the mixture for 4 h with calcium hypochlorite. Workup[6] followed by removal of solvent through a column packed with glass helices furnished the crude ester **7** (X = ^{13}COOMe). Hydrolysis of the latter and sublimation of the product gave **7a** (0.62 g, 74%) as a colorless solid. The physical properties of **7a** were consistent with those of the unlabeled substance:[8] ^{1}H NMR ($CDCl_3$) δ 10.24 (s, 1 H), 2.44 (t, 1 H, ^4J = 14.22 Hz), 2.11 (s, 6 H).

Acknowledgment. We thank the Australian Research Grants Committee for financial support.

Registry No. **1a**, 73948-77-3; **2a**, 73948-78-4; **3a**, 112043-87-5; **4a**, 73948-79-5; **5a**, 112043-88-6; **6a**, 112043-89-7; **7a**, 73948-80-8; **8a**, 87969-55-9; **10**, 112043-90-0; **14**, 112043-91-1; **16**, 112043-92-2; **17**, 112043-93-3; **18**, 112043-94-4.

Conformational Effects in the Alkali Metal Reduction of Diaryl Sulfides and Dibenzothiophene

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Received April 9, 1987

In alkali metal reductions, the carbon–sulfur bond cleavage that occurs in diaryl sulfides and similar structures such dibenzothiophene is shown to be controlled not by the relative stability of the reactive intermediates but by their degree of conformational freedom. Regardless of the stability of the reactive intermediates, diaryl sulfides suffer carbon–sulfur bond cleavage because the aryl groups are free to assume a configuration that favors cleavage. Dibenzothiophene, although similar in structure to diphenyl sulfide, does not have such freedom and therefore, instead of carbon–sulfur bond cleavage, undergoes ring hydrogenation. The behavior of di-1-naphthyl sulfide and di-4-quinolinyl sulfide support this conclusion and provide further evidence for intramolecular coupling of the aryl moieties at some reactive intermediate stage to form an episulfide type of intermediate. This is then followed by a double carbon–sulfur bond cleavage to extrude sulfur.

Alkali methal reductions in ammonia have been synthetically useful and mechanistically interesting for over 50 years.[1] While these same reactions are now frequently used in synthetic organic chemistry, there are still unresolved questions concerning mechanisms, the nature of reactive intermediates, and the effects of solvent, temperature, and structure.[2]

Our work with the alkali metal reductions of aromatic sulfur compounds has led us to investigate several of these unresolved questions. The literature shows that diaryl sulfides, such as diphenyl sulfide, are cleaved at the carbon–sulfur bond by alkali metals in ammonia to yield a thiophenol and a derivative of benzene.[3] Even with excess metal, the products of carbon–sulfur bond cleavage result, and there is no evidence for ring hydrogenation without carbon–sulfur bond cleavage.

Dibenzothiophene is similar in structure to diphenyl sulfide and can be considered as diphenyl sulfide bonded between the 2- and 2′-positions. Reductions of dibenzothiophene in liquid ammonia with 2–3 equiv of alkali metal reportedly give products of ring hydrogenation with no carbon–sulfur bond cleavage.[4,5]

The reasons for this difference in reactivity between diaryl sulfides and dibenzothiophene with alkali metals in liquid ammonia have not been clear. Differences in metals and conditions could have been sufficient to make the studies on diaryl sulfides not directly comparable to those with dibenzothiophene, and the first step in the present study was to establish the pattern reactivity of dibenzothiophene and diphenyl sulfide under identical reduction conditions with the same alkali metal.

Table I. Summary of Gas Chromatography/Mass Spectral Data for Alkali Metal Reduction Products and Reactants

reactants	m/e^a	products (yield,[b] m/e)
dibenzothiophne (1)	184	**1a** (major, 186), **1b** (minor, 188)
diphenyl sulfide (2)	188	**2a** (98.0, 78), **2b** (66.7, 110), **2c** (5.6, 218)
di-1-naphthyl sulfide (3)	286	**3** (57.4, 286), **3a** (10.4, 128), **3b** (13.0, 256), **3c** (1.0, 254), **3d** (13.0, 290), **3e** (5.1, 288)
1-naphthalenethiol (4)	160	**4a** (1.3, 130), **4b** (50.0, 162), **4c** (8.3, 322), **4d** (11.1, 318)
di-4-quinolinyl sulfide (5)	288	**5** (18.0, 288), **5a** (79.0, 256)

[a] M/e is the mass to charge ratio of moleculr ion taken from the mass spectral data. [b] Yields given are on a mole percent and were obtained by integration of the total ion chromatograms from the GC/MS data obtained on each reduction product with tetradecane as an internal standard (Experimental Section).

Results and Discussion

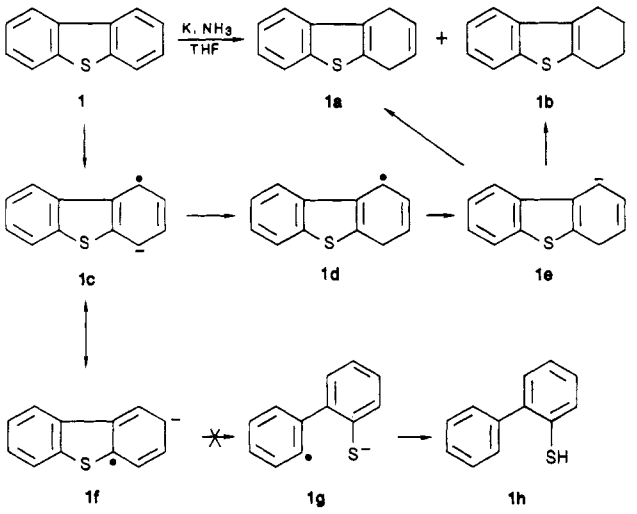
Dibenzothiophene (1), diphenyl sulfide (2), di-1-naphthyl sulfide (3), 1-naphthalenethiol (4) and di-4-quinolinyl sulfide (5) were reduced with 2 equiv of potassium metal (K^0) in liquid ammonia at −78 °C. The reduction products were characterized by gas chromatography/mass spectroscopy (GC/MS) (Table I). Schemes I–V show the probable cleavage paths of the investigated compounds.

Reduction of Dibenzothiophene (1) and Diphenyl Sulfide (2). Nature of Reactive Intermediates. Compound **1**, on reduction with potassium in liquid ammonia, gives 1,4-dihydrodibenzothiophene (**1a**) as the major product and 1,2,3,4-tetrahydrodibenzothiophene (**1b**) as

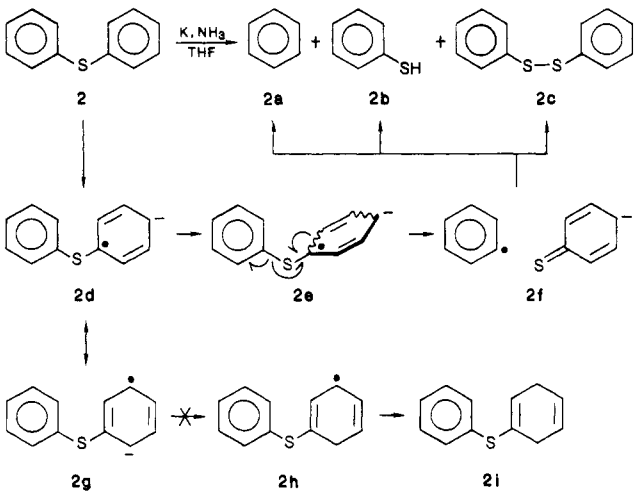
(1) Birch, A. J.; Slobbe, J. *Heterocycles* **1976**, *5*, 905.
(2) Mullen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801.
(3) Truce, W. E.; Tate, D. P.; Burdge, D. N. *J. Am. Chem. Soc.* **1960**, *82*, 2872.
(4) Huckel, W.; Nabih, I. *Chem. Ber.* **1956**, *89*, 2115.
(5) Gilman, H.; Jacoby, A. L. *J. Org. Chem.* **1938**, *3*, 108.

0022-3263/88/1953-0596$01.50/0

Scheme I



Scheme II

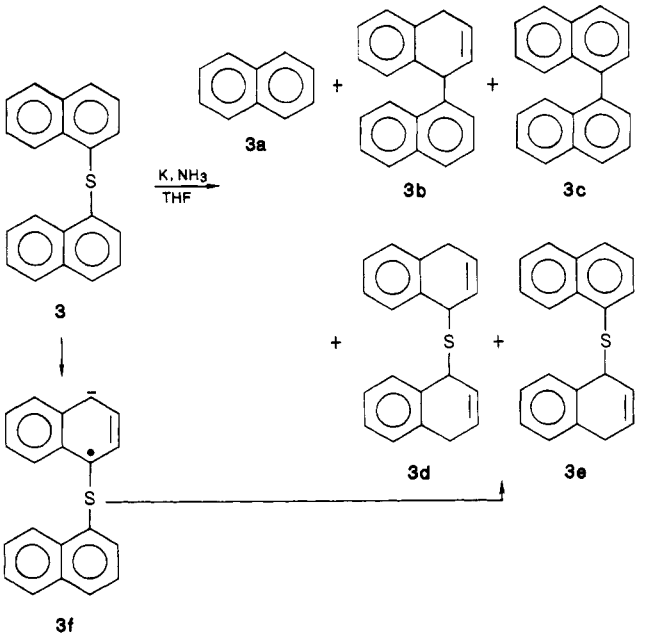


a minor product (Scheme I and Table I). The products **1a** and **1b** were identified by GC/MS and ^{13}C NMR spectra and by comparison with authentic samples synthesized by known methods.[5,6] Under identical reduction conditions (in contrast to **1**), **2** forms none of the expected dihydrodiphenyl sulfide **2i**. Instead, **2** undergoes cleavage of the carbon–sulfur bond without hydrogenation to give only benzene (**2a**), thiophenol (**2b**), and diphenyl disulfide (**2c**) (Scheme II).

These differences in reactivity may be rationalized by consideration of the possible reactive intermediates and their relative stabilities and structures. The first step in any alkali metal reduction is electron transfer from the metal to the substrate to form a radical anion.[7] The radical anion **1c** becomes protonated to **1d**, adds another electron to give **1e**, and thus forms the hydrogenation products **1a** and **1b** without carbon–sulfur bond cleavage. The radical anion **1c** does not follow the alternative path through **1g**, which would lead to the carbon–sulfur bond cleavage product **1h**.

Although the radical anion **2d** has available an analogous hydrogenation path (**2g** → **2h** → **2i**), it follows the cleavage path (**2d** → **2f** → **2a** + **2b** + **2c**) with no hydrogenation.

Scheme III



This may be because the radical anion **1c** is thermodynamically more stable than the radical anion **2d**, or alternatively, the relative stabilities may not be the controlling factor at all. The radical anion **2d** has the conformational freedom to rotate its phenyl groups (to give **2e**) and thus overlap the p orbitals containing the free electron or electron pair with the electron pair in the σ bond of the carbon–sulfur bond, which becomes cleaved. This optimum configuration for bond cleavage **2e** is not available to the radical anion **1c**, which lacks conformational freedom.

In liquid ammonia, these radical anions may be protonated either by the NH_3 or by the external proton source (NH_4Cl) added to quench the reaction, and the neutral radical ring formed (**1d**) can add another electron to form an anion (e.g., **1e**). A similar choice of cleavage versus hydrogenation paths is available to the anions thus derived from the radical anions (e.g., **1g**), but the same considerations as to relative stability and conformational freedom hold whether one is considering the radical anions, the anions, or a combination of both as the reactive intermediates. To simplify subsequent discussion, the cleavage versus hydrogenation branch point at the radical anion stage will be considered.

Relative Reactivity versus Conformational Freedom. The radical anion **3f** from di-1-naphthyl sulfide (**3**) should be less reactive than **2d**; on the basis of the loss in aromatic stabilization energy for one ring in naphthalene versus benzene,[8] the difference should be ca. 12 kcal/mol. If the reason for **2d** taking the cleavage path is that it is thermodynamically more reactive than **1c**, the increased stability of **3f** over **2d** should result in reduction chemistry observed for **1** with the formation of some sort of hydrogenation product from **3**. However, under alkali metal reduction conditions identical with those used for **1** and **2**, the reduction of **3** (Scheme III) yields mostly the products of carbon–sulfur bond cleavage; less than half of the **3** that reacts yields ring hydrogenation products with no cleavage of carbon–sulfur bond (there is 57.4 mol % unreacted **3**, Table I). All of the cleavage products have had sulfur removed completely, i.e., no 1-naphthalenethiol

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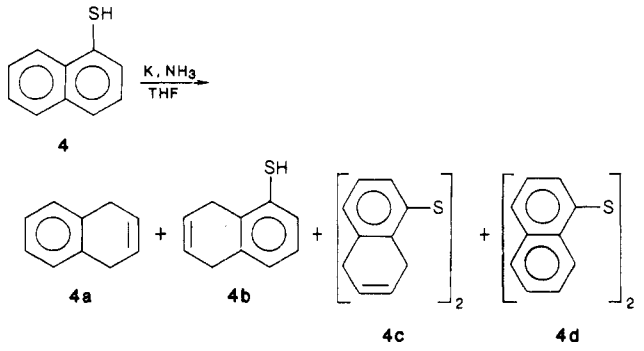
(7) Smith, H. In *Chemistry in Noionizing Solvents*; Wiley: New York, 1963; Vol. I, Part 2, p 153.
(8) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon: New York, 1985; pp 45–47.

Scheme IV



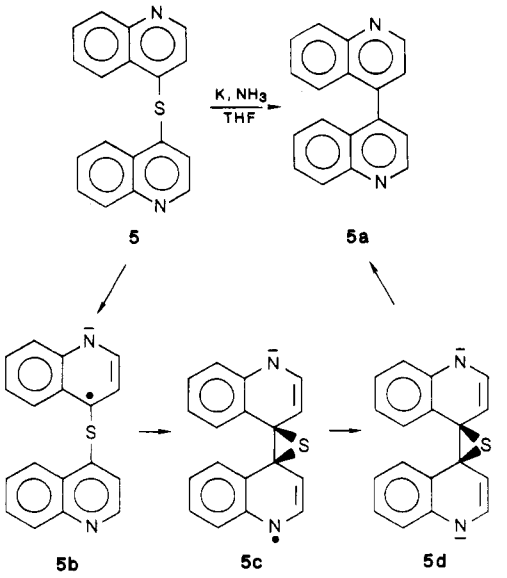
(4) was formed and a little more than 50% of the cleavage products are coupled to form naphthalene derivatives **3b** and **3c**.

The absolute structure of the binaphthalene **3c** was confirmed by comparison of its GC/MS data with that of an authentic sample of 1,1′-binaphthalene. It was found that alkali metal reduction of 1,1′-binaphthalene under identical conditions produced a naphthalene derivative with retention time and MS identical with that of **3b**; this was not observed when 2,2′-binaphthalene was reduced. This fact indicates that **3b** was derived from the reduction of **3c**; the position of double bond in **3b** was not confirmed. Similarly, the positions of the double bonds in sulfide **3d** and **3e** are not known since the products were analyzed by GC/MS. When considering **3d** and **3e** shown in Scheme III, it should be recognized that for each structure shown any of the other reasonable regioisomers are possible. Significantly, the GC/MS data showed that one and only one regioisomer for both **3d** and **3e** were present in the reduction products. 1-Naphthalenethiol (**4**) could not have been a precursor to the cleavage products since only traces 1,4-dihydronaphthalene (**4a**) and 50.0 mol % 5,8-dihydro-1-naphthalenethiol (**4b**) are produced under the alkali metal reduction conditions along with di-1-dihydronaphthyl and di-1-naphthyl disulfides **4c** and **4d** (Table I, Scheme IV). The positions of double bonds in **4b** and **4c** were not confirmed.

The result for **3** is in contrast to (i) that for **2**, which suffered a single carbon–sulfur bond cleavage to yield uncoupled products and little desulfurization and (ii) that of **1**, which undergoes only hydrogenation. This indicates that reducing the relative reactivity of the intermediate is not important, but the conformational freedom of the radical anion probably is important in determining whether cleavage or hydrogenation occurs.

The point is reinforced by the case of di-4-quinolinyl sulfide (**5**) (Scheme V). Considering the loss in aromatic stabilization energy for the nitrogen-containing ring in quinoline versus one ring in naphthalene,[9] one would expect the radical anion **5b** to be on the order of 5–7 kcal/mol more stable than the radical anion **3f** or 17–19 kcal/mol more stable than the radical anion **2d**. Reduction of **5** produced only 46% biquinoline **5a**, the result of double carbon–sulfur bond cleavage, and 51% unreacted **5** (Table I). No hydrogenated forms of **5** were observed. A single biquinoline was observed in the reduction product by GC/MS, and the most likely regioisomer is shown (**5a**), but other biquinoline regioisomers are also possibilities. Comparison of the authentic sample of the 2,2′-biquinoline showed the retention time to be significantly different in the GC/MS data.

Scheme V



In covering an energy difference of 17–19 kcal/mol, one would expect to see a significant shift to hydrogenated products if the stability of the reactive intermediates were important, particularly in the case of **5**; thus, the conformational freedom of the diaryl sulfides appears to be the significant factor that allows orbital overlap leading to bond cleavage instead of hydrogenation. [Calculations of the electron affinities of **1** and **2** using the method of M. J. S. Dewar and H. S. Rzekpa (*J. Am. Chem. Soc.* **1978**, *100*, 784) indicate that the EA of the former is only ca. 3 kcal/mol more than that the latter.] Some ring hydrogenation without carbon–sulfur bond cleavage most likely occurs in the case of **3** because electron transfer to either ring is possible. Only transfer to the sulfur–bearing ring can result in carbon–sulfur bond cleavage. The electron transfer to the other ring leaves only hydrogenation as an option; carbon–sulfur bond cleavage would not be possible in that case.

Evidence for Episulfide Intermediates. The results for **3** and **5** also indicated that as one goes to diaryl sulfides, which form increasingly stable radical anions, there is intramolecular coupling of the aryl fragments (Schemes III and V) at some reactive intermediate stage before any carbon–sulfur bond cleavage occurs. a reactive intermediate (e.g., either radical anion **5c** or dianion **5d**) containing an episulfide function would explain why cleavage products are obtained with sulfur completely removed from the moleucle and the aryl moieties coupled.

The alternative route of carbon–sulfur bond cleavage at the bisradical anion stage to extrude sulfur as X_2S, and coupling of the aryl radicals is unlikely in the case of **5**. Significantly, no quinoline, which should result by further reduction of the quinolyl radicals or the radical abstracting hydrogen atom from the solvent (such as tetrahydrofuran, the cosolvent), was found. The episulfide path and the bisradical anion path could both operate in the case of **3** since naphthalene was observed among the reduction products as well as binaphthalenes. In the case of **5**, cleavage cannot occur at the radical anion **5b**, since no 4-quinolinethione or quinoline was observed.

Similar linked diaryl systems that are not conjugated, such as the 1,2-dinaphthylethanes, yield reduction products in which both rings have reacted even with limited alkali metal.[9,10] This could be explained by an intramo-

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lecular intermediate between the two aryl rings at the monoradical stage, somewhat similar to episulfide formation.

Summary. The alkali metal reduction of a series of diaryl sulfides (**2**, **3**, **5**) indicates that it is the conformational freedom available to these molecules and their reactive intermediates that allows the orbital overlap, which in turn leads to carbon–sulfur bond cleavage. This is in contrast to **1**, which is similar in structure but does not have such conformational freedom, and so, the reactive intermediate follows exclusively a hydrogenation path. The relative reactivities of these intermediates do not appear to control cleavage versus hydrogenation. Evidence for coupling at some reactive intermediate stage (episulfide mechanism) before carbon–sulfur bond cleavage was found in the case of **3** and **5**.

Experimental Section

General Procedures. Melting points were determined on Bristoline Hot Stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM 360L (60 MHz) spectrometer with TMS as internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-900 NMR spectrometer or on a Varian XL 200 (50 MHz) spectrometer referenced to δ $CDCl_3$ = 77.0.

Materials. Dibnezothiophene (**1**), diphenyl sulfide (**2**), 1-naphthalenethiol (**4**), 4-quinolone, and 1-bromonaphthalene were purchased from Aldrich Chemical Co. and used as received. The purity was checked by GC/MS. Potassium metal, sodium metal, and ammonium chloride (NH_4Cl) were also purchased from Aldrich and used as received. Lithium aluminum hydride (LAH) was purchased from Alfa. Ammonia was purchased from Matheson Gas. Magnesium for the Grignard reaction, zinc (powder), dichloromethane (CH_2Cl_2), ethyl ether, and tetrahydrofuran (THF) were purchased from Fischer Scientific Co. THF and ethyl ether were distilled from LAH and sodium metal, respectively, before use.

GC/MS Analysis of Reduction Products. The GC/MS was a Hewlet-Packard (HP 5995) instrument with 30-m, narrow-bore, methylsilica capillary column. Ionization was accomplished at 70-eV electron mode, and detection was in the 10–800-amu range with 1-amu resolution. The injection temperature was 220 °C. Products were identified by comparison of retention time, and their characteristic mass spectra were identified by comparison with authentic materials. The following compounds: dibenzothiophene (**1**), 1,4-dihydrodibenzothiophene (**1a**), 1,2,3,4-tetrahydrodibenzothiophene (**1b**), diphenyl sulfide (**2**), benzene (**2a**), thiophenol (**2b**), diphenyl disulfide (**2c**), di-1-naphthyl sulfide (**3**), naphthalene (**3a**), 1,1′-binaphthalene (**3c**), 1-naphthalenethiol (**4**), 1,4-dihydronaphthalene (**4a**), and di-4-quinolinyl sulfide (**5**) were used for this purpose.

The yields of reduction products were obtained by integration of the total ion chromatograms from the GC/MS data obtained on each reduction product. Tetradecane was used in each case as an internal standard. Response factors were determinated by using weighed amounts of authentic compounds and tetradecane in dichlomethane and making GC/MS runs under identical conditions.

In the following cases authentic compounds were not available but response factors determined from compounds very similar in structure were used: (i) di-1-naphthyl sulfide as response factor was used to calculate the yields of sulfides **3d** and **3e** and disulfides **4c** and **4d**, (ii) 1-naphthalenethiol (**4**) was used for **4b**, and (iii) 2,2′-biquinoline was used for **5a** obtained in the reduction of **5**.

The temperature profile for GC/MS analysis of **1** reduction products was as follows: initial temperature 100 °C for 5 min, increased to 220 °C (10 °C/min) and held 25 min. The temperature profile of **2** was the following: initial temperature 25 °C for 5 min and then increased to 250 °C (10 °C/min) and held 20 min. For **3**–**5**, the following was the temperature profile: initial temperature 100 °C for 5 min and then increased to 250 °C (10 °/min) and held for 30 min.

Di-1-naphthyl Sulfide (3). To a stirred solution of 1-naphthylmagnesium bromide [obtained from 1-bromonaphthalene (10.04 g, 0.050 mol) and magnesium (1.2 g, 0.050 mol) in dry ether (30 mL)] was added dropwise thionyl chloride (3 g, 0.025 mol) in dry ethyl (30 mL) for 1 h at 5 °C. Then, the mixture was poured over ice and allowed to reach room temperature. The solid was filtered off and recrystallized from 95% ethanol to give 3.9 g (52%) of di-1-naphthyl sulfoxide as pale yellow powder, mp 165–166 °C (lit.[11] mp 166 °C).

To a suspension of di-1-naphthyl sulfoxide (5.3 g, 0.0175 mol) in concentrated hydrochloric acid (58.8 mL) and ether (100 mL) was added zinc (14.05 g, 0.025 mol) over 4 h at reflux. After cooling, the ethereal layer was separated, dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The solid residue was recrystallized from 95% ethanol to give 2.9 g (63%) of **3** as pale yellow needles: mp 104–106 °C (lit.[12] mp 106–108 °C); ^{1}H NMR δ 8.45 (m, 1 H), 7.90–6.90 (m, 6 H); ^{13}C NMR δ 133.99, 132,52, 132.35, 129.81, 128.50, 127.87, 126.99, 126.66, 125.76, 125.00.

Di-4-quinolinyl Sulfide (5). 4-Quinolinethione was obtained from 4-quinolone according to a literature procedure[13] in 62% yield, mp 158–161 °C (lit.[13] mp 158–162 °C). 4-Quinolinethione (5 g, 0.03 mol) was refluxed in toluene (150 mL) with charcoal (1.2 g, 0.10 mol) for 24 h, at which time TLC (ethyl acetate) indicated that no starting material was present. Charcoal was filtered off warm, and toluene was removed under vacuum as far as possible. The solid residue was recrystallized from a mixture of water–ethanol (1:1) to give 2.5 g (55%) of **5** as yellow needles: mp 139–141 °C (lit.[13] mp 144–147 °C); ^{1}H NMR δ 8.75 (d, J = 7.8 Hz, 1 H), 8.40–8.10 (m, 2 H), 8.00–7.50 (m, 2 H), 7.15 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 149.59, 148.21, 141.74, 130.16,130.09, 127.32, 127.12, 124.15, 123.35. Anal. Calcd for $C_{18}H_{12}N_2S$: C, 74.95; H, 4.19; N, 9.75. Found C, 74.80; H, 4.03; N, 9.35.

1,4-Dihydrodibenzothiophene (1a). Dibenzothiophene (1; 0.30 g, 0.0016 mol) in THF (7.5 mL) was added to a solution of potassium metal (0.13 g, 0.0033 mol) in liquid ammonia (8 mL) at −78 °C under nitrogen. The reaction mixture was stirred for 3 h, and solid ammonium chloride (0.30 g, 0.0056 mol) was added. The red-blue color faded, and the clear solution was allowed to warm slowly to 20 °C. After the ammonia and THF had evaporated under a stream of nitrogen, the solid white residue was extracted with CH_2Cl_2. The extracts were concentrated under vacuum and kept at 0 °C to give 0.29 g (95%) of **1a** as white crystals: mp 76 °C (lit.[5] mp 76 °C); ^{13}C NMR δ 25.22, 26.37, 120.66, 122.38, 123.25, 123.36, 126.72, 134.00, 138.51, 139.29; MS, m/e (relative intensity) 188 (M + 2, 4.4), 187 (M + 1, 17.2), 186 (M^+, 97.3), 185 (100.0).

1,2,3,4-Tetrahydrodibenzothiophene (1b). 1-(Phenylthio)-2-cyclohexanone (2.8 g, 0.013 mol) obtained according to a literature procedure[6] was heated with polyphosphoric acid (15 mL) at 100 °C for 3 h. After cooling, the reaction mixture was poured out into ice and extracted with diethyl ether (3 × 50 mL). The ethereal layer was dried over anhydrous magnesium sulfate. The ether was distilled off, and 2.0 g of a dark oil was obtained. Purification by column chromatography (silica gel, n-pentane as solvent) gave 1.7 g (67%) of **1b** as a colorless oil: bp 208–217 °C (0.05 mmHg) (lit.[6] bp 210–220 °C); ^{13}C NMR δ 22.25, 23.55, 25.57, 120.30, 122.11, 123.44, 123.65, 129.32, 136.87, 138.32, 139.68; MS, m/e (relative intensity) 190 (M + 2, 3.5), 189 (M + 1, 12.1), 188 (M^+, 78.5), 187 (100.0).

Reduction in Alkali Metal Solution of Diaryl Sulfides. Compounds **2**–**5** in THF were added to a solution of 2 equiv of potassium metal (K^0) in liquid ammonia at −78 °C under a nitrogen atmosphere. The dark blue solution changed to a red-blue and was stirred for 3 h, and 3 equiv of solid ammonium chloride was added. The clear solution was allowed to warm slowly to 20 °C. After the ammonia was evaporated, tetradecane was added as an internal standard to the THF solution. The reaction mixture was sampled by GC/MS.

Reduction of diphenyl sulfide (**2**; 1.0194 g, 0.0054 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.3011 g, 0.0015 mol) and was found to contain **2a** [0.4145 g, 0.0053 mol, 98 mol %; MS, m/e (relative

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(12) Voronkov, M. G.; Deryagina, E. N.; Ivanova, G. M. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *13*, 2400; *Zh. Org. Khim.* **1977**, *13*, 2584.
(13) Albert, A.; Barlin, G. B. *J. Chem. Soc.* **1959**, 2384.

intensity), 78 (M^+, 100.0)], **2b** [0.3905 g, 0.0036 mol, 66.7 mol %; MS, *m/e* (relative i ntensity), 112 (M + 2, 6.8), 111 (M + 1, 11.5), 110 (M^+, 100.0)], and **2c** [0.0561 g, 0.0003 mol, 5.6 mol %; MS, *m/e* (relative intensity), 220 (M + 2, 4.7), 219 (M + 1, 12.0), 218 (M^+, 57.2), 109 (100.0)].

Reduction of di-1-naphthyl sulfide (**3**; 1.1010 g, 0.0038 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.3080 g, 0.0016 mol) and was found to contain **3a** [0.0512 g, 0.0004 mol, 10.4 mol %; MS, *m/e* (relative intensity), 128 (M^+, 100.0)], one regioisomeric **3b** [0.1280 g, 0.0005 mol, 13.0 mol %; MS, *m/e* (relative intensity), 256 (M^+, 69.1), 128 (100.0)], one regioisomeric **3c** [0.01000 g, 0.000039 mol, 1.0 mol %; MS, *m/e* (relative intensity), 254 (M^+, 100.0)], one isomer of **3d** [0.1450 g, 0.0005 mol, 13.0 mol %; MS, *m/e* (relative intensity), 292 (M + 2, 2.9), 291 (M + 1, 8.4) 290 (M^+, 35.5), 129 (83.9), 128 (100.0)], one isomer of **3e** [0.0576 g, 0.0002 mol, 5.1 mol %; MS, *m/e* (relative intensity) 290 (M + 2, 7.4), 289 (M + 1, 12.8), 288 (M^+, 100)], and unreacted **3** [0.6320 g, 0.0022 mol, 57.4 mol %; MS, *m/e* (relative intensity), 288 (M + 2, 8.6), 287 (M + 1, 26.2), 286 (M^+, 100.0), 115 (80.0)].

Reduction of 1-naphthalenethiol (**4**; 0.5904 g, 0.0037 mol) yielded a THF solution of reduction products, which was analyzed by GS/MS with tetradecane (0.3180 g, 0.0015 mol) and was found to contain **4a** [0.0061 g, 0.000047 mol, 1.3 mol %; MS, *m/e* (relative intensity), 130 (M^+, 100.0), 129 (96.1)], one isomer of **4b** [0.2989 g, 0.0018 mol, 50.0 mol %; MS, *m/e* (relative intensity), 164 (M + 2, 4.0), 163 (M + 1, 8.3), 162 (M^+, 49.2), 129 (100.0), 128 (90.3)], one isomer of **4c** [0.0829 g, 00003 mol, 8.3 mol %; MS, *m/e* (relative intensity), 322 (M^+, 5.6), 290 (25.6), 162 (50.2), 160 (53.6), 128 (100.0)], and **4d** [0.1157 g, 0.007 mol, 11.1 mol %; MS, *m/e* (relative intensity), 318 (M^+, 10.6), 160 (100.0), 128 (78.8)].

Reduction of di-4-quinolinyl sulfide (**5**; 0.5004 g, 0.0017 mol) yielded a THF solution of the reduction products, which was analyzed by GC/MS with tetradecane (0.3000 g, 0.0015 mol) and was found to contain unreacted **5** [0.0864, 0.0003 mol, 18 mol%; MS, *m/e* (relative intensity), 290 (M + 2, 7.2), 289 (M + 1, 23.8), 288 (M^+, 100.2)] and only one regioisomer **5a** [0.3456 g, 0.0014 mol, 79 mol %; MS, *m/e* (relative intensity), 258 (M + 2, 2.0), 257 (M + 1, 16.7), 256 (M^+, 100), 255 (97.8)].

Acknowledgment. Enthusiasm and support for this research by Drs. R. E. Overfield and A. Kaldor are appreciated, and special thanks go to Dr. L. Ebert for informative discussions and to Hudson Luce for help with calculations.

The 193-nm Photochemistry of Some Fused-Ring Cyclobutenes: Absence of Orbital Symmetry Control

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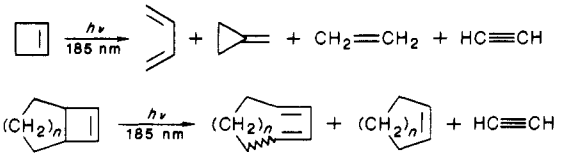
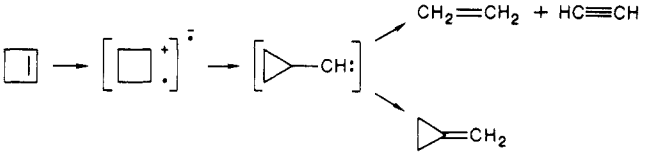
Received August 3, 1987

The photochemistry of *cis*-bicyclo[6.2.0]dec-9-ene (**1**), *cis*-bicyclo[6.2.0]deca-2,9-diene (**4**), and *trans*-bicyclo[6.2.0]deca-2,9-diene (**8**) has been examined at 193 nm in pentane solution. The photochemistry of **1** was complicated by the apparent formation of the thermally labile diene **15**, which prevented direct determination of the primary photoproducts of **1**. Dienes **4** and **8** were found to eliminate acetylene stereoselectively to give mainly the syn-elimination products **17** and **18**, respectively. Ring opening of **4** and **8** gave, as primary products, trienes **5**, **6**, and **16**, indicating that the stereospecificity suggested by the Woodward–Hoffmann rules of orbital symmetry was not followed.

The irradiation of cyclobutenes at 185 nm recently has been studied. The photoreaction of an *n*-heptane solution of cyclobutene at 185 nm yields 1,3-butadiene, methylenecyclopropane, ethylene, and acetylene.[1] Irradiation of



fused-ring cyclobutenes gives rise to conjugated cyclic 1,3-dienes, cycloalkenes, and acetylene, but no methylenecyclopropane products were detected.[2] The ring opening to butadiene is thought to be a π,π^* electrocyclic process,[1,2] and fragmentation products and the methylenecyclopropane have been suggested to come from carbenes formed via the Rydberg excited states of the cyclobutenes.[1-3]



The stereochemistry of the ring opening of cyclobutene and of the cleavage of cyclobutene to ethylene and acetylene cannot be determined for cyclobutene itself, and it was not determined for the ring-fused cyclobutenes.[4] However, the stereochemistry of cyclobutene photoreaction has been observed for the tetrasubstituted cyclobutenes *cis*- and *trans*-tricyclo[6.4.0.0^{2,7}]dodec-1-ene upon irradiation at $\lambda > 200$ nm in pentane.[5] The fragmentation reaction of these cyclobutenes occurred stereospecifically to give *Z* olefin from the cis-fused cyclobutene and *E* olefin from the trans-fused cyclobutene. This result was explained in terms of a retro [2 + 2] cycloaddition reaction, which would be expected to give the observed stereospecificity.[5] The specificity can also be explained by a

(1) (a) Adam, W.; Oppenländer, T.; Zang, G. *J. Am. Chem. Soc.* **1985**, *107*, 3921. (b) For a review of 185-nm photochemistry, see: Adam, W.; Oppenländer, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 661. Steinmetz, M. G. *Org. Photochem.* **1987**, *8*, 67.

(2) Inoue, Y.; Sakae, M.; Hakushi, T. *Chem. Lett.* **1983**, 1495.

(3) Kropp, P. J.; Fields, T. R. *J. Am. Chem. Soc.* **1974**, *96*, 7559.

(4) While this work was in progress, it has been found that bicyclo[4.2.0]oct-7-ene and *cis*- and *trans*-3,4-dimethylcyclobutene ring open upon irradiation at 185 and 193 nm in pentane to give all possible diene products: Leigh, W. J., private communication.

(5) Saltiel, J.; Lim, N. *J. Am. Chem. Soc.* **1969**, *91*, 5404.

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