[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF OREGON STATE UNIVERSITY, CORVALLIS, ORE., AND THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

Mechanisms of Reactions of Sulfinic Acids. III. The Reaction of Some Dialkyl Sulfides with *p*-Toluenesulfinic Acid

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Benzyl sulfide and butyl sulfide have been found to react rapidly with *p*-toluenesulfinic acid at 70° in acetic acid–water containing 0.3–0.7 *M* sulfuric acid. This previously unreported reaction between a sulfide and a sulfinic acid leads to the cleavage of the sulfide and the oxidation of at least one of its alkyl groups to the corresponding aldehyde. Other products which have been identified are *p*-tolyl *p*-toluenethiolsulfonate and alkyl *p*-toluenethiolsulfonate. Kinetic studies show the reaction is first order in both sulfinic acid and sulfide. It also shows the same pronounced dependence of rate on acidity and water concentration exhibited by the *p*-tolyl disulfide–*p*-toluenesulfinic acid reaction studied earlier.[2] These facts point to a mechanism involving the formation of ion III, followed by its rate-determining decomposition, probably by the sequence shown in reactions 6 and 7.

The preceding paper[2] described a new reaction between *p*-tolyl disulfide and *p*-toluenesulfinic acid. The experimental evidence indicated this reaction involved the reversible formation of the ion $ArS(O)^+S(Ar)–SAr$ and then its rate-determining decomposition to ArS^+ and $ArS(O)SAr$. This mechanism has several interesting and significant implications. In particular it suggests that other divalent sulfur compounds (X–S–Y) might react similarly to form $ArS(O)\overset{+}{S}XY$. The breakdown of such ions, other than by reversion to $ArSO^+$ and X–S–Y, could then result in novel reactions between sulfinic acids and a variety of organic sulfur compounds.

The present paper shows that such expectations can in fact be realized for at least some members of one important group, the dialkyl sulfides. Thus both benzyl and *n*-butyl sulfide react rapidly with *p*-toluenesulfinic acid under conditions similar to those used[2] for the disulfide–sulfinic acid reaction. The dependence of the rates of these reactions on water and strong acid concentration points to $ArS(O)\overset{+}{S}R_2$ as the intermediate involved in the rate-determining step. The products include, among other things, the aldehydes (benzaldehyde and *n*-butyraldehyde) derived from the alkyl group of the sulfide. To the best of our knowledge this is the first report of any sort of reaction between a sulfide and a sulfinic acid.

Results

As with the disulfide–sulfinic acid reaction,[2] at moderate sulfuric acid concentrations in acetic acid–0.56 *M* H_2O the reaction of the sulfides with sulfinic acid strongly predominates over the normal disproportionation reaction of sulfinic acids. For both benzyl and *n*-butyl sulfides the products and kinetics of the sulfide–sulfinic acid reaction have been investigated. Although the kinetic behavior is exactly the same in both cases the products are somewhat different, suggesting that there are differences in behavior subsequent to the rate-determining step.

Products of the Benzyl Sulfide–*p*-Toluenesulfinic Acid Reaction.—Benzyl sulfide (0.2 *M*) reacted with *p*-toluenesulfinic acid (0.05 *M*) in acetic acid–0.56 *M* H_2O containing 0.5 *M* sulfuric acid to give three products—*p*-tolyl *p*-toluenethiolsulfonate (I), benzaldehyde and benzyl *p*-toluenethiolsulfonate (II). These were separated by chromatography from a large amount of unreacted sulfide. Reaction of 4.0 mmoles of sulfinic acid gave 1.40 mmoles of I, 0.55 mmole of II and 0.39 mmole of benzaldehyde. The benzaldehyde yield is probably low due to losses and possible oxidation during work-up and isolation. The two thiolsulfonates account for 83% of the original *p*-tolyl groups. Small amounts of other products eluted in the same fractions as the large amount of recovered sulfide could have escaped detection, although no irregularities were found in the infrared spectra of any of the sulfide fractions.

Mechanistic considerations (see Discussion) suggest eq. 1 as a likely stoichiometry for the over-all reaction. On this basis the yields of the

$$5ArSO_2H + (C_6H_5CH_2)_2S \longrightarrow 2ArSO_2SAr + ArSO_2SCH_2C_6H_5 + C_6H_5CHO + 3H_2O \quad (1)$$

$$Ar = p\text{-tolyl}$$

three products are: I, 92%; II, 76%; and benzaldehyde, 54%.[3] Since a significant amount of benzaldehyde could well be lost during isolation, these yields seem in fairly satisfactory accord with the suggested stoichiometry.

Products of the Butyl Sulfide–*p*-Toluenesulfinic Acid Reaction.—The reaction of butyl sulfide (0.2 *M*) with *p*-toluenesulfinic acid (0.1 *M*) was studied in the same acetic acid–water–sulfuric acid solution used for the benzyl sulfide reaction. In contrast to the benzyl case only one thiolsulfonate, I, was isolated, 10.0 mmoles of sulfinic acid yielding 4.96 mmoles of I. Since this accounts for 99% of the original *p*-tolyl groups, no butyl *p*-toluenethiolsulfonate to speak of is formed. However, a substantial amount of *n*-butyraldehyde is produced. For reasons outlined in the Experimental there were difficulties in determining the exact yield of the aldehyde accurately. However, from 3.5–4.5 mmoles appear to be formed. A large amount of butyl sulfide was recovered unreacted. The fate of the sulfur atom in those sulfide molecules which do react was not definitely determined. It was established, though, that no H_2S is libe-

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[2] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2384 (1962).

[3] In calculating yields one must remember that the relative rates of the sulfide–sulfinic acid reaction and the normal disproportionation under these conditions are such that about 10% of the sulfinic acid decomposes by the normal disproportionation.

rated during the course of the reaction. In all the butyl sulfide runs an insoluble scum formed on the inside of the reaction vessel. Although not identified, it is possible this was elemental sulfur. If so, the experimental results seem in fair agreement with the stoichiometry shown in eq. 2. Based on eq. 2 the yield of I is 99% of theory. That of butyraldehyde is somewhat in excess (105–135%)

$$6ArSO_2H + (CH_3CH_2CH_2CH_2)_2S \longrightarrow 3ArSO_2SAr + 2CH_3CH_2CH_2CHO + S + 3H_2O \quad (2)$$

of that predicted, indicating that the actual reaction is probably somewhat more complex than eq. 2.

Despite the variation in and the uncertainty regarding the exact stoichiometry in the two cases, it is clear that the alkyl sulfide–sulfinic acid reaction involves in each case the cleavage of the sulfide molecule with the concomitant oxidation of at least one of the alkyl groups. That such a profound structural change can be brought about by the sulfinic acid under these conditions is certainly interesting and unexpected.

Kinetics of the Dialkyl Sulfide—*p*-Toluenesulfinic Acid Reaction.—Unlike the products, the kinetic behavior of the sulfide–sulfinic acid reactions is the same for both sulfides studied. It also is quite straightforward. As before[2,4] the progress of the reaction could be followed by titration of unreacted sulfinic acid with standard sodium nitrite solution.

Kinetic Order with Respect to Sulfinic Acid.—Figure 1 shows a typical run for each of the sulfides. Since the sulfide is present in large excess its concentration remains effectively constant during a run. The linearity of log ($ArSO_2H$) *vs.* time shows the reaction is first order in sulfinic acid.

Dependence of Rate on Sulfide Concentration.—A series of runs at varying initial sulfide concentration, but always with the sulfide in large excess, was made for each sulfide. In all cases but one, rate constants were obtained by taking the slope of the log ($ArSO_2H$) *vs.* time plot and correcting this experimental rate constant for the small contribution from the normal disproportionation reaction in the manner described in the preceding paper.[2] In the butyl sulfide run at 0.2 M H_2SO_4 the alternate procedure of ref. 2 was used.

The rate constants (k_1's) for the runs at varying sulfide concentrations are shown in Part A of Table I for benzyl sulfide and Part A of Table II for butyl sulfide. From eq. 3 it is evident that if the reactions are first order in sulfide division of the k_1 values by sulfide concentration should give a constant. This constant will be k_S, the actual rate constant for the sulfide–sulfinic acid reaction.

$$\text{Rate of sulfide–sulfinic acid reacn.} = k_1(ArSO_2H) = k_S(R_2S)(ArSO_2H) \quad (3)$$

Examination of Part A of Tables I and II shows that $k_1/(R_2S)$ is indeed constant for each sulfide, and this demonstrates the reaction is in each case first order in sulfide.

Dependence of Rate on Sulfuric Acid Concentration.—The dependence of rate on acid concentration was investigated (Part B of Tables I and II).

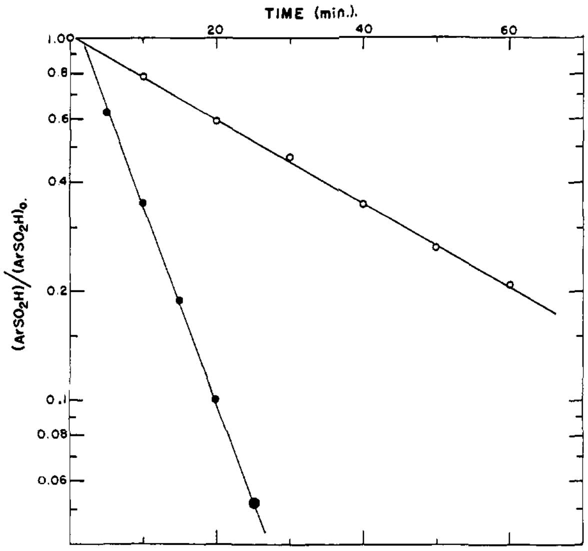

Fig. 1.—Rate of disappearance of sulfinic acid in presence of butyl and benzyl sulfides. Both runs in acetic acid–0.56 M H_2O containing 0.5 M H_2SO_4: ○, benzyl sulfide, 0.2 M, $(ArSO_2H)_0$, 0.05 M; ●, butyl sulfide, 0.2 M, $(ArSO_2H)_0$, 0.1 M.

For both sulfides the rate is strongly dependent on acid concentration. Figure 2 shows a plot of log k_1 *vs.* H_0[5] for each. Within the experimental error the slope (1.45, 1.48) is the same for both sulfides. Furthermore it is also the same as the slope of a similar plot for the *p*-tolyl disulfide–*p*-toluenesulfinic acid reaction.[2] The dependence of rate on acidity for the sulfide–sulfinic acid reaction is therefore the same as for the disulfide–sulfinic acid reaction.

TABLE I

KINETICS OF DECOMPOSITION OF *p*-TOLUENESULFINIC ACID IN THE PRESENCE OF BENZYL SULFIDE

All runs are at 70° in acetic acid–0.56 M water

(H_2SO_4), M	$(ArSO_2H)_0$, M	(R_2S), M	$k_1 \times 10^3$ sec.$^{-1}$	$10^3 \times [k_1/(R_2S)] = k_S \times 10^3$
A: Effect of benzyl sulfide concentration				
0.60	0.050	0.30	1.12	3.7
		.20	0.74	3.7
		.10	0.37	3.7
B: Effect of sulfuric acid concentration				
0.70	0.050	0.20	1.09	5.5
.60			0.74	3.7
.50			.40	2.0
.40			.26	1.3
.30			.130	0.65

Dependence of Rate on Water Concentration.—This was studied only with butyl sulfide (Part C of Table II), although the other similarities in kinetic behavior suggest the benzyl compound would have also behaved the same way. The rate is clearly strongly dependent on water concentration. Further, as Fig. 3 shows, the nature of this dependence is almost identical with that displayed by the disulfide–sulfinic acid reaction.[2] Thus these two reactions display not only the same dependence

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

(5) D. S. Noyce and L. R. Snyder, *J. Am. Chem. Soc.*, **80**, 4324 (1958).

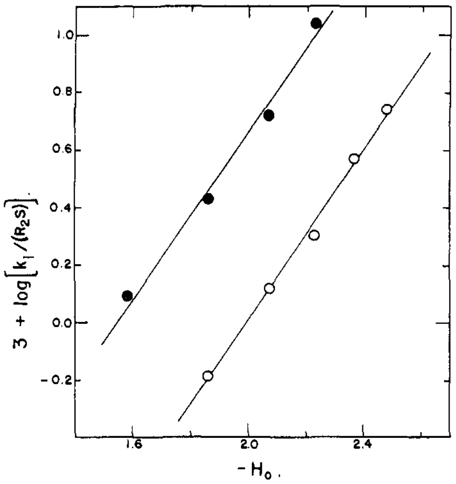


Fig. 2.—Dependence of rate on strong acid concentration: log $k_1/(R_2S)$ *vs.* $-H_0$ for runs at varying (H_2SO_4): ○, benzyl sulfide (slope, 1.48); ●, butyl sulfide (slope, 1.45).

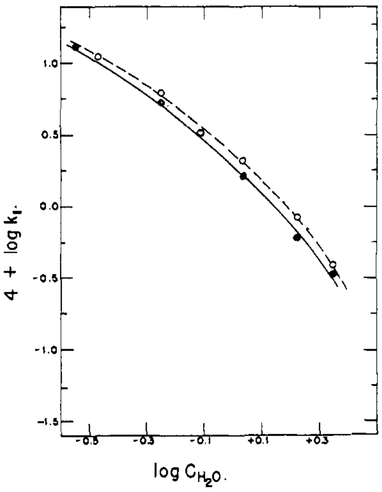


Fig. 3.—Dependence of rate on water concentration: ●, butyl sulfide runs at 0.3 *M* sulfuric acid (Part C of Table II); ○, *p*-tolyl disulfide runs at 0.5 *M* sulfuric acid (ref. 2).

on strong acid but also the same dependence on water concentration.

Discussion

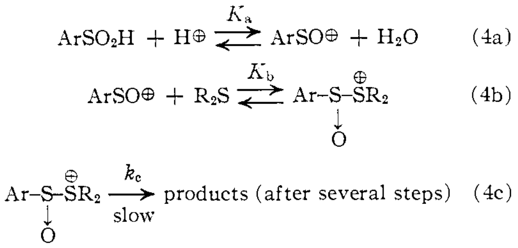
The identical kinetic behavior of the butyl and benzyl sulfide reactions strongly suggests that both proceed by the same mechanistic path through the rate-determining step. Since both are first order in sulfide and sulfinic acid, the rate-determining transition state must be derived from a molecule each of sulfide and sulfinic acid. In addition, the sulfide reactions show the same dependence on water and strong acid concentration as the tolyl disulfide–sulfinic acid reaction.[2] In the latter case the response to changing acidity or water concentration was seen as being strongly indicative of a mechanism involving the reversible formation of the ion $ArS(O)^+S(Ar)-SAr$ and then its rate-determining decomposition. By the same token the results in the present system seem readily consistent only with a mechanism involving the formation of $Ar\overset{+}{S}(O)SR_2$ followed by its rate-determining decomposition (eq. 4). For such a mechanism the rate expression is given by eq. 5a and the rate constant, k_S, by eq. 5b. The ratio of activities and activity coefficients in 5b is of exactly the same sort as that given in eq. 18 of ref. 2 as determining the dependence of the disulfide–sulfinic acid reaction on strong acid and water. The arguments given there to indicate that such a ratio could lead to the experimentally observed variation of rate with water and acid apply equally to the present case. For their exposition the reader is referred to the preceding paper.[2]

Table II

Kinetics of Decomposition of *p*-Toluenesulfinic Acid in the Presence of Butyl Sulfide

All runs are at 70° in acetic acid containing the amount of water indicated

(H_2O), *M*	(H_2SO_4), *M*	($ArSO_2H$)$_0$, *M*	(R_2S), *M*	$k_1 \times 10^3$, sec.$^{-1}$	$10^3 \times [k_1/(R_2S)] = k_S \times 10^3$
A: Effect of butyl sulfide concentration					
0.56	0.30	0.10	0.30	0.78	2.6
			.20	.53	2.7
			.15	.39	2.6
B: Effect of sulfuric acid concentration					
0.56	0.50	0.10	0.20	2.2	11
	.40			1.06	5.3
	.30			0.53	2.7
	.20			0.25	1.25
C: Effect of water concentration					
0.28	0.30	0.10	0.20	1.3	6.5
0.56				0.53	2.7
1.10				.158	0.79
1.68				.059	.30
2.22				.033	.165



$$ArSO_2H + H^{\oplus} \underset{}{\overset{K_a}{\rightleftarrows}} ArSO^{\oplus} + H_2O \qquad (4a)$$

$$ArSO^{\oplus} + R_2S \overset{K_b}{\rightleftarrows} Ar\text{-}\underset{\downarrow \atop O}{S}\text{-}\overset{\oplus}{S}R_2 \qquad (4b)$$

$$Ar\text{-}\underset{\downarrow \atop O}{S}\text{-}\overset{\oplus}{S}R_2 \xrightarrow[\text{slow}]{k_c} \text{products (after several steps)} \qquad (4c)$$

$$\left[\frac{-d(ArSO_2H)}{dt}\right] = k_cK_aK_b(ArSO_2H)(R_2S)\left[\frac{a_{H^+}f_{R_2S}f_{ArSO_2H}}{a_{H_2O}f_{*c}}\right] \qquad (5a)$$

$$k = \text{const.} \times \left[\frac{a_{H^+}f_{R_2S}f_{ArSO_2H}}{a_{H_2O}f_{*c}}\right] \qquad (5b)$$

At present the exact nature of the rate-determining step (eq. 4c) and of the subsequent reactions leading to the final products is not definitely established. One very attractive possibility for the rate-determining step, however, is eq. 6. This SNi type displacement has analogy in a reaction recently suggested by Kenney, Walsh and Davenport[6] as a step in the acid-catalyzed rearrangement of sulfoxides. Ion IV could then decompose to the aldehyde and the mixed disulfide by reaction 7, a process which has an obvious parallel in the fol-

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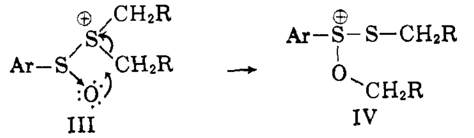
(6) W. J. Kenney, J. A. Walsh and D. A. Davenport, *J. Am. Chem. Soc.*, **83**, 4019 (1961).



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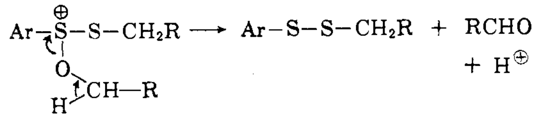
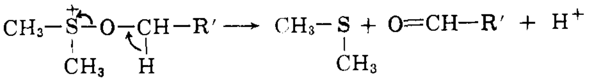


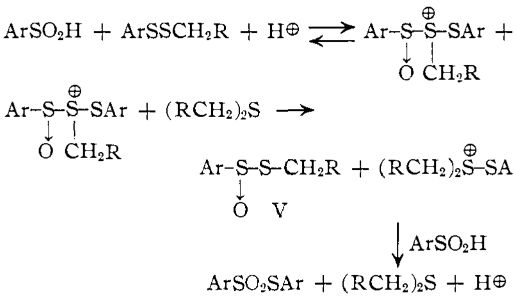
(7)

lowing step in the dimethyl sulfoxide–alkyl halide reaction.[7]



$$CH_3-\underset{CH_3}{\overset{+}{S}}-O-\underset{H}{CH}-R' \longrightarrow CH_3-\underset{CH_3}{S} + O{=}CH-R' + H^+$$

Consideration of the rates of reaction of diaryl and dialkyl disulfides with *p*-toluenesulfinic acid,[2] and of the marked catalysis of the disulfide–sulfinic acid reaction by sulfides,[2] indicates the mixed disulfide produced in eq. 7 should react with the sulfinic acid many times more rapidly than does the sulfide, with the result that $ArSSCH_2R$ will in effect be consumed as rapidly as it is formed, and its steady state concentration will be extremely small.[8] The reaction of $ArSSCH_2R$ with sulfinic acid should presumably follow the course shown in eq. 8,[2] with formation of a molecule each of $ArSO_2SAr$ and the thiolsulfinate V. Since Vinkler and Klivenyi[9] have shown that the disproportionation of thiolsulfinates is apparently acid catalyzed, V would be expected to decompose rapidly in these rather acidic solutions. Normally this decomposition would be expected to occur essentially as in eq. 9. Combination of eq. 4a,b and 6–9 leads to the over-all stoichiometry shown in eq. 10. This is in agreement with what is observed for the benzyl sulfide–*p*-toluenesulfinic acid reaction.



$$ArSO_2H + ArSSCH_2R + H^{\oplus} \rightleftarrows Ar-\underset{\downarrow \atop O}{S}-\overset{\oplus}{\underset{CH_2R}{S}}-SAr + H_2O$$

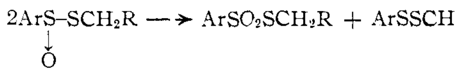
$$Ar-\underset{\downarrow \atop O}{S}-\overset{\oplus}{\underset{CH_2R}{S}}-SAr + (RCH_2)_2S \longrightarrow$$

$$Ar-\underset{\downarrow \atop O}{S}-S-CH_2R + (RCH_2)_2\overset{\oplus}{S}-SAr \quad (8)$$

V

$$\Big\downarrow ArSO_2H$$

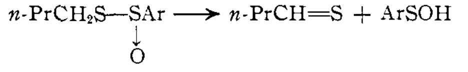
$$ArSO_2SAr + (RCH_2)_2S + H^{\oplus}$$



$$2Ar\underset{\downarrow \atop O}{S}-SCH_2R \longrightarrow ArSO_2SCH_2R + ArSSCH_2R \quad (9)$$

$$5ArSO_2H + (RCH_2)_2S \longrightarrow$$
$$2ArSO_2SAr + ArSO_2SCH_2R + RCHO + 3H_2O \quad (10)$$

The most plausible explanation we can presently offer for the different product behavior exhibited by the butyl sulfide reaction is that the decomposition of the butyl thiolsulfinate (V, R = *n*-Pr-), while still rapid, does not follow eq. 9 but instead takes an anomalous course. So little is known about the mechanism of the decomposition of thiolsulfinates in acid solution that it seems inappropriate to speculate either about why such a difference in behavior might occur or what alternate course for the decomposition seems most probable. Let us therefore only note that if the butyl thiolsulfinate were to decompose, not according to eq. 9, but by a process formally equivalent to eq. 11, and if this were followed by the sequence of steps shown in 12a-c, one would arrive at eq. 2 as the over-all stoichiometry for the butyl sulfide reaction.



$$n\text{-}PrCH_2S-\underset{\downarrow \atop O}{S}Ar \longrightarrow n\text{-}PrCH{=}S + ArSOH \quad (11)$$

$$n\text{-}PrCH{=}S + H_2O \longrightarrow H_2S + n\text{-}PrCH{=}O \quad (12a)$$

$$H_2S + ArSO_2H \longrightarrow ArSOH + S + H_2O \quad (12b)$$

$$ArSOH + ArSO_2H \longrightarrow ArSO_2SAr + H_2O \quad (12c)$$

This uncertainty regarding what steps lead to the final products of the butyl sulfide reaction should not obscure the significant aspects of this study—first, that in each case the sulfide–sulfinic acid reaction leads to cleavage of the sulfide under what are fairly mild reaction conditions, and second, that the kinetics show the reaction involves ion III as the key intermediate. The first suggests the reaction could have some practical value as a degradative tool. The second, combined with the disulfide–sulfinic acid reaction, augurs well for the existence of reactions between other weak nucleophiles and sulfinic acids. We hope in the future to investigate both this latter possibility and the scope and limitations of the sulfide–sulfinic acid reaction. As we have already seen,[2] diphenyl sulfide does not react with the sulfinic acid. Presumably this is both because of its lower nucleophilicity (smaller value of K_b in eq. 4) and the fact the ion $ArS(O)\overset{+}{S}(C_6H_5)_2$ cannot readily decompose in the manner shown in eq. 6 and 7.

Acknowledgment.—This work was materially aided by a grant from the Alfred P. Sloan Foundation.

Experimental

Butyl sulfide (Columbia Organic Chemicals) was fractionally distilled, b.p. 100° (45 mm.). **Benzyl sulfide** (Columbia Organic Chemicals) was recrystallized from ethanol; the recrystallized material was chromatographed on alumina using pentane as eluent. This was followed by another recrystallization from ethanol; m.p. 50°. ***p*-Toluenesulfinic acid** was prepared and purified as before.[4] **Benzyl *p*-toluenethiolsulfonate** was prepared from sodium *p*-toluenethiolsulfonate and benzyl chloride in aqueous acetone by a slight modification of the procedure of Loudon and Livingston.[10] Recrystallized from ethanol it melted at 57° (lit.[10] 60°).

Solvents and Standard Solutions.—The preparation of these has been previously described.[2,4]

Procedure for Kinetic Runs.—The procedure was essentially that previously used for the normal disproportionation.

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[7] N. Kornblum, W. J. Jones and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959); I. M. Hunsberger and J. M. Tien, *Chemistry & Industry*, 88 (1959).

[8] Actual conservative estimates (see Ph.D. thesis of K. W. Bowers, Univ. of S. C. for details of calculations) suggest, for example, that in the benzyl sulfide runs the steady state concentration of $ArSSCH_2R$ should be *less* than 4×10^{-4} *M* and would account for *no more than* 4% of the sulfide actually reacting. Further, at worst, the disulfide will essentially reach its steady state concentration when no more than 13% of the sulfinic acid has reacted. Due to the time required for thermal equilibrium and the speed of most of the reactions little kinetic data of value could be (or was) obtained during this part of the reaction. Therefore the buildup of $ArSSCH_2R$ to its steady state concentration would not in any event have been kinetically evident to us.

[9] E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Hung.*, **22**, 345 (1960); *Magyar Kemiai Folyoirat*, **62**, 48 (1956).

[10] J. D. Loudon and A. Livingston, *J. Chem. Soc.*, 896 (1935).

Butyl sulfide was added as a standard solution of the sulfide in acetic acid. Benzyl sulfide was weighed out and added directly. Trial experiments showed that the sulfides did not interfere with the titration of sulfinic acid by the nitrite method.

Products of the Benzyl Sulfide–Sulfinic Acid Reaction.—Benzyl sulfide (20.0 mmoles) and *p*-toluenesulfinic acid (5.00 mmoles) were dissolved and made up to 100 ml. in a solution of acetic acid–0.56 M H_2O containing 0.5 M sulfuric acid. The solution was deaerated and then heated under nitrogen at 70° for 1 hour, using the same procedure employed for the kinetic runs. At the end of this time titration of an aliquot showed 80% of the sulfinic acid (4.00 mmoles) had reacted. The reaction was stopped at this point by pouring the solution into 1 liter of distilled water. The resultant cloudy mixture was exhaustively extracted with ether. The ether extracts were washed several times with sodium bicarbonate solution. The ether solution was then dried and most of the ether removed by distillation through a 30-cm. helices-packed column. The remainder of the ether was then removed by distillation through a 35-cm. micro-Widmer column. The residue was taken up in a small amount of methylene chloride and placed on a 2 × 80 cm. column of acid-washed alumina. The column was eluted with the following solvents: 400 ml. of pentane; pentane–ether, 200 ml. 19:1; 200 ml. of 9:1; 200 ml. of 7:1; 100 ml. of 4:1; and 100 ml. of 3:1; 500 ml. of ether. Fractions of 20 ml. were collected. The solvents were removed by distillation through the micro-Widmer column to minimize product loss. The products obtained were the following: Unreacted benzyl sulfide (3.92 g., 18.5 mmoles) was identified by infrared and m.p. comparison with a known sample. *p*-Tolyl *p*-toluenethiolsulfonate (0.386 g., 1.40 mmoles) was identified by similar comparison with a known sample.[4] Benzyl *p*-toluenethiolsulfonate (0.153 g., 0.55 mmole) as obtained from the reaction was found to be identical with the prepared sample both by infrared and mixed m.p. For quantitative estimation the fractions containing benzaldehyde were treated with 2,4-dinitrophenylhydrazine in the usual way. The amount of 2,4-dinitrophenylhydrazone formed, m.p. 236°, indicated 0.39 mmole of benzaldehyde had been present. The infrared spectra of the fractions before treatment with 2,4-dinitrophenylhydrazine were equivalent to that of a known sample of benzaldehyde.

Products of the Butyl Sulfide–Sulfinic Acid Reaction.—The sulfide (20.0 mmoles) and *p*-toluenesulfinic acid (10.0 mmoles) were dissolved in the same acetic acid–water–sulfuric acid mixture used for the benzyl sulfide reaction, and the solution was deaerated. It was then heated at 70° for 1 hour. In one run the exit tube from the reaction vessel was connected to a trap containing a 2,4-dinitrophenylhydrazine solution, and nitrogen was passed through the solution throughout the decomposition. A precipitate, m.p. 121°, shown to be identical with a known sample of *n*-butyraldehyde 2,4-dinitrophenylhydrazone, formed in the trap. Tests on known mixtures of butyraldehyde in acetic acid showed, however, that the aldehyde could not be determined quantitatively by this procedure, and for this reason the following v.p.c. method was employed for that purpose. In this a sample of the reaction mixture was injected into a Perkin-Elmer model 154 vapor phase chromatograph equipped with Golay column and flame ionization detector, the column temperature being 96°. This procedure gave satisfactory separation of butyraldehyde from all other components of the mixture. However, quantitative estimation of the aldehyde was not very precise. From the average of a number of samples the aldehyde concentration in the final reaction mixture appears to be 0.04 ± 0.005 M.

The other products were investigated in a subsequent run. In this the solution at the end of the decomposition was poured into distilled water, extracted with ether, etc., in the same way as in the benzyl sulfide study. The residue after removal of the ether by distillation was chromatographed using much the same procedure as with the other sulfide. On removal of the solvent from the chromatographic fractions only two compounds were found. These were *p*-tolyl *p*-toluenethiolsulfonate (1.37 g., 4.96 mmoles) and unreacted butyl sulfide (2.1 g., 14.5 mmoles).

In another run the nitrogen exit gases were passed through a cadmium nitrate solution. No precipitate formed. In another they were passed through sodium hydroxide solution. This was subsequently heated with hydrogen peroxide to oxidize any sulfide to sulfate. On addition of barium chloride no precipitate formed. These results show clearly that hydrogen sulfide is not evolved from the reaction mixture.

In all of the butyl sulfide runs an insoluble scum formed on the surface of the solution during the course of a run. Although small in amount and not identified, this could have been elemental sulfur.

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Conformational Analysis. XXVI. Some Stereochemical Studies of the Cyclooctane Ring[1,2]

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The *cis* and *trans* isomers of 5-*t*-butylcyclooctanol have been prepared and many of their reactions have been studied by quantitative methods. The results have been interpreted in conformational terms.

Introduction

While the conformational properties of the cyclohexane ring have been studied in considerable detail,[3] comparatively little is known about the corresponding properties of the cyclooctane ring.[4] This work was undertaken in an effort to learn more about the conformational effects involved in the 8-membered ring, and it was specifically intended to show, among other things, whether or not 1,5-transannular hydride migration did occur in this ring system. It was shown quite some time ago that either 1,3- or 1,5-hydride transfer did occur,[5] the 1,5-transfer appearing more likely by analogy with what had been observed in the cyclodecane system.[6] Recently Cope and his students reported that in fact both 1,3- and 1,5-hydride transfer occurred, and they determined the ratio in a particular case.[7]

Winstein and Holness,[8] Eliel and Ro,[9] and subsequently many others have shown that by using

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[1] Paper XXV, N. L. Allinger and L. Freiberg, *J. Am. Chem. Soc.*, **83**, 5028 (1961).

[2] This research was supported by a grant from the National Science Foundation.

[3] For recent reviews see: (a) H. H. Lau, *Angew. Chem.*, **73**, 423 (1961); (b) E. L. Eliel, *J. Chem. Ed.*, **37**, 126 (1960).

[4] N. L. Allinger and S. Hu, *J. Am. Chem. Soc.*, **83**, 1664 (1961).

[5] A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

[6] H. J. Urech and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957).

[7] A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharmon *J. Am. Chem. Soc.*, **82**, 6366 (1960).

[8] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

[9] E. L. Eliel and R. S. Ro, *Chemistry & Industry*, 251 (1956).