structure of the enol rather than in that of the base. This is reasonable since the stronger the association (K_{assoc}), the more deshielded the hydroxylic proton.

The sensitivity of log K_{assoc} to δ(OH) is high. The slope of eq 14 is 0.77. A 2.7-fold change in K_{assoc} (**2a** → **2d**) results in a shift of δ(OH) by 0.71 ppm. In a single family the δ(OH) can thus serve as a sensitive tool for the degree of association. However, δ(OH) in our system is affected not only by hydrogen bonding but also by the ring currents, i.e., by the location of the OH relative to the faces of the β-mesityl rings. The regular changes in both the MesC=C dihedral angles and the R–C–O bond angle from R = H to R = *t*-Bu may contribute to the regular change of δ(OH) on changing R.

Conclusions

The α-alkyl-β,β-dimesitylethenols **2** exist in CCl_4 in a syn-type conformation and in DMSO in an anti-type conformation associated with a solvent molecule. The association constant with DMSO (K_{assoc}) decreases with α-R in the order H > Me > Et > *i*-Pr > *t*-Bu. The log K_{assoc} values are linear with σ^* of the α-substituent, indicating a major contribution from a polar effect. They decrease nonlinearly with the steric parameter E_s, probably reflecting that the association occurs at a relatively unhindered side of the molecule.

Experimental Section

Enols **1** and **2a–d** were prepared as described previously.[2,6] CCl_4 was dried over 4A molecular sieves, and the deuteriated NMR solvents were the best commercial samples. NMR spectra were recorded with a Bruker WP 200 SY pulsed FT spectrometer operating at 200.133 MHz. IR spectra were recorded with a Analect FTIR FX-6200 spectrometer.

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Registry No. 1, 54288-04-9; **2a**, 89959-15-9; **2b**, 96040-90-3; **2c**, 96040-91-4; **2d**, 89959-16-0.

Supplementary Material Available: Figure S1 showing the linearity of the plot according to eq 9 and Figure S2 showing a linear K_{assoc} vs C plots (3 pages). Ordering information is given on any current masthead page.

Conformational Effects in the Alkali-Metal Reduction of Diaryl Sulfides. 2. Evidence for Episulfide Intermediates

Manuel A. Francisco* and Argo Kurs

Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, New Jersey 08801

Alan R. Katritzky and Danuta Rasala

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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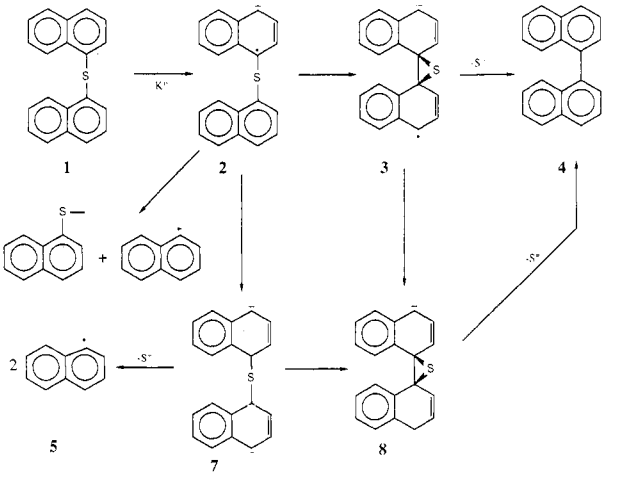
Alkali-metal reduction of a series of diaryl sulfides shows that, if both aryl moieties possess aromatic stabilization energies less than that of the phenyl group (i.e., able to generate relatively more stable radical anions), the diaryl sulfide forms an episulfide intermediate via regiospecific coupling of the aryl moieties at the stage of a reactive intermediate. The formation of the episulfide intermediate explains why double carbon–sulfur bond cleavage and extrusion of sulfur is observed only in such diaryl sulfides and why there is a preference for the formation of single regioisomeric biaryl.

Introduction

In our previous work on the alkali-metal reduction of diaryl sulfides,[1] we have shown that the conformational freedom available to the aryl groups allows maximum orbital overlap at the stage of a reactive intermediate, probably that of the radical anion (Scheme I). This overlap in turn leads to facile cleavage of the carbon–sulfur bond.[2] Molecules similar in structure to diaryl sulfides but lacking this conformational freedom, such as dibenzothiophene, cannot achieve such maximum orbital overlap during reduction. For this reason ring hydrogenation of dibenzothiophene occurs without cleavage of the carbon–sulfur bond. In diaryl sulfides that are capable of generating relatively stable radical anions (those with aryl moieties more extensively conjugated than phenyl, such as naphthyl or quinolyl), there was some evidence[1] of coupling of the aryl moieites at some reactive intermediate stage to form an episulfide which extrudes sulfur with two carbon–sulfur bond cleavages to give the corresponding

Scheme I



biaryl. The coupling was specifically shown (Scheme I) to occur before carbon–sulfur bond cleavage. The reaction, as shown, is essentially an aryl migration. Intramolecular attack of reactive intermediates such as radicals and anions

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0022-3263/88/1953-4821$01.50/0

Table I. Alkali-Metal Reduction Products, Yields, and Summary of Gas Chromatography/Mass Spectral Data

reactants (m/e[a])	products (yield,[b] m/e)
4-(1-naphthylthio)quinoline (**15**) (287)	**9** (36.3, 128), **34** (3.1, 129), **25** (8.4, 160), **38** (2.8, 257), **37** [(80.2, 255) and (13.3, 255)],[c] **15** (1.9, 287), **42** (1.6, 259)
4-(1-naphthylthio)quinoline 1-oxide (**16**) (303)	**9** (7.7, 128), **34** (1.0, 129), **37** [(2.9, 255) and (0.8, 255)],[c] **15** (1.4, 287), **32** (1.6, 318)
4-(phenylthio)quinoline (**17**) (237)	**22**[d] (81.7, 78), **34** (35.8, 129), **23** (12.6, 218), **17** (3.1, 237), **13** (16.5, 288)
4-(phentylthio)quinoline 1-oxide (**18**) (253)	**22** (54.0, 78), **34** (15.8, 129), **23** (16.0, 218), **17** (2.7, 237), **13** (1.9, 288)
phenyl 1-naphthyl sulfide (**19**) (236)	**22** (103.0, 78), **9** (2.6, 128), **25** (35.9, 160), **30** (0.22, 238), **19** (0.43, 236), **27** [(1.0, 254) and (1.3, 254)],[c] **1** (2.2, 286), **33** (4.8, 322), **32** (16.2, 318)
4-quinolinethione (**20**) (161)	**34** (3.5, 129), **40** (47.8, 260), **13** (4.7, 288), **41** (trace, 290), **39** (trace, 256),[c] **36** (trace, 163), **35** (trace, 133)
bis(4-methyl-1-naphthyl) sulfide (**21**) (314)	**24** (12.3, 142), **26** (29.0, 174), **29** (trace, 282), **31** (4.1, 316), **21** (67.0, 314), **28** (trace, 284)

[a] m/e is the mass to charge of molecular ion taken from the mass spectral data. [b] Yields given are mol % 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 (see Experimental Section). [c] Two different regioisomers. [d] Compound as shown as sketched except for **22** (benzene).

Chart I

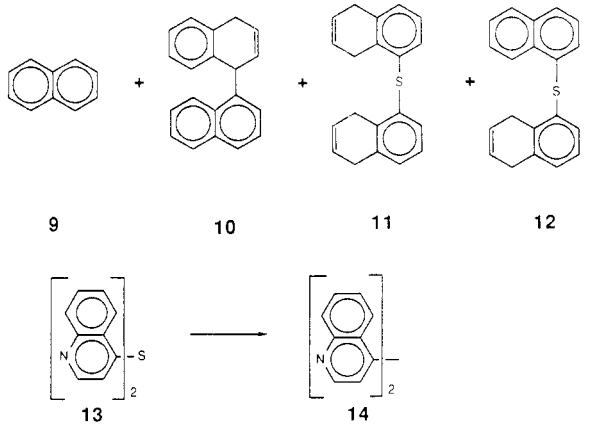
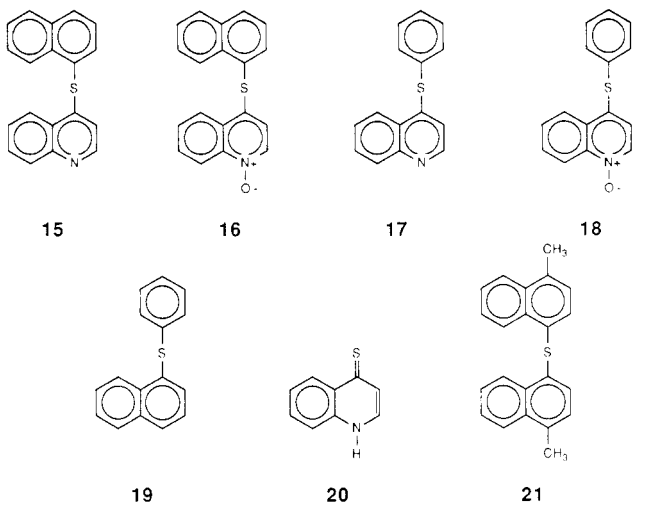


Chart II



on aryl moieties resulting in aryl migrations are rare in the case of radicals and anions.[3-9] Certainly aryl migration of the type discussed in the present study, involving an episulfide intermediate under reducing conditions, is to our knowledge the first such case reported. In this study we provide further evidence for these reactive episulfide intermediates and show further that their formation does indeed lead to the regiospecific coupling of the aryl moieties before carbon–sulfur bond cleavage.

Results and Discussion

The existence of a reactive episulfide intermediate (Scheme I) should insure regiospecific coupling of the aryl moieties. Some evidence for such regiospecificity was provided in our previous studies with di-1-naphthyl sulfide (**1**) and di-4-quinolyl sulfide (**13**). In each case when biaryls were observed as a result of reduction, there was a marked preference for the formation of one and only one regioisomer: thus **1** gave **9**–**12** and **13** gave **14** (Chart I). Nevertheless, it is possible that such apparent regiospecific coupling could result from the coupling of aryl radicals (Scheme I). Since the radicals would be generated regiospecifically, the postulated regiospecific coupling of aryl moieties in a reactive intermediate before the two C–S bond cleavages is not demonstrated.

The episulfide intermediate requires intramolecular coupling of aryl moieties. The alternative radical coupling requires that some intermolecular coupling of aryl moieties will occur. We have now investigated the alkali-metal reduction chemistry of five unsymmetrical diaryl sulfides, 4-(1-naphthylthio)quinoline (**15**), 4-(1-naphthylthio)-quinoline 1-oxide (**16**), 4-(phenylthio)quinoline (**17**), 4-(phenylthio)quinoline 1-oxide (**18**), and phenyl 1-naphthyl sulfide (**19**), to obtain stronger evidence for the regiospecific coupling of aryl moieties at some reactive intermediate stage before any cleavage of the C–S bonds (Scheme I). The reduction chemistry of 4-quinolinethione (**20**) and bis(4-methyl-1-naphthyl) sulfide (**21**) was also investigated as part of this study (Chart II).

Reductions of all compounds were conducted under identical alkali-metal reduction conditions, which were the same as those used in our previous work on diaryl sulfide reductions.[1] The results of the reduction of compounds **15**–**21** are summarized in Table I (Chart III). Evidence for the episulfide reactive intermediate is derived from the behavior of the unsymmetrical sulfides **15**–**19** with respect to their reactivity in alkali-metal reduction. They fall into two catagories. Compounds **15** and **16** generate biaryls **37** as the major products. Given the large number of possible regioisomeric biaryls that could have been produced, there is a marked preference for the formation of one in each case. The predominent reaction is two carbon–sulfur bond cleavages to extrude sulfur from the molecule. In addition to regiospecificity, only unsymmetrical biaryls are produced; there was no evidence for the formation of symmetrical biaryls.

Compounds **17**–**19** fall into the second category. The major products in each case are not biaryls but the results of only one carbon–sulfur bond cleavage. In some cases trace amounts of biaryls were generated but now more than

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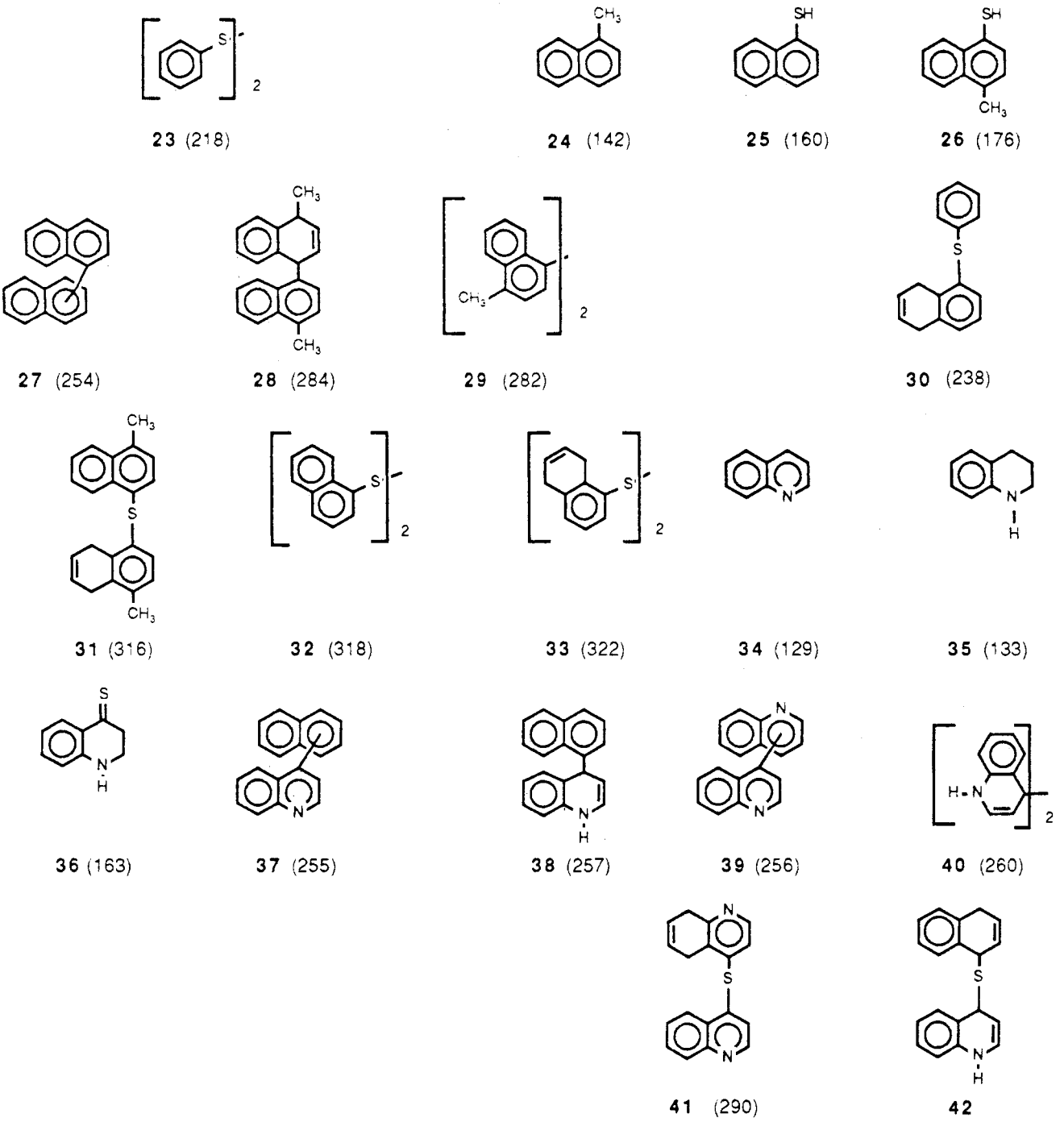
Chart III



one regioisomeric biaryl was invariably generated. No preference was observed for the formation of a single isomer. Also there was no evidence for presence of unsymmetrical biaryls. Only symmetrical biaryls were produced.

Compound **15** shows no evidence for the intermolecular coupling of aryl moieties in the reduction products. Symmetrical biaryls were not observed. Two regioisomeric, unsymmetrical biaryls **37** are formed. There is a significant preference for the formation of one of these regioisomers (presumably the 4,1′-derivative). This is strong evidence for the intramolecular coupling of aryl moieties before C–S bond cleavage via an episulfide intermediate. A small amount of a single regioisomer of a dihydrobiaryl is produced. The exact regiochemistries of the two biaryls **37** and the dihydrobiaryl **38** was not determined since the analysis was by gas chromatography with mass spectral detection. However, the significance lies in the fact that only two unsymmetrical biaryls are produced, and one of these is by far the major isomer produced. The single regioisomeric dihydrobiaryl **38** is observed; most likely it results from the reduction of the major unsymmetrical biaryl which is present in very large excess.

The other reduction products (Table I), naphthalene (**9**), quinoline (**34**), and 1-naphthalenethiol (**25**), may result from intermediates other than an episulfide. Single C–S bond cleavage of a radical anion or double C–S bond cleavage of a diradical anion would account for the formation of these three products. The radical anion and diradical anion alternatives were discussed as alternatives to the episulfide intermediate in the case of di-1-naphthyl sulfide in our previous study.[1] Note that only the episulfide reactive intermediate can account for the regioselective formation of one unsymmetrical biaryl.

The small amount of a compound generated with a mass of 259 (**42**, Table I) will be discussed further when the reduction chemistry of 4-quinolinethione (**20**) is considered.

Compound **16** gave a product slate very similar to that found for **15**. Compound **16** was reduced with the hope that it would generate reactive intermediates that were more stable than the corresponding intermediates produced in the reduction of **15**. However, the chemistry may proceed with nitrogen–oxygen bond cleavage to regenerate compound **15**, and the observed products would be derived from the subsequent reduction of **15** (Table I). However, one cannot be certain of this since both the 1-oxides (**16** and **18**) were found to be thermally unstable and to decompose in the GC/MS analysis (injection port and column) to give the respective deoxygenated sulfides (**15** and **17**). This may also explain the moderate material balances obtained in the case of the reduction products of the 1-oxides. The pure compounds **16** and **18** decomposed on the column to give **15** and **17**, respectively, which resulted in extremely broad base-line responses in the GC/MS data that could not be integrated.

The results of reduction of compounds **17–19** suggest that both the aryl rings linked directly to the sulfur must have aromatic stabilization energies less than that of a phenyl group for at least part of the reduction to proceed through an episulfide reactive intermediate (Table I). [Although the total resonance energy of naphthalene is larger than that of benzene, the loss in resonance energy for naphthalene to dihydronaphthalene is considerably less than that of benzene to dihydrobenzene.] There was no evidence for the intramolecular coupling of the aryl moieties of **17–19** at the stage of a reactive intermediate before carbon–sulfur bond cleavage (no regioselectivity and no formation of only unsymmetrical biaryls). If the first electron transfer is to the phenyl moiety, the resultant radical anion is reactive and immediately should cleave at the one C–S bond to generate thiophenol or diphenyl disulfide (**23**) (derived from thiophenol, Table I). This is what is observed for compounds **17–19**. The results with diphenyl sulfide in our previous work forshadowed this. If the first electron transfer is to the naphthyl, to the quinolyl, or to the quinolyl 1-oxide moiety, the resultant radical anion will be significantly more stable than the one generated in the phenyl moiety. However, coupling to form an episulfide intermediate will be difficult because it will require that the relatively stable radical anion break the aromatic stabilization energy of the phenyl moiety. The result is that the more stable radical anion persists either until it is protonated (hydrogenated species result) or until it cleaves at the C–S bond to form aromatic thiols, their corresponding disulfides, or both. The reactive aryl radical fragments that result from the cleavages discussed above can be reduced further or be protonated to produce aromatic compounds (as is observed with the formation of benzene, naphthalene, and quinoline) or they can couple to produce a variety of biaryls. Such reactivity has been observed in the reductive cleavage of di-2-naphthyl ether.[10] Interestingly only one regioisomeric biaryl was produced, the 2,2′-dinaphthyl, but the significance of the result was not recognized at that time.

The reductions of compounds **15–19** also yield products of single carbon–sulfur bond cleavages. In addition to the biaryls, compounds **15** and **16** generate naphthalene (**9**), 1-naphthalenethiol (**25**), and quinoline (**34**). However, no 4-quinolinethione (**20**) was observed, as one would have expected if 1-naphthalenethiol (**25**) were generated. Similarly compounds **17** and **18** generate benzene (**22**), diphenyl disulfide (**23**), and quinoline (**34**), but no 4-quinolinethione (**20**), which is expected if thiophenol were the initial cleavage product. Such products may result from the participation of reactive intermediates other than the episulfide type (i.e., radical anion and diradical anion).

The results with 4-quinolinethione (**20**) show that if it is generated it would undergo further reduction under these conditions. Under identical alkali-metal reduction conditions, compound **20** generates quinoline (**34**), biquinolines (**39**) (at least two regioisomers), a tetrahydrobiquinoline (**40**) (only one regioisomer), tetrahydroquinoline **35**, and a dihydro-4-quinolinethione (**36**) (Table I). Also observed in the reaction mixture were di-4-quinolyl sulfide (**13**) and a dihydro derivative of di-4-quinolyl sulfide (**41**). Compound **13** is most likely generated thermally from **20**, in the injection port of the GC during the GC/MS analysis. Thermal condensation of compound **20** with itself and extrution of one sulfur atom would yield the product **13**. Pure compound **20** showed only **13** when analyzed by GC/MS. The traces of **41** could result from thermal condensation of compound **20**, with the dihydro-4-quinolinethione **36** generated in the reduction.

The results with compound **21** (Table I) can be explained on the basis of the destabilization[11] by electron-donating substituents of the build up of negative charge resulting from electron transfer from the potassium metal to the aromatic ring. When there is a choice of two rings in each of the aryl moieties to which the electron may be added, destabilization may cause electron donation to occur to the ring not bearing the sulfur and methyl groups. Creation of a radical anion in this ring directs the molecule to the products of ring hydrogenation without C–S bond cleavage. Relative to di-1-naphthyl sulfide (**1**), compound **21** favors the products of ring hydrogenation without C–S bond cleavage over C–S bond cleavage products as one would expect from the electron-donating affect of the methyl groups (Table I).

Conclusions and Summary

Alkali-metal reduction chemistry of a series of diaryl sulfides shows that in the case of sulfides having two aryl moieties with aromatic stabilization energies less than that of the phenyl moiety, intromolecular coupling of the aryl moieties can occur at the stage of a reactive intermediate before carbon–sulfur bond cleavage. Such intramolecular coupling forms a reactive episulfide intermediate which extrudes sulfur in a double carbon–sulfur bond cleavage to produce a biaryl regioselectively.

Experimental Section

General. Melting points were determined on a Bristoline hot stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian XL (200 MHz, FT mode) spectrometer with TMS as an internal standard. ^{13}C NMR spectra were recorded on a Varian XL 200 (50 Hz) referenced to $\delta(CDCl_3) = 77.0$ or $\delta(DMSO) = 39.5$. Microanalyses were performed on a Carbo Erba 110 G elemental analyzer.

Analysis of the reduction products was accomplished by gas chromatography with mass spectral detection (GC/MS). The GC/MS was a Hewlett-Packard (HP 5995) instrument with a 30-m, narrow bore [0.32-mm i.d., 0.25-μm film thickness (SPB-5 phase)], fused silica capillary column (Supelco, Supelco Park, Bellefonte, PA 16823). Ionization was accomplished at 70-eV electron impact mode and detection was in the 10–800-amu range with 1-amu resolution. The injection temperature was 220 °C.

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Products were identified by comparison of characteristic retention times and mass spectra with authentic compounds. The following compounds, diphenyl sulfide, diphenyl disulfide (**23**), benzene (**22**), thiophenol, naphthalene (**9**), 1,1′-binaphthalene, 2,2′-binaphthalene, 1-naphthalenethiol (**25**), di-4-quinolyl sulfide (**13**), 4-(1-naphthylthio)quinoline (**15**), 4-(1-naphthylthio)quinoline 1-oxide (**16**), 4-(phenylthio)quinoline (**17**), 4-(phenylthio)quinoline 1-oxide (**18**), phenyl 1-naphthyl sulfide (**19**), 4-quinolinethione (**20**), and bis(4-methyl-1-naphthyl) sulfide (**21**), 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 determined by using weighed amounts of authentic compounds and tetradecane in dichloromethane or tetrahydrofuran and making GC/MS runs under identical conditions.

In the following cases authentic compounds were not available but response factors were determined from compounds very similar in structure: naphthylquinoline **37**, dihydronaphthylquinoline **38**, phenyl dihydrolnaphthyl sulfide **30**, binaphthalene **27**, tetrahydro derivative of di-1-naphthyl disulfide **33**, biquinoline **39**, tetrahydrobiquinoline **40**, dihydro-4-quinolinethione **36**, 4-methyl-1-naphthalenethiol **26**, dimethylbinaphthalene **29**, dihydro derivative of bis(dimethyl-1-naphthyl) sulfide **31**, dihydrodimethylbinaphthalene **28**.

The temperature profile for the GC/MS analyses of products from the reduction of compounds **15**, **16**, **20**, and **21** was initial temperature 100 °C for 5 min, increased to 250 °C (10 °C/min) and held for 40 min. The flow rate was 1 mL/min and the carrier gas was nitrogen. The temperature profile for the analysis of the reduction products of compounds **17–19** was initial temperature, 25 °C for 5 min, increased to 250 °C (10 °C/min) and held for 40 min. The flow rate was 1 mL/min and the carrier gas was nitrogen.

Materials. Diphenyl sulfide, benzene, thiophenol, naphthalene, 1,4-dihydronaphthalene, 1-methylnaphthalene, quinoline, 1,2,3,4-tetrahydroquinoline, diphenyl disulfide, 1,1′-binaphthalene, 2,2′-binaphthalene, 2,2′-biquinoline, 1-bromonaphthalene, 1-bromo-4-methylnaphthalene, 4-quinolone, and triphenylphosphine were purchased from the Aldrich Chemical Company and used as received. The purity was checked by GC/MS. 1-Naphthalenethiol, diethyl ether, and magnesium metal for the Grignard reagents were purchased from Fisher Scientific Co. Potassium metal (K), sodium metal (Na), and ammonium chloride were also purchased from aldrich and used as received. Lithium aluminum hydride (LAH) was purchased Alfa Products. Ammonia was purchased from Matheson Gas Products. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were purchased from Fischer Scientific Co. The THF were distilled from LAH prior to use. The diethyl ether was distilled from sodium metal prior to use.

Synthesis of Diaryl Sulfides. 4-Quinolinethione (20) was obtained from 4-quinolone in 65% yield according to the literature procedure:[12] mp 158–161 °C (lit.[12] mp 158–162 °C); ^{13}C NMR δ (DMSO) 192.34, 135.59, 132.31, 131.78, 128.51, 124.91, 124.17, 119.14.

Phenyl 1-Naphthyl Sulfide (19). To a stirred solution of 1-naphthylmagnesium bromide [obtained from 1-bromonaphthalene (8.3 g, 0.04 mol) and magnesium (0.096 g, 0.04 mol) in dry ether (25 mL)] was added diphenyl disulfide (4.4 g, 0.02 mol) in dry ether (25 mL) dropwise over 1 h at room temperature; the whole was subsequently refluxed for 6 h. The reaction mixture was then poured over ice, acidified with 10% aqueous hydrochloric acid, extracted with ether (3 × 50 mL), and dried ($MgSO_4$). The solvent was removed under vaccum and the dark oily residue was subjected to column chromatography (silica gel, *n*-hexane). The major product was crystallized from ethanol–water (1:1) to give 3.3 g (68%) of **19**, as white prisms: mp 39.0–40.5 °C (lit.[13] mp 40.0–41.0 °C, lit.[14] mp 41.5 °C); ^{13}C NMR δ 136.93, 134.21, 133.58, 132.51, 131.24, 129.15, 129.03, 128.95, 128.53, 126.90, 126.38, 126.07, 125.77, and 125.61.

4-Chloroquinoline 1-oxide was obtained from quinoline 1-oxide via 4-nitroquinoline 1-oxide according to a literature procedure[16-18] in 82% yield: mp 132–133 °C (lit.[17] mp 133–134 °C, lit.[18] mp 133 °C); ^{13}C NMR δ 141.95, 134.94, 130.95, 129.66, 129.46, 127.79, 124.96, 120.87, and 120.15.

4-(Phenylthio)quinoline 1-Oxide (18). 4-Chloroquinoline 1-oxide (3.3 g, 0.018 mol) and thiophenol (3.9 g, 0.035 mol) in anhydrous ethanol (80 mL) were stirred at room temperature for 24 h. The hydrochloride of 4-(phenylthio)quinoline 1-oxide was filtered off and dried and then neutralized with anhydrous sodium carbonated in $CHCl_3$ (150 mL). The organic layer was separated, washed with water (2 × 25 mL), and dried ($MgSO_4$). The solvent was evaporated under vacuum, and the solid residue was recrystallized from 95% ethanol to give 4.4 g (94%) of **18** as yellow prisms: mp 99–102 °C (lit.[15] mp 98–101 °C); ^1H NMR δ 8.70 (dd, J = 10.0 and J = 2.0 Hz, 1 H), 8.40–8.20 (m, 2 H), 7.75 (dd, J = 10.0 and J = 2.0 Hz, 1 H), 7.50–7.35 (m, 6 H), 6.85 (d, J = 8.0 Hz, 1 H); ^{13}C NMR δ 140.65, 135.26, 134.74, 133.27, 130.45, 129.72, 128.89, 128.58, 127.99, 124.63, 120.08, and 120.03.

4-(Phenylthio)quinoline (17). A mixture of 4-(phenylthio)quinoline 1-oxide (**18**) (3.25 g, 0.013 mol) and triphenylphosphine (7.19 g, 0.026 mol) was heated at 220–230 °C for 2 h. After cooling, the dark solid was extracted from *n*-hexane (5 × 100 mL). Then, the solution was evaporated to dryness, and the residue was separated by column chromatography (silica gel chloroform). The 4-(phenylthio)quinoline was recrystallized from ethanol–water (1:1) to give 2.1 g (69%) of **17** as pale yellow prisms: mp 84.0–85.5 °C (lit.[18] bp 190–200 °C/4 mmHg, no mp mentioned): ^1H NMR δ 8.75 (d, J = 5.2 Hz, 1 H), 8.42–8.18 (m, 2 H), 7.95–7.40 (m, 7 H), 6.87 (d, J = 5.2 Hz, 1 H); ^{13}C NMR δ 149.26, 148.38, 147.45, 135.04, 129.80, 129.62, 129.41, 128.12, 126.30, 125.81, 123.34, 117.68. Anal. Calcd for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; N, 5.90. Found: C, 76.22; H, 4.67; N, 5.61.

4-(1-Naphthylthio)quinoline 1-Oxide (16). To a stirred solution of 1-naphthalenethiol (2.55 g, 0.016 mol) and sodium methanolate (0.87 g, 0.016 mol) in anhydrous methanol (30 mL) was added 4-chloroquinoline 1-oxide (2.70 g, 0.015 mol) dropwise over 0.5 h. The reaction mixture was refluxed for 12 h and cooled, and precipitated sodium chloride was removed by filtration. The filtrate was concentrated under vacuum. The crude product was recrystallized from anhydrous ethanol to give 3.6 g (79%) of **16** as yellow needles: mp 172–174 °C; ^1H NMR δ 8.78 (d, J = 9.2 Hz, 1 H), 8.36 (d, J = 8.2 Hz, 1 H), 8.27 (d, J = 9.2 Hz, 1 H), 8.16 (d, J = 6.7 Hz, 1 H), 7.98 (d, J = 8.2 Hz, 1 H), 7.93–7.69 (m, 4 H), 7.54–7.46 (m, 3 H), 6.32 (d, J = 6.7 Hz, 1 H); ^{13}C NMR δ 140.53, 136.41, 135.15, 132.87, 134.33, 133.62, 131.16, 130.64, 128.80, 128.64, 127.68, 127.48, 126.82, 126.07, 125.93, 125.02, 124.38, 120.34, and 118.27. Anal. Calcd for $C_{19}H_{13}NOS$: C, 75.22; H, 4.32; N, 4.62. Found: C, 74.98; H, 4.12; N, 4.29.

4-(1-Naphthylthio)quinoline (15). A mixture of 4-(1′-naphthythio)quinoline 1-oxide (**16**) (2.28 g, 0.0075 mol) and triphenylphosphine (3.98 g, 0.015 mol) was heated at 160–170 °C for 2 h. After cooling, the dark solid was dissolved in benzene (5 mL) and separated by column chromatography [silica gel, benzene–ethyl acetate (4:1)]. The collected product was recrystallized from anhydrous ethanol to give 1.7 g (78%) of **15** as pale yellow prisms: mp 134.0–135.5 °C; ^1H NMR δ 8.35–8.31 (m, 2 H), 8.22 (dd, J = 8.8 and 1.0 Hz, 1 H), 8.09 (d, J = 8.3 Hz, 1 H), 7.95 (d, J = 8.3 Hz, 1 H), 7.86 (dd, J = 8.8 and 1.0 Hz, 1 H), 7.75–7.39 (m, 6 H), 6.36 (dd, J = 6.0 and 1.1 Hz, 1 H); ^{13}C NMR δ 149.23, 148.11, 147.47, 135.87, 134.36, 134.17, 131.20, 129.88, 129.64, 128.71, 127.54, 126.71, 126.32, 125.93, 125.75, 125.40, 123.40, and 117.31. Anal. Calcd for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; N, 4.87. Found: C, 78.86; H, 4.36; N, 4.58.

Bis(4-methyl-1-naphthyl) Sulfide (21). To a solution of (4-methyl-1-naphthyl)magnesium bromide [from 1-bromo-4-methylnaphthalene (10.0 g, 0.05 mol) and magnesium (1.2 g, 0.05 mol) in dry ether (35 mL) and dry benzene (35 mL)] was added thionyl chloride (3 g, 0.025 mol) in dry ether dropwise for 0.5 h

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at 0–5 °C. Then the mixture was poured over ice and allowed to reach room temperature. The organic layer was separated and dried ($MgSO_4$) and then concentrated in vacuo. The solid residue was recrystallized from benzene to give 3.2 g (47%) of bis(4-methyl-1-naphthyl) sulfoxide as pale yellow needles: mp 185–187 °C; ^1H NMR δ 8.33 (q, J = 9.2 Hz and J = 3.0 Hz, 1 H), 7.95–7.89 (m, 2 H), 7.45 (m, 2 H), 7.32 (d, J = 10 Hz, 1 H), 2.59 (s, 3 H); ^{13}C NMR δ 140.07, 139.08, 134.00, 131.20, 126.55, 128.30, 127.70, 126.65, 124.49, 122.47, 20.83. Anal. Calcd for $C_{22}H_{18}SO$: C, 79.99; H, 5.49. Found: C, 79.78; H, 5.62.

To a suspension of bis(4-methyl-1-naphthyl) sulfoxide (3.0 g, 0.009 mol) in concentrated hydrochloric acid (25 mL) and ether (50 mL) was added zinc (6.5 g, 0.1 mol) over 4 h, at reflux. After cooling, the solid was separated and recrystallized from ethyl acetate to give 1.5 g (51%) of **21**, as pale yellow plates: mp 174–175 °C; ^1H NMR δ 8.45 (d, J = 9.9 Hz, 1 H), 8.05 (d, J = 9.8 Hz, 1 H), 7.73 (m, 2 H), 7.16 (m, 2 H), 2.63 (s, 3 H), ^{13}C NMR δ 134.29, 133.24, 132.54, 130.40, 129.70, 126.69, 126.27, 126.13, 125.66, 124.69, 19.40. Anal. Calcd for $C_{22}H_{18}S$: C, 84.05; H, 5.79. Found: C, 83.84; H, 6.02.

Alkali-Metal Reduction of Diaryl Sulfides. Reduction of 15–21 was carried out by dissolving them in THF and adding the solution to 2–3 equiv of K in liquid ammonia at −78 °C under a nitrogen atmosphere. The dark blue solutions changed color and were stirred for 3 h. Three equivalents of ammonium chloride were added. After a few minutes the color of the solution faded and it became clear and was slowly allowed to warm to ambient temperature. After the ammonia was evaporated, tetradecane was added as an internal standard. The THF solution of reduction products was sampled and analyzed by GC/MS.

Reduction of 4-(1-naphthylthio)quinoline (15) (0.4882 g, 0.0017 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1563 g, 0.00079 mol) and found to contain **9** (0.079 g, 0.00062 mil, 36.3 mol %) [MS, m/e (relative intensity) 128 (M^+, 100.0)], **34** (0.0067 g, 0.00005 mol, 3.1 mol %) [MS, m/e (relative intensity) 129 (M^+, 100.0)], **25** (0.0454 g, 0.00014 mol, 8.4 mol %) [MS, m/e (relative intensity) 160 (M^+, 100.0), 128 (M − 32, 38.4)], **42** (0.0072 g, 0.00003 mol, 1.6 mol %) [MS, m/e (relative intensity) 259 (7.8), 147 (32.0), 129 (100.0)], **38** (0.0121 g, 0.00005 mol, 2.8 mol %) [MS, m/e (relative intensity) 259 (M + 2, 6.5), 258 (M + 1, 23.2), 257 (M^+, 100.0), 129 (45.9), 128 (20.5)], and two regioisomers of **37** [(0.3476 g, 0.00136 mol, 80.2 mol %) and reacted **15** (0.0090 g, 0.00003 mol, 1.9 mol %)].

Reduction of 4-(1-naphthylthio)quinoline 1-oxide (16) (0.5033 g, 0.00166 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1620 g, 0.00082 mol) and found to contain **9** (0.0165 g, 0.00013 mol, 7.7 mol %), and two regioisomers of **37** [(0.0122 g, 0.00005 mol, 2.9 mol %) and **15** (0.0066 g, 0.00002 mol, 1.4 mol %) and **32** (0.0083 g, 0.00003 mol, 1.6 mol %)].

Reduction of 4-(phenylthio)quinoline (17) (0.4140 g, 0.00175 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1594 g, 0.00081 mol) and found to contain **22** (0.1084 g, 0.00139 mol, 81.7 mol %), **34** (0.0785 g, 0.00061 mol, 35.8 mol %), **23** (0.0465 g, 0.00021 mol, 12.6 mol %), **17** (0.0125 g, 0.00005 mol, 3.1 mol %), and **13** (0.0804 g, 0.00028 mol, 16.5 mol %).

Reduction of 4-(phenylthio)quinoline 1-oxide (18) (0.4121 g, 0.00163 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1492 g, 0.00075 mol) and found to contain **22** (0.0689 g, 0.00088 mol, 54.0 mol %), **34** (0.0333 g, 0.00026 mol, 15.8 mol %), **23** (0.0567 g, 0.00026 mol, 16.0 mol %), **17** (0.0109 g, 0.00005 mol, 2.7 mol %), and **13** (0.0093 g, 0.00003 mol, 1.9 mol %).

Reduction of phenyl 1-naphthyl sulfide (19) (0.4016 g, 0.0017 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1519 g, 0.00077 mol) and found to contain **22** (0.13363 g, 0.00175 mol, 103.0 mol %), **9** (0.0057 g, 0.00004 mol, 2.6 mol %), **25** (0.976 g, 0.00061 mol, 35.9 mol %), **30** (0.009 g, 0.0000037 mol, 0.22 mol %), **19** (0.0017 g, 0.00001 mol, 0.43 mol %), and two regioisomers of **27** [(0.0040 g, 0.00002 mol, 1.0 mol %) and (0.0055 g, 0.00002 mol, 1.3 mol %)], **1** (0.0109 g, 0.00004 mol, 2.2 mol %), **33** (0.0263 g, 0.00008 mol, 4.8 mol %), and **32** (0.0875 g, 0.00028 mol, 16.2 mol %).

Reduction of 4-quinolinethione (20) (0.2743 g, 0.0017 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1515 g, 0.00077 mol) and found to contain **34** (0.0077 g, 0.00006 mol, 3.5 mol %), **40** (0.2111 g, 0.00081 mol, 47.8 mol %), **13** (0.0232 g, 0.00008 mol, 4.7 mol %), **41** (trace), and two regioisomers of **39** [(trace): MS, m/e (relative intensity) 256 (M^+, 100.0), and (trace)], and **35** (trace).

Reduction of bis(4-methyl-1-naphthyl) sulfide (21) (0.5009 g, 0.0016 mol) yielded a THF solution of reduction products, which was analyzed by GC/MS with tetradecane (0.1583 g, 0.0008 mol) and found to contain **24** (0.0280 g, 0.0002 mol, 12.3 mol %), **26** (0.0811 g, 0.00047 mol, 29.0 mol %), **29** (trace), **31** (0.0205 g, 0.00006 mol, 4.1 mol %), **28** (trace), and unreacted **21** (0.3365 g, 0.00047 mol, 67.0 mol %).

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Supplementary Material Available: Full experimental details containing additional mass spectral data on all compounds appearing in the article (7 pages). Ordering information is available on any current masthead page.