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Studies of *N*-Sulfinyl Compounds. IV.[1] The Reactions of *N*-Sulfinylanilines and -phenylhydrazines with Styrene Oxide

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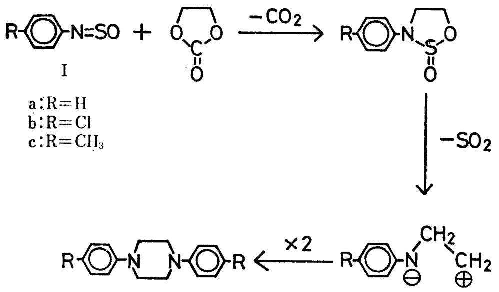
The reaction of *p*-substituted *N*-sulfinylanilines with styrene oxide in the presence of tetraethylammonium bromide gave the corresponding 1,2,4,5- and 1,2,4,6-tetraarylpiperazines, whose configurations were established on the basis of the NMR spectral studies. On the other hand, while a similar reaction of *p*-substituted *N*-sulfinylphenylhydrazines with the oxide in benzene gave the corresponding diaryl disulfide, diaryl sulfide, and *p*-substituted biphenyl, the reaction in acetonitrile did not give the biphenyl. The pathways for these reactions are suggested.

It is known that *N*-sulfinylaniline reacts as a 1,3-dipolarophile with benzonitrile oxide[2] and diphenylnitrilimine.[3] Recently, Etlis *et al.*[4] found that the reaction of *N*-sulfinylaniline with 1,2-epoxides such as ethylene oxide, propylene oxide, and epichlorohydrin, in the presence of tetraethylammonium bromide (TEABr) gave the corresponding 1,2,3-oxathiazolidine-2-oxides.

In a previous paper,[5] we reported that *p*-substituted *N*-sulfinylanilines (I) reacted with ethylene carbonate in the presence of lithium bromide or TEABr, to afford the corresponding *N*,*N'*-diarylpiperazine. The pathway for the formation of the piperazine may be illustrated by the dimerization of the intermediate derived from the expected 1,2,3-oxathiazolidine-2-oxide with the elimination of sulfur dioxide, as is shown in Scheme 1.



Scheme 1

On the basis of the above facts, the reaction of I with styrene oxide (II) which can behave like a 1,3-dipolar reagent, can be considered to result in the formation of either diaryl-1,2,3-oxathiazolidine-2-oxides or tetraarylpiperazines. However, little attention has been paid to the reaction of I with II.

When *N*-sulfinylaniline (Ia) and three molar amounts of II were heated with a small amount of TEABr in an atmosphere of nitrogen at 120°C for 7 hr, two crystalline compounds, IIIa (mp 204°C) and IVa (mp 219°C), were obtained. Both IIIa and IVa had molecular formula, of $C_{28}H_{26}N_2$ (M^+ m/e 390), which was equivalent to that of a dimer of an intermediate derived from an 1:1 adduct of Ia and II with the elimination of sulfur dioxide.

The IR spectra of IIIa and IVa did not show any bands due to the NH group, and the mass spectrum of IIIa was very similar to that of IVa. On the basis of the above observations and NMR spectra (Fig. 1), it may be deduced that IIIa and IVa are isomeric tetraphenylpiperazines.

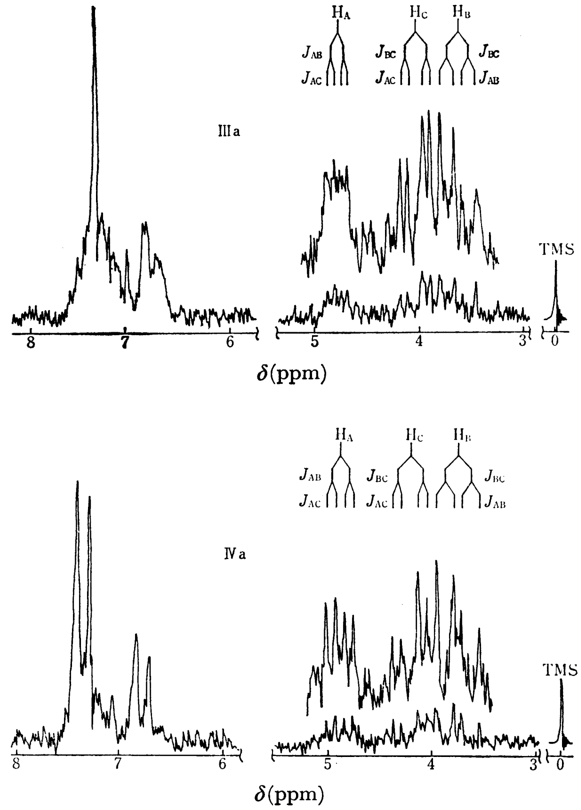


Fig. 1. NMR spectra of IIIa and IVa in $CDCl_3$

Recently, Hoberg[6] reported that the reaction of benzylidenaniline with diazomethane in the presence of diethylaluminum iodide gave 1,2,4,5- and 1,2,4,6-tetraphenylpiperazines, but their structural evidences were not given.

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[1] Part III: O. Tsuge and S. Mataka, *The Reports of the Research Institute of Industrial Science, Kyushu University*, **51**, 14 (1970).

[2] P. Rajagopalan and B. G. Advani, *J. Org. Chem.*, **30**, 3369 (1965).

[3] R. Huisgen, R. Grashey, M. Seidel, H. Knupfer, and R. Schmidt, *Ann. Chem.*, **658** 169 (1962).

[4] V. S. Etlis, A. P. Sineokov, and M. E. Sergeeva, *Khim. Geterotskil. Soedin*, 682 (1966); *Chem. Abstr.*, **66**, 55150s (1967).

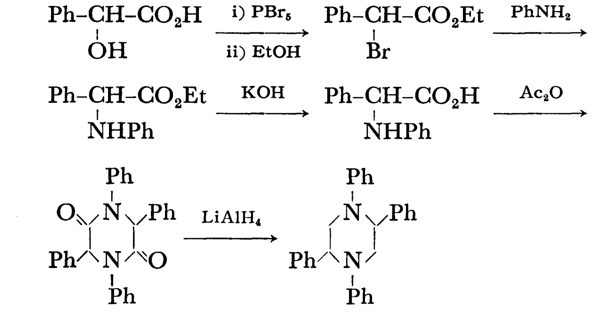
[5] O. Tsuge, S. Mataka, M. Tashiro, and F. Mashiba, This Bulletin **40**, 2709 (1967).

[6] H. Hoberg, *Ann. Chem.*, **707**, 147 (1967).

TABLE 1. TETRAARYLPIPERAZINES, III AND IV

Compound	Yield (%)	Appearance (Recryst. Solvent)*	Mp (°C)	Formula	Analysis (%) Found (Calcd) C	H	N	MW (*m/e*)
IIIa	4	colorless prisms (L)	204	$C_{28}H_{26}N_2$	85.95 (86.11)	6.73 (6.71)	7.06 (7.17)	390
IVa	14	colorless needles (L)	219	$C_{28}H_{26}N_2$	85.80 (86.11)	6.68 (6.71)	7.13 (7.17)	390
IIIb	6	colorless prisms (PB)	228—229	$C_{28}H_{24}N_2Cl_2$	73.37 (73.23)	5.04 (5.23)	6.03 (6.10)	458
IVb	17	colorless needles (PB)	160—161	$C_{28}H_{24}N_2Cl_2$	73.42 (73.23)	5.50 (5.23)	6.02 (6.10)	458
IIIc	7	colorless needles (PB)	260—261	$C_{30}H_{30}N_2$	85.90 (86.08)	7.37 (7.22)	6.52 (6.69)	418
IVc	6	colorless needles (PB)	154—155	$C_{30}H_{30}N_2$	86.12 (86.08)	7.38 (7.22)	6.74 (6.69)	418

* L: ligroin (bp 80—110°C), PB: petroleum benzine (bp 40—65°C).



Scheme 2

1,2,4,5-Tetraphenylpiperazine was synthesized by the reduction of the tetraphenylpiperazine-3,6-dione[7] prepared unequivocally from mandelic acid, as is shown in Scheme 2. The melting points of 1,2,4,5- and 1,2,4,6-tetraphenylpiperazines reported by Hoberg[6] were 214 and 202°C respectively, but the 1,2,4,5-tetraphenylpiperazine prepared by the method shown in Scheme 2 melted at 204°C. Therefore, it is clear that tetraphenylpiperazines were erroneously identified by Hoberg;[6] it seems reasonable to assume that the compound melting at 202°C is 1,2,4,5-tetraphenylpiperazine and that melting at 214°C is 1,2,4,6-isomer.

The compound IIIa was proved, by the admixed melting point and by a study of its IR spectrum, to be identical with the authentic sample of 1,2,4,5-tetraphenylpiperazine prepared by the above method. In view of the reaction process (Scheme 3) and of the melting point reported by Hoberg,[6] the compound IVa was assumed to be 1,2,4,6-tetraphenylpiperazine.

A similar reaction of *N*-sulfinyl-*p*-chloro- (Ib) or -*p*-methylaniline (Ic) with II gave the corresponding tetraarylpiperazines, IIIb and IVb or IIIc and IVc. The yields, physical properties, results of elemental analyses, and NMR spectral data of III and IV are summarized in Tables 1 and 2 respectively.

The compounds IIIb—IIIc and IVb—IVc were assigned, by a comparison of their NMR and IR spectra (Fig. 2) with those of IIIa and IVa, to be the corresponding 1,2,4,5- and 1,2,4,6-tetraarylpiperazines respectively.

TABLE 2. NMR SPECTRAL DATA OF TETRAARYLPIPERAZINES

Compound	Chemical shift[a] δ (ppm) H_A	H_B	H_C	Coupling constant (Hz) J_{AB}	J_{AC}	J_{BC}
IIIa	4.77(d.d)	3.63(d.d)	4.02(d.d)	9	4	13
IIIb	4.73(d.d)	3.57(d.d)	4.01(d.d)	8	4	13
IIIc	4.63(d.d)	3.34(d.d)	3.83(d.d)	9	4	11.5
IVa	4.85(d.d)	3.75(d.d)	4.22(d.d)	11	5.5	14.5
IVb	4.81(d.d)	3.72(d.d)	4.10(d.d)	9.5	5.5	14.5
IVc	4.79(d.d)	3.67(d.d)	4.05(d.d)	9	5	15

a) d.d: double-doublet.

In connection with a previous paper,[5] the pathway for the formation of III and IV is illustrated in Scheme 3. That is, 3,5- (A) and 3,4-diaryl-1,2,3-oxathiazolidine-2-oxides (B) are formed by the (2+3) cycload-

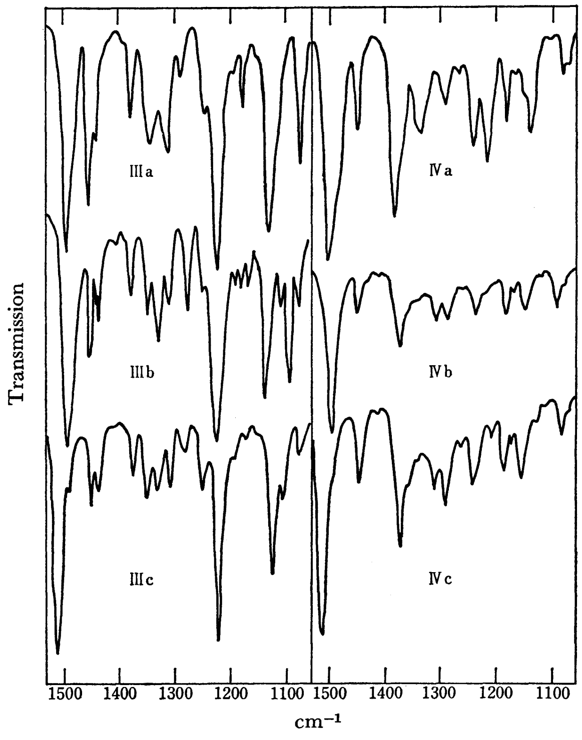


Fig. 2. IR spectra of III and IV (KBr).

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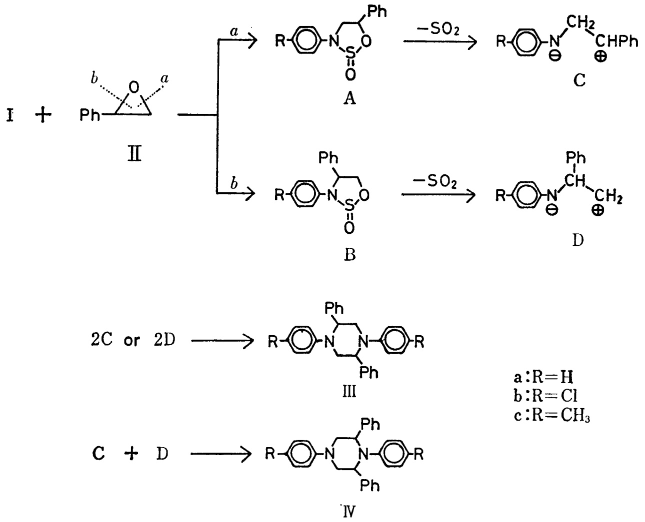
[7] H. Henze, *Ber.*, **32**, 3058 (1899).

dition of I to the 1,3-dipoles arising from the cleavage of *a* or *b* bond in II.



Scheme 3

The subsequent elimination of sulfur dioxide from A and B yields the 1,3-dipolar intermediates C and D respectively. The dimerization of C or D leads to the formation of III, while the (3+3) cycloaddition of C to D gives IV.

Three conformational isomers, III-1—III-3, and IV-1—IV-3, are possible for the respective structures of III and IV (Fig. 3).

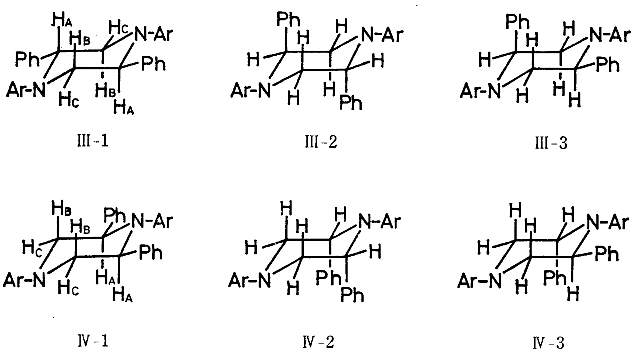


Fig. 3

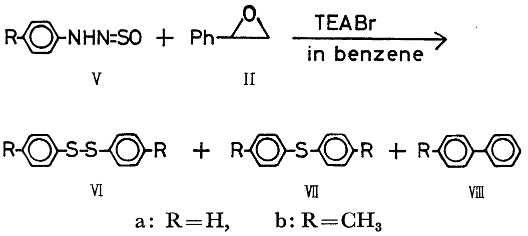
As is shown in Fig. 1 and Table 2, the NMR spectra of all the III and IVisomers showed only one double-doublet (1H+1H) and two double-doublets (each 2H) in the methine and methylene regions respectively; these facts exclude the possibility of III-3 or IV-3 for the structure of III or IV. It is well known that, in cyclohexane derivatives, the values of the vicinal axial-axial ($J_{a,a}$) and axial-equatorial coupling constants ($J_{a,e}$) are 8—13 and 2—6 Hz, and that the value of the vicinal equatorial-equatorial coupling constant ($J_{e,e}$) is invariably and significantly smaller than that of $J_{e,e}$.[8]

Consequently, it may be deduced that the most reasonable structures for III and IV are the conformers, III-1 and IV-1, in which the two phenyl groups are in equatorial positions.

There has been no study of the reaction of *N*-sulfinylphenylhydrazines (V) with a 1,3-dipole, because V is less reactive than I. It appeared of interest to investigate the reaction of V with II.

When equimolar amounts of *N*-sulfinylphenylhydrazine (Va) and II were heated with a small amount of TEABr in refluxing benzene for 16 hr, diphenyl disulfide (VIa), diphenyl sulfide (VIIa), biphenyl (VIIIa), and colorless prisms (IX), mp 156—157°C, were obtained, accompanied with a large amount of tars.

A similar reaction of *N*-sulfinyl-*p*-tolylhydrazine (Vb) with II gave *p,p'*-ditolyl disulfide (VIb), *p,p'*-ditolyl sulfide (VIIb) and 4-methylbiphenyl (VIIIb), but no 4,4'-dimethylbiphenyl was formed.



On the basis of these data, it is evident that the benzene used as the solvent participates in the formation of VIII.

When acetonitrile was used as the solvent in place of benzene, Vb reacted with II in the presence of TEABr to give only VIb and VIIb, but here the formation of VIIIb or 4,4'-dimethylbiphenyl was not observed. The products, VI, VII, and VIII, were isolated in pure forms by gas chromatography and were identified by comparison with authentic samples. Also, quantitative analyses were carried out on the basis of the areas of the individual peaks on the respective chromatograms.

The results are summarized in Table 3.

TABLE 3. REACTIONS OF V WITH II IN THE PRESENCE OF TEABr

V		II	TEABr	Solvent	Reaction time	Product			
						Total yield	Composition (ratio)		
R	(g)	(g)	(mg)		(hr)	(mg)	VI	VII	VIII
H	1.0	0.78	70	benzene	16	200	14	4	1
CH_3	0.7	0.49	40	benzene	16	250	3	2	1
CH_3	1.0	0.68	60	CH_3CN	7	190	2	1	0

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8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Ed., Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunshweig (1969), p. 286.

The reaction of Va with TEABr, or the reaction of Va with II in the absence of TEABr, did not take place, but Va was recovered quantitatively.

Many years ago, Michaelis and Ruhl[9] found that Va reacted with thionyl or acetyl chloride at a low temperature to give benzenediazonium chloride; they suggested the following reaction scheme:

$$\mathrm{PhNHN{=}SO} \longrightarrow \mathrm{PhN{=}N\text{-}SOH} \xrightarrow{\mathrm{Y\text{-}Cl}}$$

$$\mathrm{PhN{=}N\text{-}SO\text{-}Y} + \mathrm{HCl} \longrightarrow$$

$$\mathrm{PhN_2^{\oplus}Cl^{\ominus}} + \mathrm{S} + \mathrm{YOH}\ (\mathrm{Y{=}SOCl\ or\ CH_3CO})$$

However, the formation of sulfur was not observed in the reaction of V with II. On the other hand, *N*-sulfinyl-α-methylphenylhydrazine, PhN(Me)N=SO, which does not show the tendency to isomerize to the azo compound, did not react with II under the influence of TEABr, but was recovered quantitatively; this suggests that the tautomerism of the *N*-sulfinyl compound (ArNHN=SO) to the azo compound (ArN=NSOH) plays an important role in the formation of products.

On the basis of the above facts and the formation of the symmetrical diaryl sulfide VII and asymmetrical biphenyl VIII, the reaction pathway for the formation of the products, VI—VIII, can tentatively be assumed to be that shown in Scheme 4.

$$\underset{\mathrm{V}}{\mathrm{ArNHN{=}SO}} \longrightarrow \underset{\mathrm{E}}{\mathrm{ArN{=}N\text{-}SOH}}$$

$$\xrightarrow{\mathrm{II+TEABr}} \underset{\mathrm{F}}{\mathrm{ArN{=}N\text{-}SO\text{-}Z}} + \mathrm{Et_4N^{\oplus}Br^{\ominus}}$$

$$\mathrm{F} \left\langle \begin{array}{l} \longrightarrow \mathrm{Ar\cdot} + \mathrm{N_2} + \mathrm{\cdot SO\text{-}Z} \\ \longrightarrow \mathrm{ArS\cdot} + \mathrm{N_2} + \mathrm{ZO\cdot} \end{array} \right.$$

$$2\mathrm{ArS\cdot} \longrightarrow \underset{\mathrm{VI}}{\mathrm{ArS\text{-}SAr}}, \qquad \mathrm{Ar\cdot} + \mathrm{ArS\cdot} \longrightarrow \underset{\mathrm{VII}}{\mathrm{ArSAr}}$$

$$\mathrm{Ar\cdot} + \mathrm{PhH(solvent)} \longrightarrow \mathrm{ArPhH\cdot} \xrightarrow{\mathrm{-H\cdot}} \underset{\mathrm{VIII}}{\mathrm{Ar\text{-}Ph}}$$

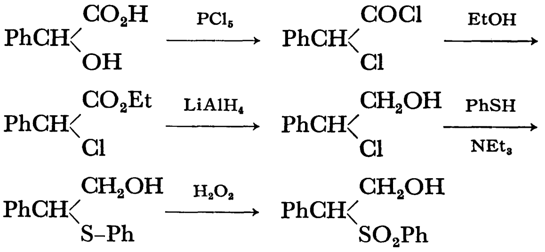
$$(\mathrm{Z{=}Ph\overset{|}{C}HCH_2OH\ or\ PhCH(OH)CH_2\text{-}})$$

Scheme 4

The intermediates (F) which are formed by the attack of 1,3-dipoles from II on the tautomer (E) of V are decomposed in two ways under these reaction conditions to yield aryl and arylthio radicals respectively. The formation of VI, VII, and VIII can be well understood in terms of the reactions shown in Scheme 4.

On the other hand, the molecular formula of compound IX (mp 156—157°C), which was obtained in a trace amount in the reaction of Va with II, was established from the molecular ion (M^+ *m/e* 262) in the mass spectrum and by elemental analysis, which showed the empirical formula to be $C_{14}H_{14}O_3S$. The IR spectrum of IX showed characteristic bands at 3480 (ν_{OH}) and at 1290 and 1140 cm^{-1} (ν_{SO_2}), while the NMR spectrum exhibited signals at 2.62 (1H, broad singlet, O*H*, exchanged with D_2O), 3.90—4.90 (3H, multiplet, >C*H* and -C*H*$_2$-), and 7.00—7.70 ppm (10H, multiplet, aromatic protons).

On the basis of the above observations, three isomers of benzenesulfonyl-phenylethanols, IX-1—IX-3, are possible for the structure of IX. However, it has been reported[10] that β-benzenesulfonyl-α-phenylethanol (IX-2) melts at 93—94°C, and the mass spectrum of IX seems to support the structure of IX-1; the fragment ion peaks appeared at *m/e* 244 (M^+-H_2O), 232 (M^+-CH_2O), 143 ($232^+-C_7H_5$), 121 (M^+-PhSO_2, base peak), 103 (121^+-H_2O, 87.7[11]), 91 ($C_7H_7^+$), and 77 (Ph^+) in the mass spectrum.

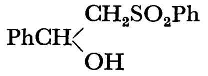


$$\mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{CO_2H}\\\mathrm{OH}\end{matrix}\right. \xrightarrow{\mathrm{PCl_5}} \mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{COCl}\\\mathrm{Cl}\end{matrix}\right. \xrightarrow{\mathrm{EtOH}}$$

$$\mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{CO_2Et}\\\mathrm{Cl}\end{matrix}\right. \xrightarrow{\mathrm{LiAlH_4}} \mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{CH_2OH}\\\mathrm{Cl}\end{matrix}\right. \xrightarrow[\mathrm{NEt_3}]{\mathrm{PhSH}}$$

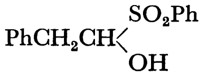
$$\mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{CH_2OH}\\\mathrm{S\text{-}Ph}\end{matrix}\right. \xrightarrow{\mathrm{H_2O_2}} \mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{CH_2OH}\\\mathrm{SO_2Ph}\end{matrix}\right.$$

IX-1



$$\mathrm{PhCH}\!\left\langle\begin{matrix}\mathrm{CH_2SO_2Ph}\\\mathrm{OH}\end{matrix}\right.$$

IX-2



$$\mathrm{PhCH_2CH}\!\left\langle\begin{matrix}\mathrm{SO_2Ph}\\\mathrm{OH}\end{matrix}\right.$$

IX-3

The compound IX was confirmed, by its admixed melting point and by a study of its IR spectrum, to be identical with β-benzenesulfonyl-β-phenylethanol (IX-1), mp 156—157°C, which was unequivocally prepared by the reaction of β-chloro-β-phenylethanol[12] with thiophenol and by subsequent oxidation with hydrogen peroxide.

However, the course of the formation of IX in the reaction of Va with II is not clear.

Experimental

All the melting and boiling points are uncorrected. The IR spectra were measured in KBr disks, and the NMR spectra were determined in deuteriochloroform at 60 MHz with a Hitachi R-20 NMR spectrometer, using TMS as the internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70eV.

Materials. The *N*-sulfinyl compounds were prepared by the reported methods[12-15] and were purified by fractional distillation or by recrystallization. *N*-sulfinylaniline (Ia), bp 80°C/12 mmHg (lit,[13] bp 80°C/12 mmHg); *N*-sulfinyl-*p*-chloroaniline (Ib), 101—102°C/5 mmHg (lit,[13]bp 237°C); *N*-sulfinyl-*p*-toluidine (Ic), bp 91.5—92°C/6 mmHg (lit,[13] bp 224°C); *N*-sulfinylphenylhydrazine (Va), mp 104.5—105.5°C (lit,[14] mp 105°C); *N*-sulfinyl-*p*-tolylhydrazine (Vb), mp 112—113°C (lit,[14] mp 112°C); *N*-sulfinyl-α-methylphenylhydrazine, mp 78°C (lit,[15] mp 77°C). The styrene oxide (II) was purified by distillation, bp 191°C.

The Reaction of Ia with II in the Presence of TEABr. After a mixture of 2.0 g of Ia and 5.2 g of II had been stirred

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[9] A. Michaelis and J. Ruhl, *Ann. Chem.*, **270**, 114 (1982).

[10] L. Field, *J. Amer. Chem. Soc.*, **74**, 3919 (1952).

[11] Observed metastable peak, *m/e*).

[12] E. L. Eliel, C. Herrmann, and J. T. Traxler, *J. Amer. Chem. Soc.*, **78**, 1193 (1956).

[13] A. Michaelis and R. Herz, *Ber.*, **23**, 3480 (1890).

[14] A. Michaelis and J. Ruhl, *ibid.*, **23**, 474 (1890).

[15] A. Michaelis, *ibid.*, **24**, 745 (1891).

with 0.45 g of TEABr under a slow stream of dry nitrogen at 120°C for 7 hr, the reaction mixture was allowed to stand overnight. A benzene solution of the mixture was then chromatographed on alumina, affording 0.75 g of colorless crystals and a large amount of resinous materials. Several fractional recrystallizations of the crystals from ligroin (bp 80—110°C) gave 0.12 g (4%) of 1,2,4,5-(IIIa), (mp 204°C) and 0.45 g (14%) of 1,2,4,6-tetraphenylpiperazines (IVa), mp 219°C.

Similar reactions of Ib and Ic with II in the presence of TEABr gave the corresponding 1,2,4,5- (IIIb and IIIc) and 1,2,4,6-tetraarylpiperazines (IVb and IVc) respectively. The yields, physical properties, and elemental analysis results are summarized in Tables 1 and 2.

The Preparation of 1,2,4,5-Tetraphenylpiperazine. *i*) Ethyl α-bromophenylacetate: A mixture of 20 g of mandelic acid and 100 g of phosphorus pentabromide was stirred at 100°C for 2 hr, and then the reaction mixture was cooled. After 20 m*l* of ethanol had been added to the mixture, it was refluxed for 10 min. The mixture was subjected to steam distillation, and then the distillate was extracted with 150 m*l* of chloroform. After the extract had been dried over anhydrous sodium sulfate, the solvent was distilled off to give a residue. The vacuum distillation of the residue gave 12 g (36%) of ethyl α-bromophenylacetate, bp 108—115°C/2 mmHg (lit,[16] bp 175°C/25 mmHg).

ii) Ethyl α-Anilinophenylacetate: After a mixture of 10.9 g of ethyl α-bromophenylacetate and 7.0 g of aniline had been stirred at 100°C for 4 hr, the reaction mixture was extracted with hot ligroin. The extract was concentrated *in vacuo* affording 9.4 g (83%) of ethyl α-anilinophenylacetate, mp 81—83°C (lit,[17] mp 83—84°C) as colorless needles.

iii) 1,2,4,5-Tetraphenylpiperazine-3,6-dione: A suspension of 8.4 g of ethyl α-anilinophenylacetate in 50 m*l* of 10% aqueous potassium hydroxide was refluxed for 3 hr, and then it was cooled. The resulting solution was neutralized with 1 N hydrochloric acid to afford a white precipitate. Filtration gave 5.6 g (75%) of crude α-anilinophenylacetic acid, mp 177—180°C (lit,[18] mp 181°C).

A mixture of 5.6 g of the acid and 2.8 g of acetic anhydride was stirred at 155°C (oil bath) for 2 hr, and then the mixture was filtered to give crystals. The crystals were washed with dilute aqueous ammonia and then diethyl ether, leaving 1.1 g (21%) of 1,2,4,5-tetraphenylpiperazine-3,6-dione, mp 258°C (decomp.) (lit,[7] mp 260°C (decomp.)).

iv) Reduction of 1,2,4,5-Tetraphenylpiperazine-3,6-dione: After a mixture of 0.1 g of 1,2,4,5-tetraphenylpiperazine-3,6-dione and 50 mg of lithium aluminum hydride in 30 m*l* of diethyl ether had been refluxed for 5 hr, the mixture was poured into water. The mixture was extracted with chloroform, and then the extract was evaporated *in vacuo*, leaving a yellowish-green, viscous oil. Purification by chromatography on alumina, using benzene as the eluent, followed by recrystallization from ligroin (bp 80—110°C), gave 10 mg (11%) of 1,2,4,5-tetraphenylpiperazine (IIIa), mp 204°C. This compound was proved, by the admixed melting point and by a study of its IR spectrum, to be identical with the compound (mp 204°C) obtained in the reaction of Ia with II.

The Reaction of Va with II in the Presence of TEABr. A solution of 1.0 g of Va and 0.78 g of II in 10 m*l* of benzene was refluxed with 70 mg of TEABr for 16 hr. The reaction mixture was then concentrated *in vacuo* to leave a red oil, which was chromatographed on alumina using benzene and then ethanol as eluents. The benzene-eluent gave 0.2 g of a pale green liquid, which was found, by gas chromatographic analysis, to be a mixture of diphenyl disulfide (VIa), diphenyl sulfide (VIIa), and biphenyl (VIIIa) (Table 3). The compounds, VIa—VIIIa, were isolated by gas chromatography, and were identified by a comparison of the IR spectra with those of respective authentic samples.

The ethanol-eluent was concentrated *in vacuo*, and the resulting residue was purified by chromatography on silica gel, using chloroform as the eluent, to give 30 mg of colorless crystals and intractable tars. The recrystallization of the crystals from benzene gave β-benzenesulfonyl-β-phenylethanol (IX), mp 156—157°C, as colorless prisms.

Found: C, 64.41; H, 5.36%. Calcd for $C_{14}H_{14}O_3S$: C, 64.11; H, 5.38%.

Similar reaction of Vb with II in benzene and acetonitrile were carried out; the results are given in Table 3. *p,p'*-Ditolyl disulfide (VIb), *p,p'*-ditolyl sulfide (VIIb), and 4-methylbiphenyl (VIIIb) formed in the reaction were isolated by gas chromatography, and were proved, by a comparison of the IR spectra, to be identical with the respective samples of VIb, VIIb, and VIIIb prepared by the reported methods.

The Preparation of β-Benzensulfonyl-β-phenylethanol. The reduction of ethyl α-chlorophenylacetate prepared by Walden's method[22] with lithium aluminum hydride in diethyl ether gave crude β-chloro-β-phenylethanol,[12] bp 164—166°C/4 mmHg.

A solution of 1.0 g of β-chloro-β-phenylethanol, 0.62 g of thiophenol, and 0.57 g of triethylamine in 10 m*l* of benzene was refluxed for 1.5 hr, and then the precipitated triethylamine hydrochloride was filtered off. The filtrate was concentrated *in vacuo* to leave 1.4 g of a yellow oil, which was used without further purification. A solution of 0.9 g of the oil and 2 m*l* of 30% hydrogen peroxide in 10 m*l* of acetic acid was stirred at room temperature for 4 days. After the reaction mixture had been poured into 50 ml of water, it was extracted twice with 50 m*l* of chloroform. The extracted was concentrated *in vacuo* to leave a viscous oil, which crystallized on standing at room temperature for a long while. Recrystallization from benzene gave 50 mg of β-benzenesulfonyl-β-phenylethanol, mp 156—157°C, as colorless prisms. This compound was proved, by the admixed melting point and by a study of its IR spectrum, to be identical with the compound (mp 156—157°C) obtained in the reaction of Va with II.

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