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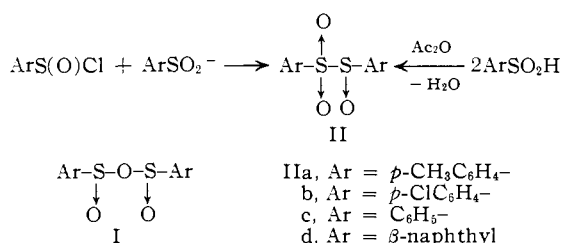
The Decomposition of Aromatic Sulfinyl Sulfones (Sulfinic Anhydrides). The Facile Homolysis of a Sulfur-Sulfur Bond¹

BY JOHN L. KICE AND NORMAN E. PAWLOWSKI

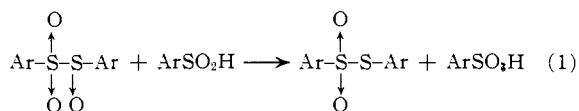
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Aromatic sulfinyl sulfones (II) undergo rapid decomposition at 50°, the rate being little affected by either solvent or the nature of the aryl group. Experiments using galvinoxyl, and the trapping of ArSO₂· radicals by an added olefin, show that the decomposition involves the facile homolysis of the sulfur-sulfur bond to give ArSO₂· and ArSO· (eq. 4). In the absence of a radical trap these radicals then recombine, yielding the sulfinyl sulfonate VI. The previously reported² reaction between II and a sulfinic acid (eq. 1) is shown actually to involve reaction of the sulfinic acid with the sulfinyl sulfonate formed by the decomposition of II. Furthermore, the stoichiometry is not quite as shown in eq. 1. Comparison of the rate of homolytic dissociation of II with the rates for such compounds as disulfides, thiolsulfonates, thiolsulfonates, etc., shows that the cleavage of the S-S bond in II occurs many times more readily than the homolytic scission of the sulfur-sulfur bond in these related compounds.

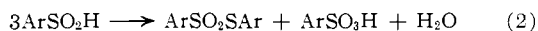
Reaction of an aromatic sulfinyl chloride with the sodium salt of the corresponding sulfinic acid,² or, alternatively, treatment of the sulfinic acid with acetic anhydride,³ results in the formation of a type of compound originally formulated³ as a sulfinic anhydride (I). Bredereck, *et al.*,² however, recently demonstrated quite convincingly that these compounds actually possess the alternative sulfinyl sulfone structure II.



Bredereck, *et al.*,² also reported what they believed was a direct reaction between a sulfinyl sulfone and the corresponding sulfinic acid in anhydrous dioxane (eq. 1), and they suggested that this same reaction was the key step in the usual disproportionation of aromatic



sulfinic acids (eq. 2). On the other hand, kinetic studies of sulfinic acid disproportionation⁴ have in-



indicated that the only mechanisms compatible with the intervention of the sulfinyl sulfone as an intermediate in the disproportionation are those in which it undergoes rate-determining unimolecular decomposition.

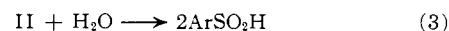
To shed further light on this problem we undertook a kinetic study of Bredereck's² sulfinyl sulfone-sulfinic acid reaction in anhydrous dioxane, and, as is described in detail in a subsequent section of this paper, we quickly found that, contrary to Bredereck's² original hypothesis, there is no *direct* reaction between the sulfinyl sulfone and the sulfinic acid under these con-

ditions. Instead, consumption of sulfinic acid occurs only as a result of its reaction with intermediates formed by a *rate-determining unimolecular* decomposition of the sulfinyl sulfone.

From these initial studies it also became apparent that aromatic sulfinyl sulfones undergo unimolecular thermal decomposition amazingly readily, and we were naturally interested in determining the mechanism of this process. The present paper reports the results of several lines of investigation directed toward that end. From these results it appears that the sulfinyl sulfones decompose by homolytic fission of the S-S bond and furthermore do so extremely rapidly as compared to the ease with which other S-S bonds are known to undergo homolytic dissociation.

Results

p-Toluenesulfinyl *p*-Tolyl Sulfone. Kinetics of Decomposition.—Aromatic sulfinyl sulfones are readily hydrolyzed to two molecules of the corresponding sulfinic acid (eq. 3).⁴ Because of this, studies of their thermal decomposition must be carried out in anhy-



drous media. However, at the same time, this ease of hydrolysis makes it possible to follow the thermal decomposition by removing aliquots of the anhydrous reaction solution and adding them to an equal volume of aqueous 2 *N* sulfuric acid; the liberated sulfinic acid is then titrated with sodium nitrite solution.⁴ Following the disappearance of sulfinyl sulfone in this way also ensures that the kinetics measure only the rate of the thermal decomposition, since the occurrence of any adventitious hydrolysis of the sulfinyl sulfone in the reaction solution would not result with this analytical method in any decrease in the apparent sulfinyl sulfone titer.

In anhydrous dioxane *p*-toluenesulfinyl *p*-tolyl sulfone (IIa) decomposes quite rapidly at 50°, even in the absence of sulfinic acid. The decomposition follows good first-order kinetics (Fig. 1) and has a half-life of about 30 min. Table I lists data on the rate of decomposition of IIa in dioxane at four temperatures. From these data Δ*H** is calculated to be 27.6 kcal./mole and Δ*S**, +11.2 e.u.

Effect of Sulfinic Acid on Rate.—If Bredereck's² hypothesis of a direct reaction between a sulfinyl sulfone and a sulfinic acid were correct, the rate of disappearance of IIa in the presence of added *p*-

(1) (a) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant AF-AFOSR-106-63. (b) Part of this work has appeared in preliminary form: J. L. Kice and N. E. Pawlowski, *J. Org. Chem.*, **28**, 1162 (1963).

(2) H. Bredereck, A. Wagner, H. Beck, and R. J. Klein, *Ber.*, **93**, 2736 (1960); H. Bredereck, A. Wagner, E. H. Beck, H. Berlinger, and K.-G. Kottenhahn, *Angew. Chem.*, **70**, 268 (1958).

(3) E. Knoevenagel and L. Pollack, *Ber.*, **41**, 3323 (1908).

(4) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

TABLE I
KINETICS OF THE DECOMPOSITION OF *p*-TOLUENESULFINYL
p-TOLYL SULFONE

Solvent	Temp., °C.	(IIa) ₀ , M	(Ar- SO ₂ H) ₀ , M	k ₁ × 10 ⁴ , sec. ⁻¹	
Dioxane	29.3	0.050	0.00	0.21 ^a	
	39.5	.050	.00	1.01 ^a	
	49.3	.050	.00	3.9	
		.048	.05	3.8	ΔH* = 27.6 kcal.
		.050	.10	4.0	
	50.8	.025	.00	4.8 ^a	ΔS* = +11.2 e.u.
.050		.00	4.6 ^a		
.050		.05	4.6 ^a		
Acetonitrile	29.3	.052	.00	0.39 ^a	
	39.3	.050	.00	1.45 ^a	ΔH* = 24.8 kcal.
	49.3	.050	.00	5.4	ΔS* = +1.8 e.u.
			.05	4.6	

^a Average of several runs.

toluenesulfonic acid should be much faster than in its absence. That this is not the case is evident both from Table I and Fig. 1. These results show that the addition of 1 or 2 molar equiv. of sulfonic acid leads to no increase, within the experimental error, in the rate of disappearance of the sulfinyl sulfone. Thus, any consumption of sulfonic acid under these conditions must be the result of its subsequent reaction with intermediates formed by an *initial rate-determining unimolecular* decomposition of the sulfinyl sulfone, not of any bimolecular reaction between the sulfinyl sulfone and the sulfonic acid.

Products of the Decomposition of IIa in the Presence and Absence of Added Sulfonic Acid.—Although added *p*-toluenesulfonic acid has no effect on the kinetics of the decomposition of IIa, the decomposition products obtained in its presence are significantly different from those in its absence. Furthermore, sulfonic acid is consumed in an amount approaching that expected from the stoichiometry of eq. 1.

The manner in which the products were investigated was as follows: In each experiment at the end of the decomposition an aliquot was removed and titrated by the nitrite procedure to determine residual sulfonic acid. Another aliquot was added to water, and the mixture was titrated with dilute sodium hydroxide. (This measures the amount of titratable acid present; This will include any residual sulfonic acid, any *p*-toluenesulfonic acid formed in the decomposition, and any of the latter acid which might be formed by the hydrolysis of any very readily hydrolyzed decomposition products on addition of the dioxane aliquot to water.) The remainder of the reaction solution was then treated with a large volume of water, and the mixture was extracted with ether. The ether-soluble products were then separated by chromatography and identified.

The results of the product studies are shown in Table II. In the presence of at least 1 molar equiv. of added sulfonic acid the decomposition yields essentially equal amounts of *p*-tolyl *p*-toluenethiolsulfonate and *p*-toluenesulfonic acid. About 0.9 mole of each is formed per mole of IIa decomposed. Somewhat less than 1 mole of sulfonic acid is consumed per mole of IIa reacting. Evidently the reaction does not have exactly the stoichiometry suggested by Brederick.²

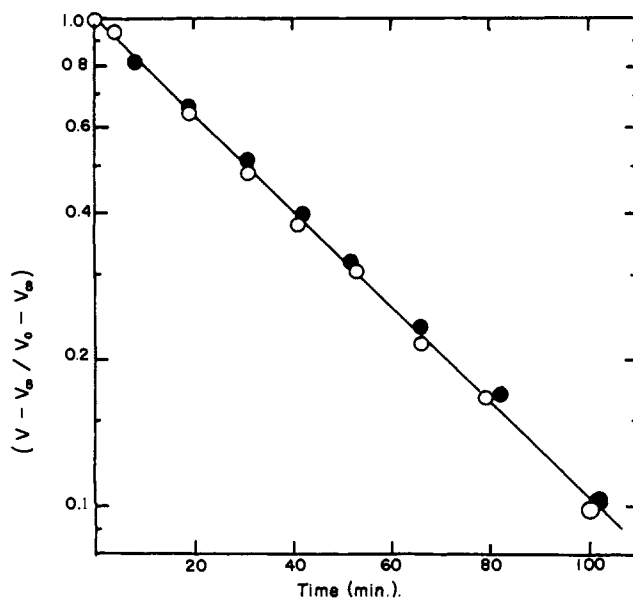


Fig. 1.—Kinetics of decomposition of IIa in dioxane: ○, 0.05 M IIa, 0.00 M ArSO₂H; ●, 0.05 M IIa, 0.05 M ArSO₂H; temp., 49.3°. *V* is the volume of standard nitrite required to titrate an aliquot after hydrolysis of IIa (see text).

In the absence of added sulfonic acid the product composition is markedly different. Although the yield of sulfonic acid remains about the same, the yield of thiolsulfonate is much lower (0.17 mole/mole IIa), and a sizable amount of *p*-tolyl disulfide (0.25 mole/mole IIa) is now isolated. During the decomposition in the absence of sulfonic acid the solution turns a light yellow. This color is discharged immediately on addition of a small amount of water or sulfonic acid.⁵

TABLE II
PRODUCTS OF THE DECOMPOSITION OF IIa IN DIOXANE AT 50°
Initial reactants

IIa, concn., M	0.050	0.043	0.042
<i>p</i> -Toluenesulfonic acid, concn., M	0.000	0.042	0.086
Products, mmole/mole of IIa			
<i>p</i> -Tolyl <i>p</i> -toluenethiolsulfonate	0.17	0.93	0.96
<i>p</i> -Tolyl disulfide	.25	0.00	0.00
Titratable acid ^a	.89	1.07	2.08
Residual <i>p</i> -toluenesulfonic acid	.00	0.13	1.15
<i>p</i> -Toluenesulfonic acid ^b	.89	.94	0.93
Mmoles sulfonic acid consumed/ mmole IIa		.86	0.89 ^c

^a Titration of aliquot to brom thymol blue end point with 0.1 N sodium hydroxide. ^b Mmole *p*-toluenesulfonic acid = (mequiv. titratable acid - mmole residual sulfonic acid). Identity of acid established in separate experiment by isolation as its *p*-toluidine salt (see Experimental). ^c Not corrected for small amount of disproportionation of sulfonic acid (eq. 2).

Effect of Solvent on Rate.—The rate of decomposition of IIa was also measured in carefully dried acetonitrile. The data are shown in Table I. The decomposition rate is not much altered by the change in solvent. Interestingly, the activation parameters ΔH* and ΔS* do change rather markedly, the change in one, however, being almost completely compensated for by the change in the other.

(5) These results for the products formed in the absence of added sulfonic acid differ from those originally reported in ref. 1b in that the yield of disulfide is much higher and that of thiolsulfonate much lower. In the early studies fewer precautions were taken to keep the system truly anhydrous during the decomposition. This has been shown to be responsible for the difference observed.

Although no direct measure of solvent ionizing power, such as Z -value⁶ or ionization rate of *p*-methoxyneophyl *p*-toluenesulfonate,⁷ is presently available for pure dioxane, one would certainly expect that it would definitely be a less-ionizing solvent than acetonitrile. Since the change from dioxane to acetonitrile produces only a modest increase in the rate of decomposition of IIa, it suggests that the reaction is not very sensitive to solvent ionizing power.

Galvinoxyl Studies.—The current reagent-of-choice for detecting and counting radical intermediates in organic reactions is the stable free radical galvinoxyl.⁸ Preliminary experiments showed that in dioxane at 30° galvinoxyl did not react at an appreciable rate with either *p*-toluenesulfonic acid (0.05 *M*) or *p*-tolyl *p*-toluenethiolsulfonate (0.05 *M*). It did, however, react quite rapidly with *p*-toluenesulfonic acid, the reaction showing second-order kinetics, first order in galvinoxyl and first order in sulfonic acid. To avoid trouble from this reaction the IIa used in the galvinoxyl studies was treated in a special way to ensure the removal of any last traces of *p*-toluenesulfonic acid (see Experimental).

The zero-order disappearance of galvinoxyl in the presence of various concentrations of the sulfinyl sulfone at 29.3° was then determined. The results are shown in Table III. In the last column of the table are values of the apparent efficiency of radical production, as estimated from the ratio of the zero-order rate of galvinoxyl disappearance to the over-all rate of decomposition of IIa, as calculated from the data of Table I. These efficiency values, f , are reasonably constant and of sufficient magnitude (~ 0.3) to suggest that the decomposition of IIa results to at least an appreciable extent in the formation of trappable radical intermediates.

TABLE III
DECOMPOSITION OF IIa IN THE PRESENCE OF GALVINOXYL
AT 29.3° IN DIOXANE

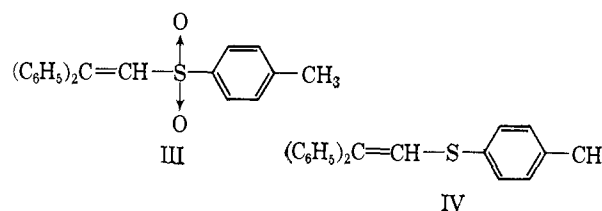
(IIa) $\times 10^2$, <i>M</i>	(G) ₀ $\times 10^3$, ^a <i>M</i>	$k_0 \times 10^7$, ^b <i>M</i> sec. ⁻¹	$[k_0/2k_1(\text{IIa})] = f^c$
1.24	0.8	1.73	0.33
2.9	.8	3.3	.27
5.4	.8	5.9	.26
1.9	1.7	2.5	.31
0.80	1.9	0.87	.26
			Av. 0.28

^a (G)₀, initial concn. of galvinoxyl. ^b k_0 , zero-order rate of disappearance of galvinoxyl. ^c k_1 is first-order rate of decomposition of IIa in dioxane at 29.3° (see Table I).

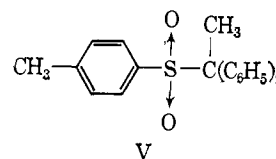
Decomposition of IIa in the Presence of Diphenylethylene.—If radical intermediates are involved in the decomposition of IIa, carrying out the reaction in the presence of an olefin susceptible to radical attack should hopefully lead to radical-olefin reaction products.

Compound IIa (0.07 *M*) was decomposed in a dioxane solution containing 1.8 *M* added 1,1-diphenylethylene. Besides some *p*-tolyl *p*-toluenethiolsulfonate (0.23 mole/mole IIa), there was isolated a sizable amount (0.20 mole/mole IIa) of *p*-tolyl 2,2-diphenyl-

vinyl sulfone⁹ (III) and 0.18 mole/mole IIa *p*-tolyl 2,2-diphenylvinyl sulfide⁹ (IV).



It was important to demonstrate that III could not arise from reaction with the olefin of any sulfinic acid which might somehow be formed in the course of the decomposition of IIa in the presence of the olefin. This was done by subjecting a dioxane solution of the olefin, *p*-toluenesulfonic acid, and a small amount of *p*-toluenesulfonic acid to the same conditions used for the other experiments. No III was formed. Interestingly, a small amount of *p*-tolyl 1,1-diphenylethyl sulfone (V) was isolated; V apparently arises by the acid-catalyzed addition of some of the sulfinic acid to the olefin. Investigation of the possible generality of such a reaction of sulfinic acids and olefins is planned.



Influence of Sulfinyl Sulfone Structure on Rate of Decomposition.—The variation of the rate of decomposition with structure of the sulfinyl sulfone was investigated with a series of aromatic sulfinyl sulfones. The reactions were followed by the same procedure used for IIa. All showed good first-order kinetics. The results are given in Table IV.

TABLE IV
KINETICS OF THE DECOMPOSITION OF AROMATIC SULFINYL
SULFONES IN DIOXANE

Compound	Temp., °C.	(ArSO ₂ SOAr) ₀ , <i>M</i>	$k_1 \times 10^4$, sec. ⁻¹		
II d	49.3	0.039	6.0		
		.059	6.2		
		.080	5.1		
II c	49.3	.050	4.8		
		.100	4.8		
		.05	6.4 ^a		
II b	39.3	.05	1.4 ^a	$\Delta H^* = 28.1$ kcal.	
		29.3	.05	0.33 ^a	$\Delta S^* = +14.3$ e.u.
		.05	0.33 ^a		

^a Average of several runs.

It is evident that there are no large changes in rate with change in the nature of the aryl group of the sulfinyl sulfone. Comparison of the data for the *p*-chlorophenyl, phenyl, and *p*-tolyl (Table I) compounds suggests that electron-releasing substituents in the aromatic ring retard the decomposition and electron-withdrawing ones accelerate it, but the effect is small.

Discussion

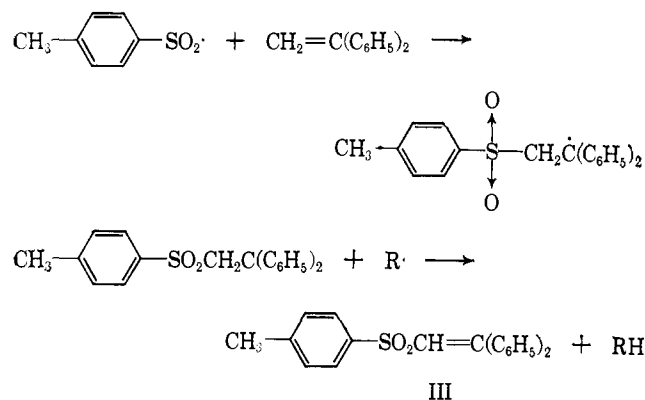
The decompositions of the various aromatic sulfinyl sulfones all follow good first-order kinetics. Although decomposition in the presence of added sulfinic acid

(6) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261 (1958).
 (7) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).
 (8) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962); P. D. Bartlett and C. Ruchardt, *ibid.*, **83**, 1756 (1960); D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *ibid.*, **85**, 1938 (1963); W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

(9) H. Potter, *ibid.*, **76**, 5472 (1954).

leads to consumption of sulfinic acid, the rate of decomposition is the same as in the absence of sulfinic acid. Clearly, there is *no direct* reaction between sulfinic acid and sulfinyl sulfone, such as Bredereck, *et al.*,² suggested. Rather, the sulfinic acid must be consumed by virtue of reaction with intermediates formed as a result of a *rate-determining unimolecular* decomposition of the sulfinyl sulfone.

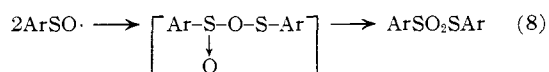
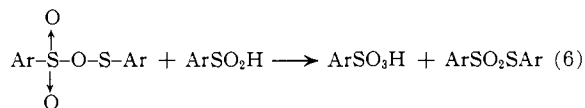
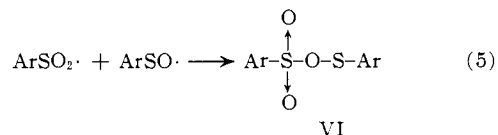
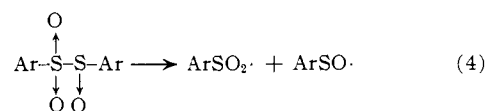
Several lines of evidence suggest that this rate-determining unimolecular decomposition of the sulfinyl sulfone is a homolytic reaction. First, there are the galvinoxyl results, which indicate that about 30% of the sulfinyl sulfone decomposing yields trappable free radicals. Second, the formation of an appreciable quantity of *p*-tolyl 2,2-diphenylvinyl sulfone (III) when IIa is decomposed in the presence of diphenylethylene is hard to account for except by a sequence such as



in which a *p*-toluenesulfonyl radical first adds to the olefin double bond and the resulting radical then undergoes an H-atom transfer with some other radical present in the solution. The only alternative route to III would be an initial addition of *p*-CH₃C₆H₄SO₂⁺, followed by loss of a β-proton from the resulting carbonium ion. However, there are several indications¹⁰ that sulfonylium ions such as *p*-CH₃C₆H₄SO₂⁺ are highly unstable species which are formed only under very forcing conditions. It hardly seems likely they could be formed under the mild conditions of the present experiments. Third, the relative insensitivity of the rate of decomposition of IIa to solvent ionizing power argues against a rate-determining heterolysis of the sulfur-sulfur bond. All things considered, the most reasonable proposal for the rate-determining step of the sulfinyl sulfone decomposition would seem to be the reaction shown in eq. 4 (Chart I).

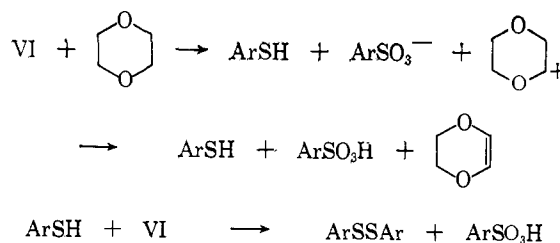
Formation of the products isolated under various reaction conditions can then be accounted for as follows. In the absence of a good radical trap such as diphenylethylene almost all of the radicals generated in eq. 4 recombine as shown in eq. 5, giving the sulfonyl sulfonate VI. This compound should resemble a very reactive sulfonyl halide in its chemical behavior. As such it would be expected to react readily (eq. 6) with any sulfinic acid present, yielding 1 molecule each of thiolsulfonate and sulfonic acid. We think that those few ArSO₂· radicals which do not disappear by eq. 5 react by abstracting a hydrogen atom from the solvent (eq. 7). It is the occurrence of this reaction which causes the consumption of sulfinic acid to be

CHART I
MECHANISM OF SULFINYL SULFONE DECOMPOSITION



somewhat less than that required by eq. 1, for not only does an ArSO₂· which reacts by eq. 7 cause less VI to be formed per mole of II decomposing, but it also replenishes in part the added sulfinic acid consumed in eq. 6. Those ArSO· radicals which do not react by eq. 5 are assumed to undergo mutual termination as in eq. 8. That termination of two ArSO· radicals gives the thiolsulfonate as the final product is strongly indicated by the work of Topping and Kharasch.¹¹

In the absence of added sulfinic acid the small amount of ArSO₂H formed in eq. 7 reacts by eq. 6 with an equimolar amount of VI from reaction 5. This reaction and eq. 8 account for much of the limited amount of thiolsulfonate formed under those conditions. Because of the small amount of sulfinic acid formed, most of the sulfonyl sulfonate is of course left to react in another fashion. Because this other path is significantly slower than eq. 6, the concentration of VI becomes large enough during the decomposition of II for the solution to become yellow colored. Assignment of the yellow color to VI is consistent with the fact it is instantly discharged by addition of water or sulfinic acid. The other reaction path for VI apparently yields sulfonic acid and disulfide as the principal products. Just how these are formed is not certain at present, but the report¹² that sulfonyl chlorides can attack ethers suggests the dioxane solvent probably plays a role in the reaction. Besides the disulfide and the sulfonic acid there are formed small amounts of at least several other, as yet unidentified, compounds, one of which contains a carbonyl function. One possible route to the disulfide and sulfonic acid might be

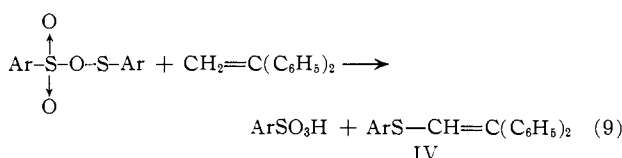


(11) R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962).

(12) D. R. Hogg, as quoted by N. Kharasch in "Organic Sulfur Compounds," Vol. 1, Pergamon Press, New York, N. Y., 1961, p. 387.

(10) F. Klages and K. Hobeisel, *Ber.*, **96**, 2057 (1963).

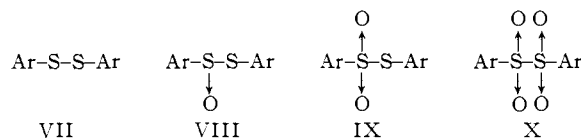
The galvinoxyl results, which indicate that not all the IIa decomposing yields trappable free radicals, suggest that a good deal of the sulfinyl sulfonate VI results from cage recombination of $\text{ArSO}_2\cdot$ $\text{ArSO}\cdot$ radical pairs. That being the case, some VI should still be formed even in the presence of diphenylethylene. Once formed under such conditions, VI should react very readily with the olefin, which is present in high concentration, and, by analogy with the reaction of sulfinyl chlorides with olefins such as *p*-methoxystyrene,¹³ the product will be the unsaturated sulfide IV (eq. 9). As outlined earlier, the unsaturated sul-



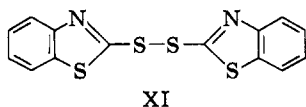
fone III is thought to be formed by addition of an $\text{ArSO}_2\cdot$ radical to the olefin, followed by a hydrogen abstraction, quite possibly by another $\text{ArSO}_2\cdot$ radical. Since no olefin- $\text{ArSO}\cdot$ radical adducts were observed, we tentatively suggest that these radicals may be considerably less reactive than $\text{ArSO}_2\cdot$ toward the olefin and that, despite its presence, they react by eq. 8, thereby producing most of the thiol sulfonate formed under these conditions.

We have seen that the various facets of the sulfinyl sulfone decomposition seem best explained by a radical mechanism involving an initial homolytic cleavage of the sulfur-sulfur bond of II (eq. 4). Probably the most striking and interesting feature of the decomposition is the fact that this homolytic cleavage occurs much more readily than the homolytic dissociation of the S-S bonds in such related compounds as disulfides, thiol sulfonates, thiol sulfonates, or α -disulfones. This becomes evident from the comparisons in the following paragraphs.

First, although aromatic disulfides (VII) undergo homolytic dissociation slowly at elevated temperatures,¹⁴ the rate of dissociation of one of the more



readily dissociated, 2,2'-dibenzothiazolyl disulfide (XI), is only 7×10^{-7} sec.⁻¹ at 56°,¹⁵ a value about one-thousandth that for k_1 for IIa at the same temperature.



Barnard¹⁶ has suggested that one way in which aromatic thiol sulfonates (VIII) can undergo disproportionation is by a radical mechanism involving dissociation into $\text{ArSO}\cdot$ and $\text{ArS}\cdot$. However, experiments in these laboratories¹⁷ have shown that in the absence

(13) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956).

(14) For a summary of the evidence see W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 42-45.

(15) R. E. Davis and C. Perrin, *J. Am. Chem. Soc.*, **82**, 1590 (1960).

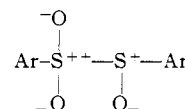
(16) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(17) C. G. Venier, unpublished results.

of added strong acid the rate of disproportionation in solution is very slow even at 65°. Obviously here too homolytic fission of the S-S bond must occur much more slowly than in the case of the sulfinyl sulfones.

Third, although their chemistry has not been studied extensively, there is nothing to indicate that aromatic α -disulfones (X) are very unstable thermally. Similarly, there are no reports of a facile homolytic dissociation of the S-S bond in an aromatic thiol sulfonate (IX).

Among the known compounds containing a single sulfur-sulfur linkage the sulfinyl sulfones thus appear to be unique as regards the extreme ease of dissociation of the S-S bond.¹⁸ Our first thought was that this facile decomposition results from the unfavorable repulsion of the two somewhat electron-deficient sulfur atoms



which leads to an increase in the free energy of II and a weakening of the sulfur-sulfur bond. Indeed the effects of aryl *p*-substituents are in qualitative accord with this concept, the electron-withdrawing halogen accelerating the rate of decomposition, and the electron-donating methyl retarding it. However, this cannot be the only factor responsible for the fast rate, for if it were, one would expect the α -disulfones X to decompose even more readily, which, of course, they do not. That being the case, it seems necessary also to assume that the $\text{ArSO}\cdot$ radical is a species of significantly lower energy than $\text{ArSO}_2\cdot$. This plus the dipole repulsion could then explain why II, and apparently XII,¹⁸ decompose so much more readily than X.

Experimental

Materials. *p*-Toluenesulfinyl *p*-tolyl sulfone (IIa), *p*-chlorobenzenesulfinyl *p*-chlorophenyl sulfone (IIb), and 2-naphthalenesulfinyl 2-naphthyl sulfone (IIc) were all prepared and purified as described by Bredereck, *et al.*² It was found that a purer product was obtained if a slight excess of sulfinyl chloride over sodium salt of the sulfonic acid was used in the preparation. **Benzenesulfinyl phenyl sulfone** (IIc) was prepared in an analogous manner from benzenesulfinyl chloride and sodium benzenesulfinate. After purification it melted at 78°, lit.³ 66-67°. However, infrared spectra showed that the present material was identical with some prepared by the Knoevenagel and Pollack³ procedure. (A similar difference in melting points was also observed by Bredereck, *et al.*,² for IIa prepared by their method and that prepared by the earlier procedure.³) *p*-Toluenesulfinic acid was prepared and purified as outlined in a previous paper.⁴ **Galvinoxyl.**—The method of Kharasch and Joshi²⁰ was used to prepare the compound. It was purified by recrystallization from ethanol; m.p. 158°.

Solvents.—**Dioxane** was purified by the method described by Wiberg.²¹ As suggested by him,²¹ it was kept anhydrous and peroxide-free by addition of some of the sodium ketyl of benzophenone. Small batches of solvent were then fractionally dis-

(18) There is one group of compounds, as yet unisolated, which may equal or exceed the sulfinyl sulfones in ease of homolytic cleavage of the S-S bond. These are the α -disulfoxides (XII), $\text{Ar}-\text{S}(\rightarrow\text{O})-\text{S}(\rightarrow\text{O})-\text{Ar}$. Thus, Barnard and Percy's results¹⁹ on the oxidation of VIII with hydrogen peroxide have led them to suggest that the first step of the reaction is oxidation of VIII to XII and that the latter compound then undergoes rapid dissociation into two $\text{ArSO}\cdot$.

(19) D. Barnard and E. J. Percy, *Chem. Ind. (London)*, 1332 (1960).

(20) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(21) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 246.

tilled from this solution as needed; b.p. 100.5°. **Acetonitrile.**—Reagent grade acetonitrile was first distilled from calcium hydride. It was then refluxed over phosphorus pentoxide and fractionally distilled from it; b.p. 82°.

Procedure for Kinetic Runs.—A weighed sample of the sulfinyl sulfone was dissolved in dioxane or acetonitrile. If sulfinic acid was also going to be used in the run this was then added, and the solution was made up to volume with solvent. The solution was placed in a reaction vessel of the type described by Kice and Bowers,⁴ deaerated with dry nitrogen at room temperature or below for 10–15 min., and then placed in the constant temperature bath. During the course of a run the solution was always kept under nitrogen, and aliquots were removed without exposing the remaining solution to the atmosphere.

Once an aliquot was removed it was added to an equal volume of 1.5 *N* aqueous sulfuric acid. This hydrolyzes any sulfinyl sulfone to the sulfinic acid (eq. 3). The amount of sulfinic acid in the aliquot was then determined by titration with standard nitrite solution.⁴

In the runs without added sulfinic acid the final titer was always zero, but naturally this is not true for the runs with any excess added sulfinic acid. In those cases the final titer was not zero, and one must accordingly plot $\log(V - V_\infty/V_0 - V_\infty)$ vs. time rather than $\log(V/V_0)$. In addition, in runs with a large excess of sulfinic acid the infinity titer drifted slowly downward owing to the slow disproportionation of the residual sulfinic acid according to eq. 2. Fortunately, the rate of the disproportionation was slow enough compared to the reaction under study that it was easy to estimate what the infinity titer would have been in the absence of any interference from the disproportionation and also to correct the measured titration volumes for the small amount of disproportionation which occurred during the course of the sulfinyl sulfone-sulfinic acid reaction. Such corrected V_∞ and V values were used in making the plots of these runs.

Galvinoxyl Studies.—Because preliminary studies indicated that galvinoxyl reacted quite readily with *p*-toluenesulfonic acid, special precautions were taken to ensure that the IIa used for the galvinoxyl studies was entirely free of sulfinic acid. Specifically, 1 g. of IIa was dissolved in 25 ml. of dry benzene, and the solution was placed on a 1.5 × 10 cm. column of 50% anhydrous magnesium sulfate-50% dried Celite. After eluting the column with about 25 ml. of benzene, the next 25–30 ml. of eluate was collected and evaporated to dryness under vacuum below room temperature. The residue was then kept for 1 hr. at room temperature under 0.1 mm. vacuum; IIa purified in this way gave good initial zero-order kinetics for galvinoxyl disappearance. Without this treatment the initial rate of disappearance of galvinoxyl was faster and no longer zero order in galvinoxyl.

The galvinoxyl runs were carried out in the apparatus shown in Fig. 2. Section C is a standard 1-cm. Beckman Pyrex cell. Before use the whole apparatus was carefully dried and baked out in an oven. A weighed sample of IIa was placed in A, and a known volume of a solution of galvinoxyl in dioxane was introduced into B. The apparatus was connected to a vacuum line through D, the contents frozen, and stopcock E was then opened. After the system had been evacuated, the stopcock was closed, and the contents of B were melted. This degassing procedure was repeated once more, and then dry prepurified nitrogen was admitted into the apparatus. The stopcock was closed, and the apparatus removed from the line. The IIa in A was now dissolved in the solution in B, and, once solution was effected, the final solution was allowed to flow into cell C. The apparatus was then placed in the cell compartment of a Beckman Model DB spectrophotometer, which was thermostated at 29.3°, and the disappearance of galvinoxyl was followed by measuring the change in optical density at 570 $m\mu$ with time.

Product Studies. Decomposition of IIa in the Absence of Sulfinic Acid.—A weighed amount of IIa was placed in a flask and a known amount of dioxane was distilled in. The solution was then deaerated and decomposed at 50° in the same manner as in the kinetic runs. Titration of an aliquot of the final solution for residual sulfinic acid showed none to be present. Another aliquot was slowly added to water, and the resulting mixture was titrated to the brom thymol blue end point with 0.1 *N* sodium hydroxide.

To the remainder of the solution was then slowly added ten times its volume of water, and the resulting mixture was extracted three times with small portions of ether. The ether extracts were washed with dilute sodium bicarbonate, and then with water. The ether was dried over sodium sulfate and then evaporated

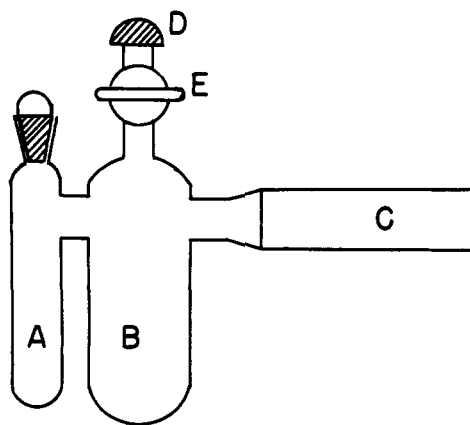


Fig. 2.—Apparatus for galvinoxyl-IIa studies.

under reduced pressure. The residue was chromatographed on alumina using successively hexane, hexane-benzene mixtures, benzene, benzene-ether mixtures, and ether as eluents. Two main fractions were obtained. The first of these, eluted with hexane, was shown to be identical with a known sample of *p*-tolyl disulfide. The second, eluted with benzene, was identical with a known sample of *p*-tolyl *p*-toluenethiolsulfonate.⁴

In a separate experiment the aqueous layer after the ether extraction was evaporated to dryness. The residue consisted of slightly violet colored crystals which had an infrared spectrum essentially identical with that of a known sample of *p*-toluenesulfonic acid. Confirmation of their identity was provided by conversion to the *p*-toluidine salt, m.p. 196–198°, lit.²² 197°, using the procedure described by Fieser.²²

Decomposition of IIa in the Presence of Sulfinic Acid.—A solution of IIa and *p*-toluenesulfonic acid in dioxane was made up, deaerated, and the IIa decomposed in exactly the same manner as in the product study above. After the reaction was finished, aliquots were removed and titrated for residual sulfinic acid and titratable acid, respectively. The remainder of the solution was then worked up in the same way as in the product study in the absence of added sulfinic acid.

Upon chromatography only one fraction was found in the ether extracts. This was *p*-tolyl *p*-toluenethiolsulfonate. No *p*-tolyl disulfide was isolated.

Decomposition of IIa in the Presence of Diphenylethylene.—Compound IIa (3.50 mmoles, 1.03 g.) was dissolved in some dioxane, 15.6 g. of 1,1-diphenylethylene²³ was added, and the solution was made up to 50 ml. with additional dioxane. The solution was deaerated, and the IIa was decomposed in the usual way. At the end of the reaction the solution was worked up in the same manner as in the other product studies.

Upon chromatography of the residue from the ether extract there was obtained first a large amount of unchanged diphenylethylene. The third major fraction eluted was *p*-tolyl *p*-toluenethiolsulfonate (0.80 mmole, 0.220 g.). Before and after the thiolsulfonate two new products were eluted. Their identity was established in the manner described in the succeeding paragraphs.

***p*-Tolyl 2,2-Diphenylvinyl Sulfone (III).**—After the thiolsulfonate there was eluted 0.240 g. of III, m.p. 102–103° after recrystallization from ethanol-water (lit.⁹ 103–103.5°). The infrared spectrum of III showed strong absorption at 1325 and 1150 cm^{-1} . The n.m.r. spectrum showed no resonance between 4–10 τ except for a singlet attributed to the tolyl methyl group at 7.67 τ (intensity, 3). The other resonances were a complex pattern attributed to the aromatic protons between 2.4 and 3.0 τ (intensity, 14.5) and a sharp singlet attributed to the vinyl hydrogen at 3.1 τ (intensity, 1). The ultraviolet absorption spectrum in 95% ethanol showed λ_{max} at 275 $m\mu$ (ϵ 18,200). For comparison, phenyl 2-phenylvinyl sulfone has λ_{max} at 275 $m\mu$ (ϵ 26,200).²⁴

***p*-Tolyl 2,2-Diphenylvinyl Sulfide (IV).**—Before the thiolsulfonate there was eluted 0.185 g. of IV, m.p. 82–83° after recryst-

(22) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 145.

(23) "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

(24) V. Baliah and Sp. Shanmuganathan, *J. Indian Chem. Soc.*, **36**, 31 (1958).

tallization from ethanol-water (lit.⁹ 84°). Like III the n.m.r. spectrum of IV shows only the tolyl methyl resonance at 7.67 τ (intensity, 3) in the region 4–10 τ . There was a series of reso-

nances attributed to the aromatic protons (τ , 2.4–3.0; intensity, 14) and a sharp singlet at 3.3 τ (intensity, 1). The ultraviolet spectrum in 95% ethanol had a maximum at 310 m μ (ϵ 24,000).

[CONTRIBUTION FROM THE SHIONOGI RESEARCH LABORATORY, SHIONOGI & CO., LTD., FUKUSHIMA-KU, OSAKA, JAPAN]

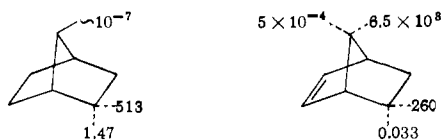
Substituent Effects and Homobenzylic Conjugation in *anti*-7-Benzonorbornenyl *p*-Bromobenzenesulfonate Solvolyses¹⁻⁴

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A series of 4'-substituted *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonates was prepared and the acetolysis of these sulfonates proceeds with retention of configuration. The relative rates of CH₃O, CH₃, H, Cl, Br, and NO₂ derivatives at 77.60° were 53.7, 5.7, 1, 0.045, 0.030, and 1.39×10^{-4} , respectively. The data indicate major participation by the aromatic ring, facilitating acetolysis. The rate data are not correlated by the Hammett relationship, $\log(k/k_0) = \rho\sigma$, or by the modified Hammett relationship, $\log(k/k_0) = \rho\sigma^+$. They are correlated with good precision by ($\sigma^+ + \sigma$) or by ($\sigma_p^+ + \sigma_m^+$), yielding straight lines with $\rho = -2.40$ or -2.55 . The implications of this correlation in terms of the precise nature of the participation in the transition state for the acetolysis are discussed.

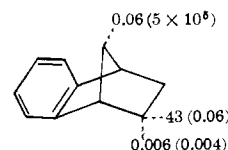
The solvolytic behavior of norbornyl systems have provided many well-known examples for the demonstration of anchimeric assistance to ionization. Acetolytic reactivities (at 25°, relative to cyclohexyl *p*-bromobenzenesulfonate) of 5- and 7-norbornenyl and of 7- and 2-norbornyl *p*-bromobenzenesulfonates are summarized as⁵



The most remarkable rate enhancement was observed on the 7-*anti*-norbornenyl system.⁶ The mere introduction of a double bond into the saturated 7-norbornyl system accelerated the acetolysis rate by a factor of 10^{11} . This large rate enhancement indicates participation by the double bond, facilitating ionization of the sulfonate group.

The solvolyses of 2- and 7-benzonorbornenyl derivatives were found by Bartlett and Giddings⁷ to parallel qualitatively the results in the analogous norbornenyl system. In the case of *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonate, the acetolysis rate was faster than that of 7-norbornyl *p*-bromobenzenesulfonate by a factor of 5×10^5 , in contrast to the much larger factor of 10^{11} provided by the double bond of the *anti*-7-nor-

bornenyl derivative. The acetolysis rates of benzonorbornenyl *p*-bromobenzenesulfonates relative to cyclohexyl and the corresponding norbornyl *p*-bromobenzenesulfonate (shown in parentheses) at 25° are summarized^{5,7a}



In spite of the smaller factor exerted by the aromatic ring in the *anti*-7-benzonorbornenyl derivatives, it is evident that participation must be quite important in accounting for the enhanced rates observed in these derivatives.

At the present time there is considerable discussion as to the precise nature of the participation in the solvolysis of derivatives of this kind, and of the precise structure of the carbonium ions produced in the ionization stage.^{6b,8} It appeared to us that some light might be thrown on this interesting question by examining the effect of substituents in *anti*-7-benzonorbornenyl derivatives on the rate of acetolysis. Accordingly, we undertook the synthesis of a number of 4'-substituted *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonates and a study of their rates of acetolysis.⁹

Results

Preparations.—Most of the 4'-substituted benzonorbornadienes (I, II, III, IV, and V), which were required in the present study as the starting materials, were prepared in high yields by our modification¹⁰ of Wittig's procedure.¹¹ The introduction of a benzoyloxy group into the *anti*-7-position of the above dienes was achieved

(8) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963), and references therein.

(9) It should be pointed out that the effect of methoxy substituents in the 3'- and 6'-positions of *anti*-7-benzonorbornenyl system was previously examined by G. A. Wiley, and that in the mid-course of this work we learned Professor Streitwieser's prediction based on molecular orbital theory for a part of our results. Refer to A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 389.

(10) H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Japan*, **37**, 40 (1964).

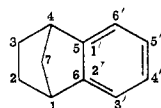
(11) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

(1) Paper V of a series on Bicyclic Systems; Paper IV: H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964).

(2) Some of the results of this paper appeared in preliminary form: H. Tanida, *J. Am. Chem. Soc.*, **85**, 1703 (1963).

(3) Presented, in part, at the 14th Organic Reaction Mechanism Symposium of the Chemical Society of Japan in Fukuoka, Oct., 1963.

(4) The ring system of benzonorbornadiene and its numbering are shown as



(5) For a recent review, see J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(6) (a) S. Winstein, M. Shatavsky, C. J. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963), and references therein.

(7) (a) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).