Amine hydrochloride precipitated immediately upon addition of the reactants except when tri-*n*-butylamine was used in ether. In the latter case no precipitate was noticed until almost all of the reactants had been combined when a second liquid phase sometimes appeared. After being stirred for 1 hr. with the ice-bath removed, the volatile products and solvents more volatile than α-methylallyl chloride were flash distilled into a Dry Ice trap and then fractionated. The reaction quantities were as in A with 11.0 g. (0.139 mole) of pyridine, 26.5 g. (0.139 mole) of N,N-diisopropyl-*o*-toluidine, 25.7 g. (0.139 mole) of tri-*n*-butylamine or 14.9 g. (0.139 mole) of 2,6-lutidine. Exceptions are noted in Table II.

C. Table III Experiments were done as described in A and B above and were on the same scale. Exceptions are noted in Table III.

Distillation Analysis of α- and γ-Methylallyl Chlorides.—The reaction mixtures after treatment as described above were carefully fractionated through a concentric tube vacuum jacketed column, the fractionating section of which consisted of a 30 cm. long, 6.5-mm. Truebore rod within an 8-mm. Trubore tube. The column was equipped with a solenoid operated, total condensation, partial takeoff head and was determined to have 35-plate efficiency at total reflux. Holdup was about 1.5 ml. About 10 fractions were collected in the course of an analysis in such a way that only a binary mixture was present in any specific fraction with the exception of runs which yielded less than 10% of one of the chlorides. Toward the end of each distillation, a small amount of chlorobenzene was added as a pusher to ensure isolation of the entire yield of chlorides. The boiling range, weight and refractive index of each fraction was recorded and the composition was obtained from calibration curves of refractive index plotted against weight per cent. of the components of the various binary mixtures encountered. The analysis was shown to be accurate within 4% by distillation of known synthetic mixtures of α- and γ-methylallyl chlorides in various solvents containing hydrogen chloride and sulfur dioxide as contaminants. Small amounts of these contaminants were frequently present in the first few fractions along with traces of thionyl chloride and were destroyed by treatment of these fractions with several drops of water followed by addition of a small amount of anhydrous potassium carbonate. The blanks showed that little, if any, isomerization of α- and γ-methylallyl chlorides occurred during the distillation analyses within the accuracy stated. That α- and γ-methylallyl chlorides are relatively stable has also been demonstrated by Catchpole and Hughes.[24] Optically active α-methylallyl chloride racemized 12% when isolated from liquid sulfur dioxide. The values reported in Table I are uncorrected for this racemization. In one experiment, the absence of *cis*-γ-methylallyl chloride in the product was established by infrared spectroscopy.

The possibility that reaction between thionyl chloride and the butenols in the absence of a tertiary amine was not completed in the times described but was still proceeding during distillation analysis must be considered; however, unpublished results[25] pertaining to attempted isolation of γ-methylallyl chlorosulfinate indicate that the reactions were essentially completed before fractionation was begun.

Determination of pK_a of the tertiary amines used in this work employed the method of Thompson[26] in which the *p*H value of a solution of a tertiary amine in the presence of an excess of standard hydrochloric acid was measured and used directly for calculation of pK_a. For preparation of 75% alcohol–water solutions, an accurately weighed sample of tertiary amine was dissolved in 25 ml. of standard aqueous hydrochloric acid and made up to 100 ml. with 96.5% ethanol which had been distilled from potassium carbonate. The results are summarized in Table IV.

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[24] A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 4 (1948).

[25] F. F. Caserio, Jr., Ph.D. Thesis, U.C.L.A., 1954.

[26] G. Thompson, *J. Chem. Soc.*, 1113 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

The Thermal Decomposition of Thiolsulfonates. II

BY JOHN L. KICE[1] AND FRED M. PARHAM

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Study of the thermal decomposition of a series of diphenylmethanethiolsulfonates, $(C_6H_5)_2CHSO_2SR'$, reveals the following pronounced dependence of the relative rate of decomposition on R′: C_6H_5–, 25; $C_6H_5CH_2$–, 1; CH_3–, 0.3; *n*-C_4H_9, 0.2. The principal products of the decompositions $[(C_6H_5)_2CHSR' + SO_2]$ and the variation in rate with solvent establish the mechanistic kinship of these and the previously studied[2] decompositions of $(C_6H_5)_2CHSO_2SCH_2C_6H_5$ and $C_6H_5CH_2SO_2SCH_2C_6H_5$. When taken together with these previous results the present data require a mechanism involving heterolytic cleavage of *both* the $C-SO_2$ and SO_2-S bonds in the transition state of the rate-determining step. One acceptable mechanism is an initial equilibrium followed by a rate-determining decomposition of the first-formed ion-pair, $RSO_2SR' \rightleftarrows [RSO_2^{\oplus} \ldots {}^{\ominus}SR'] \rightarrow [R^{\oplus} \ldots {}^{\ominus}SR'] + SO_2$. The possible general significance of these data in view of the previously noted[2] similarities between the thiolsulfonate decomposition and such SNi reactions as the decomposition of chlorocarbonates and chlorosulfites is discussed. The extent of deuteration of the diphenylmethane and tetraphenylethane formed in the decomposition of $(C_6H_5)_2CHSO_2SCD_2C_6H_5$ has been determined; the results permit some further conclusions to be drawn concerning the origin of these products in the decomposition of the diphenylmethanethiolsulfonates.

Recent work[2] has shown that the thiolsulfonates $RSO_2SCH_2C_6H_5$, where R = $(C_6H_5)_2CH$– or $C_6H_5CH_2$–, undergo thermal decomposition in inert solvents in the temperature range 130–200° with essentially quantitative evolution of sulfur dioxide and the formation of varying amounts of $RSCH_2C_6H_5$, RH, stilbene, R–R and dibenzyl disulfide. Investigation of the kinetics of the decomposition has shown that for both thiolsulfonates the reaction is a simple first-order process whose rate is notably dependent on solvent, being faster in relatively polar solvents (nitrobenzene, benzonitrile) than in non-polar solvents (bromobenzene, methylnaphthalene, etc.). Under comparable conditions the benzhydryl compound decomposes about 150 times more rapidly than the α-toluenethiolsulfonate. These facts, together with the failure of added diphenylmethanethiolsulfonate to accelerate the polymerization of styrene in bromobenzene, led to the proposal of a mechanism for the thiolsulfonate decomposition (eq. 1) involving a rate-determining heterolytic fission of the $C-SO_2$ bond followed by recombination of the fragments with loss of sulfur dioxide in either of two ways. The minor products of the decomposition, tetraphenylethane and the disulfide, were believed to result from either subsequent

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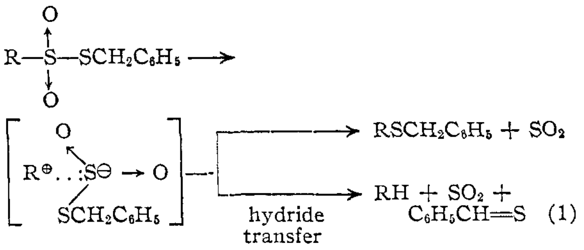
(1) To whom inquiries should be addressed: Department of Chemistry, Oregon State College, Corvallis, Ore.

(2) J. L. Kice, F. M. Parham and R. M. Simons, THIS JOURNAL, **82**, 834 (1960).



$$C_6H_5CH{=}S \longrightarrow C_6H_5CH{=}CHC_6H_5 + S$$

reactions of some of the products first formed or from a minor concomitant radical decomposition of the thiolsulfonate.

In continuing these studies we have now examined the behavior of a series of diphenylmethanethiolsulfonates, $(C_6H_5)_2CHSO_2SR'$ (I). We find that their rate of decomposition is strongly dependent on the nature of the group R′ in a manner analogous to the effect of R′ on the acidity of the corresponding mercaptan, R′SH. This result indicates that both the C–SO₂ and SO₂–S bonds are broken (or weakened) in the transition state of the rate-determining step and accordingly requires some modification of the mechanism originally proposed. Moreover, in view of the previously noted[2] similarities between the thiolsulfonate decomposition and a number of SNi reactions,[3–5] this most recent finding may be of considerable interest in connection with the mechanistic details of SNi processes in general.

We have also prepared α,α-dideuteriobenzyl diphenylmethanethiolsulfonate, $(C_6H_5)_2CHSO_2SCD_2C_6H_5$, and studied its decomposition, with particular emphasis on the extent of deuteration of the diphenylmethane and tetraphenylethane formed as products. The results permit a better delineation of the possible routes for the formation of these compounds, and in particular, they rule out our previously preferred mechanism[2] for the formation of the latter hydrocarbon.

Results

The decomposition of the phenyl (Ib, R′ = C_6H_5–), methyl (Ic, R′ = CH_3–), *n*-butyl (Id, R′ = *n*-C_4H_9–) and α,α-dideuteriobenzyl (Ie, R′ = $C_6H_5CD_2$–) esters of diphenylmethanethiolsulfonic acid has been studied, and the results have been combined with those previously obtained[2] with the benzyl ester Ia. The preparation and decomposition of the deuterated ester is discussed later in a separate section. Of the other thiolsulfonates, all except Ic have been previously prepared.[6] The methyl ester Ic was prepared from methyl mercaptan by a similar procedure. Several attempts to prepare the carboethoxymethyl ester (R′ = $EtOOCCH_2$–) by this same procedure from ethyl thioglycolate failed.

Kinetics of the Thiolsulfonate Decompositions.—Since product studies (*vide infra*) show the decompositions of the thiolsulfonates take a course similar to that previously observed for Ia, it is not surprising that their kinetics can be followed conveniently by the method employed earlier for the benzyl ester[2]—measurement of the rate of evolution of sulfur dioxide.

The rates of decomposition of the thiolsulfonates have been determined in bromo- and nitrobenzene, good first-order kinetics being observed in all cases. The results of the various runs are shown in Table I. As was found with Ia, the rates of decomposition of Ib, Ic and Id are all considerably greater in nitrobenzene than in bromobenzene, in accord with expectations based on a heterolytic mechanism for the decomposition.

TABLE I

RATE OF DECOMPOSITION OF $(C_6H_5)_2CHSO_2SR'$

R′	Solvent	Temp., °C.	$(RSO_2\text{-}SR')_0$, *M*	$k_1 \times 10^5$, sec.⁻¹	ΔH*, kcal.	ΔS*, e.u.
C_6H_5-	C_6H_5Br	134.1	0.030	11.7		
			.097	11.8		
		125.1	.032	5.0		
			.099	5.3		
		115.0	.029	2.1	27.3	−9.8
			.102	2.1		
	$C_6H_5NO_2$	115.0	.043	20		
CH_3–	C_6H_5Br	142.1	.031	0.37		
	$C_6H_5NO_2$	142.1	.030	3.00		
			.089	3.25		
n-C_4H_9–	C_6H_5Br	142.1	.031	0.3		
	$C_6H_5NO_2$	142.1	.030	2.16		
			.071	2.02		

With the phenyl ester the temperature dependence of the rate constant was determined in bromobenzene, permitting the calculation of Δ*H** and Δ*S** for Ib in this solvent.

In Table II are shown the relative rates of decomposition of the diphenylmethanethiolsulfonates at 142° in nitrobenzene (either as directly determined or extrapolated from data at other temperatures). Included also is a relative rate for benzyl α-toluenethiolsulfonate estimated from data at higher temperatures,[2] as well as Δ*H** for Ia, Ib and the α-toluenethiolsulfonate.

TABLE II

EFFECT OF STRUCTURE ON RATE OF DECOMPOSITION OF RSO_2SR'

R–	R′–	Relative rate of decomp. at 142° in nitrobenzene	ΔH* (kcal.) in C_6H_5Br
$(C_6H_5)_2CH$–	*n*-C_4H_9–	0.21	
	CH_3–	0.31	
	$C_6H_5CH_2$–[a]	1.00	30.5
	C_6H_5–	25[b]	27.3
$C_6H_5CH_2$–	$C_6H_5CH_2$–[a]	0.006[c]	37.0[d]

[a] Ref. 2. [b] Determined from data at 115° assuming $\Delta H^*_{C_6H_5NO_2} = \Delta H^*_{C_6H_5Br}$, which (see ref. 2) is true for Ia. [c] Value is ratio of rate constants for the α-toluenethiolsulfonate and Ia in chloronaphthalene at 142°. [d] In chloronaphthalene; however, other studies[2] indicate Δ*H** not noticeably solvent dependent.

It is clear that changes in both R and R′ have a significant effect on the rate of thermal decomposition of RSO_2SR', and also that these rate effects

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[3] K. B. Wiberg and T. M. Shryne, THIS JOURNAL, **77**, 2774 (1955).

[4] (a) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak and W. G. Young, *ibid.*, **80**, 5965 (1958); (b) K. L. Oliver and W. G. Young, *ibid.*, **81**, 5810 (1959).

[5] E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 308 (1952); **75**, 3182 (1953); **76**, 794 (1954).

[6] H. J. Backer, J. S. Boerma and H. Kloosterziel, *Rec. trav. chim.*, **72**, 612 (1953).

seem to result primarily from changes in ΔH^*. The mechanistic significance of these findings will be considered in the Discussion.

Products of Decomposition of Ib and Ic.—To ensure that the decompositions being studied kinetically took a course similar to that for Ia we have determined the products formed when Ib and Ic are decomposed in dilute bromo- or nitrobenzene solution (0.1 *M*). The results are shown in Table III. As with Ia the yields of sulfur dioxide are essentially quantitative, and the major organic product in each case is the appropriate benzhydryl sulfide, this being formed, as before, in greater yield in nitrobenzene.

TABLE III

DECOMPOSITION PRODUCTS OF $(C_6H_5)_2CHSO_2SR'$

Reaction product	Yields are in mole % thiolsulfonate $R' = C_6H_5$		$R' = CH_3$	
	C_6H_5-Br– 125° under N_2 30 hr.	C_6H_5-NO_2– 120° under N_2 8 hr.	C_6H_5Br– reflux under N_2 53 hr.	C_6H_5-NO_2– 142° under N_2 40 hr.
Sulfur dioxide	98	99	92	104[d]
$(C_6H_5)_2CHSR'$	70	85	49	63
Diphenylmethane	7	[a]	21	7
R'SSR'	11	2.5	0.3[c]	[b]
$(C_6H_5)_2CHCH(C_6H_5)_2$	6	1	7	<1
Thiobenzophenone	0	0	0	0
"Thioformaldehyde"	..	..	[e]	[b]

[a] Qualitatively identified, not determined quantitatively. [b] Not determined. [c] Some may be lost because of its volatility; see Experimental. [d] Initial products slowly decompose on prolonged heating in $C_6H_5NO_2$. [e] Tentatively identified.

With the phenyl ester the amount of disulfide formed in bromobenzene is larger than in the case of Ia and the amount of diphenylmethane considerably less. Since we have now definitely shown (*vide infra*) that the majority of the diphenylmethane formed in the decomposition of Ia results from a disproportionation between the benzhydryl and benzylthiyl groups, the reason for the lower yield of the hydrocarbon with Ib is readily apparent. Also deserving of comment is the absence of thiobenzophenone as a minor reaction product in the decompositions of Ib and Ic. This product was believed[2] to be formed in the decomposition of Ia by reaction 2. In the present cases the analogous reaction should occur at a much lower rate due to the lack of resonance

$$(C_6H_5)_2\dot{C}{-}SCH_2C_6H_5 \longrightarrow (C_6H_5)_2C{=}S + C_6H_5CH_2\cdot \quad (2)$$

stabilization of the resulting phenyl or methyl radicals. In line with this is the isolation in the decomposition of Ib in bromobenzene of a small amount of unidentified higher molecular weight material whose infrared spectrum suggests it might contain $(C_6H_5)_2\underset{|}{C}SC_6H_5$ groups.

We might also note that experiment showed benzhydryl phenyl sulfide was thermally stable in bromobenzene solution under our reaction conditions.

To date we have not examined the products of the decomposition of Id. However, the results with Ib and Ic in both solvents are so consistent with expectations based on our previous study of Ia[2] that we feel quite sure Id behaves in a closely related fashion.

Preparation and Decomposition of the α,α-Dideuteriobenzyl Ester.—To synthesize Ie, α,α-dideuteriobenzyl alcohol was prepared by $LiAlD_4$ reduction of methyl benzoate; this carbinol was then converted to α,α-d_2-benzyl mercaptan,[7] and the mercaptan reacted with diphenyldiazomethane and sulfur dioxide in the usual fashion[6] to give the deuterated thiolsulfonate. Analysis[8] showed Ie contained 2.01 atoms of D per molecule.

One kinetic run with Ie in bromobenzene at 142° gave an experimental first-order rate constant of 7.3×10^{-6} sec.$^{-1}$. This is about 10% lower than that measured earlier[2] for the undeuterated ester. We believe this difference is probably outside experimental error and is therefore indicative of a small isotope effect ($k_H/k_D \cong 1.1$). There are a number of possible explanations for this effect, two of the most plausible being given in the footnote below.[9] However, in view of the limited data available it seems inappropriate to discuss this matter in any greater detail.

In another experiment the approximate yields of the various decomposition products of Ie in refluxing bromobenzene were determined. Comparison with the results for Ia[2] showed a slight increase in the yield of benzhydryl benzyl sulfide, a slight decrease in the yield of stilbene, and an essentially unchanged yield of diphenylmethane; although, for the reasons outlined below,[11] we think the actual yield of this hydrocarbon is probably also somewhat lower with Ie than with the undeuterated compound. The magnitudes of the changes in the yields of these three products, although in the expected direction, clearly indicate that the formation of stilbene and diphenylmethane is subject to only a small isotope effect at best. Arguments indicating such an observation can

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(7) R. L. Frank and P. V. Smith, THIS JOURNAL, **68**, 2103 (1946).

(8) Deuterium analyses are by Mr. Josef Nemeth, University of Illinois.

(9) If the mercaptans follow the pattern observed with the carboxylic acids and ammonium ions[10] $C_6H_5CD_2SH$ should be a slightly weaker acid (~10%) than $C_6H_5CH_2SH$. In view of the pronounced dependence of the rate of decomposition of RSO_2SR' on the acidity of R'SH, it would then be reasonable to expect the deuterated thiolsulfonate to decompose slightly slower than the undeuterated compound. The second possibility is that the mechanism of the decomposition is as shown in eq. i, with k_{ii} and $k_{iii} < k_{-i}$. This gives $k_{exp} = k_i(k_{ii} + k_{iii})/k_{-i}$, with the result that any isotope effect involving k_{iii} (and

$$RSO_2SCH_2C_6H_5 \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}}$$

$$[\text{ion-pair}] \begin{cases} \xrightarrow{k_{ii}} RSCH_2C_6H_5 + SO_2 \\ \xrightarrow[k_{iii}]{} RH + SO_2 + C_6H_5CHS \end{cases} \quad (i)$$

certainly a small one seems likely) will lead to a lower experimental first-order rate constant than is observed with the undeuterated compound.

(10) E. A. Halevi and M. Nussim, *Bull. Res. Council Israel*, **5A**, 263 (1956); *Tetrahedron*, **1**, 174 (1957); *Abstr. 16th Int. Cong. Pure Appl. Chem.*, **II**, 27 (1957).

(11) Due to its volatility losses of diphenylmethane can occur if the residues of the chromatographic fractions containing this compound are subject to too prolonged vacuum treatment at room temperature in an effort to remove the last traces of solvent. That this may have happened in the early product studies reported in ref. 2 is suggested by the fact that a later product run on Ia in bromobenzene gave a 27% yield rather than 22% of the hydrocarbon.

be consistent with the postulated mechanism for the decomposition are given in the Discussion.

Of greatest interest to us, however, was the extent of deuteration of the diphenylmethane and tetraphenylethane formed in the decomposition of Ie. Analysis of the diphenylmethane was effected by infrared comparison with a standard sample of α-deuteriodiphenylmethane prepared by $LiAlD_4$ reduction of benzophenone and hydrogenolysis of the acetate of the resulting deuteriobenzhydrol. The diphenylmethane from Ie was found to contain 0.82 atom of D per molecule. Although this demonstrates that the majority of the diphenylmethane is formed by a reaction involving transfer of a hydrogen from the benzylthiyl to the benzhydryl group, in agreement with the mechanism previously proposed[2] (eq. 1), it also shows that a significant portion ($\sim$20%) of the diphenylmethane arises by some other route not involving the benzylthiyl hydrogens. One attractive possibility is the sequence 3–5, evidence for the occurrence of reactions 4 and 5 having been obtained in the previous paper.[2] This finding that

$$R'S\cdot + (C_6H_5)_2CHSR' \longrightarrow R'SH + (C_6H_5)_2\dot{C}SR' \quad (3)$$

$$R'SH + (C_6H_5)_2CHSO_2SR' \longrightarrow R'SSR' + (C_6H_5)_2CHSO_2H \quad (4)$$

$$(C_6H_5)_2CHSO_2H \longrightarrow (C_6H_5)_2CH_2 + SO_2 \quad (5)$$

not all the diphenylmethane from Ia arises by hydrogen transfer from the benzyl group ties in nicely with our observation that a considerably reduced but nonetheless significant amount of this hydrocarbon is produced in the decomposition of the phenyl ester, where, of course, a similar hydrogen transfer cannot occur.

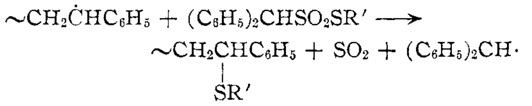
Based on analogy to certain arguments and evidence presented by Moureau,[12] we previously suggested[2] that the principal path for the formation of tetraphenylethane in the decomposition of Ia was through reaction of diphenylmethane with some of the thiobenzaldehyde before the latter decomposed to stilbene (eq. 6). This reaction was then thought to be followed principally by eq. 7 and 8. If this postulate were correct the tetraphenylethane isolated from the decomposition of the deuterated benzyl ester should be partially deuterated, containing at the least 0.41 atom of D per molecule. Actual analysis showed it to contain only 0.03 atom of D per molecule. This result demonstrates conclusively that our original formulation was wrong and that no significant portion of the tetraphenylethane arises from further reactions of initially formed diphenylmethane. Presently acceptable routes for the formation of tetraphenylethane will be considered in detail in the next section.

$$(C_6H_5)_2CH_2 + C_6H_5CH{=}S \longrightarrow (C_6H_5)_2CH\cdot + C_6H_5CH_2S\cdot \quad (6)$$

$$C_6H_5CH_2S\cdot + (C_6H_5)_2CHSO_2SCH_2C_6H_5 \longrightarrow SO_2 + (C_6H_5CH_2S{-})_2 + (C_6H_5)_2CH\cdot \quad (7)$$

$$2(C_6H_5)_2CH\cdot \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \quad (8)$$

Effect of Ib on the Polymerization of Styrene.—Unlike Ia,[2] addition of Ib (0.0075 *M*) to a solution of styrene (2 *M*) in bromobenzene at 115° produced a 1.5-fold increase in the rate of polymerization, the experiments being carried out in the manner previously described.[2] Actually the rate of radical decomposition of Ib may be somewhat larger than seems at first indicated by this result. This is because the presence of Ia was earlier shown[2] to cause some retardation, presumably by reaction 9, which replaces the styryl


(9)

$$\sim CH_2\dot{C}HC_6H_5 + (C_6H_5)_2CHSO_2SR' \longrightarrow \sim CH_2\underset{\substack{| \\ SR'}}{C}HC_6H_5 + SO_2 + (C_6H_5)_2CH\cdot \quad (9)$$

radical with the less reactive benzhydryl radical; and retardation by eq. 9 can obscure to a greater or less extent initiation due to homolytic decomposition of the thiolsulfonate. A similar problem was faced by Ferrington and Tobolsky[13] in studying the effect of tetramethylthiuram disulfide on the polymerizations of methyl methacrylate and styrene. Fortunately in the present case it seems possible to set an upper limit on the rate of reaction 9, since the rate of evolution of SO_2 in the presence of styrene is not appreciably greater ($\leq$10%) than in its absence. Combining this with an estimate of the behavior of a benzhydryl radical in such a system, which can be made from some data of Cohen and Wang,[14] one can arrive at an upper limit for the rate of radical decomposition of Ib.[15] Such calculations suggest that homolytic decomposition could account for as much as 5% of the decomposition of Ib in bromobenzene. Similarly, despite the fact that the rate of polymerization of styrene actually decreases with increasing concentration of Ia,[2] it is possible for there to be as much as 6% radical decomposition in the decomposition of Ia in bromobenzene. Our previous analysis[2] did not adequately take into account the extent to which retardation by eq. 9 might mask initiation occurring through homolytic decomposition of the thiolsulfonate. (However, it must be emphasized that the above figures represent upper limits and that the actual rate of homolytic decomposition may well be considerably smaller in both cases.)

Consequently, although our previous conclusion[2] that the decomposition of the thiolsulfonates occurs even in non-polar solvents primarily by a heterolytic mechanism remains unchanged, it is now possible that much of the tetraphenylethane and disulfide formed as minor by-products could result from homolytic decomposition of some of the thiolsulfonate (eq. 10), followed by reactions 7 and 8.

$$(C_6H_5)_2CHSO_2SR' \longrightarrow (C_6H_5)_2CH\cdot + SO_2 + R'S\cdot \quad (10)$$

The R'S· radicals formed in 10 could also react in part as in eq. 3.

A possible non-radical route to disulfide is the reaction of thiolsulfonate with an $R'S^-$ ion from the heterolytic decomposition (eq. 11). The diphenylmethanesulfinate anion formed in eq. 11

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[12] R. C. Moureau, *Bull. soc. chim. France*, [5] **22**, 918, 922, 1044, 1049, 1164 (1955).

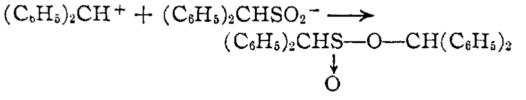
[13] T. E. Ferrington and A. V. Tobolsky, THIS JOURNAL, **77**, 4510 (1955); **80**, 3216 (1958).

[14] S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

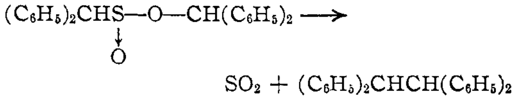
[15] The actual derivation and calculations will not be given here, since although not difficult, they are long and involved. They are given in detail in the Ph.D. thesis of F. M. Parham, University of South Carolina, 1960.

$$R'S^- + (C_6H_5)_2CHSO_2SR' \rightarrow R'SSR' + (C_6H_5)_2CHSO_2^- \quad (11)$$

could then combine with a benzhydryl carbonium ion. We originally rejected this route because we felt this latter reaction would give benzhydryl sulfone, a compound presumably stable and therefore isolable under our reaction conditions. However, the recent report[16] that triethyl phosphite reacts with alkyl alkanethiolsulfonates (RSO_2SR') to give chiefly $(EtO)_2P(O)SR'$ and the ethyl alkanesulfinate $RS(O)OEt$, rather than the corresponding sulfone, suggests that reaction of the carbonium ion and diphenylmethanesulfinate might well lead to benzhydryl diphenylmethanesulfinate (eq. 12). Decomposition of this compound according to eq. 13 could then lead to tetraphenylethane. An indication that diphenylmethanesulfinates may decompose thermally to give tetraphenylethane is provided by combination of the Polish authors' findings[16] with the unpublished observation in this Laboratory[17] that triethyl phosphite and Ia react readily at room temperature in bromobenzene, and that refluxing the resulting solution for 24 hr. leads to the formation in >90% yield of $(EtO)_2P(O)SCH_2C_6H_5$ and tetraphenylethane, the remaining products not being identified.



$$(C_6H_5)_2CH^+ + (C_6H_5)_2CHSO_2^- \longrightarrow (C_6H_5)_2CH\underset{\overset{\downarrow}{O}}{S}{-}O{-}CH(C_6H_5)_2 \quad (12)$$



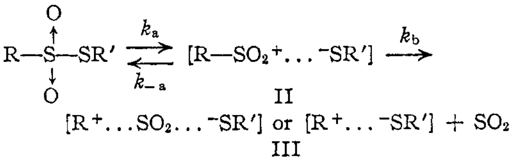
$$(C_6H_5)_2CH\underset{\overset{\downarrow}{O}}{S}{-}O{-}CH(C_6H_5)_2 \longrightarrow SO_2 + (C_6H_5)_2CHCH(C_6H_5)_2 \quad (13)$$

Discussion

All evidence to date in this and the previous investigation[2] indicates the thermal decomposition of thiolsulfonates is primarily a heterolytic reaction. The data in Table II demonstrate clearly that the rate of decomposition of RSO_2SR' is markedly dependent on the nature of *both* R– and R'–, and that the dependence on R' parallels its effect on the acidity of the corresponding mercaptans, R'SH.[18] Probably one may legitimately question the absolute accuracy of these mercaptan pK_a's in view of the frequent lack of agreement between the results of different workers.[19] Nevertheless, it is abundantly clear that the relative ease of decomposition of the thiolsulfonates is qualitatively that which would be expected from consideration of the possible resonance and inductive contributions of the various R' groups toward stabilization of a partial negative charge on sulfur. Furthermore, the order benzyl > methyl > *n*-butyl is exactly the reverse of what would be predicted from inductive considerations for the alternate heterolysis, $RSO_2SR' \rightarrow R^- \ldots SO_2 \ldots {}^+SR'$, leading to the formation of a sulfenium ion and a positive charge on the sulfide sulfur. These results consequently suggest that the sulfide sulfur atom has considerable anionic character in the transition state of the thiolsulfonate decomposition and also require that the earlier mechanism[2] (eq. 1) be modified in such a way that *both* the R–SO_2 and the SO_2–S bonds are broken (or weakened) in the transition state of the rate-determining step.[20]

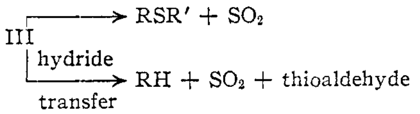
Comparison of the 170-fold difference in the rates of decomposition of Ia and benzyl α-toluenethiolsulfonate with the much larger difference (10^4–10^5 fold) shown by the solvolysis rates of benzhydryl and benzyl chlorides[22] suggests that the aralkyl fragment in the thiolsulfonate decomposition has notably less carbonium ion character in the transition state of the rate-determining step than is the case in the solvolysis reaction.

One mechanism which is in accord with this and the other facts is shown in eq. 14. This involves an initial reversible ionization of the thiolsulfonate to ion pair II, followed by a rate-determining decomposition of II to ion pair III. The principal products of the reaction could then be formed by collapse of III in either of two ways (eq. 15).



$$R{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}SR' \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} \underset{\text{II}}{[R{-}SO_2^+ \ldots {}^-SR']} \xrightarrow{k_b} [R^+ \ldots SO_2 \ldots {}^-SR'] \text{ or } \underset{\text{III}}{[R^+ \ldots {}^-SR']} + SO_2 \quad (14)$$

This mechanism predicts the observed first-order dependence on thiolsulfonate and leads to an experimental first-order rate constant, $k_1 = k_ak_b/(k_{-a} + k_b)$. For k_b rate-determining (*i.e.*, $k_b < k_{-a}$) this reduces to $k_1 = k_ak_b/k_{-a}$. In this situation the rate of decomposition of RSO_2SR' will be determined by the difference in the free energies of the thiolsulfonate and the transition state for the reaction $\text{II} \xrightarrow{k_b} \text{III}$. To compare the effect of changing R from benzyl to benzhydryl in the present case with the solvolysis of RX we must therefore consider the transition state for II → III and compare it with the transition state for the ionization step in halide solvolysis ($R{-}X \rightarrow [R^+ \ldots {}^-X]$). In the latter reaction, for the reasons discussed by Hammond,[23] the transition state



$$\text{III} \longrightarrow RSR' + SO_2 \quad (15a)$$

$$\text{III} \xrightarrow[\text{transfer}]{\text{hydride}} RH + SO_2 + \text{thioaldehyde} \quad (15b)$$

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[16] J. Michalski, T. Modro and J. Wieczorkowski, *J. Chem. Soc.*, 1665 (1960).

[17] R. M. Simons, unpublished work.

[18] J. Maurin and R. A. Paris, *Compt. rend.*, **232**, 2428 (1951). These authors give the following pKa's in ethanol: C_6H_5SH, 8.3; $C_6H_5CH_2SH$, 11.8; *n*-C_4H_9SH, 12.4. Although the acidity of CH_3SH was not measured, consideration of the inductive effects of the three alkyl groups suggests it should be intermediate between benzyl and *n*-butyl.

[19] J. P. Danehy and C. J. Noel, THIS JOURNAL, **82**, 2511 (1960)

[20] The possibility that the observed effects result only from the inductive effect of the various R' groups on the stability of $R'SSO_2^-$ would appear to be ruled out by consideration of the relative rates of decomposition of the phenyl, benzyl and *n*-butyl esters. If only the inductive effect of R' was important the rate of decomposition of the phenyl ($\sigma^* = +0.60$)[21] ester would be faster than the benzyl ($\sigma^* = +0.22$)[21] by about the same factor as the benzyl is faster than the *n*-butyl ($\sigma^* = -0.13$).[21] Since the phenyl ester actually decomposes considerably faster than this, additional stabilization of the negative charge by phenyl (through resonance with the aromatic ring) seems indicated.

[21] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556–675.

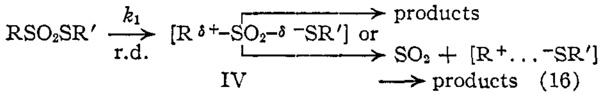
[22] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956); S. Winstein, A. H. Fainberg and E. Grunwald, THIS JOURNAL, **79**, 4146 (1957).

[23] G. S. Hammond, *ibid.*, **77**, 334 (1955).

must resemble the products ($R^+ \ldots {}^-X$) much more closely than it does the reactants, and the R group must have very considerable carbonium ion character. On the other hand, the $R\text{–}SO_2^+ \rightarrow R^+ + SO_2$ reaction involves the formation of R^+ from another unstable intermediate, and it therefore seems reasonable to believe the transition state of this reaction will occur at an earlier point along the reaction coördinate representing cleavage of the $R\text{–}SO_2$ bond, with the result that the group R will have less carbonium ion character in the transition state than is found in the solvolysis of the halides. As a consequence the difference in the rates at which the benzyl and benzhydryl compounds undergo the reaction will be less than in the halide solvolysis.

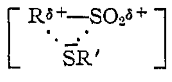
Moreover, an additional factor can operate to diminish the difference further. From the picture above it is evident that the sulfonyl sulfur atom will bear a partial positive charge in the transition state of reaction II → III. Consideration of the purely inductive effect of R on the stability of this positive charge on sulfur leads to the conclusion that inductively $(C_6H_5)_2CH^{\delta+}\text{–}SO_2^{\delta+}$ will be destabilized relative to $C_6H_5CH_2^{\delta+}\text{–}SO_2^{\delta+}$ because benzhydryl ($\sigma^* = +0.41$)[21] is a more strongly electron-withdrawing group than benzyl ($\sigma^* = +0.22$).[21] This will bring the energies of the two transition states closer together than would otherwise be the case and, of course, will lead to a smaller difference in the rates of decomposition of the benzyl and benzhydryl compounds.

Alternatively one could propose a mechanism for the decomposition involving a rate-determining ionization to an intermediate such as IV (eq. 16).



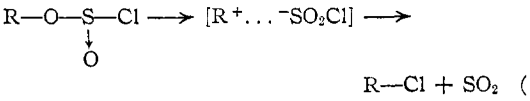
$$RSO_2SR' \xrightarrow[\text{r.d.}]{k_1} \underset{\text{IV}}{[R^{\delta+}\text{–}SO_2\text{–}^{\delta-}\,{}^-SR']} \text{ or } \begin{cases} \longrightarrow \text{products} \\ \longrightarrow SO_2 + [R^+ \ldots {}^-SR'] \longrightarrow \text{products} \end{cases} \quad (16)$$

In IV, of course, R cannot be a full-fledged carbonium ion else one should get a dependence of rate on R comparable to the solvolysis of halides. Although in a sense IV represents a new type of intermediate for reactions of this sort, this is not adequate cause for preferring eq. 14, especially in view of the statement[24]: "Because of the character of intimate ion pairs, there is no sharp distinction between such an ion pair and a covalently bound intermediate in a so-called cyclic rearrangement. *These are not qualitatively distinct but form extremes in a graded series.*" We should also point out that ionization to intermediates of this sort might proceed not to IV but to one (V) in which part of the positive charge was centered on the sulfonyl group.

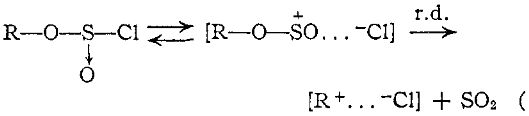


V

The evidence presently at hand does not seem sufficient to permit a meaningful decision between these various alternatives. This, however, should not obscure the significance which the obvious involvement of both the $R\text{–}SO_2$ and $SO_2\text{–}S$ bonds may have for the mechanism of SNi reactions in general. We have noted[2] that the thiolsulfonate decomposition has a number of features in common with such SNi reactions as the decomposition of chlorocarbonates[3,4b] and chlorosulfites.[4a,5] Thus both show a similar dependence of rate on solvent and take a principal course which can be represented as $R\text{–}Y\text{–}X \rightarrow R\text{–}X + Y$. The rates of decomposition of a series of chlorosulfites, $RO\text{-}SOCl$,[4a] or chlorocarbonates, $ROCOCl$,[3,4b] parallel the stability of the carbonium ions, R^+, showing that ionization of the R–O bond is involved in the rate-determining step. Two mechanisms have been suggested for these reactions, one,[3,4] (eq. 17a) involving a rate-determining fission of only the R–O bond, and the other[4a,5] (17b), akin to eq. 14, an initial equilibrium followed by rate-determining cleavage of the R–O bond.



$$R\text{—}O\text{—}\underset{\substack{\downarrow \\ O}}{S}\text{—}Cl \longrightarrow [R^+ \ldots {}^-SO_2Cl] \longrightarrow R\text{—}Cl + SO_2 \quad (17a)$$



$$R\text{—}O\text{—}\underset{\substack{\downarrow \\ O}}{S}\text{—}Cl \rightleftharpoons [R\text{—}O\text{—}\overset{+}{S}O \ldots {}^-Cl] \xrightarrow{\text{r.d.}} [R^+ \ldots {}^-Cl] + SO_2 \quad (17b)$$

However, all of these mechanistic studies[3,4,5] have naturally involved the same group, chlorine, in the place occupied by R'S– in the thiolsulfonate decomposition, with the result that there has actually been no way of determining if the S–Cl (or C–Cl) bond was also broken (or weakened) in the rate-determining step. The present study has clearly shown that both the $R\text{–}SO_2$ and $SO_2\text{–}S$ bonds are involved in the thiolsulfonate decomposition, and the possible relationship between this reaction and the chlorosulfite and chlorocarbonate decompositions suggests that in these other reactions breaking of more than just the R–O bond may be involved.

In this connection, however, it ought to be pointed out that the chlorocarbonate and chlorosulfite decompositions show a much more pronounced dependence of rate on R, which is quantitatively very similar to that exhibited by the limiting solvolysis of the corresponding halides and tosylates.[3,4,22] For that reason any mechanism involving multiple bond cleavage, if applicable, would presumably not be as shown in eq. 17a, but rather as in eq. 18.

$$ROSOCl \rightleftharpoons [R^+ \ldots {}^-SO_2Cl] \xrightarrow{\text{r.d.}} [R^+ \ldots {}^-Cl] + SO_2 \quad (18)$$

In any event, the present results definitely suggest the desirability of investigations aimed at determining whether similar mechanisms are involved in the majority of SNi reactions.

The consistency of the proposed mechanism with the small isotope effect observed for the formation of diphenylmethane and stilbene from Ie remains to be considered. We believe there are at least three reasons for expecting a quite small isotope effect for a reaction such as 15b under our reaction conditions: (1) Hydride transfers to carbonium ions have generally shown rather small isotope effects ($k_H/k_D = 1.8 - 2.5$ at 25°)[25,26]; (2) the temperature of our experiments was ~156°,

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(24) S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958).

(25) P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956).

(26) R. Stewart, *Can. J. Chem.*, **35**, 766 (1957).

and for a given reaction the magnitude of k_H/k_D decreases with increasing temperature[27]; (3) Lewis and Boozer[5] reported no measurable isotope effect for the formation of pentene in the decomposition in isoöctane of 2-pentyl chlorosulfite fully deuterated in the 1- and 3-positions. Thus in a closely related reaction, also in a non-polar solvent, loss of a proton from the ion pair intermediate has been shown to be subject to an extremely small isotope effect even though in 80% ethanol loss of a proton from the *t*-amyl carbonium ion is subject to an isotope effect of 1.8.[28] Consequently, we feel it quite possible that the hydride transfer in 15b may also exhibit a smaller isotope effect than might otherwise be expected.

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Experimental

Phenyl diphenylmethanethiolsulfonate (Ib) and butyl diphenylmethanethiolsulfonate (Id) were prepared by previously described procedures.[6] Recrystallized from 95% ethanol, Ib melted 120–121° dec. The butyl ester was recrystallized from ethanol–hexane, m.p. 111–112°.

Methyl diphenylmethanethiolsulfonate (Ic) was synthesized by the same general procedure.[6] Passage of sulfur dioxide through a solution of 0.09 mole of diphenyldiazomethane and 0.09 mole of methyl mercaptan in 100 ml. of anhydrous ether contained in a flask equipped with a Dry Ice condenser and cooled in an ice–salt-bath gave discharge of the diphenyldiazomethane color and precipitation of an orange solid. Repeated recrystallization of the solid from 95% ethanol, with the aid of decolorizing charcoal, gave 3.1 g. (12%) of Ic, m.p. 133–134°. *Anal.* Calcd. for $C_{14}H_{14}O_2S_2$: C, 60.43; H, 5.07; S, 23.00. Found: C, 60.39; H, 5.11; S, 23.18.

Benzhydryl Phenyl Sulfide.—Five grams (0.025 mole) of benzhydryl chloride[29] and 5.0 g. of thiophenol (0.045 mole) were heated on the steam-bath for 3 hr. The crystalline mass which formed on cooling was recrystallized from ethanol, giving 3.7 g. (54%) of the sulfide, m.p. 81–82° (lit.[30] 82°).

Benzhydryl Methyl Sulfide.—Benzhydryl mercaptan was prepared by the method described by Fukuda[31] for substituted benzhydryl mercaptans. Three grams of the mercaptan (b.p. 121–122° (1 mm.)) was added to a solution of 0.35 g. of sodium in 10 ml. ethanol. To this was then added 2.2 g. of methyl iodide in 5 ml. ethanol. The solution was refluxed for 10 hr., after which most of the ethanol was removed under reduced pressure, and the residue was poured into water. The sulfide was extracted with ether, the ether removed, and the residue crystallized from hexane at −20°, giving 2.0 g. (62%) of sulfide, m.p. 27–32° (lit.[32] 33°).

Preparation of Deuterated Compounds. **α,α-Dideuteriobenzyl Diphenylmethanethiolsulfonate (Ie).**—To 3 g. of 98% $LiAlD_4$ (0.07 mole) in 125 ml. of ether was slowly added 19.4 g. (0.14 mole) of methyl benzoate in 50 ml. ether. After stirring for 0.5 hr. the mixture was hydrolyzed, and the ether layer was separated and dried over sodium sulfate. Removal of the ether and fractional distillation of the residue gave 10.0 g. (65%) of the α-d_2-alcohol, b.p. 76–77° (4 mm.). The infrared spectrum of the deuterated carbinol had three peaks at 4.55, 4.70 and 4.80μ that were absent in undeuterated benzyl alcohol. The aliphatic C–H absorption of the undeuterated alcohol at 3.4–3.5μ was absent.

α,α-Dideuteriobenzyl mercaptan was then prepared from this α-d_2-benzyl alcohol using Frank and Smith's procedure.[7] The yield was 8.8 g. (70%), b.p. 63–64° (7 mm.). The mercaptan was used immediately and was not further characterized.

The mercaptan was converted to the thiolsulfonate by the method described for Ia.[2] Recrystallization of the 13 g. of crude product so obtained from ethanol gave 6.9 g. (27%) of Ie, m.p. 144–145° dec. Analysis[8] showed 11.13 atom % excess D, corresponding to 2.01 atoms of D per molecule of Ie.

α-Deuteriodiphenylmethane.—To 1.02 g. of $LiAlD_4$ in 100 ml. of ether was slowly added 17.4 g. of benzophenone in 100 ml. of ether. The reaction mixture was worked up in the usual manner, recrystallization of the ether residue from hexane giving 12.6 g. (71%) of α-*d*-benzhydrol, m.p. 64–66°. Refluxing 9.06 g. of the carbinol, 8.5 g. of sodium acetate trihydrate and 60 ml. of acetic anhydride for 7 hr. gave the acetate. On working up the reaction mixture there was obtained, after recrystallization from hexane, 9.44 g. (83%) of α-*d*-benzhydryl acetate, m.p. 42–43°.

The acetate was dissolved in 50 ml. of dry ethyl acetate, and the solution was shaken with 0.5 g. of 10% Pd/C under 2 atm. pressure of hydrogen. After hydrogen absorption ceased, the solution was filtered, the ethyl acetate removed, and the residue chromatographed on alumina. The hexane eluates were evaporated, and the residue was distilled under reduced pressure, b.p. 98–100° (3 mm.). The α-*d*-diphenylmethane, 6.0 g. (70%), solidified on standing at room temperature. Its infrared spectrum showed an absorption band at 4.60μ while the aliphatic C–H absorption at 3.4μ was less intense than in the undeuterated hydrocarbon. Analysis[8] gave 7.40 and 7.49 atom % excess D, equivalent to an average value of 0.895 atom of D/per molecule.

Decomposition of Ib in Bromobenzene.—The decomposition of Ib (1.713 g., 5.02 mmoles) in bromobenzene (50 ml.) was carried out in the manner described for Ia.[2] The solution was heated at 125° for 30 hr. Titration of the iodine remaining in trap C indicated a sulfur dioxide yield of 4.91 mmoles.

Removal of the solvent under reduced pressure left a semi-solid residue, which when treated with 10 ml. of hexane left 0.291 g. of insoluble solid; this was filtered off. Cooling the filtrate at −20° overnight gave 0.328 g. of additional solid. Infrared comparison with a known sample showed this second solid fraction was benzhydryl phenyl sulfide. This was confirmed by m.p. and mixed m.p. determinations on a once-recrystallized portion of the material. In an earlier experiment fractional crystallization of the first solid fraction had shown it to be a mixture of tetraphenylethane and benzhydryl phenyl sulfide. Infrared examination of synthetic mixtures of these two compounds showed the amount of sulfide could be estimated fairly accurately from the intensity of the band at 6.30μ. In this manner the first solid fraction was analyzed as 70% sulfide–30% tetraphenylethane by wt.

The products remaining in the hexane filtrate after removal of the two solid fractions were separated by chromatography using the same procedure employed for Ia.[2] The identity and yield of the various products was established in the following manner.

Diphenylmethane.—The first fractions contained diphenylmethane contaminated with a little bromobenzene, the amount of the hydrocarbon being determined as before.[2] A subsequent fraction consisted of diphenyl disulfide plus a little diphenylmethane. The amount of disulfide could be estimated accurately from the intensity of its infrared absorption at 6.30μ. The remainder of this fraction was assumed to be diphenylmethane.

Diphenyl Disulfide.—Subsequent fractions consisted of almost pure diphenyl disulfide, m.p. 59–63°, a much better separation of sulfide and disulfide being obtained than was the case with Ia.[2] The total amount of disulfide, including that in the fraction contaminated with diphenylmethane, was 0.120 g.

Benzhydryl phenyl sulfide was found in an essentially pure state in those fractions eluted subsequent to the disulfide. Infrared spectra confirmed the identity of the material. Combination with that already isolated in the solid fractions gave a total yield of 0.959 g.

Tetraphenylethane.—The last major fraction from the chromatogram was treated with a little cold hexane and the insoluble material (0.021 g.) filtered off, m.p. 206–207°, infrared spectrum same as tetraphenylethane. Combined with the tetraphenylethane in the first solid fraction this gives a total of 0.105 g. The hexane-soluble material had

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[27] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[28] V. J. Shiner, Jr., THIS JOURNAL, **75**, 2925 (1953).

[29] H. Gilman and J. Kirby, *ibid.*, **48**, 1733 (1926).

[30] R. Knoll, *J. prakt. Chem.*, **221**, 40 (1926)

[31] H. Fukuda, *J. Pharm. Soc. Japan*, **72**, 1472 (1952); *C. A.*, **47**, 8706 (1953)

[32] L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1596 (1955).

an infrared spectrum similar in some respects to benzhydryl phenyl sulfide but notably different in others. Its identity has not been established although it is thought it may contain $(C_6H_5)_2\underset{|}{C}-SC_6H_5$ groups.

Decomposition of Ib in Nitrobenzene.—Using the same general procedure, 1.716 g. of Ib in 50 ml. of nitrobenzene was heated at 115° for 8 hr. The solvent was fractionally distilled under reduced pressure, and the residue was treated with ~10 ml. of hexane and cooled in ice. The solid (0.953 g.) which separated was filtered off, m.p. 77–79°. An infrared spectrum and mixed m.p. established definitely that it was benzhydryl phenyl sulfide. An additional 0.236 g. of sulfide was isolated from chromatography of the hexane filtrate giving a total of 1.189 g.; other products isolated from the chromatography and quantitatively determined: diphenyl disulfide, 0.027 g.; tetraphenylethane, 0.016 g.

Decomposition of Ic in Bromobenzene.—A solution of 1.349 g. of Ic in 50 ml. of bromobenzene was refluxed for 53 hr., the decomposition being carried out in the manner described for Ia.[2] Sulfur dioxide (4.43 mmoles) was determined as before.[2] The small amount of liquid which collected in trap B during the decomposition was examined by vapor phase chromatography. Comparison with the retention times of a synthetic mixture of **dimethyl disulfide** and bromobenzene established the presence of the former. The actual amount of disulfide was very small, 1.4 mg., but it is quite possible that because of its volatility the majority was entrained past trap B by the nitrogen stream. This seems especially likely since subsequent v.p.c. examination of the bromobenzene distillate failed to reveal the presence of any additional disulfide in the reaction mixture.

Removal of the solvent was followed by treatment of the residue with 5–10 ml. of hexane. The solution was cooled, and the solid which separated was filtered off. Infrared examination of this solid showed the presence of a small amount (0.011 g.) of undecomposed Ic as evidenced by characteristic absorption bands at 7.47, 7.62 and 8.86μ. Recrystallization, m.p. and mixed m.p. showed the remainder of the material (0.104 g.) to be **tetraphenylethane**.

Chromatography of the hexane filtrate was carried out in the fashion already described.[2] **Diphenylmethane** (0.174 g.) was identified and estimated as before.[2] Also isolated in an essentially pure state was an additional 0.017 g. of **tetraphenylethane**. A series of consecutive fractions, weighing a total of 0.506 g., and all having an infrared spectrum essentially identical to that of a known sample of **benzhydryl methyl sulfide**, were obtained.

In the course of the decomposition some white solid sublimed into the lower part of the condenser of the decomposition flask. This was not readily soluble in any of the common solvents and could not be mechanically removed because of the construction of the apparatus. It is our belief that this material is a product derived from **thioformaldehyde** produced in the decomposition, although it was not definitely identified.

Decomposition of Ic in Nitrobenzene.—Using the same procedure as in bromobenzene, 1.387 g. of Ic in nitrobenzene (50 ml.) was heated at 142° for 40 hr. The initially colorless solution darkened noticeably during the last stages of the decomposition, apparently due to breakdown of some of the initial decomposition products of Ic. This presumably accounts for the apparent SO_2 yield (5.20 mmoles, 104% of theory).

Removal of the nitrobenzene and chromatography of the residue gave 0.36 mmole of diphenylmethane and 3.15 mmoles of benzhydryl methyl sulfide.

Decomposition of Ie in Bromobenzene.—The decomposition of the deuterated thiolsulfonate (1.79 g. in 50 ml. of bromobenzene) was carried out in the usual manner[2] using a reflux period of 28 hr. **Sulfur dioxide** (4.58 mmoles) and **thiobenzophenone** (0.13 mmole) were determined as before.[2]

The residue after removal of the solvent was chromatographed.[2] Through the use in the present case of slightly more alumina diphenylmethane was cleanly separated from stilbene. Infrared examination also showed the **diphenylmethane** (0.190 g.) to be free of bromobenzene. The intensity of its infrared absorption at 4.60μ was then determined neat in a 0.05-mm. cell and compared with those of known mixtures of α-*d*-diphenylmethane–diphenylmethane. (The optical densities of the latter had been shown to follow Beer's law.) The optical density was 0.91 times that of the pure "standard" sample of α-*d*-diphenylmethane. Given the deuterium content of the latter, this indicates 0.815 atom of D per molecule in the diphenylmethane from Ie.

Because deuteration eliminates the 10.4μ band **stilbene** could not be determined as before.[2] However, dideuteriostilbene possesses a very sharp C–D absorption at 4.45μ which is clearly distinct from those of the other products. A pure sample of the olefin was obtained by recrystallization of the appropriate fractions from a preliminary run, and its optical density at 4.45μ was compared with those of the chromatography fractions. The total yield of stilbene so indicated was 0.34 mmole (7%). Incidentally, the lack of any 4.45μ absorption in the diphenylmethane fractions confirms the absence of stilbene in those fractions.

Benzhydryl benzyl sulfide, m.p. 70–72° (0.806 g.), was isolated as with Ia.[2] Deuterium analysis[8] on a portion of this material recrystallized from ethanol showed 11.01 atom % excess D, or 1.98 atoms of D per molecule, indicating no loss of deuterium during the work-up procedure. The residues of the mother liquors from the original sulfide isolation were estimated to contain an additional 0.045 g. of sulfide.

Tetraphenylethane was isolated as previously described.[2] The material from several runs was further purified by recrystallization from ethanol and analyzed[8] for deuterium. Found: 0.15 atom % excess D or 0.03 atom of D per molecule.

Kinetic Studies of the Decompositions.—The procedure used has already been described in detail,[2] as has the purification of solvents for both kinetic and product studies.

Decomposition of Ib in Presence of Styrene.—The procedure was the same as in the earlier paper[2] except that the experiments were carried out at 115° and a 2 *M* solution of styrene in bromobenzene was employed.