and distilled under reduced pressure (1 mm) giving 20.5 g (90%) of the sulfides. The oxidation by peroxybenzoic acid in chloroform gave, in almost quantitative yields, a mixture of ethylenic sulfones from which compounds **5** and **6** can be isolated by column chromatography on silica gel (eluents petroleum ether (bp 30–60°)-ethyl ether 2:1). The chromatographic separation was almost quantitative (over-all yields on sulfides >90%).

The acetic acid solution was poured in iced water and extracted with ether. The ethereal extract has been worked up as the ethyl acetate solution giving a mixture of the three sulfones **5, 6** and **7** (see Table I).

Identification of Sulfones 5, 6, and 7.—The three sulfones, recrystallized from petroleum ether, gave satisfactory analyses for 1:1 adducts in the oxidized form [*Anal.* Calcd for $C_{13}H_{17}ClO_2S$: Cl, 12.99; S, 11.75. Found. (**5**, mp 84–85°): Cl, 13.00; S, 11.68. (**6**, mp 88–89°) Cl, 13.12; S, 11.71. (**7**, mp 83–84°) Cl, 13.15; S, 11.90]. Hydrogenation of **5** and **6** over 5% palladium–charcoal in ethanol (3.5 atm for 4 hr at room temperature) yielded the same (1,2,2-trimethyl)propyl *p*-tolyl sulfone (**8**). Hydrogenation of **7** yielded (3,3-dimethyl)butyl *p*-tolyl sulfone (**9**).

(1,2,2-Trimethyl)propyl *p*-tolyl sulfone (8) has been synthesized by oxidation of the corresponding sulfide **10** with peroxybenzoic acid in chloroform, mp 67–68° from methanol. *Anal.* Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39; S, 13.34. Found: C, 64.96; H, 8.39; S, 13.20.

(3,3-Dimethyl)butyl *p*-tolyl sulfone (9) was obtained by oxidation of the corresponding sulfide **11**, mp 97–98° from methanol. *Anal.* Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39; S, 13.34. Found: C, 64.82; H, 8.39; S, 13.28.

(1,2,2-Trimethyl)propyl *p*-tolyl sulfide (10) was obtained by reaction of *p*-bromobenzensulfonic acid (1,2,2-trimethyl)propyl ester[20] with sodium *p*-toluenethiolate in ethanol, bp 118–120° (1 mm). *Anal.* Calcd for $C_{13}H_{20}S$: C, 74.93; H, 9.68; S, 15.41. Found: C, 74.09; H, 9.44; S, 15.30.

(3,3-Dimethyl)butyl *p*-tolyl sulfide (11), obtained by reaction of 1-bromo-3,3-dimethylbutane with sodium *p*-toluenethiolate in ethanol, had bp 104–106° (1 mm). *Anal.* Calcd for $C_{13}H_{20}S$: C, 74.93; H, 9.68; S, 15.41. Found: C, 75.16; H, 9.59; S, 15.10.

Registry No.—*t*-Butylacetylene, 917-92-0; **5**, 19519-80-3; **6**, 19519-81-4; **7**, 19519-66-5; **8**, 19519-67-6; **9**, 19519-68-7; **10**, 19519-69-8; **11**, 19519-70-1.

Acknowledgments.—We thank Professor F. Taddei, Istituto di Chimica Organica e di Chimica Industriale, Bologna, for the nmr spectra.

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Organosulfur Derivatives of Azulene. III. Di-1-azulyl Sulfide, Sulfoxide, and Sulfone[1a]

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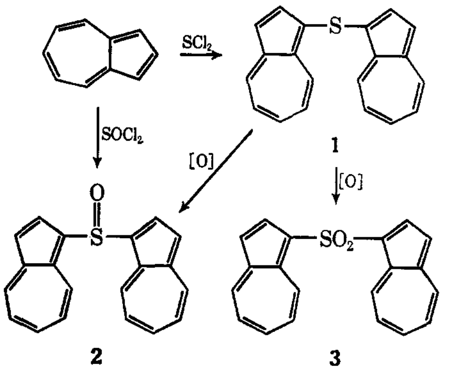
Earlier papers in this series have described the preparation and properties of some methyl and phenyl 1-azulyl sulfides[2] and the corresponding sulfoxides and sulfones.[3] This paper is concerned with the symmetrical derivatives di-1-azulyl sulfide (**1**), di-1-azulyl sulfoxide (**2**), and di-1-azulyl sulfone (**3**).

It is known that aromatics react with sulfur dichloride to form symmetrical diaryl sulfides[4] and with thionyl chloride to form symmetrical diaryl sulfoxides.[5] Azulenes react with benzenesulfenyl chloride to give phenyl 1-azulyl sulfides[2,6] and with methanesulfinyl and benzenesulfinyl chlorides to give methyl and phenyl 1-azulyl sulfoxides.[3] Also, it was reported[7] that the reaction of the sodium salt of 1-azulenesulfonic acid with thionyl chloride gave azulene-1-sulfonyl-3-sulfinyl dichloride. Therefore, it was expected that di-1-azulyl sulfide (**1**) and di-1-azulyl sulfoxide (**2**) should result from the reaction of azulene with sulfur dichloride and thionyl chloride, respectively.

Azulene reacted vigorously with sulfur dichloride in anhydrous ether at −78° to give an 18% yield of the blue, crystalline di-1-azulyl sulfide (**1**). The sulfide (**1**) was characterized by its elemental analysis, its nmr spectrum, which was characteristic of a 1-substituted azulene, and its visible spectrum with λ_{max} 598 $m\mu$. Much unreacted azulene was recovered from this reaction as well as a considerable amount of polymeric green solid. Variations in reaction conditions such as different solvents (tetrahydrofuran, chloroform, or acetonitrile), different temperatures (−45 or −111°), or the inclusion of pyridine did not increase the yield of the sulfide (**1**).

A 21% yield of di-1-azulyl sulfoxide (**2**) was obtained from the reaction of azulene with thionyl chloride in acetonitrile at −45°. The sulfoxide (**2**), a purple, crystalline solid, had λ_{max} 557 $m\mu$ and a band at 9.75 μ (S═O) in its infrared (ir) spectrum. The sulfide (**1**) was isolated in very low yield from one of the reactions between azulene and thionyl chloride.[8] When the reaction was carried out at −70° in anhydrous ether, another product, a red solid which eluted before the sulfoxide (**2**), was isolated in low (*ca.* 4%) yield. This red solid was later identified as di-1-azulyl sulfone (**3**) (Scheme I). An attempt to form the sulfone (**3**)

SCHEME I



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by treating azulene with sulfuryl chloride was unsuccessful, yielding unreacted azulene and a small amount of green oil which probably contained 1-chloro- and 1,3-dichloroazulene. When the sulfide was oxidized by sodium metaperiodate in refluxing methanol for 1 hr, the sulfoxide **2** was obtained in good yield (78%) along with a small amount (5%) of the sulfone **3**. A similar oxidation of **1** for 24 hr afforded di-1-azulyl sulfone (**3**) in good (81%) yield. The sulfone was characterized by its elemental analysis, its λ_{max} at 541 mμ, the bands in its ir spectrum at 7.72 and 8.93 μ, and its nmr spectrum.

A few attempts to prepare tri-1-azulylsulfonium chloride were carried out. It has been reported[9] that triarylsulfonium chlorides result from the reaction of the arene with thionyl chloride and aluminum chloride. Azulene was allowed to react with thionyl chloride and anhydrous stannic chloride in acetonitrile at −45°. A small amount of purple solid was obtained from the dichloromethane extract by twice precipitating it by addition to anhydrous ether. This purple solid, which was suspected to be tri-1-azulylsulfonium chloride, was rather unstable, and we were not able to obtain it in pure form. On heating, it decomposed, turning black, at about 150°.

The shift of the visible band of azulene due to methyl- and phenylthio,[2] methyl- and phenylsulfinyl,[3] and methyl- and phenylsulfonyl[3] groups substituted at the 1 position has been reported and discussed. It is known that electron-withdrawing substituent groups at the 1 position of azulene cause hypsochromic shifts,[10] and the observed shifts of −9 mμ for a phenylthio group, −32 mμ for a phenylsulfinyl group, and −47 mμ for a phenylsulfonyl group are consistent with their relative electron-withdrawing character. In comparison, the spectral shifts (Table I) for the sulfide **1** (+18 mμ), the sulfoxide **2** (−20 mμ), and the sulfone **3** (−36 mμ) are all more bathochromic than the corresponding phenyl derivatives. Since azulene is electron rich at the 1 position, one would expect a 1-azulyl group to donate electron density to an attached sulfur atom and that a 1-azulylthio, 1-azulenesulfinyl, or 1-azulenesulfonyl group would be less electron withdrawing than the corresponding substituent group which has a phenyl in place of the 1-azulyl moiety.

TABLE I

PRINCIPAL VISIBLE ABSORPTION MAXIMA AND SPECTRAL SHIFTS OF DI-1-AZULYL SULFIDE, SULFOXIDE, AND SULFONE

Compound	λ_{max}, mμ	$\Delta\lambda_{max}$, mμ
(1-Az)$_2$S (**1**)	598[a]	+18[a]
(1-Az)$_2$SO (**2**)	557[b]	−20[b]
(1-Az)$_2$SO$_2$ (**3**)	541[b]	−36[b]

[a] Cyclohexane solution. [b] Chloroform solution.

Experimental Section[11]

Di-1-azulyl Sulfide (1).—To a stirred solution of 640 mg (5.00 mmol) of azulene in approximately 50 ml of anhydrous ether, kept at −78° under an argon atmosphere was added a solution of 0.19 ml (310 mg, 3.0 mmol) of sulfur dichloride in 10 ml of anhydrous ether dropwise over a period of 2 hr. The reaction mixture was poured into ice water and the layers were separated. The aqueous layer was extracted several times with ether, leaving much insoluble green solid behind. Solvent was removed from the combined blue-green ethereal extracts, and the residue was chromatographed over acid-washed alumina. A large blue band which contained unreacted azulene (222 mg) was eluted with petroleum ether, and the darker blue band was eluted with 1:1 petroleum ether–dichloromethane. A large green band followed. The blue-green oily residue from the second band was recrystallized from petroleum ether containing traces of dichloromethane to give 130 mg (18% gross, 28% net yield) of dark blue crystals of di-1-azulyl sulfide (**1**): mp 87–88°; uv max (cyclohexane) 238 mμ (log ϵ 4.56), 278 (4.77), shoulder at 293 (4.66), 337 (3.93), and 371 (4.07); visible max (cyclohexane) 598 mμ (log ϵ 2.73) 622 (2.73), and shoulder at 680 (2.52); nmr (CDCl$_3$) τ 1.23 (d, J = 9 Hz, H-8), 1.82 (d, J = 9 Hz, H-4), 2.27 (d, J = 4 Hz, H-2), 2.75 (d, J = 4 Hz, H-3), and 2.4–3.1 (m, H-5, H-6, H-7).

Anal. Calcd for $C_{20}H_{14}S$: C, 83.87; H, 4.93. Found: C, 83.75; H, 4.99.

Di-1-azulyl Sulfoxide (2). A. By Oxidation of 1.—A mixture of 170 mg (0.596 mmol) of di-1-azulyl sulfide, 0.70 ml of 1 M aqueous sodium metaperiodate, and 25 ml of methanol was refluxed until tlc (silica gel G, dichloromethane) showed that most of sulfide (front-running blue spot) had reacted and that di-1-azulyl sulfone (intermediate red spot) was being produced (*ca.* 1 hr). Water was added and the mixture was extracted with ether and then with dichloromethane. The organic extracts were combined and dried (MgSO$_4$), and the solvent was removed. The residue was chromatographed over acid-washed alumina; the small blue band which contained 14 mg of unreacted sulfide was eluted with 2:1 petroleum ether–dichloromethane. A small red band which yielded 10 mg (5%) of di-1-azulyl sulfone (**3**), mp 188–189°, was eluted with dichloromethane, and the large purple band was eluted with 1:1 ether–acetone. The residue from the purple eluate was recrystallized from a petroleum ether–dichloromethane mixture to give 140 mg (78%) of di-1-azulyl sulfoxide (**2**): purple crystals; mp 94–95°; uv max (CHCl$_3$) 282 mμ (log ϵ 4.78), shoulder at 298 (4.40), 336 (4.14), and 373 (4.20); visible max 557 mμ (log ϵ 2.91); ir (CHCl$_3$) 9.81 μ (S═O); nmr (CDCl$_3$) τ 1.05 (d, J = 9 Hz, H-8), 1.65 (d, J = 9 Hz, H-4), 2.07 (d, J = 4 Hz, H-2), 2.70 (d, J = 4 Hz, H-3) and 2.3–2.7 (m, H-5, H-6 and H-7).

Anal. Calcd for $C_{20}H_{14}OS$: C, 79.44; H, 4.67. Found: C, 79.14; H, 4.55.

B. From Azulene and Thionyl Chloride.—A solution of 0.188 ml (180 mg, 1.5 mmol) of freshly distilled thionyl chloride in 8 ml of dry acetonitrile was added dropwise over a period of 15 min to a stirred, cooled (−45°) mixture of 387 mg (3.02 mmol) of azulene and 25 ml of acetonitrile kept under a dry nitrogen atmosphere. The temperature of the reaction mixture was allowed to rise to −40°, 0.10 ml of pyridine was added, and this mixture was poured into water. The purple mixture was extracted with dichloromethane. Solvent was removed from the organic extract, and the residue was chromatographed over acid-washed alumina. Dichloromethane eluted a large green band which had a small blue front. Some small brown, yellow, and pink bands were eluted before the large purple band (1:1 ether–acetone). The purple eluate yielded 95 mg (21%) of **2** as a purple, crystalline solid, mp 94.5–95.5°. An ir spectrum of this product (chloroform solution) was identical with the ir spectrum of the product above.

Di-1-Azulyl Sulfone (3).—A mixture of 193 mg (0.675 mmol) di-1-azulyl sulfide, 1.5 ml of aqueous 1 M sodium metaperiodate, and 25 ml of methanol was refluxed for 24 hr. The reaction mixture was treated in a manner similar to that (method A) above. Chromatography gave a small blue band, eluted with 1:4 dichloromethane–chloroform, which contained 20 mg of unreacted sulfide and a large red band, eluted with dichloromethane.

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(9) S. Smiles and R. L. Rossignol, *J. Chem. Soc.*, **89**, 698 (1906).

(10) (a) E. Heilbronner in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, New York, N. Y., 1959, Chapter V; (b) A. G. Anderson, Jr., and B. M. Steckler, *J. Amer. Chem. Soc.*, **81**, 4941 (1959).

(11) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded using a Beckman IR-5; ultraviolet and visible spectra were taken on a Cary 14. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as the internal marker. Coupling constants were taken directly from the spectra and are apparent values. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich., or by Berkeley Analytical Laboratories, Berkeley, Calif.

The red eluate yielded 175 mg (81%) if di-1-azulyl sulfone (**3**): red crystals; mp 187–188°; uv max ($CHCl_3$) 276 mμ (log ε 4.67), 296 (4.57), 306 (4.53), 366 (4.09), and 381 (4.10); visible max 541 mμ (log ε 2.95) and a shoulder at 625 (2.45); ir ($CHCl_3$) 7.72 and 8.93 μ (SO_2); nmr τ 0.55 (d, *J* = 10 Hz, H-8), 1.58 (d, *J* = 10 Hz, H-4), 1.62 (d, *J* = 4 Hz, H-2), 2.72 (d, *J* = 4 Hz, H-3) and 2.0–2.7 (m, H-5, H-6, and H-7).

Anal. Calcd for $C_{20}H_{14}SO_2$: C, 75.44; H, 4.43; S, 10.07. Found: C, 75.41; H, 4.42; S, 9.79.

Registry No.—**1**, 19254-87-6; **2**, 19254-88-7; **3**, 19254-89-8.

The Reduction of Nitroso Compounds with Diborane

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In continuation of our studies of the reduction of unsaturated nitrogen functions with diborane,[1] we are now reporting the results with aromatic nitroso compounds, *gem*-nitronitroso, *gem*-chloronitroso, and *gem*-nitrooximino compounds.

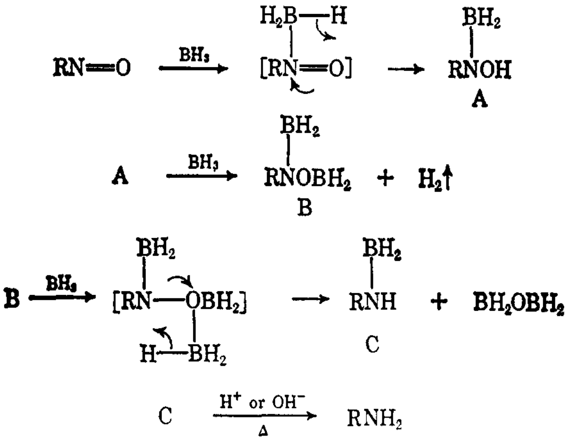
The reduction of aromatic nitroso compounds catalytically or with atomic hydrogen to amines is well documented in the literature.[2] Treatment of *p*-nitrosophenol with sodium borohydride led to *p*-aminophenol (42%);[3] however, nitrosobenzene itself was reduced to azoxybenzene in 73% yield.[3]

As shown by representative examples in Table I, the reduction of aromatic nitroso compounds with diborane at 25° afforded the corresponding amines in good yields. It is of interest to point out that while *p*-nitroso-N,N-dimethylaniline was reduced to 1-amino-4-dimethylaminobenzene in 64% yield, the product of reduction with lithium aluminum hydride was 4,4′-azobis(N,N-dimethylaniline) (80%).[4]

In general the reactions were found to be highly exothermic, and 1 equiv of hydrogen was evolved immediately after the addition of diborane, although no acidic hydrogen was present in the starting material. Hydrogen evolution was also observed by Boyer and Ellzey[3] when *o*-dinitrosobenzene was treated with sodium borohydride.

By employing nitrosobenzene (**1**) as a model compound, it was found that the yield of amine was, over a wide range, independent of the amount of hydride ion per mol of **1**.[5]

On the basis of quantitative measurements of hydride consumption (3 equiv of hydride ion were consumed in the reduction, 1 equiv of which was evolved as hydrogen *prior* to hydrolysis) it is proposed that the reduction of aromatic nitroso compounds with diborane involves essentially four steps (eq 1–4).



$$RN{=}O \xrightarrow{BH_3} \left[\overset{H_2B-H}{RN{=}O}\right] \longrightarrow \underset{\mathbf{A}}{\overset{BH_2}{RNOH}} \tag{1}$$

$$\mathbf{A} \xrightarrow{BH_3} \underset{B}{\overset{BH_2}{RNOBH_2}} + H_2\uparrow \tag{2}$$

$$\mathbf{B} \xrightarrow{BH_3} \left[\overset{BH_2}{RN}-\underset{H-BH_2}{OBH_2}\right] \longrightarrow \underset{C}{\overset{BH_2}{RNH}} + BH_2OBH_2 \tag{3}$$

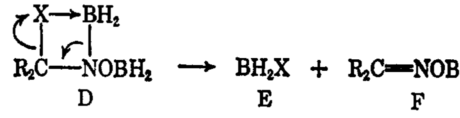
$$C \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RNH_2 \tag{4}$$

Although intermediates A, B, and C are represented as monomeric, it is quite possible that they are polymeric in nature. The electrophilic attack of diborane on nitrogen in step 1 explains the formation of a hydroxyl group in intermediate A by a four-centered hydride transfer. In step 2, the electrophilic attack on the hydroxyl proton[6] is supported by the fact that hydrogen was evolved during the reaction *prior* to hydrolysis. The possibility of the formation of a hydroxylamine intermediate such as B is based on our findings that phenylhydroxylamine was readily reduced by diborane to aniline (65%) at 25°.[7] The remaining steps 3 and 4 are similar to those proposed for the reduction of oxime ethers with diborane.[1]

A recent report by Exner,[8] that 1,1-nitronitrosocyclohexane (**2**) was converted into cyclohexanone oxime (79%) at 15° on treatment with lithium aluminum hydride, prompted us to investigate the reaction of *gem*-nitronitroso compounds with diborane. It was found that the reaction of **2** with diborane at 25° gave the hydroxylamine, N-cyclohexylhydroxylamine, in 71% yield. As shown in Table II similar results were obtained with 2,2-nitronitrosopropane (**3**), 1,1-chloronitrosocyclohexane (**4**), and 1-nitropropanal oxime (**5**).

It was established that in these reactions the nitro and chloro groups were eliminated in the reduction, for the hydrolysates of the reaction mixtures gave positive tests for these ions.

Our observations that, as in the case of aromatic nitroso compounds, hydrogen was evolved prior to hydrolysis and that the same amount of hydride was consumed makes it very likely that steps 1 and 2 also apply to the reduction of compounds **2–5**. However, the important difference lies in the elimination step which leads to an oxime intermediate F (eq 5). Further



$$\underset{D}{\overset{X\rightarrow BH_2}{R_2C-NOBH_2}} \longrightarrow \underset{E}{BH_2X} + \underset{F}{R_2C{=}NOBH_2} \tag{5}$$

reaction of F with diborane and subsequent hydrolysis would lead to the hydroxylamine.[9]

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[1] For previous publications, see H. Feuer and D. M. Braunstein, *J. Org. Chem.*, **34**, 1817 (1969).

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[5] The reduction of **1** with 3.5 and 8.0 equiv of hydride ion gave aniline in yields of 73.8 and 74.2%, respectively.

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[7] It was previously found that the reduction of aliphatic hydroxylamines to amines with diborane required a temperature range of about 105–110°.[1]

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