Organosulfur Derivatives of Azulene. II. 1-Azulyl Sulfoxides and Sulfones[1,2]

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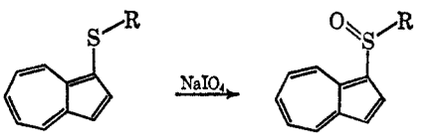
The preparation and properties of some methyl and phenyl 1-azulyl sulfoxides and sulfones are reported. The sulfoxides and sulfones were obtained by oxidation of the corresponding sulfides. Also the sulfoxides were prepared by electrophilic substitution of methanesulfinyl or benzenesulfinyl chloride on azulene. This method represents a new procedure for the synthesis of unsymmetrical diaryl sulfoxides. The methyl 1-azulyl sulfones could be prepared by electrophilic substitution on azulene by methanesulfonyl chloride, but attempted substitution of azulene by benzenesulfonyl chloride was unsuccessful. The spectral shifts of the visible band of azulene due to the organosulfur substituents are reported and discussed.

Only a few functional group classes of organosulfur derivatives of azulene have been reported, and these usually have the sulfur atom attached to the 1 position. A series of methyl and phenyl 1-azulyl sulfides have been prepared.[4] Some derivatives of 1-azulenethiol and 1,3-azulenedithiol, *viz.*, thiocyano, S-acetylthiol, and disulfide, were reported by Anderson and McDonald.[5] Many different azulenesulfonic acids are known. Sulfonation of guaiazulene gives substitution at the 3 position, or at the 2 position and on the 1-methyl group, depending on the sulfonating agent.[6] The expected 1-azulenesulfonic acids are obtained from the sulfonation of azulene and 4,6,8-trimethylazulene.[7] Treatment of 6-chloro-4,8-dimethylazulene with sulfur and sodium sulfide is reported[8a] to give the corresponding 6-azulyl disulfide, while a 6-azulenethiol was obtained by nucleophilic displacement on ethyl 6-bromoazulene-1,3-dicarboxylate with sodium hydrosulfide.[8b]

It is believed that examination of the properties of these organosulfur derivatives of azulene will contribute some information to the problem of sulfur bonding. Azulene has some unique properties which make it a valuable tool for these studies. Spectral shifts caused by substituent groups can be evaluated in terms of electronic and steric effects.[9] Variation in electronic effects is provided by the nonuniform π-electron densities[9a] around the ring, and the propinquity of the 1 and 8 positions allows one to examine steric effects. Hopefully then, interpretation of the spectral shifts due to substituent groups which have the sulfur atom attached to the ring will allow an evaluation of the bonding between sulfur and an aromatic ring.

Sulfoxides.—No azulyl sulfoxides have previously been recorded in the literature. We have prepared methyl and phenyl 1-azulyl sulfoxides by the sodium metaperiodate oxidation of the corresponding methyl and phenyl 1-azulyl sulfides and also by electrophilic substitution of methanesulfinyl and benzenesulfinyl chlorides on the azulene substrate. The azulene moiety of these sulfoxides is azulene itself, 4,6,8-trimethylazulene, or guaiazulene (1,4-dimethyl-7-isopropylazulene).

Oxidation of the methyl and phenyl 1-azulyl sulfides[2] by an aqueous, methanolic mixture of sodium metaperiodate[10] proved to be an excellent method for the synthesis of the sulfoxides. For example, methyl 1-azulyl sulfide (**1a**) was oxidized to methyl 1-azulyl sulfoxide (**2a**), mp 75.5–76.5°, in 93% yield. Methyl



1a, R=CH_3
b, R=C_6H_5

2a, R=CH_3
b, R=C_6H_5

1-(4,6,8-trimethylazulyl) sulfoxide (**3**), mp 78.5–79.5°, and methyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfoxide (**4**), mp 95–95.5°, were obtained in comparable yields by the oxidation of the corresponding sulfides.

It was found that more vigorous conditions were required to oxidize phenyl 1-azulyl sulfides. Refluxing the reaction mixture (70–75° temperature) for several hours was a satisfactory procedure. Phenyl 1-azulyl sulfoxide (**2b**), mp 65.5–67°, was obtained from the sulfide **1b** in 82% yield. Similar oxidation of 1-phenylthio-4,6,8-trimethylazulene (**5**) and 3-phenylthioguaiazulene (**6**) gave the corresponding 1- and 3-phenylsulfinyl derivatives **7** and **8** of trimethylazulene and guaiazulene, respectively.

The oxidation of **1b** also yielded a small amount of another crystalline product, a red solid melting at 134–135°. Likewise, a red-purple solid, mp 143–146°, was isolated in low yield from the oxidation of **6**. These solids had no sulfoxide absorption band in the infrared, but they did show sulfone bands[11] at *ca.* 7.7 and 8.7 μ.[12]

The identity of these methyl and phenyl 1-azulyl sulfoxides was established by their spectral data and elemental analyses (Table I). A strong sulfoxide band[11] at *ca.* 9.7 μ was apparent in their infrared spectra. Their visible spectra show the hyposochromic shift (Table II) expected for an azulene bearing an electron-withdrawing group in the 1 position.[9] Also their

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(2) Part I: L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, **30**, 2715 (1965).

(3) National Science Foundation Undergraduate Research Participant, 1964–1965.

(4) Reference 2 and references therein.

(5) A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959).

(6) W. Meir, D. Meuche, and E. Heilbronner, *Helv. Chim. Acta*, **46**, 1929 (1963).

(7) W. Schroth and K. Achtelik, *Z. Chem.*, **3**, 426 (1963).

(8) (a) K. Hafner, H. Patzelt, and H. Kaiser, *Ann.*, **656**, 24 (1962); (b) T. Nozoe, K. Takase, and M. Tada, *Bull. Chem. Soc., Japan*, **38**, 247 (1965).

(9) (a) E. Heilbronner, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter V; (b) A. G. Anderson, Jr., and B. M. Steckler, *J. Am. Chem. Soc.*, **81**, 4941 (1959); (c) M. Scholz and W. Treibs, *Z. Elektrochem.*, **65**, 120 (1961).

(10) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(11) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 54.

(12) These compounds were subsequently identified as the respective sulfones, phenyl 1-azulyl sulfone (**11**) and phenyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfone (**14**).

TABLE I

METHYL AND PHENYL 1-AZULYL SULFOXIDES

Sulfoxide[a]	Mp[b] °C	Yield, % By oxidn[c]	Yield, % By substn[d]	S=O[e] band, μ	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1-MeSO-Az (2a)	75.5–76.5	93	38	9.74	$C_{11}H_{10}OS$	69.44	5.30	69.47	5.30
1-PhSO-Az (2b)	70–70.5[f]	82	54	9.77	$C_{16}H_{12}OS$	76.16	4.80	76.09	5.15
1-MeSO-TMA (3)	81–81.5[f]	89	70	9.74	$C_{14}H_{16}OS$	72.37	6.94	72.36	6.58
1-PhSO-TMA (7)	79–81.5	75	71	9.77	$C_{19}H_{18}OS$	77.51	6.16	77.60	6.09
3-MeSO-Gz (4)	95–95.5	91	68	9.76	$C_{16}H_{20}OS$	73.80	7.74	74.01	7.94
3-PhSO-Gz (8)	88.5–90.5	68	57	9.80	$C_{21}H_{22}OS$	78.21	6.88	77.85	6.92

[a] Az = azulene, TMA = 4,6,8-trimethylazulene, Gz = guaiazulene. [b] All melt with decomposition. [c] From oxidation of corresponding sulfide. [d] From substitution on azulene hydrocarbon by methanesulfinyl or benzenesulfinyl chloride. [e] In chloroform solution. [f] Analytical sample.

TABLE II

PRINCIPAL VISIBLE ABSORPTION MAXIMA AND SPECTRAL SHIFTS OF 1-AZULYL SULFOXIDES

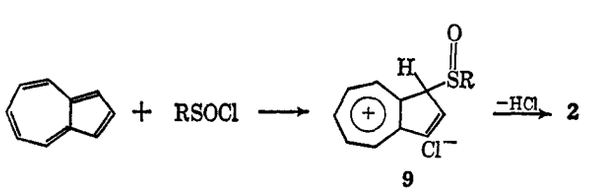
Compd[a]	Cyclohexane λ_{max}, mμ	Cyclohexane $\Delta\lambda_{max}$,[b] mμ	Cyclohexane $\Delta\nu_{max}$,[b] cm^{-1}	Chloroform λ_{max}, mμ	Chloroform $\Delta\lambda_{max}$,[b] mμ	Chloroform $\Delta\nu$,[b] cm^{-1}
1-MeSO-Az (2a)	566	−14	430	550	−27	880
1-PhSO-Az (2b)	554	−26	810	545	−32	1020
1-MeSO-TMA (3)	543	−4	140	526	−17	590
1-PhSO-TMA (7)	530	−17	590	516	−27	960
3-MeSO-Gz (4)	596	−9	250	577	−23	660
3-PhSO-Gz (8)	578	−27	770	567	−33	970

[a] Az = azulene, TMA = 4,6,8-trimethylazulene, Gz = guaiazulene. [b] Shift measured relative to parent azulene, *viz.* Az, TMA, or Gz.

nmr spectra have the expected pattern for 1 and 3 substitution plus the additional methyl or phenyl group. Since azulene always undergoes electrophilic substitution in the 1 position[9a] and the spectra of these compounds are consistent with 1 substitution, there seems little doubt that these compounds are 1-azulyl sulfoxides.

Another possible route to the 1-azulyl sulfoxides would be direct electrophilic substitution on the azulene by an alkane- or arenesulfinyl chloride. It was found that treatment of an acetonitrile solution of the azulene at *ca.* −45° with methane- or benzenesulfinyl chloride,[13] followed by addition of pyridine at −30°, is also a satisfactory method for the preparation of methyl and phenyl 1-azulyl sulfoxides. Colder reaction temperatures are to be avoided because the solvent freezes. Warmer temperatures cause extensive decomposition.

During the addition of the sulfinyl chloride a solid, usually reddish brown, would be formed; when pyridine was added, it would disappear, and the solution would generally assume the color of the product. Therefore this solid is presumed to be the adduct (*e.g.*, **9**) of the azulene with the sulfinyl chloride.



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Preparation of the methyl and phenyl sulfoxides of 4,6,8-trimethylazulene (**3** and **7**) and of guaiazulene (**4** and **8**) by this method resulted in fair (57 to 72%) yields. However substitution on azulene itself gave much poorer (38 to 34%) yields of sulfoxides **2a** and **2b**. A modification of the reaction of azulene with benzenesulfinyl chloride, in which the reaction was carried out at 0° in dichloromethane and pyridine was omitted, gave a somewhat better (54%) yield. Much unreacted azulene was recovered from this reaction. However the use of these conditions in the attempted preparation of **8** led to much decomposition, and gave no sulfoxide. The use of dry ether at room temperature in the reaction of 4,6,8-trimethylazulene with benzenesulfinyl chloride (followed by addition of pyridine) gave a 9% (33% net) yield of **7**. Although preparation of methyl and phenyl 1-azulyl sulfoxides by this substitution method gives lower yields than the oxidation of sulfides, it affords a direct route from azulene.

It is well known that symmetrical diaryl sulfoxides can be prepared by the reaction of the arene with thionyl chloride and aluminum chloride,[14] and this reaction most likely involves the formation of the arenesulfinyl chloride which then substitutes on another aromatic ring. Also it has been reported[15] that highly reactive aromatic compounds, *e.g.*, napthyl ethers, undergo this reaction in the absence of the catalyst. However the preparation of unsymmetrical diaryl sulfoxides or alkyl aryl sulfoxides by reaction of an arene with an arenesulfinyl or alkenesulfinyl chloride has been relatively unexplored. Douglass and Farah[16] have reported the synthesis of methyl phenyl sulfoxide in 26% yield from the reaction of methanesulfinyl chloride with benzene in the presence of aluminum chloride. Phenyl *p*-tolyl sulfoxide has been prepared in a similar manner using *p*-toluenesulfinyl chloride in place of methanesulfinyl chloride, but details of this reaction are not readily available.[17] From these reports and our results, it would seem that this method would provide a convenient preparation of such sulfoxides. Since sulfoxides are easily reduced,[18] this would be another route to the corresponding sulfides. Probably, activated aromatics such as phenols and aryl ethers and heterocyclics like thiophene and pyrrole would undergo this reaction without the need for a catalyst. A Friedel–Crafts catalyst would most likely be required for nonactivated aromatics.

(13) I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).

(14) H. H. Szmant, in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 158.

(15) C. A. Silveradd, *Chem. Ind.* (London), **45**, 36 (1926).

(16) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 805 (1958).

(17) A. Schöberl, and A. Wagner ["Houben-Weyl, Methoden der Organischen Chemie," Vol. 9, 4th ed, Georg Thieme Verlag, Stuttgart, Germany, 1955, p 217] report that C. Courtot and P. Chiffert (Dissertation, Nancy, 1932) prepared phenyl *p*-tolyl sulfoxide by the reaction of benzene with *p*-toluenesulfinyl chloride in the presence of aluminum chloride.

(18) Reference 14, p 159.

These 1-azulyl sulfoxides are not very stable. They decompose when left in chlorinated solvents, and this decomposition occurs more rapidly in concentrated solutions or at elevated temperatures. Some of the nmr samples, in deuteriochloroform solution, decomposed very rapidly. The sulfoxides containing the guaiazulene or 4,6,8-trimethylazulene moiety seem to be more unstable, and the methyl sulfoxides of these are the most unstable. The sulfoxides do not decompose on alumina. They do decompose in acidic (hydrochloric acid) media, but not in basic (ammonium hydroxide) solution. Traces of pyridine on the solids also seem to accelerate decomposition. In general the decomposition products were not crystalline and were not investigated further. Occasionally the parent azulene would be produced. Notably, the treatment of **3** with dilute hydrochloric acid gave a substantial amount of 4,6,8-trimethylazulene. All of the sulfoxides melt with decomposition; consequently, the melting points of different samples are somewhat variable.

Sulfones.—Oxidation of the methyl and phenyl 1-azulyl sulfides to the sulfones required more vigorous conditions and gave lower yields than oxidation to the sulfoxides. Methyl 1-azulyl sulfide (**1a**) could be oxidized to methyl 1-azulyl sulfone (**10**), a red, crystalline solid, mp 154–156.6°, in 76% yield, by an excess of sodium metaperiodate in refluxing methanol solution over a period of 24 hr. Phenyl 1-azulyl sulfone (**11**) was obtained by a similar oxidation of **1b** in 78% yield. Oxidation of phenyl 1-azulyl sulfoxide (**2b**) also gave **11** in good yield. However, the corresponding sulfides of guaiazulene and 4,6,8-trimethylazulene were more difficult to oxidize and gave low yields of the sulfones. Refluxing a methanolic mixture of methyl 1-(4,6,8-trimethylazulyl) sulfide and excess sodium metaperiodate for 48 hr gave only 22% of methyl 1-(4,6,8-trimethylazulyl) sulfone (**12**). A similar oxidation of **5**, with a reaction period of 14 hr, gave phenyl 1-(4,6,8-trimethylazulyl) sulfone (**13**) in 23% yield. No sulfone could be obtained from sodium metaperiodate oxidation of the methyl sulfide of guaiazulene, and only an 11% yield of phenyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfone (**14**) resulted from the oxidation of the phenyl sulfide of guaiazulene (**6**).

The use of *m*-chloroperbenzoic acid as the oxidizing agent also was investigated. A low (11%) yield of methyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfone (**15**) was obtained from the oxidation of the corresponding sulfide in benzene solvent. The sulfones **12** and **14** were also produced by *m*-chloroperbenzoic acid oxidation of the corresponding sulfides in yields comparable with those obtained by the use of sodium metaperiodate.

A few attempts were made to oxidize the sulfides to sulfones using hydrogen peroxide in acetic acid. Mild conditions (room temperature or slightly above) gave mostly sulfoxide, some unreacted sulfide, and a little sulfone, and more vigorous conditions (100°) led to extensive decomposition.

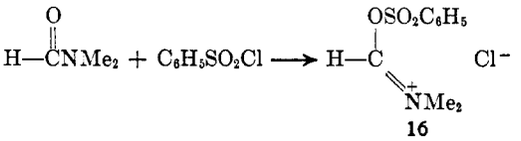
The observed difficulty in oxidation of the sulfides having 4,6,8-trimethylazulene or guaiazulene as the azulene moiety is probably due to steric hindrance. These compounds have a *peri*-8-methyl group which would greatly hinder approach of the oxidizing agent.

A well-known method for the preparation of aryl sulfones is the reaction of an arene with a sulfonyl chloride in the presence of a Friedel–Crafts catalyst.[19] The reaction of azulene with methanesulfonyl chloride provided another route to the methyl 1-azulyl sulfones. Although a catalyst was not required, elevated temperatures and a polar solvent were necessary to get substitution to occur. A refluxing acetonitrile solution of azulene and methanesulfonyl chloride gave, after 14 hr, an 86% yield of **10**. However, similar treatment of 4,6,8-trimethylazulene gave only a 36% yield of **12**. One reaction of guaiazulene with methanesulfonyl chloride gave a very low (8%) yield of **15**, mp 87.5–88.5°. However, this reaction could not be repeated.

Although satisfactory elemental analyses could not be obtained for **15**, there seems little doubt about its structure. The sulfone[11] bands at 7.72 and 8.73 μ, its visible spectral shift of -48 mμ, and the methods of synthesis strongly support the proposed structure.

No phenyl 1-azulyl sulfones could be prepared by the reaction of an azulene with benzenesulfonyl chloride. Many different conditions (nonpolar solvent and a Friedel–Crafts catalyst, polar solvent and no catalyst, low or elevated temperatures) were tried and none were successful. Mild conditions would give mostly unreacted azulene, while more vigorous conditions yielded green and/or brown decomposition products. Azulene and guaiazulene were both tried as substrates. Attempted phenylsulfonylations using benzenesulfonyl chloride and silver perchlorate[20] in nitromethane or with benzenesulfonic anhydride[21] were also unsuccessful.

In one reaction between guaiazulene and benzenesulfonyl chloride, when dimethylformamide was used as the solvent, a brown, crystalline solid, mp 82.5–84°, was isolated. This product had a carbonyl peak in the infrared at 6.1 μ, and it was subsequently identified as 3-guaiazulenecarboxaldehyde.[22] Apparently the formylation of guaiazulene occurred *via* a modified Vilsmeier–Haack reaction,[23] in which the benzenesulfonyl chloride assumed the usual role of phosphorous oxychloride and reacted with the solvent to form the adduct **16**. Phosgene and thionyl chloride[24] have been



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used in place of phosphorous oxychloride in the Vilsmeier–Haack reaction, but apparently benzenesulfonyl chloride has not been so employed.

It is interesting to compare the relative reactivities of sulfenyl, sulfinyl, and sulfonyl chlorides toward azulene. Benzenesulfenyl chloride reacts with azulene most rapidly;[25] the adduct is formed rapidly at $-70°$ in anhydrous ether. Under the same conditions, there is no reaction of azulene with benzenesulfinyl chloride. A more polar solvent (acetonitrile) is required for their reaction, and, as noted, benzenesulfonyl chloride and

(19) F. R. Jensen and G. Goldman, in "Friedel–Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1319.
(20) H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 887 (1955).
(21) F. Muth, ref 17, p 551.
(22) K. Hafner and C. Bernhard, *Ann.*, **625**, 108 (1959).
(23) G. A. Olah and S. J. Kuhn, ref 19, p 1211.
(24) Reference 23, p 1220.
(25) K. Hafner, A. Stephan, and C. Bernhard, *Ann.*, **650**, 42 (1961).

TABLE III

METHYL AND PHENYL 1-AZULYL SULFONES

Sulfone[a]	Mp, °C	Yield, % By oxidn[b]	Yield, % By substn[c]	SO_2[d] bands, μ	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1-$MeSO_2$-Az (10)	156–157[e]	76	86	7.69, 8.87	$C_{11}H_{10}O_2S$	64.05	4.89	63.81	4.54
1-$PhSO_2$Az (11)	134–135	78	0	7.72, 8.78	$C_{16}H_{12}O_2S$	71.61	4.51	71.58	4.55
1-$MeSO_2$-TMA (12)	130.5–131[e]	22	36	7.76, 8.88	$C_{14}H_{16}O_2S$	67.71	6.50	67.82	6.95
1-$PhSO_2$-TMA (13)	196–199[e]	23		7.79, 8.79	$C_{19}H_{18}O_2S$	73.51	5.84	73.67	5.79
3-$MeSO_2$-Gz (15)	87.5–88.5	11	8	7.72, 8.83	$C_{16}H_{20}O_2S$	69.52	7.29	70.29	7.90
3-$PhSO_2$-Gz (14)	151–152	11	0	7.79, 8.74	$C_{21}H_{22}O_2S$	74.52	6.55	74.67	6.51

[a] Az = azulene, TMA = 4,6,8-trimethylazulene, Gz = guaiazulene. [b] From oxidation of the corresponding sulfide. [c] From substitution on azulene hydrocarbon by the sulfonyl chloride. [d] In chloroform solution. [e] Analytical sample.

azulene do not react at room temperature whether in a polar or nonpolar solvent or in the presence of a Lewis acid. In line with our results is the observation that sulfinyl chlorides react much more rapidly with methanol than do sulfonyl chlorides.[26] These data are explicable in terms of how easily the chlorine is displaced from the sulfur. As the sulfur atom becomes increasingly oxygenated, it becomes more electron deficient, and it becomes more difficult to displace the negative chloride ion from it.

That these products are methyl and phenyl 1-azulyl sulfones is established by their spectral data and elemental analyses (Table III). Their infrared spectra show sulfone bands[11] at *ca.* 7.7 and 8.8 μ. Their visible spectra show the strong hypsochromic shift (Table IV) expected for an azulene bearing a strongly electron-withdrawing group in the 1 position.[9] Also their nmr spectra have the expected pattern for 1 substitution plus the additional methyl or phenyl group. The fact that the methyl sulfones could be prepared by two different methods provides additional evidence for their structures. The methyl and phenyl 1-azulyl sulfones described herein are stable, crystalline solids. They are not very soluble in nonpolar solvents. In chromatography the sulfone will elute before the corresponding sulfoxide.

TABLE IV

PRINCIPAL VISIBLE ABSORPTION MAXIMA AND SPECTRAL SHIFTS OF 1-AZULYL SULFONES[a]

Compd[b]	λ_{max}, mμ	$\Delta\lambda_{max}$[c] mμ	ν_{max}, cm^{-1}	$\Delta\nu_{max}$,[c] cm^{-1}
1-$MeSO_2$-Az (10)	530	−47	18,870	1540
1-$PhSO_2$-Az (11)	530	−47	18,870	1540
1-$MeSO_2$-TMA (12)	500	−43	20,000	1580
1-$PhSO_2$TMA (13)	499	−44	20,040	1620
3-$MeSO_2$-Gz (15)	552	−48	18,120	1450
3-$PhSO_2$-Gz (14)	552	−48	18,120	1450

[a] Chloroform solution. [b] Az = azulene, TMA = 4,6,8-trimethylazulene, Gz = guaiazulene. [c] Shift measured relative to parent azulene, *viz.*, Az, TMA, or Gz.

Spectral Shifts.—It is well known that electron-withdrawing groups in the 1 position of azulene will cause a shift of the visible band of azulene to lower wavelengths, and that the magnitude of the shift is roughly proportional to the electron-withdrawing strength of the group.[9] Therefore the hypsochromic shifts shown by the 1-azulyl sulfoxides (Table II) and sulfones (Table IV) are expected. Also the greater shifts caused by the sulfonyl group are consistent with the greater electron-withdrawing power of that group.[27]

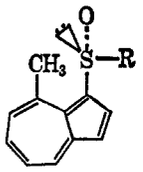
In contrast to the sulfones which show little change in spectral shift, the spectral shifts of the sulfoxides change considerably as the structure is varied. A phenylsulfinyl group causes a significantly stronger hypsochromic shift than the methylsulfinyl group. A similar effect was noted for the methyl and phenyl 1-azulyl sulfides, where the methylthio group caused a moderately strong bathochromic shift but the phenylthio group effected a weak hyposochromic shift.[2] A rationalization of these data could be based on the qualitative interpretation proposed by Anderson and Steckler[9b] for spectral shifts due to substituents in the 1 position. Their explanation considers the effect of the group in helping to stabilize (or destabilize) the ground state, which is electron rich in the 1 position, and the excited state, which is electron poor in this position. Both the sulfinyl group and the sulfonyl group will stabilize the ground state and destabilize the excited state by their electron-withdrawing inductive and resonance effects. However the sulfinyl group, unlike the sulfonyl group, still has an unshared pair of electrons on the sulfur atom, and these electrons might be released to the azulene ring in the excited state.

If there is electron-withdrawing conjugation of the lone pair with the benzene ring, this effect, coupled with the electron-withdrawing inductive effect of the phenyl group, will cause a drift of the lone pair into the benzene ring. This will make the phenylthio and phenylsulfinyl groups more electron withdrawing than the methylthio and methylsulfinyl groups. As a result, the ground state of the 1-azulyl phenyl sulfides and sulfoxides will be more stabilized, and the excited state will be less stabilized by donation of the lone pair, than for the corresponding methyl derivatives. No such effect is possible for the sulfones since there is no unshared pair of electrons on the sulfur atom.

Another observation from the spectral data is that the sulfoxides of guaiazulene and trimethylazulene show smaller shifts than do the sulfoxides of azulene itself. In contrast, the specific structure of the azulene moiety in the sulfones has essentially no effect on the spectral shift. A possible rationalization of these data would once again take into account the lone pair of electrons on the sulfur atom of the sulfoxides. The sulfinyl group in methyl or phenyl 1-azulyl sulfoxide (2a or 2b) should show fairly free rotation, but the *peri*-methyl group in the trimethylazulyl and guaiazulyl sulfoxides will hinder its rotation. These derivatives will probably

(26) I. B. Douglass, *J. Org. Chem.*, **30**, 633 (1965).

(27) The σ *para* value for the CH_3SO_2 group is +0.72 compared with +0.49 for the CH_3SO group: J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.



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have favored conformations such as **17**, and there could be effectively more electron donation of the lone pair to the azulene ring in **17** than in **2a** and **2b** where the sulfinyl group is freely rotating. Therefore the excited states of trimethylazulyl and guaiazulyl methyl sulfoxides should be more stabilized and show smaller hypsochromic shifts than **2a**. The observation that the difference between the shifts for the methyl sulfoxides is greater than the difference between the phenyl sulfoxides is consistent with the explanation proposed above, since there is relatively less electron release from the phenyl sulfoxides.

The visible maxima of the methyl sulfoxides show a shift of approximately 17 mμ to lower wavelengths when the solvent is changed from cyclohexane (nonpolar) to the more polar chloroform, while the phenyl sulfoxides show a somewhat smaller solvent shift. This rather strong solvent shift[9a] indicates strong dipolar interaction (presumably hydrogen bonding) between the sulfinyl group and chloroform. A solvent effect on the S=O band in the infrared is also evident, as this band for **4** occurs at 9.52 μ in carbon tetrachloride and at 9.76 μ in chloroform solution.

Experimental Section[28]

Unless otherwise specified, the petroleum ether used was reagent grade, bp 30–60°. The dry acetonitrile employed as a reaction solvent was freshly distilled from phosphorous pentoxide. Alumina used for chromatography was Merck acid washed. Azulene was purchased from Henley and Co., guaiazulene was obtained from Fluka AG (Switzerland), and 4,6,8-trimethylazulene was prepared according to a published procedure.[29]

Benzenesulfinyl chloride was prepared from benzenethiol and chlorine according to the general procedure of Douglass, *et al.*[13] The product was an orange-red liquid: bp 98° (5 mm), $n^{21}D$ 1.6068 [lit.[13] 71–72° (1.5 mm) $n^{25}D$ 1.6062].

Methanesulfinyl chloride was prepared according to the procedure of Douglass, *et al.*[13] The product was a light yellow liquid: bp 52–55° (30 mm), $n^{22}D$ 1.5063 [lit.[13] 55–59° (40 mm), $n^{25}D$ 1.500].

Methyl 1-Azulyl Sulfoxide (2a). Method A.—A mixture of 117 mg of methyl 1-azulyl sulfide[2] (**1a**), 16 ml of 0.05 *M* aqueous sodium metaperiodate solution, and 25 ml of methanol was stirred, under nitrogen, at room temperature for 40 min. The crystalline residue left after the usual work-up[30] was recrystallized from petroleum ether (bp 60–110°) to give 119 mg (93%) of **2a** as a purple, crystalline residue: mp 75.5–76.5° dec; $\lambda_{max}^{CHCl_3}$ 298 mμ (log ε 4.60), 341 (3.74), 354 (3.59), and 548 (2.59).

Method B.—A stirred mixture of azulene (402 mg, 3.14 mmoles) in 25 ml of dry acetonitrile under dry nitrogen was cooled to −50°,[31] and a solution of 0.226 ml (3.2 mmoles) of methanesulfinyl chloride in 7 ml of dry acetonitrile was added dropwise over a period of 10 min. A purplish red solid formed. The mixture was allowed to warm to −35° and 0.33 ml (4.1 mmoles) of pyridine was added. The residue left after the usual work-up[30] was chromatographed. A blue band (which contained some unreacted azulene), a green, and a pink band were eluted with dichloromethane. A large purple band was eluted with 20:1 acetone–methanol and eventually yielded 225 mg (38%) of **2a**: mp 73.5–76.5° dec, $\lambda_{max}^{CHCl_3}$ 550 mμ. A mixture melting point of this product with that from method A was 73.5–75.5° dec. An infrared spectrum of this product was identical with that of the product from method A. The nmr spectrum showed the typical pattern for a 1-substituted azulene with H-8 and H-4 as doublets[32] at τ 1.13 and 1.55, H-2 a doublet at 1.68, and the methyl group of CH_3SO as a strong, sharp singlet at 7.02. The remainder of the ring protons appeared as a complex multiplet at τ 2.0–2.8.

Phenyl 1-Azulyl Sulfoxide (2b). Method A.—A mixture of 136 mg (0.577 mmole) of phenyl 1-azulyl sulfide[2] (**1b**), 20 ml of methanol, and 7.0 ml of 0.10 *M* sodium metaperiodate was refluxed (approximately 75°) under nitrogen for 90 min. Chromatography of the residue from the work-up[30] gave a small, red-purple band, eluted with 4:1 chloroform–dichloromethane, and a large, purple band, eluted with 4:1 ether–acetone. The small, red-purple band yielded 26 mg of a red, crystalline solid, mp 134–135°. Its infrared spectrum showed bands characteristic of sulfones at 7.7 and 8.75 μ. This compound was identified as phenyl 1-azulyl sulfone (**11**). The purple band yielded 123 mg (82%) of phenyl 1-azulyl sulfoxide (**2b**) as red crystals: mp 65.5–67° dec; $\lambda_{max}^{CHCl_3}$ 286 mμ (log ε 4.58), 296 (4.66), 343 (3.79), 358 (3.75), and 544 (2.58). The nmr spectrum showed the expected pattern with H-8 and H-4 as doublets[32] at τ 0.98 and 1.56, H-2 a doublet at 2.12, and a complex multiplet at 2.2–2.7. An analytical sample, purified by rechromatography, had mp 70–70.5° dec.

Method B.—To a stirred solution of 64 mg (0.50 mmole) of azulene in 20 ml of dichloromethane, cooled to 0° and kept under dry nitrogen, was added 0.50 ml (67 mg, 0.42 mmole) of benzenesulfinyl chloride, whereupon the mixture became red-purple. After 15 min the reaction mixture was washed with water, the solvent was removed *in vacuo*, and the residue was chromatographed. Unreacted azulene (34 mg) was eluted with 1:1 petroleum ether–dichloromethane and a red band was eluted with 2:1 ether–acetone. The red eluate yielded 57 mg, a 57% (92% from consumed azulene) yield of red crystals: mp 66.5–67.5° dec, $\lambda_{max}^{CHCl_3}$ 545 mμ. An infrared spectrum of this product was identical with that of the product from method A.

Methyl 1-(4,6,8-Trimethylazulyl) Sulfoxide (3). Method A.—A mixture containing 136 mg (0.630 mmole) of methyl 1-(4,6,8-trimethylazulyl) sulfide,[2] 20 ml of methanol, and 7.5 ml of 0.10 *M* sodium metaperiodate was stirred under nitrogen at 35° for 60 min. After the usual work-up[30] chromatography gave a small, blue band, eluted with petroleum ether–dichloromethane, and a large, red band eluted with acetone. The red eluate yielded 130 mg (89%) of methyl 1-(4,6,8-trimethylazulyl) sulfoxide as a red, crystalline solid: mp 78.5–79.5° dec; $\lambda_{max}^{CHCl_3}$ 305 mμ (log ε 4.61), 350 (4.61), 364 (3.59), and 527 (2.80). An analytical sample, prepared by rechromatography had mp 81–81.5°.

Method B.—To a solution of 523 mg (2.94 mmoles) of 4,6,8-trimethylazulene in 20 ml of dry acetonitrile, cooled to −45° and kept under nitrogen, was added, dropwise, a solution of 0.216 ml (3.00 mmoles) of methanesulfinyl chloride in 5 ml of dry acetonitrile. This mixture (some orange solid had formed) was allowed to warm to −20° and 0.35 ml (4.3 mmoles) of pyridine was added. Chromatography of the residue from the usual work-up[30] gave a blue-purple band, eluted with dichloromethane, a brown and a green band, eluted with ether, and a large, purple-red band eluted with 20:1 acetone–methanol. The eluate from the last band contained 476 mg (70%) of **3** as red crystals: mp 74–76° dec, $\lambda_{max}^{CHCl_3}$ 526 mμ. A rechromatographed sample had mp 79–80° and mmp 77–80° when mixed with the product from method A. An infrared spectrum of this product was identical with that of the product from method A.

An nmr spectrum showed H-2 and H-3 as doublets[32] at τ 1.66 and 2.58, H-5 and H-7 at 2.82, CH_3SO methyl at 7.15, and 8-, 4-, and 6-methyl groups at 7.00, 7.18, and 7.38.

(28) 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 in deuteriochloroform solution with tetramethylsilane as the internal marker, using a Varian A-60 spectrometer, and chemical shifts are reported as τ values. Coupling constants were taken directly from the spectra and are apparent values. Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mülheim, Germany, or by Berkeley Analytical Laboratories, Berkeley, Calif.

(29) K. Hafner, *Angew. Chem.*, **70**, 419 (1958).

(30) The usual work-up consisted of pouring the reaction mixture into an aqueous salt solution, extracting the mixture with dichloromethane or ether, and removal of the solvent *in vacuo*.

(31) Some of the solvent froze.

(32) The observed coupling constants are *ca.* 4 cps for protons in the five-membered ring and *ca.* 11 cps for those on the seven-membered ring.

Phenyl 1-(4,6,8-Trimethylazulyl) Sulfoxide (7). Method A.—A mixture containing 69 mg (0.25 mmole) of phenyl 1-(4,6,8-trimethylazulyl) sulfide,[33] 20 ml of methanol, and 6.0 ml of 0.05 *M* sodium metaperiodate (nitrogen atmosphere) was stirred at 70° for 2 hr. Chromatography of the residue from the usual work-up[30] gave a small, purple band, eluted with 4:1 petroleum ether–dichloromethane, and a large, red band, eluted with 4:1 ethanol–ether. The residue from the red eluate was recrystallized from Skellysolve B, giving 55 mg (75%) of **7** as red crystals: mp 73–75° dec; $\lambda_{max}^{CHCl_3}$ 308 mμ (log ε 4.67), 352 (3.94), 368 (3.78), and 517 (2.85).

Method B.—A solution of 0.31 ml (2.6 mmoles) of benzenesulfinyl chloride in 8 ml of dry acetonitrile was added dropwise to the cooled (−45°) solution of 4,6,8-trimethylazulene (436 mg, 2.56 mmoles) in 20 ml of dry acetonitrile (dry nitrogen atmosphere). The mixture (an orange-red solid had formed) was allowed to warm to −30° and 0.45 ml (5.6 mmoles) of pyridine was added. Following the usual work-up,[30] chromatography gave a purple band, eluted with 1:1 petroleum ether–dichloromethane, a brown band with dichloromethane, and a large, red-purple band with 2:1 acetone–ether. From the last band was obtained 535 mg (71%) of **7** as a red, crystalline solid: mp 79–81.5° dec, $\lambda_{max}^{CHCl_3}$ 516 mμ. This product, when mixed with a repurified sample of the compound from method A, had mp 78–80.5° dec. An infrared spectrum of this product was identical with that of the product from method A.

The nmr spectrum showed H-2 as a doublet[32] at τ 2.15, a complex multiplet at 2.3–2.7, H-5 and H-7 a singlet at 2.95, and the 8-, 4-, and 6-methyl groups at 6.79, 7.16, and 7.38.

Methyl 1-(3,8-Dimethyl-5-isopropylazulyl) Sulfoxide (4). Method A.—A mixture containing 154 mg (0.632 mmole) of methyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfide[2] 25 ml of methanol, and 8.0 ml of 0.10 *M* sodium metaperiodate solution was stirred at ice-bath temperature for 30 min (nitrogen atmosphere). Chromatography of the residue from the work-up[30] gave a small, blue band, eluted with petroleum ether and a large, purple band, eluted with acetone. The purple eluate yielded 149 mg (91%) of **4** as a purple, crystalline solid: mp 95–95.5° dec; $\lambda_{max}^{CHCl_3}$ 297 mμ (log ε 4.50), shoulder at 390 (4.46), 358 (3.82), 375 (3.90), and 577 (2.72).

Method B.—A solution of 0.216 ml (3.00 mmoles) of methanesulfinyl chloride in 7 ml of dry acetonitrile was added dropwise to a cooled (−45°) solution of 584 mg (2.95 mmoles) of guaiazulene in 12 ml of dry acetonitrile (dry nitrogen atmosphere). Chromatography of the residue from the work-up[30] gave a brown and a green band, eluted with dichloromethane, a large, purple band, eluted with 1:1 ether–acetone, and a large, green band. From the purple eluate was obtained 520 mg (68%) of **4** as a purple, crystalline solid: mp 89–90° dec, $\lambda_{max}^{CHCl_3}$ 577 mμ. An infrared spectrum of this product was essentially identical with that of the product from method A.

The nmr spectrum showed H-2 and H-4 as overlapping signals at τ 1.71 and 1.72, H-7 and H-6 as doublets[32] at 2.83 and 2.48 (each peak of this doublet was further split, J = 2 cps, into a doublet), CH_3SO methyl at 7.15, the 8- and 3-methyl at 6.98 and 7.35, and the isopropyl methyl doublet at 8.64.

Phenyl 1-(3,8-Dimethyl-5-isopropylazulyl) Sulfoxide (8). Method A.—A mixture of 76.5 mg (0.25 mmole) of phenyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfide, 20 ml of methanol, and 6.0 ml of 0.05 *M* sodium metaperiodate was refluxed (approximately 73°) for 5 hr. Chromatography of the residue left after the usual work-up[30] gave a blue band (5 mg of unreacted sulfide), eluted with 1:1 petroleum ether–dichloromethane, a purple-red band, eluted with 2:1 dichloromethane–ether, and a large, purple band, eluted with 5:1 ether–acetone. Sixteen milligrams of a red, crystalline solid, mp 143–146°, was obtained from the red-purple band, The infrared spectrum of this compound had no sulfoxide band, but it did have bands at 7.7 and 8.7 μ which are indicative of a sulfone. This compound was identified as phenyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfone (**14**).

From the purple eluate was obtained 55 mg (68%) of the sulfoxide as a purple, crystalline solid: mp 88.5–90.5° dec; $\lambda_{max}^{CHCl_3}$ 250 mμ (log ε 4.34), 302 (4.49), 313 (4.47), shoulder at 367 (3.93), 381 (4.03), and 567 (2.76).

Method B.—A solution of 0.24 ml (2.0 mmoles) of benzenesulfinyl chloride in 5 ml of dry acetonitrile was added dropwise to the cooled (−45°) solution of 401 mg (2.02 mmoles) of guaiazulene in 20 ml of dry acetonitrile (nitrogen atmosphere). The red-purple reaction mixture (some solid had formed) was allowed to warm to −30° and 0.36 ml (4.5 mmoles) of pyridine was added, whereupon the solid disappeared, and the mixture became purple. Chromatography of the residue left from the usual work-up[30] gave a blue and a green band, eluted with dichloromethane, and a large, purple band, eluted with 2:1 ether–acetone. The purple eluate yielded 369 mg (57%) of (**8**) as a purple, crystalline solid: mp 84–86.5°, $\lambda_{max}^{CHCl_3}$ 567 mμ. The infrared spectrum of this product was identical with that of the product from method A.

The nmr spectrum showed H-4 as a doublet (J = 2 cps) at τ 1.73, H-2 as a singlet at 2.27, a complex multiplet at 2.3–2.8, 8- and 3-methyl groups at 6.78 and 7.48, and the isopropyl methyl doublet at 8.65.

Methyl 1-Azulyl Sulfone (10). A. By Substitution.—A mixture containing 128 mg (1.00 mmole) of azulene, 7.0 ml of dry acetonitrile, and 0.080 ml (1.0 mmole) of methanesulfonyl chloride was refluxed for 14 hr. The reaction mixture was poured into salt water and extracted with dichloromethane. The solvent was removed, and the residue was chromatographed on Merck acid-washed alumina. A small, blue band, which contained 3 mg of unreacted azulene was eluted with dichloromethane. The large, red-purple band was eluted with an ether–acetone mixture and yielded 178 mg (86%) of methyl 1-azulyl sulfone (**10**) as a red-purple, crystalline solid: mp 153–156°; ultraviolet and visible absorption data, $\lambda_{max}^{CHCl_3}$ 281 mμ (log ε 4.69), 285 (4.65), 292 (3.75), shoulder at 334 (3.69), 340 (3.72), 356 (3.70), 530 (2.70), and shoulders at 555 (264) and 607 (2.23).

The nmr spectrum showed a strong, sharp singlet at τ 6.82 (methyl group) and a typical pattern for a 1-substituted azulene with H-8 and H-4 as doublets[32] at 0.68 and 1.43, H-2 and H-3 as doublets at 1.70 and 2.63, and a complex multiplet at 2.1–2.5. An analytical sample, prepared by rechromatography, had mp 156–157.°

B. By Oxidation.—A mixture containing 235 mg (1.35 mmoles) of methyl 1-azulyl sulfide,[2] 3.2 ml of a 1.0 *M* solution of sodium metaperiodate, and 25 ml of methanol was refluxed for 14 hr. A tlc analysis (silica gel G, 1:1 ligroin–ethyl acetate) showed only about 40% product, so another 0.5 ml of the sodium metaperiodate solution was added and refluxing was continued for another 10 hr. The red mixture was poured into a salt solution and extracted with dichloromethane. The solvent was removed and the residue was chromatographed over Merck acid-washed alumina. A large, purple-red band was eluted with 20:1 ether–acetone; two, following, small, purple bands were eluted with 5:1 ether–acetone. From the red eluate was obtained 211 mg (76%) of methyl 1-azulyl sulfone as a red-purple, crystalline solid, mp 154–156.5°. This product appeared to be identical (visible and infrared spectra; mmp 152–154°) with the product obtained above.

Phenyl 1-Azulyl Sulfone (11). A. By Oxidation of Sulfide.—A mixture containing 441 mg (1.87 mmoles) of phenyl 1-azulyl sulfide,[2] 4.75 ml of 1 *M* sodium metaperiodate and 20 ml of methanol was refluxed for 14 hr. The red reaction mixture was poured into salt water and extracted with dichloromethane. The solvent was removed and the residue chromatographed on Woelm neutral alumina. The large red-purple band was eluted with 5:1 ether–acetone, and the small purple band was eluted with a 2:1 ether–acetone mixture. The purple band yielded 40 mg (8%) of phenyl 1-azulyl sulfoxide (**2b**), while the red-purple band gave 391 mg (78%) of phenyl 1-azulyl sulfone (**11**) as a red-purple, crystalline solid: mp 134–135.5°; ultraviolet and visible absorption data, $\lambda_{max}^{CHCl_3}$ 290 mμ (log ε 4.66), 299 (4.72), 337 (3.76), 347 (3.78), 363 (3.90), 530 (2.71), and shoulders at 560 (2.65) and 615 (2.19). The nmr spectrum of **11** showed H-8 and H-4 as doublets[32] at τ 0.68 and 1.60, H-2 as a doublet at 1.66, and a complex multiplet at 1.9–2.8.

B. By Oxidation of Sulfoxide.—A mixture of 91 mg (0.36 mmole) of phenyl 1-azulyl sulfoxide, 0.5 ml of 1 *M* sodium metaperiodate solution, and 20 ml of methanol was refluxed for 20-hr. A tlc analysis of the reaction mixture showed about 50% completion, so another 0.25 ml of the sodium metaperiodate solution was added and refluxing was continued for an additional 23 hr. Water was added, and this mixture was extracted with a mixture of dichloromethane and carbon tetrachloride. The solvent was removed, and the residue was chromatographed on Merck acid-washed alumina. A large, red-purple band was eluted with 1:1-dichloromethane–ether and a small, purple band with 4:1 ether–acetone. The red-purple eluate yielded 81 mg

(33) K. Hafner, A. Stephan, and C. Bernhard, *Ann.*, **650**, 42 (1961).

(84%) of the sulfone **11** as a crystalline solid, mp 133–134°. This product was combined with that from method A, and this mixture was chromatographed (homogeneous) to give a crystalline solid, mp 134.5–135°.

Methyl 1-(4,6,8-Trimethylazulyl) Sulfone (12). A. By Substitution.—A mixture of 170 mg (1.00 mmole) of 4,6,8-trimethylazulene, 0.080 ml (1.0 mmole) of methanesulfonyl chloride, and 8 ml of dry acetonitrile was refluxed for 12 hr. The mixture was poured into salt water and extracted with dichloromethane. The solvent was removed, and the residue was chromatographed on Merck alumina. A large, purple band, containing unreacted trimethylazulene, was eluted with dichloromethane, and the red band was eluted with 5:1 ether–acetone. The red eluate yielded 89 mg (36%) of methyl 1-(4,6,8-trimethylazulyl) sulfone (**12**) as a red, crystalline solid: mp 126–129.5°; ultraviolet and visible absorption data, $\lambda_{max}^{CHCl_3}$ 252 mμ (log ε 4.44), shoulder at 293 (4.64), 303 (3.72), 346 (3.82), 362 (4.64), and 500 (2.93). The nmr spectrum showed H-2 and H-3 as doublets[32] at τ 1.72 and 2.73, H-5 and H-7 as singlets at 2.57 and 2.63, 8-methyl and sulfone methyl overlapping at 6.63, 4-methyl at 7.12 and 6-methyl at 7.33. An analytical sample, rechromatographed on acid-washed alumina, had mp 130.5–131°.

B. By Oxidation.—A mixture containing 455 mg (2.10 mmoles) of methyl 1-(4,6,8-trimethylazulyl) sulfide,[2] 4.5 ml of 1 *M* sodium metaperiodate, and 30 ml of methanol was refluxed for 24 hr, then another 2.0 ml of the metaperiodate solution was added, and refluxing was continued for another 24 hr. The red reaction mixture was poured into salt water and extracted with dichloromethane. The residue left after removal of solvent was chromatographed over Merck acid-washed alumina. Dichloromethane eluted a yellow band and then an orange band. A brown band was eluted with ether and a red band with 1:1 ether–acetone. The red eluate yielded 54 mg of methyl 1-(4,6,8-trimethylazulyl) sulfoxide (**3**), mp 73.5–77°, while the orange eluate afforded 117 mg (22%) of crude sulfone **12**. This product had the same spectra (visible and infrared) as that from method A.

Phenyl 1-(4,6,8-Trimethylazulyl) Sulfone (13).—A mixture of 389 mg (1.40 mmoles) of phenyl 1-(4,6,8-trimethylazulyl) sulfide,[33] 3.5 ml of 1 *M* sodium metaperiodate, and 20 ml of methanol was refluxed for 14 hr, and then poured into salt water. Extraction with dichloromethane, and removal of solvent left a crystalline solid which was chromatographed on Woelm neutral alumina. An orange-red band was eluted with 5:1 dichloromethane–ether, a green band with 3:1 dichloromethane–ether, and the large, red band with 2:1 ether–acetone. The red eluate presumably contained the sulfoxide **7**, but it decomposed before it could be identified. The orange-red band yielded 99 mg (23%) of phenyl 1-(4,6,8-trimethylazulyl) sulfone (**13**) as orange-red crystals: mp 195–200°; ultraviolet and visible absorption data, $\lambda_{max}^{CHCl_3}$ 252 mμ (log ε 4.45), 306 (4.71), 347 (3.92), 364 (3.79), and 499 (2.99). The nmr spectrum showed H-2 as a doublet[32] at τ 1.75, a complex multiplet at 2.1–2.8, 8-methyl at 6.95, 4-methyl at 7.08, and 6-methyl at 7.40. An analytical sample, rechromatographed on Woelm neutral alumina, had mp 196–199° dec.

Phenyl 1-(3,8-Dimethyl-5-isopropylazulyl) Sulfone (14).—A mixture containing 1,370 mg (4.37 mmoles) of phenyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfide,[2] 10 ml of 1 *M* sodium metaperiodate, and 60 ml of methanol was heated at *ca.* 45° for 48 hr. A tlc analysis of the brown reaction mixture indicated some sulfone was present along with decomposition products; no starting material or intermediate sulfoxide was observed. Water was added to the reaction mixture and it was extracted with dichloromethane. The residue from the organic extract was chromatographed on Merck acid-washed alumina. A 1:1 petroleum ether–dichloromethane mixture eluted a small, blue band, a large, brown-green band, while a 1:5 mixture of these solvents eluted a purple band. The residue from the purple eluate crystallized when triturated with cyclohexane, yielding 164 mg (11%) of phenyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfone: mp 151–152° dec; ultraviolet and visible absorption data, $\lambda_{max}^{CHCl_3}$ 248 mμ (log ε 4.51), 298 (4.55), 310 (4.52), 378 (3.99), and 552 (2.84). An nmr spectrum showed H-4 as a weakly split doublet (J = 2 cps) at τ 1.63, H-2 a singlet at 1.72, a complex multiplet at 2.0–2.8, 8-methyl at 6.99, 3-methyl at 7.40, and the isopropyl methyl doublet (J = 7 cps) at 8.63.

Guaiazulene with Benzenesulfonyl Chloride and DMF.—To a solution of 200 mg (1.01 mmoles) of guaiazulene in 20 ml of redistilled N,N-dimethylformamide was added 0.16 ml (1.25 mmoles) of benzenesulfonyl chloride. The solution immediately darkened and evolved gas. Pyridine (0.5 ml) was added and after a few minutes the mixture was hydrolyzed. This mixture was extracted with ether, the ethereal extract was dried over sodium sulfate, and the solvent was removed. The residue was dissolved in petroleum ether and chromatographed on Merck acid-washed alumina to give a large, blue band, eluted with petroleum ether, a small, purple band, eluted with 4:1 dichloromethane–ether, a small, green band, eluted with ether, and a red-brown band, eluted with acetone. Unreacted guaiazulene (105 mg) was obtained from the blue band. The solid material from the red-brown band was rechromatographed (purple eluate), yielding 41 mg of crystalline 3-guaiazulenecarboxaldehyde, mp 82.5–84°. A further rechromatography gave a product, mp 84–85° (lit.[22] 85–86°), which was identical with the authentic material (mmp 84–85.5°, with identical ultraviolet, visible, and infrared spectra).[34]

Methyl 1-(3,8-dimethyl-5-isopropylazulyl) Sulfone (15). A. By Substitution.[35]—A mixture of 200 mg (1.01 mmoles) of guaiazulene, 0.081 ml (1.0 mmole) of methanesulfonyl chloride, and 10 ml of dry acetonitrile was refluxed under a dry nitrogen atmosphere for 22 hr. The reaction mixture was poured into salt water and extracted with dichloromethane. The solvent was removed, and the residue was chromatographed over Merck alumina. A large blue band (unreacted guaiazulene) was eluted with a petroleum ether–dichloromethane mixture, a green band was eluted with dichloromethane, and a small purple band was eluted with 1:5 ether–dichloromethane. The purple eluate yielded 22 mg (8%) of crude methyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfone (**15**). The crude sample was rechromatographed on Merck acid-washed alumina. It crystallized when triturated with ether: mp 87.5–88.5° (softened at 77–87°); ultraviolet and visible absorption data, $\lambda_{max}^{CHCl_3}$ 248 mμ (log ε 4.41), 297 (4.60), shoulder at 307 (4.45), 363 (3.76), 376 (3.84), and 552 (2.78).

B. By Oxidation.—A solution of 222 mg (0.91 mmole) of methyl 1-(3,8-dimethyl-5-isopropylazulyl) sulfide[2] and 430 mg of 80% *m*-chloroperbenzoic acid (344 mg, 2.0 mmoles of oxidant) in 25 ml of dry benzene was stirred at room temperature. The solution rapidly turned from blue to purple. Tlc analysis (alumina, methylene chloride) of the reaction mixture indicated that the sulfide was rapidly converted to the sulfoxide which was then slowly oxidized to the sulfone. However, a component identified as guaiazulene was also appearing as the reaction proceeded. After approximately 1.5 hr the reaction mixture was concentrated and chromatogaphed over acid-washed alumina. Dichloromethane eluted a blue band (guaiazulene), a yellow band, and a purple band. From the purple eluate was obtained 27 mg (11%) of crude sulfone **15**, mp 84.5–89°. This product had spectra (ultraviolet, visible, and infrared) identical with that of the product from method A.

A large, purple band was eluted with acetone. This band probably contained the sulfoxide **4**, but the residue from the eluate decomposed and was not identified.

Registry No.—**2a**, 10437-66-8; **2b**, 10437-67-9; **3**, 10437-68-0; **4**, 10464-97-8; **7**, 10437-69-1; **8**, 10487-80-6; **10**, 10437-70-4; **11**, 10437-71-5; **12**, 10437-72-6; **13**, 10437-73-7; **14**, 10437-74-8; **15**, 10437-75-9.

(34) We are grateful to Mr. Warren W. Schroeder for obtaining these data.

(35) Several attempts to repeat the preparation of this sulfone by this method were unsuccessful.