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The Reaction of Sulfinic Acids with *N*,*N*-Dimethylaniline

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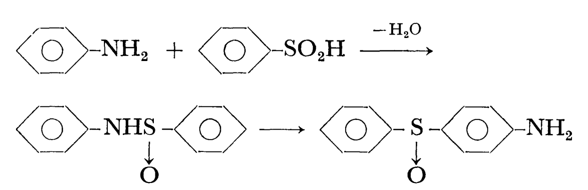
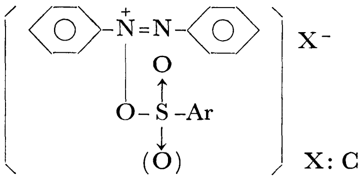
When *N*,*N*-dimethylaniline was allowed to react with *p*-toluenesulfinic acid, unusual demethylation products, *i.e.*, *p*-(*N*,*N*-dimethylamino)benzyl *p*-tolyl sulfone and *p*-(*N*-methylamino)benzyl *p*-tolyl sulfone were obtained. *N*-*p*-Toluenesulfonylmethyl-*N*-methylaniline was proposed to be a discrete intermediate, which undergoes intermolecular rearrangement in the presence of acid eventually to afford the above products. Similar results were obtained for the reaction of *N*-methylaniline with *p*-toluenesulfinic acid.

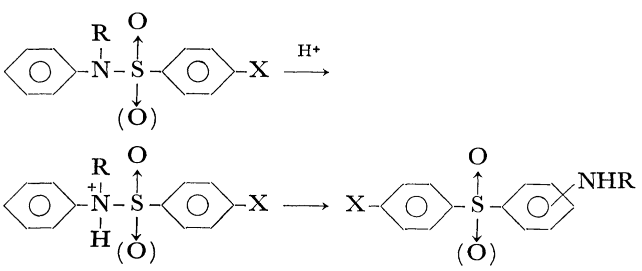
The reaction of benzenesulfinic acid with phenylhydrazine is known to give benzenesulfonyl phenylhydrazide,[1] presumably proceeding *via* a dehydrated intermediate, benzenesulfinyl phenylhydrazide. A similar reaction with aniline has also been suggested to proceed through sulfinamide to give a rearranged product of *p*-aminophenyl phenyl sulfoxide.[2]



This reaction is an example of sulfinyl migration from neutral nitrogen atom to the *para* position of the aniline ring, although the rearrangement may proceed after protonation of the nitrogen. A few reactions of sulfonyl and sulfonate migration, on the other hand, are known to proceed from the quartenary nitrogen atom. The reactions of azoxybenzene with arenesulfinyl chloride,[3] arenesulfonyl chloride,[4] and with arenesulfonic anhydride[5] are considered to proceed *via* either an intramolecular or intermolecular nucleophilic attack of sulfinate or sulfonate ion on the benzene ring to form the final products.



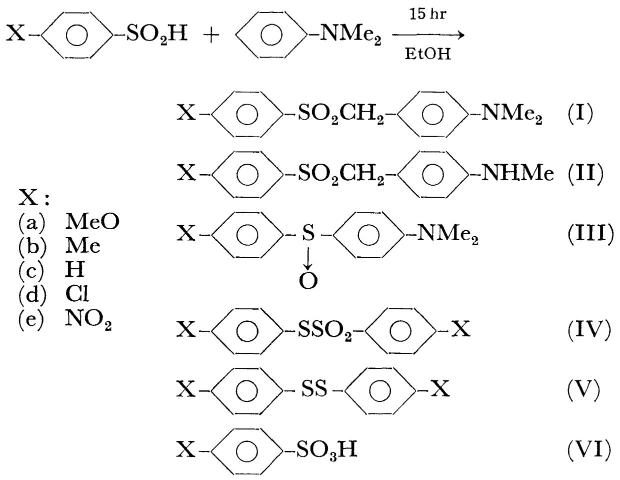
In contrast to the nucleophilic rearrangement of sulfinate or sulfonate groups, electrophilic rearrangements are well known. The rearrangement of benzenesulfinanilide to *p*-aminophenyl phenyl sulfoxide[6] and that of benzenesulfonanilide to *o*-aminophenyl phenyl sulfone[7] in concentrated sulfuric acid are considered to preceed *via* cationic rearrangement of sulfinyl or sulfonyl groups.



In order to clarify the ambiguity of the sulfinyl and sulfonyl rearrangements, we have reexamined the reaction of aniline with benzenesulfinic acid using *N*,*N*-dimethylaniline as a substrate. The neutral intermediate, sulfinanilide, can not be formed in this reaction as in the case of aniline. The reaction is expected to give *p*-aminophenyl phenyl sulfone by the nucleophilic attack of the sufinate on the *N*,*N*-dimethylanilinium ion, analogous to the reaction of azobenzene with benzenesulfinic acid to give *p*-benzenesulfonyl azobenzene.[8] However, we found that the reaction gave complex products, one of which was derived from the demethylation of the *N*-methyl group. In this paper, we deal with the reaction of *N*,*N*-dimethylaniline with benzenesulfinic acid, referring mainly to the intermediates of the reaction and also some other reactions with the related compounds.

Results and Discussion

N,*N*-Dimethylaniline was allowed to react with excess *p*-toluenesulfinic acid in refluxing ethanol for 15 hr. *p*-(*N*,*N*-Dimethylamino)benzyl *p*-tolyl sulfone (Ib) and *p*-(*N*-methylamino)benzyl *p*-tolyl sulfone (IIb) were found to be the major products and *p*-(*N*,*N*-dimethylamino)phenyl *p*-tolyl sulfoxide (IIIb) a minor product along with the disproportionation products of *p*-toluenesulfinic acid such as *p*-tolyl *p*-toluenethiolsulfonate (IVb), *p*,*p*′-ditolyl disulfide (Vb) and *p*-toluenesulfonic acid (VIb). Several *p*-substituted benzenesulfinic acids, allowed to react similarly, were found to give the



(1)

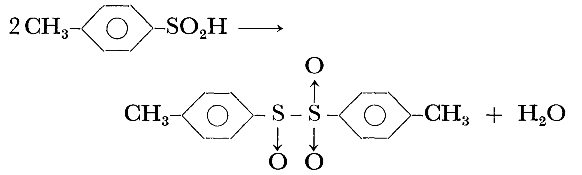
TABLE 1. PRODUCTS OF THE REACTION OF *N,N*-DIMETHYLANILINE WITH EXCESS ARENESULFINIC ACID[a)]

X		Solvent	Yield of products (%) I	II	III
a)	MeO	EtOH	32	3.4	3.6
b)	Me	EtOH	22	23	4.7
		CH_3CN	18	18	4
		Benzene	17	10	4.5
c)	H	EtOH	12	39	6
d)	Cl	EtOH	5	18	trace
e)	NO_2	EtOH	11	trace	9

a) Yields were obtained on the basis of the amount of *N,N*-dimethylaniline used.

corresponding products shown in Eq. (1). The yields except for those of the disproportionation products of the sulfinic acid are given in Table 1.

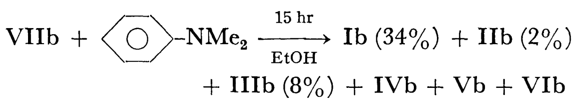
Products IV, V, and VI are considered to be formed by the disproportionation of the sulfinic acid.[9)] This was confirmed by an experiment involving the refluxing of the sulfinic acid alone in ethanol. The mechanism of the disproportionation of the sulfinic acid suggested by Kice *et al.* includes sulfinylsulfone (VII) as the intermediate[10)] which is known to be decomposed by the attack of a nucleophile.[11)]



(VIIb)

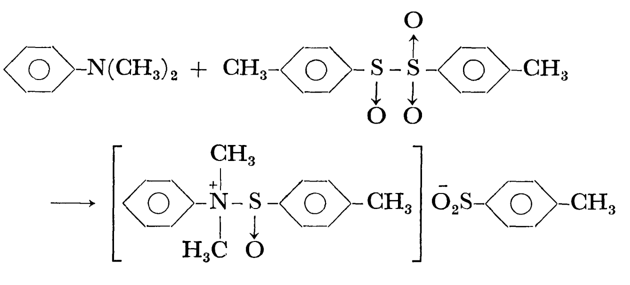
In the reaction of *N,N*-dimethylaniline with *p*-toluenesulfinic acid, the nucleophilic attack of aniline on the intermediate, VIIb is plausible.

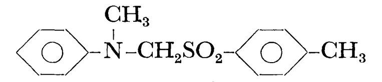
The reaction of *N,N*-dimethylaniline with an equimolar amount of *p*-tolyl *p*-toluenesulfinyl sulfone (VIIb) was carried out. As expected, *p*-(*N,N*-dimethylamino)-benzyl *p*-tolyl sulfone (Ib), *p*-(*N*-methylamino)benzyl *p*-tolyl sulfone (IIb) *p*-(*N,N*-dimethylamino)phenyl *p*-tolyl sulfoxide (IIIb) were obtained as the main products along with disproportionation products of the sulfinic acid as shown in the following.



(2)

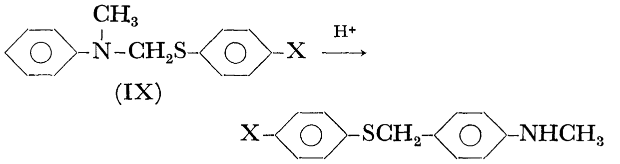
As to the mechanism of the reaction of the sulfinyl sulfone with *N,N*-dimethylaniline, the demethylation is considered to proceed through *N*-*p*-toluenesulfonylmethyl-*N*-methylaniline (VIIIb) as an intermediate as in the case of similar Pummerer[12)] or Polonovski reactions.



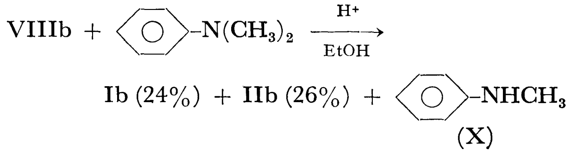


(VIIIb)

Succeeding rearrangements of VIIIb should proceed quite easily in view of the acid-catalyzed rearrangement of *N*-arenesulfenylmethyl *N*-methylaniline (IX).[13)]



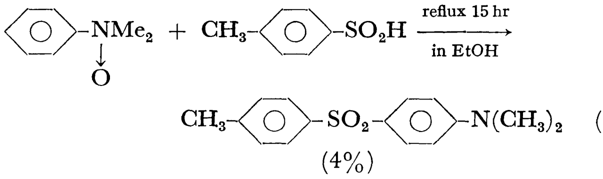
N-*p*-Toluenesulfonylmethyl-*N*-methylaniline (VIIIb) was prepared from *p*-toluenesulfinic acid, formaldehyde and *N*-methylaniline and was refluxed in ethanol with a trace amount of *p*-toluenesulfinic acid. *p*-(*N*-Methylamino)benzyl *p*-tolyl sulfone (IIb) was found as the product of the acid-catalyzed rearrangement of VIIIb. The rearrangement of VIIIb with an equimolar amount of *N,N*-dimethylaniline was found to give Ib, IIb, and *N*-methylaniline.



(3)

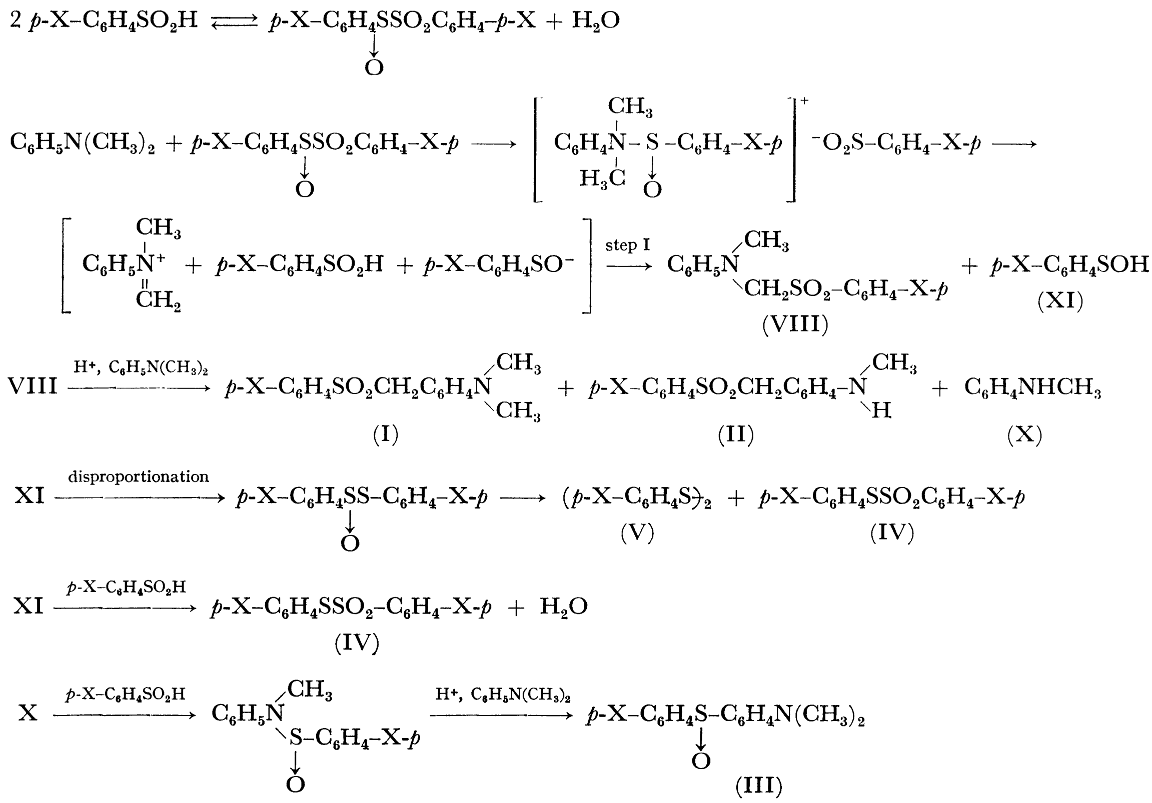
The formation of Ib and *N*-methylaniline indicates the reaction to be an intermolecular rearrangement of VIIIb to give IIb.

The overall processes of the reaction of *N,N*-dimethylaniline with arenesulfinic acid can thus be written as shown in Scheme 1. In relation to the reaction of *N,N*-dimethylaniline with *p*-toluenesulfinic acid, we examined the reaction of *N,N*-dimethylaniline *N*-oxide with *p*-toluenesulfinic acid. *p*-(*N,N*-Dimethylamino)-phenyl *p*-tolyl sulfone was isolated as follows. The sulfone is presumed to be formed *via* the Bamberger type rearrangement process.[14)]



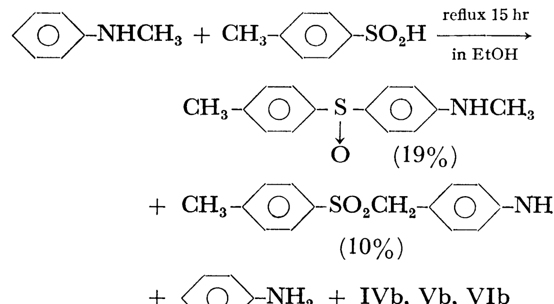
(4)

We carried out the reaction of *N*-methylaniline with



Scheme 1.

p-toluenesulfinic acid under the same conditions and obtained *p*-(*N*-methylamino)phenyl *p*-tolyl sulfoxide and *p*-(*N*-methyl)aminobenzyl *p*-tolyl sulfone as follows.



(5)

However, *N*,*N*-dimethylbenzylamine and *N*-methylmorpholine did not undergo any demethylation reaction with arenesulfinic acid. This reaction apparently takes place only in the cases of *N*-methyl and *N*,*N*-dimethyl aromatic amines because of the formation of the stabilized anilinium ion formed in the reaction.

Experimental

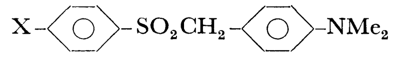
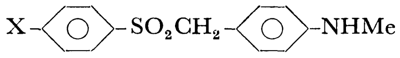
Materials. *p*-Toluenesulfinic acid was prepared by the reduction of *p*-toluenesulfonyl chloride by the usual method.[15] *p*-Nitrobenzenesulfinic acid was prepared by the alkaline hydrolysis of *p*-nitrobenzenesulfinyl chloride which was synthesized by the oxidative chlorination of *p*,*p*′-dinitrodiphenyl disulfide by bubbling Cl_2 in methylene chloride.[16] Mp p-X-C_6H_4-SO_2H: X: OCH_3 97—98 °C, CH_3 85 °C, H 81 °C, Cl 92—93 °C, NO_2 135 °C. *p*-Tolyl *p*-toluenesulfinylsulfone was prepared from *p*-toluenesulfinyl chloride and sodium *p*-toluenesulfinate according to the process given by Bredereck *et al.*[17] *N*,*N*-Dimethylaniline *N*-oxide was prepared by the oxidation of *N*,*N*-dimethylaniline with H_2O_2.[18] *N*-*p*-Toluenesulfonylmethyl-*N*-methylaniline was prepared as follows: Formalin (1.04 g) was added to *p*-toluenesulfinic acid (2.0 g, 0.013 mol) in methanol (3 ml). An equimolar amount of *N*-methylaniline in 15 ml methanol was then added to the reaction mixture with stirring at room temperature. The white crystals precipitated were filtered off and washed with dilute Na_2CO_3. *N*-*p*-Toluenesulfonylmethyl-*N*-methylaniline was obtained. (2.7 g, mp 107—110 °C).

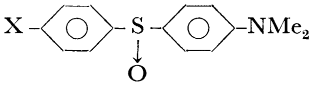
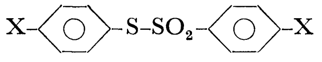
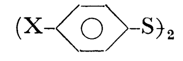
Reaction of N,N-*Dimethylaniline with Arenesulfinic Acid.* A typical run was carried out as follows: *N*,*N*-Dimethylaniline (0.5 g, 0.004 mol) was refluxed with *p*-toluenesulfinic acid (2 g, 0.013 mol) in absolute ethanol (1 ml) for 15 hr. After evaporation of the solvent, the residue was dissolved in $CHCl_3$ and the solution was extracted with water. *p*-Toluenesulfonic acid was obtained from the water layer. The compound was identified by comparison of the *S*-benzyl isothiouronium salt of the acid (mp 181—182 °C) with that of the authentic sample. The $CHCl_3$ layer was dried over Na_2SO_4 and chromatographed on silica gel with $CHCl_3$ as an eluent. *p*-(*N*,*N*-Dimethylamino)benzyl *p*-tolyl sulfone and *p*-(*N*-methyl)aminobenzyl *p*-tolyl sulfone were obtained. The former was identified by comparison of the physical properties with those of the authentic sample[19] and the structure of the latter was confirmed by IR, NMR, and elemental analysis. Found: C, 65.42; H, 6.22; N, 5.08%. Calcd for $C_{15}H_{17}NO_2S$: C, 65.26; H, 6.13; N, 5.01%.

p-(*N*,*N*-Dimethyl)aminophenyl *p*-tolyl sulfoxide was identified by comparison of the physical properties with those of the authentic sample prepared by the methylation of *p*-aminophenyl *p*-tolyl sulfoxide (mp 140—142 °C). Melting points of the products are given in Table 2.

Reaction of N,N-*Dimethylaniline with* p-*Tolyl* p-*Toluenesulfinyl Sulfone.* An ethanol solution of *N*,*N*-dimethylaniline

Table 2. Melting points of the products obtained by the reaction of *N,N*-dimethylaniline with arenesulfinic acids

	X	Products	
			
a)	MeO	146—148 °C	
b)	Me	192—193 °C	156—157 °C
c)	H	147 °C	158—159 °C
d)	Cl	158 °C	164—166 °C
e)	NO^2	201 °C	

	X	Products		
				
a)	MeO		44— 45 °C	91— 93 °C
b)	Me	140—141 °C	46 °C	75— 76 °C
c)	H	130 °C	60— 61 °C	45 °C
d)	Cl		70— 71 °C	134—135 °C
e)	NO_2	150—152 °C	180—181 °C	154—155 °C

(0.5 g, 0.004 mol) and an equimolar amount of *p*-tolyl *p*-toluenesulfinyl sulfone was refluxed for 15 hr. Analysis was carried out as described above.

Rearrangement of N-p-*Toluenesulfonylmethyl* N-*Methylaniline in the Presence of Acid.* An ethanol solution of *N-p*-Toluenesulfonylmethyl *N*-methylaniline (0.2 g) with a trace amount of *p*-toluenesulfinic acid was refluxed for 15 hr. *p*-(*N*-Methyl)-amino)benzyl *p*-tolyl sulfone (0.14 g) was obtained.

Reaction of N-p-*Toluenesulfonylmethyl* N-*Methylaniline with* N,N-*Dimethylaniline.* An ethanol solution of the title compound (0.5 g, 0.0018 mol) was refluxed for 15 hr with an equimolar amount of *N,N*-dimethylaniline and a trace amount of HCl. *p*-(*N,N*-Dimethylamino)benzyl *p*-tolyl sulfone (0.12 g), *p*-(*N*-methylamino)benzyl *p*-tolyl sulfone (0.13 g) and *N*-methyl- and *N,N*-dimethylanilines were isolated from the reaction mixture by chromatography on silica gel with $CHCl_3$ as an eluent.

Reaction of N,N-*Dimethylaniline* N-*Oxide with* p-*Toluenesulfinic Acid.* An ethanol solution of the *N*-oxide (1 g, 0.007 mol) and the sulfinic acid (3.4 g, 0.0021 mol) was refluxed for 15 hr. *p*-(*N,N*-Dimethylamino)phenyl *p*-tolyl sulfone (0.065 g, mp 212 °C), *p,p'*-ditolyl disulfide (0.037 g), *p*-tolyl *p*-toluenethiolsulfonate (0.30 g) and *p*-toluenesulfonic acid were obtained.

Reaction of N-*Methylaniline with* p-*Toluenesulfinic Acid.* An ethanol solution of *N*-methylaniline (0.5 g, 0.047 mol) and *p*-toluenesulfinic acid (2.2 g, 0.014 mol) was refluxed for 15 hr. *p*-(*N*-Methylamino)benzyl *p*-tolyl sulfone (0.105 g) and *p*-(*N*-methylamino)benzyl *p*-tolyl sulfoxide (0.214 g, mp 146—147 °C) were obtained along with *p,p'*-ditolyl disulfide, *p*-tolyl *p*-toluenethiolsulfonate and *p*-toluenesulfonic acid.

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