at C-1 which corresponds to 94% carbanion formation. These experiments thus reveal that **4d** is a weak acid.

Comparison was then made of the rates of deuterium exchange into the methylene hydrogens of **4d**, acenaphthene (**29**), and diphenylmethane (**30**) by heating solutions of the hydrocarbons

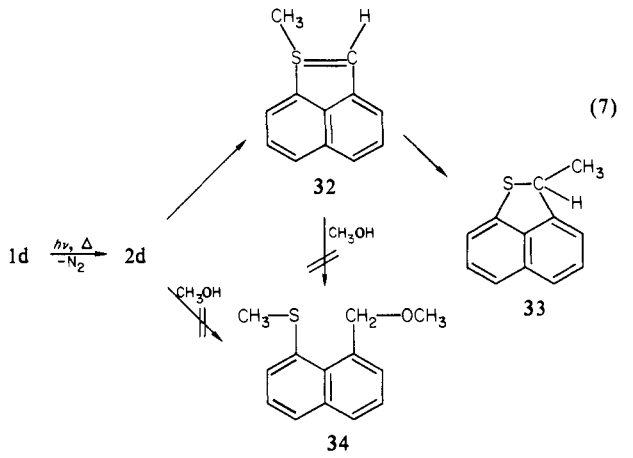


29 30 31

in sodium dimsylate/dimethyl-d_6 sulfoxide at 75 °C and monitoring the exchange by NMR methods. Deuterium incorporation into **4d** to give **4f** occurs relatively slowly. At 75 °C, deuterium exchange into **29** and **30** is faster than into **4d** by factors of at least 40 and 7200, respectively.[19] It is therefore apparent that a major factor in the resistance of **4d** to base lies in the inability of the naphthalene nucleus to delocalize developing negative charge at C-1 because of the molecular strain in a transition state having the character of **31**.[16] Further study of **4a** and **4d** will be summarized in subsequent publications.

Photolysis and Thermolysis of 1d. Study was then initiated of possible peri interaction of the thiomethyl group and the carbenic center of 8-(methylthio)-1-naphthylidene (**2d**). Photolysis (25 °C) and thermolysis (78 °C) of **1d** were thus found to result in nitrogen evolution and formation of 2-methyl-2*H*-naphtho[1,8-*cd*]thiophene (**33**, eq 7, >19%) along with oligomers.[20] Irradiation and thermal decomposition of the sodium salt of **15d** also gives **33** and the products of higher molecular weights.[20] Thiophene derivative **33** is a low melting air-sensitive solid which is assigned upon comparison of its spectral characteristics and physical properties (see Experimental Section) with literature values.[21]

Photolysis and thermolysis of **1d** and the sodium salt of **15d** are of interest in that nitrogen is last, and the carbene (**2d**) apparently formed reacts intramolecularly on sulfur (eq 7) to give

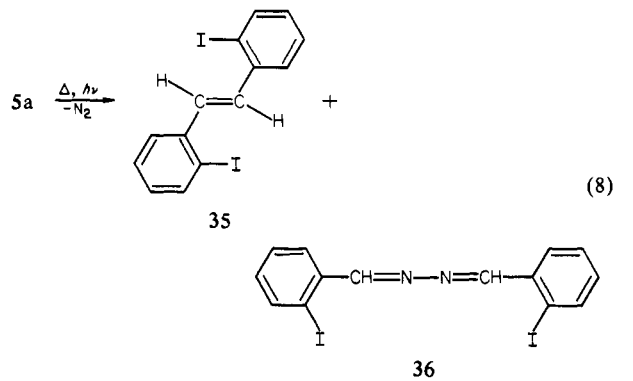


(7)

32 33 34

ylide **32** which undergoes thia-Stevens rearrangement[22] to **33**. Conversion of **32** to **33** is formally equivalent to methyl migration in 2-methyl-1-phenyl-2-thianaphthalene at 40 °C to yield 1-methyl-1-phenyl-2-thiochromene efficiently.[23] In the present system attempts to isolate **32** or effect its interception with methanol by conversion to methyl [8-(methylthio)-1-naphthyl]-methyl ether (**34**) were unsuccessful. Further, thermolysis of the sodium salt of **15d** in methanolic sodium methoxide leads to **33** rather than **32**. The various photolytic and thermal decomposition experiments for **1d** and the sodium salt of **15d** are thus noteworthy in that they imply rapid attack of the carbenic center of **2d** on sulfur at C-8 and subsequent methyl migration in **32** with great facility.

Thermolysis and Photolysis of 5a and 5b. Decomposition of **5a** and **5b** was then investigated in attempts to effect formation of intramolecular products of types **7** and **8** (eq 2). Thermolysis of **5a** in chlorobenzene at ~132 °C however yields *trans*-bis(*o*-iodophenyl)ethylene[24] (**35**, eq 8, 24%), *o*-iodobenzalazine (**36**,



(8)

35 36

17%), and amorphous products. Similar results are obtained upon photolysis of **5a** in ethyl ether at 20 °C. There was no evidence however for 7-iodobenzocyclopropene (**8a**; eq 2) or its recognizable derivatives. Further, ylide **7a** could not be detected as a discrete intermediate although a carbene representable as **6a** is apparently generated in the thermolyses and photolyses.

The behavior of *o*-(methylthio)benzylidene (**6b**) is more definable than that of **6a**. Thus, **5b** thermolyzes in refluxing chlorobenzene (~132 °C) to 4,5-dihydrobenzo[*b*]thiophene (**37**, eq 9, 40%) along with *trans*-bis[*o*-(methylthio)phenyl]ethylene (**38**, 22%) and *o*-(methylthio)benzalazine (**39**, 23%).[25] Further, photolysis of **5b** in ethyl ether results in selective insertion of **6b**

(18) (a) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 2328. (b) Ashby, E. C. *Q. Rev., Chem. Soc.* **1967**, *21*, 259. (c) Ashby, E. C. *Bull. Soc. Chim. Fr.* **1972**, 2133.

(19) The reactivity factors for **4d**, **29**, and **30** based on the relative rates of exchange for any single methylene hydrogen are thus 1:20:7200.

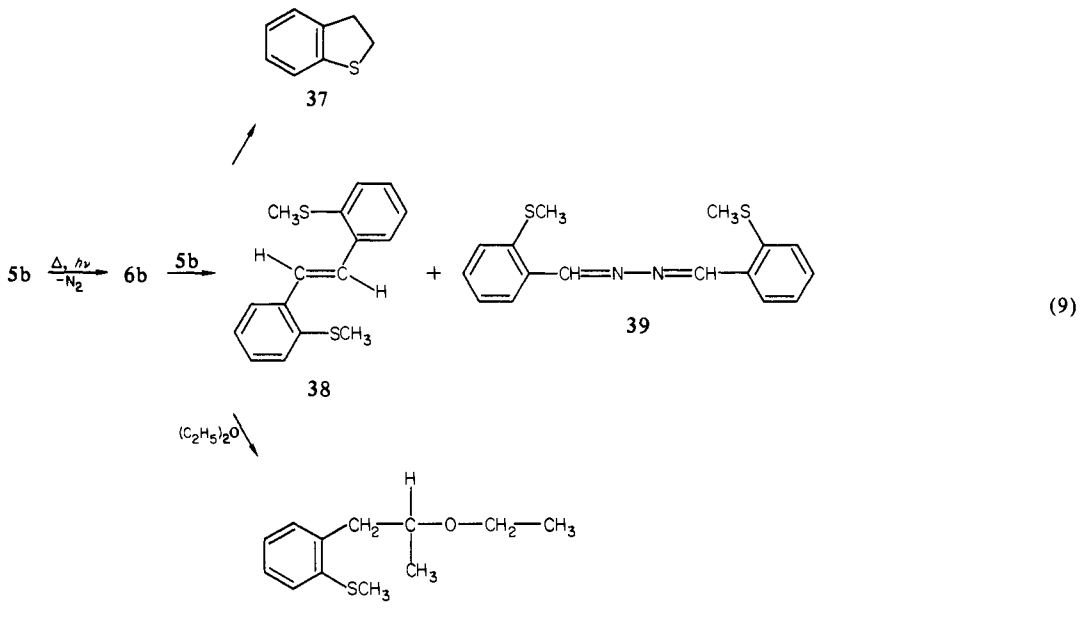
(20) The structures of these products were studied extensively without resolution. See Experimental Section.

(21) (a) Hawthorne, D. G.; Porter, Q. N. *Aust. J. Chem.* **1966**, *19*, 1909. (b) Hawthorne, D. G.; Porter, Q. N. *Ibid.* **1968**, *21*, 171.

(22) Olsen, A.; Currie, B. "The Chemistry of the Thiol Group", Part 2; Patai, S. Ed.; Wiley: New York, 1974; pp 561–566.

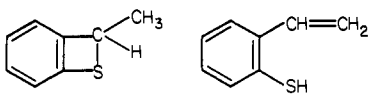
(23) Stackhouse, J.; Maryanoff, B. E.; Senkler, G. H.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 5650.

(24) The trans stereochemistry of **35** was assigned on the basis of IR absorption at 955 cm^{-1} and NMR absorption at δ 7.10.



(9)

into α-hydrogen of the solvent to form 2-(2-ethoxy-1-propyl)-thioanisole (**40**, 32%) along with **38** (56%) and **39** (6%).[25] Since neither ylide **7b** nor its isomerization products: 2-methylbenzothiete (**41**) and/or 2-vinylbenzenethiol (**42**)[3] nor derivatives thereof were found in these experiments, it cannot yet be concluded that there is bonding interaction of the methylthio moiety and the carbenic center in **6b**.



41 42

Study of possible generation of sulfur and halo ylides of type **7** is being continued.

Experimental Section

Anhydro-8-(hydroxymercuri)-1-naphthoic Acid (10).[26] 1,8-Naphthalic anhydride (99.1 g, 0.50 mol) was suspended in aqueous sodium hydroxide (70.2 g, 1.75 mol, in 3000 mL of water) and refluxed until the solid material dissolved. The excess base was neutralized with glacial acetic acid (50 mL), and a solution of mercuric acetate, prepared by dissolving mercuric oxide (110.1 g, 0.51 mol) in hot glacial acetic acid (250 mL) and diluting with water (500 mL), was added in one portion. After the mixture was refluxed 30 min, additional glacial acetic acid (90 mL) was added to the white slurry, resulting in slow evolution of carbon dioxide. The slurry was refluxed 48 h, cooled, and filtered. The highly insoluble solid was washed with water and then dried under vacuum at 105 °C overnight to give **10**, a tan storable powder: 184 g (~100%).

8-Bromo-1-naphthoic Acid (11).[27] Anhydro-8-(hydroxymercuri)-1-naphthoic acid (190.1 g, 0.514 mol) suspended in glacial acetic acid (750 mL) and water (120 mL) was stirred vigorously at 0 °C. Sodium bromide (341.0 g, 1.66 mol) in water (620 mL) and bromine (84.5 g, 29 mL, 0.53 mol) were added slowly while the reaction temperature was maintained at 0–5 °C. The resulting slurry was then slowly heated to 100 °C and poured on ice (1500 g). The precipitate was washed with water, dissolved in hot aqueous sodium hydroxide (120 g, 3 mol, in 250 mL of water), and filtered through Celite. When the filtrate was acidified with concentrated hydrochloric acid (250 mL) and cooled, acid **11** was obtained as white crystals: 85.6 g (67.4%); mp 174–175 °C (lit.[28] 174–175 °C). Extraction of the Celite with benzene (750 mL) and concentration of the extract yielded 1,8-dibromonaphthalene as yellow crystals:[26b] 11.4 g (8%); mp 106–109 °C (lit.[29] 109–110 °C).

(8-Bromo-1-naphthyl)methanol (12). A solution of naphthoic acid **11** (200.8 g, 0.8 mol) and thionyl chloride (992.0 g, 600 mL, 8.4 mol) was refluxed 6 h and concentrated under reduced pressure. Crystallization of the residue from hexane yielded 8-bromo-1-naphthoyl chloride: 180.0 g (86%); mp 66–68 °C.[30]

8-Bromo-1-naphthoyl chloride (160.0 g, 0.61 mol) in ethyl ether (500 mL) was added to lithium aluminum hydride (17.5 g, 0.46 mol) suspended in ethyl ether (500 mL). After addition was complete, the mixture was refluxed 5 h, cooled, and hydrolyzed with saturated aqueous sodium sulfate. When the ether layer was dried ($MgSO_4$) and concentrated at reduced pressure, the residue obtained yielded **12** as a pale yellow solid: 130 g (88%); mp 86–87 °C.[31] Anal. Calcd for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 55.78; H, 3.85.

8-Bromo-1-naphthaldehyde (13). A. Dimethyl sulfide (37.2 g, 45 mL, 0.6 mol) was added to *N*-chlorosuccinimide (80.0 g, 0.6 mol) suspended in toluene (2000 mL) at 0 °C. When the mixture was cooled to −25 °C, alcohol **12** (70.8 g, 0.3 mol) dissolved in toluene (700 mL) was introduced slowly and the solution was stirred for 2.5 h at −25 °C. After addition of triethylamine (45.0 g, 50 mL, 0.45 mol), the mixture was warmed to ~25 °C overnight, filtered, concentrated, poured into ether, and filtered. The ether solution was extracted with 1 N hydrochloric acid, saturated sodium bicarbonate and sodium chloride, dried ($MgSO_4$), and vacuum concentrated. Crystallization led to **13** as a slight yellow solid: 63.0 g (85%); mp 89–90 °C;[31] IR (mull, cm^{-1}) 1660 (aldehyde C=O), 1600, 1550, 1490, 826, 792, 750 (aromatic); NMR ($CDCl_3$, δ) 7.12–8.02 (m, 6 H, aromatic), 11.32 (s, 1 H, CHO); mass spectrum, *m/e* 234.236 (M^+).

B. Chlorox (200 mL of a 5.25% aqueous solution of sodium hypochlorite) was added to (8-bromo-1-naphthyl)methanol (9.5 g, 40 mmol) in ethyl acetate (200 mL). After introduction of benzyltriethylammonium chloride (1 g) for phase transfer, the mixture was stirred vigorously for 30 h and pentane was added. The organic layer was washed with water, dried, and concentrated. Crystallization yielded **13** (7.6 g, 81%) identical with a previous sample.

8-Bromo-1-naphthaldehyde *p*-Tosylhydrazone (15a). *p*-Tosylhydrazide (1.9 g, 10.2 mmol) was added to a solution of **13** (2.34 g, 10 mmol) in 95% ethanol (15 mL), and the mixture was warmed. After addition of concentrated hydrochloric acid (3 drops), the solution was cooled to ~25 °C to effect crystallization. Recrystallization of the solid

(25) The products of thermolysis and photolysis of 2-(*n*-butylthio)-4-nitrophenyldiazomethane and 2-(*sec*-butylthio)-4-nitrophenyldiazomethane are corresponding stilbenes and sulfones. Insertion processes corresponding to conversion of **6b** to **37** were not observed. Garner, G. V.; Mobbs, D. B.; Suschitzky, H.; Millership, J. S. *J. Chem. Soc.* **1971**, 3693.

(26) (a) The present procedure is a modification[26b] of that of: Leuck, G. J.; Perkins, R. P.; Whitmore, F. C. *J. Am. Chem. Soc.* **1929**, *51*, 1831. See also: Newman, M. S.; Vander Zwan, M. C. *J. Org. Chem.* **1972**, *38*, 319. (b) Private communication: Engler, T. A., The Ohio State University, Columbus, Ohio. (c) Mercuric acetate (CP) is a little more reliable but considerably more expensive than commercial mercuric oxide for the above mercuration.

(27) An improved and more complete modification[26b] of the procedure of: Corbellini, A.; Fossati, V. *Rend. R. Ist. Lomb. Sci. Lett.* **1936**, *69*, [2], 264, 265.

(28) Rule, H. G.; Pursell, W.; Brown, R. R. H. *J. Chem. Soc.* **1934**, 168.

(29) (a) Fieser, L. F.; Seligman, A. M. *J. Am. Chem. Soc.* **1939**, *61*, 139. (b) Yields of 1,8-dibromonaphthalene as high as 16% have been obtained in these brominations.

(30) Identical with an authentic sample.

(31) The product reported is of proper IR, NMR, and mass spectra.

from 95% ethanol yielded **15a**: 3.78 g (94%); mp 193–195 °C (with decomposition).[31] Anal. Calcd for $C_{18}H_{15}BrN_2O_2S$: C, 53.61; H, 3.75. Found: C, 53.52; H, 3.65.

8-Iodo-1-naphthoic Acid. Iodine (44.5 g, 0.175 mol) was added to **10** (63.0 g, 0.17 mol) dissolved in aqueous potassium iodide (120 g, 0.72 mol in 600 mL of water). The mixture was refluxed 15 h, cooled, and filtered. Sodium thiosulfate (20 g, 0.13 mol) in water (100 mL) was then added, and the solution was acidified with hydrochloric acid. The crude product was filtered, dissolved in hot acetone, decolorized with charcoal, concentrated, and crystallized from chloroform to give 8-iodo-1-naphthoic acid: 41.5 g (82%), mp 163.5–164.5 °C (lit.[27,31] 164–165 °C).

(8-Iodo-1-naphthyl)methanol. Methyl 8-iodo-1-naphthoate was prepared (98.5%) by esterification of 8-iodo-1-naphthoic acid in methanol with diazomethane (as generated from *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide) in ethyl ether at 0 °C: mp 59–60 °C (lit.[32] 59 °C).

Diisobutylaluminum hydride solution (60.0 g, 0.105 mol as a 25% solution in hexane) was added dropwise to methyl 8-iodo-1-naphthoate (15.6 g, 0.05 mol) in ethyl ether (200 mL) at −50 °C. After the mixture had been stirred 30 min at −40 °C, 50% aqueous methanol (20 mL) was added dropwise, the mixture was warmed to ~25 °C, and 3 N hydrochloric acid was added until the aluminum salts dissolved. On workup of the ether layer and recrystallization of the product from carbon tetrachloride, (8-iodo-1-naphthyl)methanol was obtained: 13.5 g (95%); mp 85.5–87 °C.[31] Anal. Calcd for $C_{11}H_9IO$: C, 46.51; H, 3.19. Found: C, 46.24; H, 3.02.

8-Iodo-1-naphthaldehyde. 8-Iodo-1-naphthaldehyde (1.40 g, 62%; mp 73–74 °C)[31] was prepared by oxidation of (8-iodo-1-naphthyl)methanol (2.27 g, 8 mmol) with *N*-chlorosuccinimide (1.6 g, 12 mmol), dimethyl sulfide (1 g, 1.2 mL, 16 mmol), triethylamine (1.2 g, 1.7 mL, 12 mmol), and toluene (100 mL) at −20 °C. Reaction of 8-iodo-1-naphthaldehyde with semicarbazide hydrochloride and sodium acetate in refluxing ethanol/water gave 8-iodo-1-naphthaldehyde semicarbazone (70%), mp 231–233 °C (with decomp).[31] Anal. Calcd for $C_{12}H_{10}IN_3O$: C, 42.50; H, 2.97; N, 12.39; I, 37.42. Found: C, 42.64; H, 2.93; N, 12.30; I, 37.59.

8-Iodo-1-naphthaldehyde *p*-Tosylhydrazone (15b). 8-Iodo-1-naphthaldehyde (2.82 g, 10 mmol) and *p*-tosylhydrazide (1.95 g, 10.5 mmol) in warm 95% ethanol (30 mL) and concentrated hydrochloric acid (3 drops) yielded **15b**: 4.35 g (95%); mp (from 95% ethanol) 197.5–198 °C.[31] Anal. Calcd for $C_{18}H_{15}IN_2O_2S$: C, 48.01; H, 3.36; I, 28.18. Found: C, 47.91; H, 3.27; I, 28.30.

(8-Iodo-1-naphthyl)diazomethane (1b). Sodium hydride (0.10 g as a 57% slurry in mineral oil) was added to **15b** (0.45 g, 1 mmol) in dichloromethane (15 mL). The slurry was stirred until hydrogen was no longer evolved, protected from light, warmed, filtered, and vacuum evaporated to give **1b**, a dark red oil: 0.20 g (68%); IR (neat, cm^{-1}) 2070 (C=N_2), 1550, 1450, 1250, 815, 788, 753 (aromatic); NMR (CCl_4, δ) 6.65 (s, 1 H, CH=N_2), 6.72–8.20 (m, 6 H, aromatic).

5,8-Dichloro-1-naphthoic Acid. Chlorine was bubbled into a slurry of anhydro-8-(hydroxymercuri)-1-naphthoic acid (37 g, 0.1 mol) in glacial acetic acid until the solid dissolved. The solution was filtered and concentrated under vacuum. Crystallization of the residue from aqueous ethanol and then benzene yielded 5,8-dichloro-1-naphthoic acid: 8.5 g, 27%; mp 188–190 °C (lit.[31,33] 190.3–191 °C).

Methyl 5,8-Dichloro-1-naphthoate. Methyl 5,8-dichloro-1-naphthoate was prepared by addition of diazomethane in ethyl ether to 5,8-dichloro-1-naphthoic acid in methanol/ethyl ether at −78 to 0 °C: 79%; mp 73–75 °C.[31] Anal. Calcd for $C_{12}H_8Cl_2O_2$: C, 56.50; H, 3.16. Found: C, 56.82; H, 3.20.

(5,8-Dichloro-1-naphthyl)methanol. Reduction of methyl 5,8-dichloro-1-naphthoate with diisobutylaluminum hydride in ethyl ether at −20 °C (as for 8-iodo-1-naphthyl alcohol) yielded (5,8-dichloro-1-naphthyl)methanol: 5.8 g (95%); mp 132–133 °C.[31] Anal. Calcd for $C_{11}H_8Cl_2O$: C, 58.18; H, 3.55. Found: C, 58.08; H, 3.60.

5,8-Dichloro-1-naphthaldehyde. Oxidation of 5,8-dichloro-1-naphthyl alcohol in toluene with *N*-chlorosuccinimide/dimethyl sulfide/triethylamine at −20 °C (as for 8-iodo-1-naphthyl alcohol) gave 5,8-dichloro-1-naphthaldehyde (78%), mp 139–140 °C (from methanol at −20 °C) (lit.[34] 139–140 °C), oxime mp 207–210 °C (lit.[34] 199–200 °C).

5,8-Dichloro-1-naphthaldehyde *p*-Tosylhydrazone (15c). Refluxing 5,8-dichloro-1-naphthaldehyde and *p*-tosylhydrazide in 95% ethanol containing hydrochloric acid led to **15c** (97%), mp 200–202 °C (with decomp).[31] Anal. Calcd for $C_{18}H_{14}Cl_2N_2O_2S$: C, 54.97; H, 3.59. Found: C, 54.87; H, 3.50.

(5,8-Dichloro-1-naphthyl)diazomethane (1c). Tosylhydrazone **15c** (2.0 g, 5 mmol) and sodium methoxide (1.0 g, 17.5 mmol) in methanol (35 mL) was refluxed 1 h. The resulting dark red solution was poured onto ice and extracted with pentane. The pentane extracts were washed with water and saturated brine and vacuum evaporated to give **1c**, an unstable red oil: 880 mg (74%); IR (mull, cm^{-1}) 2060 (diazo), 1580, 1560, 1375, 1280, 820, 740 (aromatic); NMR ($CDCl_3$, δ) 6.57 (s, 1 H, CH=N_2), 6.81–8.21 (m, 5 H, aromatic).

Thermolysis of the Sodium Salt of 15a. Sodium hydride (135 mg, 3.3 mmol as a 57% dispersion in mineral oil) was washed with hexane and added in portions to **15a** (1.2 g, 3 mmol) slurried in dichloromethane (20 mL). When the mixture was evaporated to dryness, chlorobenzene (20 mL) was added and the solution was heated to 120 °C for 0.5 h. The reaction mixture, upon filtration and cooling, gave 9-bromo-3*H*-benz[*e*]indazole (**18a**): 370 mg (50%); mp 231–232 °C; IR (mull, cm^{-1}) 1610, 1600, 1530, 945, 855, 815, 760 (aromatic); NMR ($CDCl_3$/Me_2SO-d_6, δ), 7.15–8.10 (m, 6 H, aromatic), 9.21 (s, 1 H, CH=N) 13.8 (br s, exch, 1 H, NH); mass spectrum, *m/e*(calcd) 245.9793, *m/e*(obsd) 245.9797, difference 2 ppm. Anal. Calcd for $C_{11}H_7BrN_2$: C, 53.47; H, 2.86; Br, 32.34; N, 11.34. Found: C, 53.29; H, 2.68; Br, 32.42; N, 11.22.

TLC analysis of the crude reaction mixture using hexane, chloroform, and ethyl ether showed no other mobile products.

Thermolysis of 1b. A solution of **1b** (0.15 g, 0.51 mmol) in chlorobenzene (5 mL) was refluxed for 0.5 h. The mixture on cooling deposited a solid which recrystallized from chlorobenzene to give 9-iodo-3*H*-benz[*e*]indazole (**18b**): 80 mg (53%); mp 217–218 °C; mass spectrum, *m/e* 294; osm mol wt 308 in dimethylformamide; IR (KBr, cm^{-1}) 1610, 1540, 945, 868, 822, 762 (aromatic); NMR ($CDCl_3$/Me_2SO-d_6, δ) 7.22–8.34 (m, 5 H, aromatic), 9.55 (s, 1 H, CH=N) 13.8 (br s, exch, 1 H, NH); UV max (95% EtOH) 334 (ϵ 2520), 283 (9000), 247 (40 500), 207 nm (24 400). Anal. Calcd for $C_{11}H_7IN_2$: C, 44.92; H, 2.34; I, 43.15; N, 9.53. Found: C, 44.65; H, 2.46; I, 43.07; N, 9.65.

Thermolysis of the Sodium Salt of 15b. Chlorobenzene (15 mL) was added to a mixture derived from **15b** (3.0 g, 6.7 mmol), sodium hydride (1.0 g as a 57% slurry in mineral oil, washed with hexane), dichloromethane (10 mL), and chlorobenzene (10 mL). The pale yellow solution was refluxed 0.5 h, filtered through diatomaceous earth, cooled, and filtered. The product, on recrystallization from chlorobenzene, yielded **18b**, 1.02 g (52%), mp 217–218 °C, identical with that previously characterized.

Reduction of 18b and 18a to 3*H*-Benz[*e*]indazole (21). A slurry of **18b** (100 mg, 0.34 mmol) and lithium aluminum hydride (200 mg, 5.2 mmol) in ethyl ether (30 mL) was stirred 4 days at room temperature. After sufficient 6 N hydrochloric acid had been added to dissolve the inorganic salts, the aqueous layer was extracted with ethyl ether. The aqueous layer was neutralized with sodium hydroxide and extracted further with ethyl ether. The ether extracts were washed with water and saturated sodium chloride, dried, and concentrated. Recrystallization of the residue resulted in **21**, 60 mg (97%), mp 234–235 °C, identical with a sample prepared by the method of ref 10: IR (KBr, cm^{-1}) 3250–2700 (several, NH, aromatic CH), 1650 (hetero C=N), 1600, 1540, 945, 860, 815, 780, 750 (aromatic); NMR ($CDCl_3$/Me_2SO-d_6, δ) 7.40–8.40 (m, 6 H, aromatic), 8.48 (s, 1 H, CH=N), 13.18 (br, s, exch, 1 H, NH); UV max (95% EtOH) 328 (ϵ 2280), 287 (8650), 242 (27 000), 230 nm (33 200); mass spectrum, *m/e*(calcd) 168.0687, *m/e*(obsd) 168.9690, difference 1.9 ppm. Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.65. Found: C, 78.37; H, 4.80; N, 16.52.

In a similar experiment **18a** was reduced by lithium aluminum hydride to **21** identical with that obtained above.

Conversion of *N*-(1-Methyl-2-naphthyl)-*N*-nitrosoacetamide (19) to 21. Nitrosoamide **19** (0.98 g) was prepared according to the procedure of ref 10. A solution of **19** in benzene (20 mL) was then warmed to 50 °C for 2 h. The crude product, on filtration and recrystallization from ethanol, was identified as **21**, 0.6 g (76%); mp 234–235 °C (lit.[10] 234–235 °C), identical with the previous samples. The structure **21** was clearly indicated from its spectral properties.[31]

Thermolysis of 1c. Heating **1c** (880 mg, 3.7 mmol) in chlorobenzene (20 mL) at 120 °C for 0.5 h, cooling the mixture, and recrystallization of the precipitate from chlorobenzene yielded 6,9-dichloro-3*H*-benz[*e*]-indazole (**18c**): 400 mg (45%); mp 266–267 °C; IR (KBr, cm^{-1}) 1610, 1590, 1490, 1100, 1090, 1030, 950, 850, 832, 803 (aromatic); NMR ($CDCl_3$/Me_2SO-d_6, δ) 7.51–8.26 (m, 5 H, aromatic), 9.00 (s, 1 H, CH=N) 13.6 (br s, exch, 1 H, NH); mass spectrum, *m/e*(calcd) 235.9908, *m/e*(obsd) 235.9911, difference 1.5 ppm. Anal. Calcd for $C_{11}H_6Cl_2N_2$: C, 55.73; H, 2.55. Found: C, 55.80; H, 2.62.

The filtrate was evaporated to dryness and the residue purified by column chromatography on silica gel using hexane/chloroform (80/20, v/v) as eluent. The only isolable product was *trans*-bis(5,8-dichloro-1-naphthyl)ethylene (**22a**): 115 mg (15%); mp 232–234 °C from ethanol; IR (KBr, cm^{-1}) 1590, 1500, 1395, 1350, 1180, 1100, 1050, 935, 820, 810, 755 (aromatic), 970 (trans C=C); NMR ($CDCl_3$, δ) 6.85–8.24 (m); mass spectrum for $C_{22}H_{12}{}^{35}Cl_4$, *m/e* 416 (M^+), 381 ($M^+ - {}^{35}Cl$), 346

(32) Goldstein, H.; Francey, P. *Helv. Chim. Acta* **1932**, *15*, 1362.
(33) Koptyug, V. A.; Komagorov, A. M.; Chzhu, V. P.; Petrov, V. P. *Zh. Org. Khim.* **1966**, *2*, 465.
(34) Price, C. C.; Vooh, S. T. *J. Org. Chem.* **1949**, *14*, 111.

($M^+ - {}^{35}Cl_2$), 311 ($M^+ - {}^{35}Cl_3$), 276 ($M^+ - {}^{35}Cl_4$); exact mass, *m/e*(calcd) 415.9693, *m/e*(obsd) 415.9700, difference 1.7 ppm.

1-Naphthaldehyde *p*-Tosylhydrazone (15e). Cooling a refluxing mixture of 1-naphthaldehyde (4.5 g, 30 mmol) and *p*-tosylhydrazide (5.6 g, 30 mmol) in methanol (25 mL) yielded **15e**, 8.8 g (85%), mp 130–132 °C, with decomposition.[31] Anal. Calcd for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97. Found: C, 66.49; H, 5.03.

1-Naphthyldiazomethane (1e). A mixture of **15e** (6.6 g, 24 mmol), sodium methoxide (2.0 g, 38 mmol) and methanol (20 mL) was refluxed (20 min), poured on ice, and extracted with pentane. The pentane extract was washed with water and saturated sodium chloride solution, dried, and concentrated to **1e**, 2.8 g (82%), an unstable reddish pink solid: IR (neat, cm^{-1}) 2100 (C=N_2), 1580, 1510, 1410, 790, 760 (aromatic).

Thermolysis of 1e in Benzene. A mixture of **1e** (1.0 g, 6 mmol) and benzene (85 mL) was refluxed until the pink color was discharged. The benzene was removed under reduced pressure and the residue separated by column chromatography on silica gel using petroleum ether as eluent. Three main fractions were as follows: (1) 7-(1-Naphthyl)cycloheptatriene (**24**): 330 mg (25%); NMR (CCl_4, δ) 3.35 (br t, 1 H, H at C_7), 5.41 (br d of d, 2 H, H at $C_{3,4}$), 5.92–6.31 (m, 2 H, H at $C_{2,5}$), 6.60 (t, 2 H, H at $C_{1,6}$), 6.5–8.0 (m, 7 H, aromatic). Attempted purification by vapor phase chromatography (10 ft × $^1/_4$ in 12.5% QF-1 on Chromosorb W, isothermal at 200 °C) resulted in rearrangement to 1-(1-naphthyl)cycloheptatriene (**25**): IR (near, cm^{-1}) 3100–2900 (several, aromatic, aliphatic, vinylic CH), 1600, 1500, 1010, 800, 750, 720 (aromatic); NMR (CCl_4, δ) 2.38–2.92 (m, 2 H, H at C_7), 5.10–5.61 (m, 1 H, H at C_2), 6.50–6.75 (m, 2 H, H at $C_{4,5}$), 6.50–6.75 (m, 2 H, H at $C_{3,6}$), 7.04–8.00 (m, 7 H, aromatic); mass spectrum, *m/e*(calcd) 218.1095, *m/e*(obsd) 218.1098, difference 1.5 ppm. Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.35; H, 6.60. (2) *trans*-Bis(1-naphthyl)ethylene (**22b**): 350 mg (42%); mp 161–162 °C (lit.[35b] 161 °C, 163–164 °C). (3) 1-Naphthalazine (**26**): 200 mg (22%); mp 156–157 °C from ethanol, identical with a sample prepared from 1-naphthaldehyde and hydrazine. Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23. Found: C, 85.45; H, 5.22.

1-Bromo-1*H*-cyclobuta[*de*]naphthalene (4a).[36] Sodium hydride (4.60 g in mineral oil, 0.1 mol) was washed with pentane, slurried in dry dichloromethane (700 mL), and cooled to 0 °C, and then **15a** (40.2 g, 0.1 mol) was added very slowly. Stirring was continued for 15 min after hydrogen evolution ceased. The resulting yellow solution was evaporated to dryness. The sodium 8-bromo-1-naphthaldehyde *p*-tosylhydrazonate was slurried in ethyl ether (2300 mL) and irradiated for 16 h with a 450-W Hanovia 679A36 high-pressure mercury arc lamp under nitrogen. The mixture was filtered and the solvent removed under reduced pressure. The residue was absorbed onto silica gel (300 g) and column chromatography using hexane as eluent gave the following: (1) 1-Bromo-1*H*-cyclobuta[*de*]naphthalene (**4a**): 9.3 g (43%), recrystallized from ethanol; mp 102–104 °C; IR (KBr, cm^{-1}) 1600, 1460, 1145, 980, 820, 785, 775, 680 (aromatic), 475 (C-Br); NMR ($CDCl_3$, δ) 6.76 (s, 1 H, H at C_1), 7.18 (d of d, 2 H, J = 5 and 2 Hz, H at $C_{2,7}$), 7.30–7.68 (m, 4 H, H at C_{3-6}); ^{13}C NMR ($CDCl_3$, δ) 51.9 (1 C, C_1), 115.8 (2 C, $C_{2,7}$), 122.9 (2 C, $C_{4,5}$), 126.3 (1 C, C_9), 131.4 (2 C, $C_{3,6}$), 143.6 (2 C, $C_{1a,7a}$), 145.1 (1 C, C_8); mass spectrum, *m/e* 218, 220 (M^+), 139 (M^+ – Br); osm mol wt ($CHCl_3$) 215. Anal. Calcd for $C_{11}H_7Br$: C, 60.13; H, 3.22. Found: C, 60.03; H, 3.09. (2) *trans*-Bis(8-bromo-1-naphthyl)ethylene (**22c**): 4.3 g (10%), recrystallized from chloroform; mp 203–204 °C; IR (KBr, cm^{-1}) 910, 820, 810, 760, 710, 680 (aromatic); NMR ($CDCl_3$, δ) 6.00–8.00 (m); mass spectrum for $C_{22}H_{14}Br_2$, *m/e*(calcd) 435.9463, *m/e*(obsd) 435.9469, difference 1.5 ppm.

Reaction of 4a with Aqueous Silver Nitrate. Silver nitrate (170 mg, 1 mmol) in water (6 mL) was added to **4a** (218 mg, 1.0 mmol) in dioxane. The mixture was protected from light and stirred 20 h at 60 °C. The mixture was filtered, poured onto ice (25 g), and extracted with ethyl ether. The ether extracts were washed with water, dried, concentrated, and chromatographed on silica gel using 80/20 petroleum ether/chloroform as eluent to give the following: (1) A mixture of **4a** and 1-(1*H*-cyclobuta[*de*]naphthyl) nitrate (**4b**): mass spectrum, *m/e* 201 (M^+); IR (KBr, cm^{-1}) 1640, 1275 (nitrate ester), 855 (aromatic). (2) 1-Naphthaldehyde (**28**): 40 mg (26%), identical with an authentic sample. All attempts to isolate 1-hydroxy-1*H*-cyclobuta[*de*]naphthalene (**27**) were unsuccessful.

1*H*-Cyclobuta[*de*]naphthalene (4d). The Grignard reagent prepared by refluxing **4a** (218 mg, 1 mmol) and magnesium (40 mg) in ethyl ether for 18 h was hydrolyzed with ammonium chloride solution. The ether extract was washed with 1 N hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using petroleum ether (bp 30–60 °C) as eluent. Preparative GPC (10 ft × $^1/_4$ in of 12.5% QF-1 on Chromosorb W, isothermal at 135 °C) of the product yielded **4d**: 87 mg (67%); IR (neat, cm^{-1}) 3030, 1470, 1000, 795, 765 (aromatic) 2960, 1340 (aliphatic CH); NMR ($CDCl_3$, δ) 4.80 (s, 2 H, H at C_1), 7.1 (d of d, 2 H, J = 5 and 2 Hz, H at $C_{2,7}$), 7.25–7.65 (m, 4 H, H at $C_{3,6}$); ^{13}C NMR ($CDCl_3$, δ) 47.3 (1 C, C_1, $J_{^{13}C-H}$ = 143.4 Hz), 117.1 (2 C, $C_{2,7}$), 121.3 (2 C, $C_{4,5}$), 125.4 (1 C, C_9), 130.6 (2 C, $C_{3,6}$), 141.6 (2 C, $C_{1a,7a}$), 146.3 (1 C, C_8); mass spectrum, *m/e*(calcd) 140.0626, *m/e*(obsd) 140.0628, difference 1.4 ppm. Anal. Calcd for $C_{11}H_8$: C, 94.25; H, 5.75. Found: C, 94.19; H, 5.78.

NMR Spectrum of 4d. A sample of **4d** (35 mg, 0.25 mmol; purified by VPC) dissolved in anhydrous carbon disulfide containing 1% tetramethylsilane was sealed in a NMR tube under vacuum. The NMR spectrum at ambient temperature exhibited the characteristic bridge singlet at δ 4.8. The probe was cooled to −100 °C. The low-temperature spectrum also exhibited a singlet at δ 4.8 with no evidence for an AB quartet, 7.1 (d of d, 2 H, ortho), and 7.25–7.65 (m, 4 H, meta and para).

NMR Spectrum of 4c. Bromide **4a** (219 mg, 1 mmol) in anhydrous tetrahydrofuran-d_8 was added to sublimed magnesium (25 mg, 1 mmol), and the mixture was refluxed for 2 h. After the solution was cooled to room temperature, an aliquot (0.5 mL) was sealed in a dry NMR tube under reduced pressure. The NMR spectrum at ambient temperature exhibited absorptions at δ 3.95 (s, 1 H, bridge proton), 6.65 (m, 2 H, ortho) and 7.0 (m, 4 H, meta and para).

Attempted Exchange of 4d with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol-*d* and with Sodium Dimsylate-d_5 in Dimethyl-d_6 Sulfoxide, Respectively. (a) A mixture of **4d** (35 mg, 0.25 mmol) in *tert*-butyl alcohol-*d* (0.6 mL) containing a small amount of sublimed potassium *tert*-butoxide was tumbled in a NMR tube for 12 h after which NMR analysis revealed that no exchange had occurred. Additional potassium *tert*-butoxide was added and the solution tumbled for 10 h. There was still no change in the NMR spectrum of the initial **4d**. (b) Sodium dimsylate-d_5 in dimethyl-d_6 sulfoxide (prepared by heating sodium hydride in excess dimethyl sulfoxide-d_6 at ~80 °C) was added to **4d** in dimethyl sulfoxide-d_6, and the mixture was tumbled for 24 h. No exchange was detectable by NMR methods.

Reaction of 4d with *tert*-Butyllithium in Tetrahydrofuran. *tert*-Butyllithium (1.6 mmol) in hexane was added to **4d** (52.5 mg, 0.375 mmol) in tetrahydrofuran (5 mL) at room temperature. The mixture was stirred 1 h and quenched with deuterium oxide. The hydrocarbon product isolated (40 mg, 76%) was a 94:6 mixture of 1-deuterio-1*H*-cyclobuta-[*de*]naphthalene (**4f**) and **4d** (NMR analysis).

Relative Rates of Deuterium Exchange into 4d, Acenaphthene (29), and Diphenylmethane (30). Solutions of **4d**, **29**, and **30**, respectively, in dimethyl-d_6 sulfoxide (~0.6 M) containing sodium dimsylate-d_5 (0.08 M) were heated to 75 °C. Deuterium exchange into each hydrocarbon sampled was monitored by NMR. The exact masses of the deuterated products were checked by MS methods. The percentage deuterium incorporated into the hydrocarbons as a function of time is as follows: (1) **4d**, 32% (20 h), 46% (40 h), 88% (13 days), 92%, (32 days); (2) **29**, 46.5% (0.5 h), 84% (1.5 h), 96.5% (20 h); (3) **30**, 89% (2 min), 95% (0.5 h). When the sodium dimsylate is added to a solution of fluorene in dimethyl-d_6 sulfoxide, the mixture turns deep red instantly and NMR reveals that 100% exchange of the methylene hydrogens of fluorene occurs.

8-(Methylthio)-1-naphthaldehyde (14). A mixture of **13** (350 mg, 1.5 mmol) and cuprous methylmercaptide (160 mg, 1.5 mmol) was heated at 160 °C under argon for 2 h, poured into water (30 mL), and extracted with ethyl ether. After workup, the product was chromatographed on silica gel using 80/20 hexane/ether as eluent and recrystallized from hexane at −20 °C to give **14**: 220 mg (72%); mp 43–44 °C; IR (KBr, cm^{-1}) 1680 (aldehyde C=O), 1610, 1510, 835, 800, 760 (aromatic); NMR ($CDCl_3$, δ) 2.30 (s, 3 H, SCH_3), 7.20–7.82 (m, 6 H, aromatic), 11.10 (s, 1 H, CHO); mass spectrum for $C_{12}H_{10}OS$, *m/e*(calcd) 202.0446, *m/e*(obsd) 202.0449, difference 1.5 ppm.

8-(Methylthio)-1-naphthaldehyde *p*-Tosylhydrazone (15d). *p*-Tosylhydrazide and **14** in solution in refluxing methanol and hydrochloric acid (cat) yielded **15d** (87%),[31] mp 148–150 °C. Anal. Calcd for $C_{19}H_{18}N_2O_2S_2$: C, 61.60; H, 4.90. Found: C, 61.51; H, 4.96.

[8-(Methylthio)-1-naphthyl]diazomethane (1d). Reaction of **15d** (as for preparation of **1b**) with sodium methoxide in refluxing methanol for 2 h and product isolation yielded **1d** (39%) as an unstable red oil: IR (neat, cm^{-1}) 2060 (C=N_2).

Thermolysis of the Sodium Salt of 15d. Thermal and Photolytic Decomposition of 1d. A. Excess sodium hydride was added to **15d** (2.0 g, 5.5 mmol) in dichloromethane (30 mL), the mixture was filtered, the solvent was vacuum evaporated, and the residue was slurried in benzene

(35) (a) Elbs, K. *J. Prakt. Chem.* **1893**, *47*, 44. (b) Hahn, W. E.; Zimnicki, J. *Rocz. Chem.* **1969**, *43*, 95.

(36) Essentially identical results are obtained upon photolysis of **1a** in ethyl ether. Photolysis of the sodium salt of **15a** is much less laborious however than photolysis of **1a**.

and refluxed 1 h. The mixture was filtered and chromatographed on silica gel with 90/10 petroleum ether/chloroform as three main fractions: (1) A light yellow oil which was purified by repeated preparative gas chromatography (5 ft × 1/4 in. of 12.5% SE-30 on Chromosorb W, 230 °C) and identified as 2-methyl-2*H*-naphtho[1,8-*cd*]thiophene ($C_{12}H_{10}S$, **33**), an air- and light-sensitive, colorless to pale yellow oil, ~200 mg (19%). A considerable portion of the **33** decomposed during the gas chromatography: IR (neat, cm^{-1}) 3030, 2990, 2920 (aromatic, aliphatic CH), 1575, 1485, 815, 795, 770 (aromatic); NMR ($CDCl_3$, δ, sealed under argon) 1.73 (d, 3.1 H, J = 7 Hz, ($CHCH_3$), 5.23 (q, 1 H, J = 7 Hz, $SCHCH_3$), 7.2–7.6 (m, 6.6 H, aromatic). Irradiation of the doublet at δ 1.73 causes the quartet at δ 5.23 to collapse to a singlet; mass spectrum, m/e 186 (M^+), 171 ($M^+ - CH_3$); exact mass, m/e(calcd) 186.0503, m/e(obsd) 186.0506, difference 1.6 ppm. (2) Several fractions of a partially oxidized amorphous red-brown material of unassigned structure, corresponding to two units of $C_{12}H_{10}S$ plus an atom of oxygen,[37] yield approximately 250 mg; IR (KBr, cm^{-1}) 1575, 1490, 822, 796, 765 (aromatic); NMR ($CDCl_3$, δ) 0.9 (br s), 1.22 (br s), 1.94 (br m), 2.23 (br s), 5.32–6.01 (br m), 6.32–7.60 (br m); mass spectrum, m/e 171 $(C_{11}H_7S)^+$, 185 $(C_{12}H_9S)^+$, 201 $(C_{12}H_9SO)^+$, several minor peaks at higher m/e. Anal. Calcd for $(C_{24}H_{20}S_2O)_n$: C, 74.19; H, 5.19; S, 16.50. Found: C, 74.94; H, 5.17; S, 16.45. (3) A sparingly soluble tan polymeric material:[37] mp >265 °C from dimethylformamide; IR (KBr, cm^{-1}) 1580, 1490, 822, 797, 775, 765, 750 (aromatic); mass spectrum, m/e 171 $(C_{11}H_7S)^+$, 185 $(C_{12}H_9S)^+$, several minor peaks at higher m/e. Anal. Calcd for $(C_{12}H_{10}S)_n$: C, 77.38; H, 5.41; S, 17.21. Found: C, 76.69; H, 4.39; S, 18.48.

B. A mixture of **1d** (400 mg, 1.0 mmol) and benzene (15 mL) was refluxed 2 h. Solvent removal and thin layer chromatography gave three fractions essentially identical with those from thermolysis of **15d**.

C. A slurry of the sodium salt of **15d** (prepared from 2.0 g, 5.5 mmol of **15d** and sodium hydride) in ethyl ether (180 mL) was irradiated 2.5 h at −15 °C with a 450-W Hanovia 679A36 high-pressure mercury arc lamp. Acidic methanol (50 mL) was added, and the mixture was filtered, concentrated, diluted with ethyl ether, washed with saturated sodium bicarbonate and sodium chloride solutions, dried, and vacuum distilled (100–125 °C (0.1 mm)). Gas chromatography of the volatile product led to isolation of **33**. No methyl [8-(methylthio)-1-naphthyl]methyl ether (**34**) was detected.

The distillation residue was separated by column chromatography on silica gel into two fractions essentially identical with the second and third fractions obtained in experiments A and B above, respectively.

Thermolysis and Photolysis of (*o*-Iodophenyl)diazomethane (5a). A. A slurry of sodium hydride (0.32 g, 7.0 mmol) and **16a** (2.8 g, 7.0 mmol) in dichloromethane was stirred at room temperature for 72 h while protected from light. The resulting red-orange solution was filtered and concentrated under reduced pressure. When the residue of **5a** was dissolved in chlorobenzene (80 mL), the solution was refluxed 1 h. TLC analysis showed the presence of two products. Removal of the chlorobenzene under vacuum and column chromatography (silica gel; hexane and hexane/chloroform as eluents) of the residue led to two main fractions: (1) *trans*-Bis(*o*-iodophenyl)ethylene (**35**): 260 mg (17%); mp 127–128.5 °C from hexane; IR (KBr, cm^{-1}) 3030 (w), 1570, 1440, 1420 (m), 1010, 755, 710 (s) (aromatic), 955 (trans C=C); NMR ($CDCl_3$, δ) 6.72–7.93 (m); mass spectrum for $C_{14}H_{10}I_2$, m/e(calcd) 431.8896, m/e(obsd) 431.8903, difference 2 ppm. Anal. Calcd for $C_{14}H_{10}I_2$: C, 38.92; H, 2.33. Found: C, 38.93; H, 2.37. (2) *o*-Iodobenzalazine (**36**): 380 mg (24%); mp 185–187 °C (lit.[21] 182 °C) from ethanol, identical with a sample prepared from *o*-iodobenzaldehyde and hydrazine hydrate. The remainder of the reaction product was brown amorphous material.

B. Photolysis of an ethyl ether solution (180 mL) of **5a** (prepared as above) under nitrogen for 2 h (450-W Hanovia 679A36 high-pressure mercury arc), TLC analysis, and column chromatography (as in previous experiment) revealed **35**, **36**, and unidentifiable amorphous material.

***o*-(Methylthio)benzaldehyde *p*-Tosylhydrazone (16b).** *o*-(Methylthio)benzaldehyde was prepared (94%) by oxidation of *o*-(methylthio)-benzyl alcohol in toluene with *N*-chlorosuccinimide/dimethyl sulfide/triethylamine (as for 8-chloro-1-naphthaldehyde): bp 78–83 °C (0.15 mm) (lit.[38] 89–91 °C (0.4 mm)). Reaction of *p*-tosylhydrazide with *o*-(methylthio)benzaldehyde in refluxing methanol (5 drops of concentrated HCl) resulted in **16b** (74%), mp 118–120 °C.[31] Anal. Calcd for $C_{15}H_{16}N_2O_2S_2$: C, 56.23; H, 5.03. Found: C, 56.09; H, 4.95.

Thermolysis of the Sodium Salt of 16b. Sodium hydride (1.0 g, 24 mmol) was used to convert **16b** (2.09 g, 6.25 mmol) to its sodium salt in dichloromethane (20 mL). The salt was handled as previous sodium salts of *p*-tosylhydrazones in this study and converted to [*o*-(methylthio)phenyl]diazomethane (**5b**) in refluxing benzene (2 h).

Decomposition of **5b** was effected in refluxing chlorobenzene (35 mL). TLC analysis of the crude reaction mixture revealed three mobile products. Column chromatography on silica gel using gradient elution from petroleum ether to 50/50 (v/v) petroleum ether/dichloromethane yielded three main fractions: (1) 2,3-Dihydrobenzo[*b*]thiophene (**37**): 340 mg (40%), purified by preparative gas chromatography (12 ft × 5/16 in 12.5% SE30 on Chromosorb W); IR (neat, cm^{-1}) 3100–2800 (several, aromatic CH, aliphatic CH), 1580, 1460, 1250, 1120, 1060, 745 (aromatic); NMR ($CDCl_3$, δ), 3.21 (s, 4 H, SCH_2CH_2Ar), 6.76–7.21 (m, 4 H, aromatic); mass spectrum, m/e 136 (M^+). Anal. Calcd for C_8H_8S: C, 70.54; H, 5.92. Found: C, 70.60; H, 6.01. (2) *trans*-Bis[(*o*-methylthio)phenyl]ethylene (**38**): 190 mg (22%), recrystallized from petroleum ether; mp 95–97 °C; IR (KBr, cm^{-1}) 3100–2950 (several, aromatic and vinylic CH), 1580, 1470, 1040, 765, 728 (aromatic), 965 (trans C=C); NMR ($CDCl_3$, δ) 2.42 (s, 6 H, $2SCH_3$), 6.78–7.28 (m, 10 H, aromatic and vinylic); mass spectrum, m/e 272 (M^+). Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.37; H, 5.99. (3) (*o*-Methylthio)benzalazine (**39**):[31] 220 mg (23%), recrystallized from dichloromethane/petroleum ether; mp 117.5–118.5 °C. Anal. Calcd for $C_{16}H_{16}N_2S_2$: C, 63.96; H, 5.37. Found: C, 63.75; H, 5.41.

Photolysis of 5b. Irradiation of **5b**, prepared in situ as in the previous experiment, in ethyl ether (180 mL) at 20 °C through Pyrex with a 450-W Hanovia 679A36 UV source and TLC indicated three mobile reaction products. Column chromatography as in the previous experiment resulted in the following: (1) **37**: 480 mg (56%), spectroscopically identical with the previous sample. (2) **38**: 50 mg (6%), identical with the previous sample. (3) *o*-(2-Ethoxy-1-propyl)thioanisole (**40**): 420 mg (32%); IR (neat, cm^{-1}) 3050–2880 (several, aromatic and aliphatic CH), 1580, 1470, 745 (aromatic), 1380 (C–S–C), 1100 (C–O–C); NMR ($CDCl_3$, δ) 1.0–1.3 (superimposed t, d, 6 H, CH_2CHCH_3 and OCH_2CH_3), 2.44 (s, 3 H, SCH_3), 2.75–3.9 (m, 5 H, $ArCH_2CHCH_3$ and OCH_2CH_3), 7.05–7.32 (m, 4 H, aromatic); mass spectrum for $C_{12}H_{18}OS$, m/e(calcd) 210.1078, m/e(obsd) 210.1080, difference 1 ppm.

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Registry No. 1a, 54125-10-9; **1b**, 85864-89-7; **1c**, 85882-54-8; **1d**, 85865-02-7; **1e**, 10378-55-9; **4a**, 54125-11-0; **4b**, 54125-13-2; **4c**, 85864-98-8; **4d**, 24973-91-9; **4f**, 85864-99-9; **5a**, 85865-04-9; **5b**, 85865-08-3; **9** (anhydride), 81-84-5; **10**, 6314-27-8; **11**, 1729-99-3; **11** (acid chloride), 56268-44-1; **11** (Z = I), 13577-19-0; **11** (Z = I, methyl ester), 85864-85-3; **12**, 14938-58-0; **12** (Z = I), 85864-84-2; **13**, 85864-82-0; **13** (Z = I), 85864-86-4; **13** (Z = I, semicarbazone), 85864-87-5; **14**, 85865-00-5; **15a**, 85864-83-1; **15a**·Na, 54125-09-6; **15b**, 85864-88-6; **15b**·Nd, 85864-94-4; **15c**, 85864-92-2; **15d**, 85865-01-6; **15d**·Na, 85865-03-8; **15e**, 19350-73-3; **16a**, 85865-05-0; **16b**, 70401-49-9; **16b**·Na, 85865-07-2; **16b** (aldehyde), 7022-45-9; **18a**, 54125-15-4; **18b**, 85864-93-3; **18c**, 85864-96-6; **19**, 85864-95-5; **21**, 232-89-3; **22a**, 85864-97-7; **22b**, 1233-36-9; **22c**, 54125-12-1; **24**, 56360-04-4; **25**, 56360-01-1; **26**, 2144-00-5; **28**, 66-77-3; **29**, 83-32-9; **29**-d_4, 16333-90-7; **30**, 101-81-5; **30**-d_2, 3947-98-6; **33**, 10397-12-3; **35**, 27686-42-6; **36**, 85865-06-1; **37**, 4565-32-6; **38**, 85865-09-4; **39**, 85865-10-7; **40**, 85865-11-8; 1,8-dibromonaphthalene, 17135-74-9; *p*-tosylhydrazide, 1576-35-8; 5,8-dichloro-1-naphthoic acid, 6680-11-1; methyl 5,8-dichloro-1-naphthoate, 85864-90-0; (5,8-dichloro-1-naphthyl)methanol, 85864-91-1; 5,8-dichloro-1-naphthaldehyde, 64256-53-7; silver nitrate, 7761-88-8; fluorene, 86-73-7; fluorene-d_2, 778-60-9; *o*-(methylthio)benzyl alcohol, 33384-77-9.

(37) Efforts to oxidize, reduce or degrade these fractions to identifiable products have been unsuccessful.

(38) Crawford, R. J.; Woo, C. *Can. J. Chem.* **1965**, *43*, 3178.