The Thermal Decomposition of Benzenediazo Sulfones. II. Benzyl Benzenediazo Sulfone[1]

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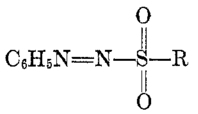
The thermal decomposition of benzyl benzenediazo sulfone (**1b**) has been examined in benzene, cumene, and diphenylmethane. In all three solvents the principal final products are sulfur dioxide, benzaldehyde phenylhydrazone, and N-benzyl benzaldehyde phenylhydrazone (**2**). The yield of **2** relative to the unsubstituted phenylhydrazone is largest in diphenylmethane and much smaller in benzene. Nmr experiments reveal that an intermediate is formed during the decomposition in benzene, and examination of the other spectral properties of this intermediate compound suggests that it is $PhCH_2N{=}NPh$. It subsequently isomerizes to benzaldehyde phenylhydrazone. Experiments using the Koelsch radical (**3**) as a radical scavenger suggest that in benzene the decomposition of **1b** involves a chain reaction. Two possible mechanisms for such a process, eq 1 and 2, are suggested, but no decision between them is possible at this time. In diphenylmethane the chain length appears to be considerably smaller, as suggested by the slower rate of disappearance of **1b** and the increased yields of **2**, which is thought to be a chain-termination product.

In the course of some other work the interesting compound benzyl benzenediazo sulfone (**1b**) was prepared. Some preliminary studies[2] revealed that its thermal decomposition in nonpolar solvents took a quite different course from that which had been observed by Overberger and Rosenthal[3] for the decomposition of the analogous phenyl compound **1a**. Since subsequent work[4] has shown that the decomposition of methyl benzenediazo sulfone (**1c**) behaves in a manner similar to that of **1a**, the decomposition of the benzyl compound **1b** obviously also follows a different pattern than the thermal decomposition of simple alkyl benzenediazo sulfones like **1c**. Indeed the study of the decomposition of **1b** which we report in the present paper suggests that the reaction is a rather complex process which appears to possess a number of most unusual features.



$$C_6H_5N{=}N{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}R$$

1a, R = C_6H_5
b, R = $C_6H_5CH_2$
c, R = CH_3

Unfortunately, even after fairly extensive study of the decomposition of **1b**, we still cannot say that we fully understand all the facets of the process. However, since some important parts of the overall picture seem to be fairly well established, and since we plan no further work on the decomposition of **1b** or other diazo sulfones in the forseeable future, it seems worthwhile to report our results at this time, in the hope that they may stimulate others to unravel some of the remaining complexities of this most intriguing system.

Results

Products of Decomposition of 1b in Nonpolar Solvents.—Samples of benzyl benzenediazo sulfone (**1b**) were decomposed in three different nonpolar solvents—benzene, cumene, and diphenylmethane. The decompositions in cumene and diphenylmethane were carried out at 80°, that in benzene at 55°. In every case the reaction was done under a nitrogen atmosphere and a slow stream of nitrogen was passed through the solution during the decomposition to remove sulfur dioxide as it was formed. The nitrogen stream was subsequently passed through a trap containing a known amount of standard iodine, and the amount of sulfur dioxide being produced was determined quantitatively in this way. After decomposition was complete the other products were separated and purified by various chromatographic procedures (see Experimental Section), and their identity was established by appropriate comparisons with known samples. The results of the various product studies on the decomposition of **1b** are shown in Table I. Besides the reaction products shown, each decomposition also produced some intractable, tarry material that we were unable to separate chromatographically into identifiable compounds. The amount of such tarry material was, however, significantly less than the amount formed in the decomposition of **1c** under the same conditions.[4]

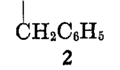
TABLE I

THERMAL DECOMPOSITION PRODUCTS OF BENZYL BENZENEDIAZO SULFONE IN NONPOLAR SOLVENTS[a]

Products, (mol/mol of **1b**)	Benzene, 55°	Cumene, 80°	Diphenylmethane, 80°
Sulfur dioxide	0.66	0.57	0.80
Benzaldehyde phenylhydrazone	0.55	0.46	0.34
N-Benzyl benzaldehyde phenylhydrazone	0.06	0.12	0.16
Biphenyl	0.02	...	...
Azobenzene	<0.01	...	...
Toluene	0.00	0.01	0.05
Benzene	(solvent)	0.11	0.15

[a] Initial concentration of **1b**, 0.08–0.10 *M*.

In all three solvents the principal products of the decomposition of **1b** are the same, sulfur dioxide and benzaldehyde phenylhydrazone ($C_6H_5{=}NNHC_6H_5$). Another product formed in every case is N-benzyl benzaldehyde phenylhydrazone (**2**), its yield being smallest in the solvent where the yield of benzaldehyde phenylhydrazone is largest and largest in the solvent where



$$\underset{\displaystyle CH_2C_6H_5}{C_6H_5N}{-}N{=}CHC_6H_5$$

2

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[1] This research supported by National Science Foundation Grant GP-1975.

[2] R. H. Engebrecht, Ph.D. Thesis, Oregon State University, 1964.

[3] C. A. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, **82**, 108, 117 (1960).

[4] J. L. Kice and R. S. Gabrielsen, *J. Org. Chem.*, **35**, 1004 (1970).

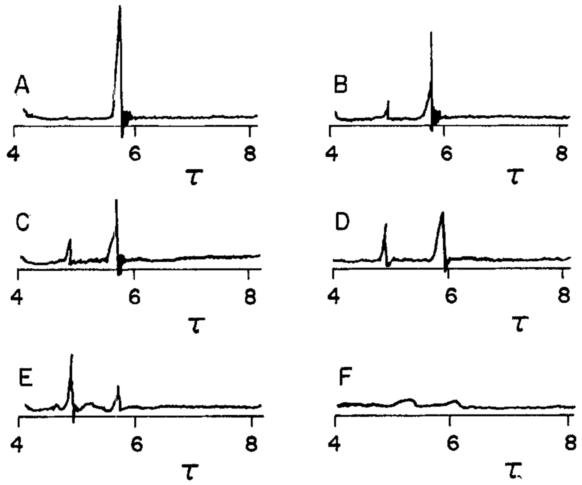

Figure 1.—Nmr spectra of solution during the course of the decomposition of **1b** (0.20 *M*) in benzene at 55°: curve A, initial solution; curve B, 2 hr; curve C, 3 hr; curve D, 4 hr; curve E, 5 hr; curve F, 8 hr.

the yield of the hydrazone is smallest. In cumene and diphenylmethane significant amounts of benzene (0.11–0.15 mol/mol **1b**) are formed. Whether this also happens in benzene as solvent one of course cannot tell. Some toluene is formed in the decomposition in diphenylmethane, much less in the one in cumene, and none that could be detected in the one in benzene. One of the most interesting facts is that no bicumyl or *sym*-tetraphenylethane were isolated from the decompositions in cumene and diphenylmethane, respectively. This is, of course, in striking contrast to the situation in the decomposition of the methyl diazo sulfone **1c**.[4]

Formation of an Intermediate During the Decomposition of 1b in Benzene.—The nmr spectrum of **1b** possesses a sharp singlet at τ 5.75 owing to the CH_2 protons of the benzyl group. During the decomposition of the diazo sulfone in benzene this peak decreases steadily in intensity and eventually disappears completely. As it decreases in intensity another sharp singlet begins to be seen at τ 4.92. This new peak increases in intensity up until the time when the original peak at τ 5.75 has almost vanished and then rapidly disappears itself. Figure 1 shows the appearance of the region from τ 4.0–6.0 with time for a typical decomposition of a 0.20 *M* solution of **1b** in benzene at 55°. Comparison of the integrated intensity of the signal at τ 4.92 at its maximum with that of a known amount of an internal standard (cyclohexane) suggests that at its peak the concentration of the intermediate responsible for the singlet at τ 4.92 is quite appreciable (0.40 mol/mol of **1b** originally present, if the signal at τ 4.92 is due to a CH_2 group).

In a second experiment another 0.20 *M* solution of **1b** in benzene was heated at 55° until nmr measurements showed that there was essentially no **1b** remaining (as indicated by the disappearance of the singlet at τ 5.75) and a maximum amount of the intermediate responsible for the singlet at τ 4.92. The solution was then frozen, and the benzene was pumped off under vacuum. Infrared, visible, and ultraviolet spectra were then taken on the residue. (That the intermediate was still present in the residue was shown by redissolving a portion of it and examining its nmr spectrum.) The infrared spectrum (in $CHCl_3$) showed no important absorption bands other than those present in benzaldehyde phenylhydrazone. In particular, there were no bands present that could be attributed to either a sulfonyl (>SO_2) or a sulfinyl (>SO) group. The ultraviolet spectrum showed an absorption maximum at 335 mμ, but this is not particularly informative, since samples removed from the decomposition after the intermediate has disappeared show a maximum at 337 mμ, and benzaldehyde phenylhydrazone also is reported[5] to have a maximum close to this wavelength. The most significant spectral finding regarding the intermediate came from the visible spectrum of the residue. This showed a weak maximum at 405 mμ which was *not* present in the spectrum of samples removed from the decomposition after the intermediate had disappeared. O'Connor[6] has shown that compounds of the type $RN{=}NC_6H_5$ have low-intensity (ε 128–156) absorption maxima in the 400–407-mμ region.

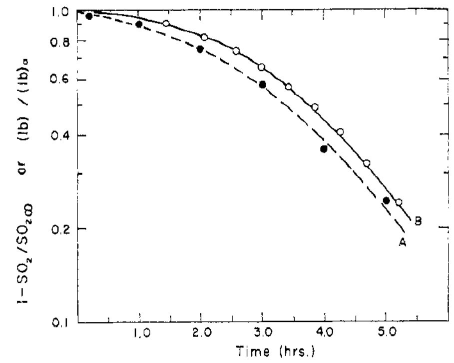

Figure 2.—Decomposition of **1b** (0.20 *M*) in benzene at 55°: curve A, ●, $[\mathbf{1b}]/[\mathbf{1b}]_0$ determined by following the intensity of the nmr singlet at τ 5.75; curve B, ○, log $(1 - SO_2/SO_{2\infty})$ as followed by SO_2 evolution.

Rate of Decomposition of 1b under Various Conditions.—The rate of the decomposition can be followed by two different procedures: (1) measurement of the decrease with time in the intensity of the nmr peak at τ 5.75 owing to the methylene protons of the benzyl group of **1b**; (2) measurement of the rate at which sulfur dioxide is evolved from the decomposition.

The nmr method could be applied only to decompositions of fairly concentrated (0.20 *M*) solutions of **1b**. In benzene at 55° under such conditions, the data for both nmr and sulfur dioxide evolution experiments when plotted in a first-order fashion give curved plots of the type shown in Figure 2. Although the results are not as reproducible from run to run as one would like, it appears that the rate of disappearance of **1b** as measured by nmr and the rate of formation of sulfur dioxide are the same. This is consistent with the fact that infrared spectra of the intermediate that forms under such conditions (*vide supra*) showed that it did not apparently contain either a sulfonyl or a sulfinyl group.

The decomposition of much more dilute (*ca.* 0.01 *M*) solutions of **1b** in benzene at 55° was followed by the sulfur dioxide evolution method. Under these conditions there is a pronounced "induction period" of *ca.* 2 hr, during which time sulfur dioxide is evolved at only a very slow rate. This is then followed by a relatively rapid evolution of the gas, which follows reasonably good first-order kinetics (Figure 3, curve A).

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[5] H. R. Stevens and F. W. Ward, *J. Chem. Soc.*, **125**, 1324 (1924).

[6] R. O'Connor, *J. Org. Chem.*, **26**, 4375 (1961).

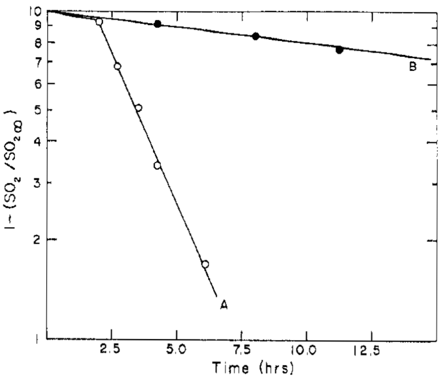

Figure 3.—Plot of log $(1 - SO_2/SO_{2\infty})$ *vs.* time for the decomposition of **1b** (0.01 *M*) in benzene at 55°: curve A, ○, no added **3**; curve B, ●, 4 × 10^{-3} *M* added **3**.

We also measured the rate of evolution of sulfur dioxide from a 0.01 *M* solution of **1b** in benzene to which had been added 0.004 *M* α,γ-bis(biphenylene)-β-phenylallyl[7] (**3**). This stable free radical is known to be a very good reagent for scavenging reactive free radicals.[8,9] In the presence of **3** (curve B, Figure 3), one sees that the "induction period" prior to rapid evolution of sulfur dioxide is dramatically prolonged. We assume that the induction period observed in the absence of **3** is the result of the presence of a small amount of an impurity in either **1b** or the solvent which is also an effective inhibitor of a radical chain reaction.

We also determined the rate of decomposition of **1b** (0.08–0.10 *M*) in cumene and diphenylmethane at 80° by the sulfur dioxide evolution method. Under these conditions the decomposition showed only a rather short induction period. The apparent first-order rate constant, as measured from the slope of the plot of log $(1 - SO_2/SO_{2\infty})$ *vs.* time, is, however, much smaller than one might have expected, given the slope of the plot of the data for the decomposition in benzene at 55°. Thus the slope after the induction period in curve A of Figure 3 corresponds to a rate constant of 1.1 × 10^{-4} sec^{-1} for the decomposition of **1b** in benzene at 55°, which is just about the same as the rate constant of 1.5 × 10^{-4} sec^{-1} calculated from the slope of a first-order plot of the data for the decomposition in diphenylmethane at 80°.

Rate of Free-Radical Production in the Decomposition of 1b in Benzene.—This was investigated over the temperature range of 55–80° using the same scavenging technique employing the Koelsch radical **3** outlined in detail in the accompanying paper[4] on the decomposition of **1c**. As was also true in the decomposition of **1c**, the disappearance of **3** followed good zero-order kinetics under conditions where **1b** was present in considerable excess over **3**. A typical plot is shown in Figure 4. The results for the various runs are summarized in Table II.

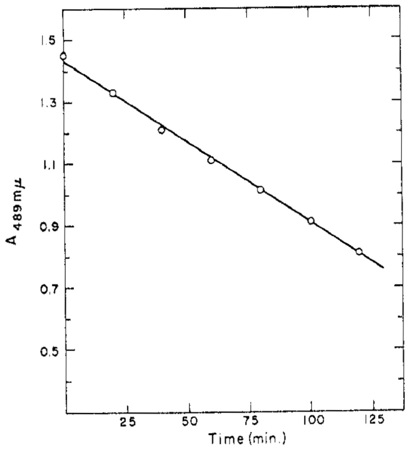

Figure 4.—Plot of the optical density at 489 mμ *vs.* time for the decomposition of **1b** (1.0 × 10^{-4} *M*) in the presence of **3** (5 × 10^{-5} *M*) in benzene at 60°.

Table II

Decomposition of 1b in the Presence of 3 in Benzene

[**1b**] × 10^4, *M*	[**3**]$_0$ × 10^4, *M*	Temp, °C	k_0 × 10^9, *M* sec^{-1} [a]	k_i × 10^5, sec^{-1} [b]
1.0	0.50	54.8	1.2	0.60
		60.0	2.7	1.3
		65.0	6.2	3.1
		70.0	12	6.0
		80.0	24	12

[a] k_0 is the zero-order rate constant for disappearance of **3**. [b] k_i is the first-order rate constant for dissociation of **1b** into radicals, estimated by assuming $k_0 = 2k_i$[**1b**].

From the zero-order rate constants, k_0, for the disappearance of **3** one can calculate k_i, the first-order rate constant for the decomposition of **1b** into pairs of scavengable free radicals, by assuming that $k_0 = 2k_i$[**1b**]. At 55° in benzene, k_i is only 6% of the apparent overall rate of decomposition of **1b**, as determined from the rate of evolution of SO_2 in the absence of added Koelsch radical (curve A, Figure 3), but it is almost exactly equal to the rate constant (0.7 × 10^{-5} sec^{-1}) estimated from curve B of Figure 3 from the rate of evolution of SO_2 from **1b** in the presence of added Koelsch radical at this same temperature. One also finds that k_i at 80° in benzene is approximately the same as the rate constant for the decomposition of **1b** in diphenylmethane at this temperature, as measured by the SO_2-evolution method.

Discussion

Several features of the results suggest that in benzene the decomposition of the benzyl diazo sulfone **1b** is a chain reaction. Thus there is the fact that the overall rate of decomposition of **1b** under such conditions is *ca.* 20 times faster than the apparent rate of dissociation of **1b** into free radicals, as measured using the Koelsch radical as a radical scavenger; *i.e.*, in benzene k_d for **1b** = $20k_i$ for **1b**. More important is the fact (Figure 3) that the addition of Koelsch radical results in a dramatic decrease in the rate of disappearance of **1b**, as measured by SO_2 evolution, k_d in the presence of Koelsch radical being about equal to k_i, rather than 20 times larger, as it is in the absence of added **3**.

As shown by the nmr experiment in Figure 1, decomposition of **1b** in benzene leads to the formation of appreciable amounts of an unstable intermediate compound. This compound decomposes on further heating of the solution, and, in view of the large amount of it which is present, must in so doing yield chiefly benzaldehyde phenylhydrazone, which is the principal final organic product of the decomposition of **1b**. The un-

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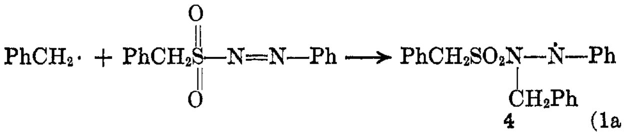
[7] C. F. Koelsch, *J. Amer. Chem. Soc.*, **79**, 4439 (1957).

[8] R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965).

[9] R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

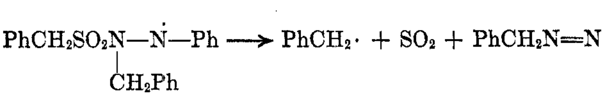
stable intermediate compound has a sharp singlet in the nmr at τ 4.92. It also appears to have a weak maximum in the visible at 405 mμ. Both of these observations, plus the fact that it presumably goes on chiefly to benzaldehyde phenylhydrazone, are consistent with its being formulated as 1′-phenyl benzeneazomethane ($PhCH_2N{=}NPh$). O'Connor[6] has shown that compounds of the structure $RN{=}NPh$ have a low-intensity absorption maximum (ϵ 128–156) in the 400–407-mμ region, and the methylene protons of ω-azotoluene ($PhCH_2N{=}NCH_2Ph$) appear as a sharp singlet at τ 5.15.[10] Also 1′-phenyl benzeneazomethane is known to isomerize readily to benzaldehyde phenylhydrazone.[11,12]

There would seem to be two possible ways that 1′-phenyl benzeneazomethane might be formed in a chain-type decomposition of **1b**. The first of these (eq 1) involves addition of a benzyl radical to the N=N double bond of **1b**, followed by cleavage of the radical **4** thus formed into 1′-phenyl benzeneazomethane, sulfur dioxide, and a benzyl radical; the benzyl radical can then add to another molecule of **1b**. The alternate possibility (eq 2) involves a reaction sequence initiated by abstraction of one of the hydrogens of the methylene group of **1b** (eq 2a). This is followed (eq 2b) by an intramolecular addition to the N=N double bond, which gives **6**. This latter radical loses sulfur dioxide rapidly (eq 2c) to give radical **7**, which can continue the chain by abstracting a hydrogen atom from another molecule of **1b** (eq 2d). This last hydrogen atom transfer to **7** should lead to a mixture of 1′-phenyl benzeneazomethane and benzaldehyde phenylhydrazone.



$$PhCH_2\cdot + PhCH_2S(=O)_2{-}N{=}N{-}Ph \longrightarrow PhCH_2SO_2N{-}\dot{N}{-}Ph \ (\text{N-}CH_2Ph)$$

4 (1a)



$$PhCH_2SO_2N(CH_2Ph){-}\dot{N}{-}Ph \longrightarrow PhCH_2\cdot + SO_2 + PhCH_2N{=}NPh$$

(1b)

$$R\cdot + PhCH_2SO_2N{=}NPh \longrightarrow RH + Ph\dot{C}HSO_2N{=}NPh \qquad (2a)$$

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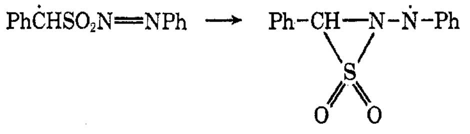
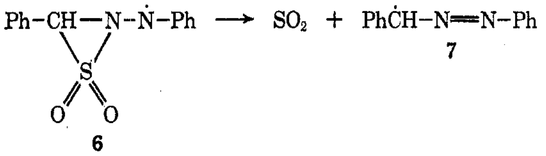


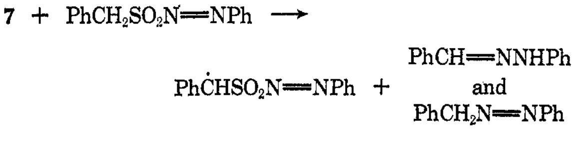
(2b)

6



(2c)

6 **7**



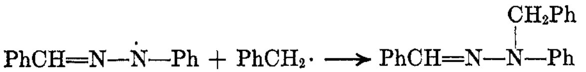
$$7 + PhCH_2SO_2N{=}NPh \longrightarrow Ph\dot{C}HSO_2N{=}NPh + \begin{matrix} PhCH{=}NNHPh \\ \text{and} \\ PhCH_2N{=}NPh \end{matrix} \qquad (2d)$$

Both eq 1 and 2 involve the addition of a free radical to an N=N double bond as a key step. Although such additions have received little study, one should note that the reaction of azobenzene with benzaldehyde in the presence of *t*-butyl peroxide to produce 1-benzoyl-1,2-diphenylhydrazine is believed[13] to involve the addition of a benzoyl radical to the N=N double bond of azobenzene, and Pryor and Guard[14] have remarked that $Ph_3CN{=}NPh$ appears to capture free radicals rather effectively and suggested that this is because addition of a free radical to the N=N double bond of a phenylazo compound gives rise to a relatively stable free radical, $>N{-}\dot{N}{-}\dot{P}h$. Therefore it is reasonable to suggest that additions such as those shown in eq 1a or 2b could be part of the chain decomposition of **1b**.

Initiation of the chain decomposition in benzene presumably involves radicals derived from the homolytic dissociation of **1b** (eq 3). If eq 2 is the correct representation of the chain-decomposition sequence, then initiation of individual chains is most reasonably formulated as proceeding by abstraction of a hydrogen atom from **1b** by a phenyl radical (eq 2a, R· = Ph·), and their termination would presumable involve coupling of radical **7** with a benzyl radical (eq 4), thereby accounting for the small amount of N-benzyl benzaldehyde phenylhydrazone also found as a reaction product.

$$PhCH_2SO_2N{=}NPh \longrightarrow$$

$$[PhCH_2SO_2\cdot + PhN_2\cdot] \xrightarrow[-N_2]{-SO_2} PhCH_2\cdot + Ph\cdot \qquad (3)$$



$$PhCH{=}N{-}\dot{N}{-}Ph + PhCH_2\cdot \longrightarrow PhCH{=}N{-}N(CH_2Ph){-}Ph \qquad (4)$$

7 **2**

Alternatively, if eq 1 is the correct representation of the reaction sequence responsible for the chain decomposition, initiation would be *via* attack of a benzyl radical from eq 3 on **1b**, in the manner shown in eq 1a. In that event it seems most reasonable to assume that the phenyl radicals also produced in eq 3 would disappear chiefly by abstracting hydrogen atoms from either $PhCH_2N{=}NPh$ or **1b**, and then to assume that a sizable fraction of the radicals **7**, which would result either directly or indirectly from this process, would then terminate chains by reacting with benzyl radicals in the manner shown in eq 4.

Either chain-decomposition sequence can therefore be satisfactorily reconciled with the behavior of the decomposition of **1b** in benzene. As far as the results in the other solvents are concerned, one will recall that in diphenylmethane the ratio of the yield of N-benzyl benzaldehyde phenylhydrazone to that of benzaldehyde phenylhydrazone is *ca.* five times larger than it is in benzene, and that the overall rate of disappearance of **1b** is considerably slower in this solvent than in benzene. Both of these results are consistent with the idea that the chain length for the decomposition of **1b** is much smaller in diphenylmethane. *A priori* one might have expected diphenylmethane to have such an effect, since abstraction of one of its hydrogens by either an initiating or a chain-carrying radical would lead to a

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(10) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

(11) D. Y. Curtin and J. A. Ursprung, *ibid.*, **21**, 1221 (1956).

(12) J. Thiele, *Justus Liebigs Ann. Chem.*, **376**, 239 (1910).

(13) M. S. Kharasch, M. Zimmerman, W. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **18**, 1045 (1953).

(14) W. A Pryor and H. Guard, *J. Amer. Chem. Soc.*, **86**, 1150 (1964).

$Ph_2CH\cdot$ radical, which should be relatively unreactive and therefore reluctant to continue the chain. The only problem is that one would also expect as a result of this process to see various compounds containing a benzhydryl group among the products of the decomposition of **1b** in diphenylmethane. We did not isolate any such compounds, although it is possible that they might have either been missed, or, alternatively, that most of the Ph_2CH groups wound up in the intractable, tarry fraction that is always part of the products of the decomposition of **1b**.

Another point of some concern is the fact that in diphenylmethane, where chain decomposition of **1b** is presumably considerably repressed, the yield of benzene is still only 0.15 mol/mol of **1b** decomposing. One might have expected it to be considerably higher, although one should certainly also note that even in the decomposition of the methyl diazo sulfone (**1c**) in this solvent it was only 0.25 mol/mol of **1c**;[4] in that case there was presumably less chain (or induced) decomposition of the diazo sulfone than in the present system.[4] Perhaps in both cases one has a portion of the diazo sulfone decomposing by an acid-catalyzed, nonradical route. Certainly there was some evidence for this in the decomposition of **1c**.[4]

From the last two paragraphs of the preceding discussion it should be clear that, despite the fact that either eq 1 or 2 seem to offer a plausible explanation for the rapid, chain-type decomposition of **1b** in benzene, there are still a number of aspects of the decomposition of **1b**, particularly in other solvents, that are either not well understood or somewhat difficult to rationalize with either of the suggested mechanisms. For this reason, any speculation about which of the two, eq 1 or 2, is the more reasonable mechanism for the chain decomposition seems unwarranted at this time. Neither may in fact be correct, although, despite a great deal of thought, we have been unable to come up with any alternatives that come as close to explaining all the experimental facts as do either eq 1 or 2.

The important point that does seem, however, to emerge clearly from both this study and that described in the accompanying paper[4] is that the thermal decomposition of alkyl benzenediazo sulfones can be an extremely complex process that certainly is worth further investigation. It is our hope that this presentation of our experimental results will stimulate others to do the additional definitive work necessary to establish with real certainty just what is going on mechanistically in systems of this type.

Experimental Section

Synthesis of 1b.—Crude α-toluenesulfinic acid, 7.1 g, prepared by the reaction sequence outlined by Kice, Engebrecht, and Pawlowski[15] was dissolved in 150 ml of methanol. To this solution was added 5 ml of water and 38.2 g of sodium bicarbonate. The solution was stirred until evolution of carbon dioxide ceased and filtered, and the filtrate evaporated to dryness under reduced pressure at room temperature. The sodium α-toluenesulfinate so obtained, 6.76 g (38.0 mmol), was dissolved in 40 ml of cold water. This solution was extracted with one 20-ml portion of ether, the ether layer was discarded, and the aqueous layer was stirred at 0–5° while a solution of 7.25 g (38.0 mmol) of benzenediazonium fluoroborate in 250 ml of water was slowly added. Ten minutes after the addition was complete the yellow precipitate which had formed was filtered off and washed with cold water. After drying, the precipitate was dissolved in 70 ml of benzene, and the solution was filtered through some magnesium sulfate. *Ca.* 200 ml of hexane was added to the benzene filtrate. After the solution had cooled, the bright yellow precipitate which had formed was filtered off, and the crystals were again recrystallized from benzene–hexane, yielding 6.0 g (62%) of benzyl benzenediazo sulfone: mp 97–99° dec; ultraviolet spectrum (cyclohexane) λ_{max} 290 mμ (ε 14,200) and 438 (129); ir (chloroform) 1350 (s) and 1145 and 1162 cm^{-1} (s), all owing to the sulfone group.

Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76; S, 12.32. Found: C, 60.38; H, 4.64; N, 10.64; S, 12.54.

Purification of Solvents.—These were purified as described in an accompanying paper.[4]

Thermal Decomposition of 1b. Product Studies.—The general procedure for carrying out the decompositions was the same as that described for **1c** in the accompanying paper,[4] as was the method used for determining the amount of sulfur dioxide evolved.

Decomposition in Benzene.—After the decomposition was complete, a small aliquot of the final solution was withdrawn and subjected to glpc on a 15-ft XF-1150 (15% on firebrick) column. The chromatogram showed benzene (the solvent) to be the only volatile component. The remaining solution was evaporated under reduced pressure to remove the solvent, and the residue was chromatographed on alumina. Elution with hexane gave biphenyl, 0.02 mol/mol of **1b**. Elution with 80:20 hexane–benzene afforded a very small amount of azobenzene. Elution with 50:50 hexane–benzene gave N-benzyl benzaldehyde phenylhydrazone, mp 108–109° (lit.[16] mp 111°), identical in all respects with a known sample.[16] Elution with pure benzene gave benzaldehyde phenylhydrazone, mp 156–158°, identical in all the usual respects with a known sample.[17]

Decomposition in Cumene.—At the end of the decomposition a glpc analysis on a small aliquot showed three peaks with retention times identical with those of a prepared mixture of benzene, toluene, and cumene.

The cumene and other volatiles were removed from the remainder of the final solution by vacuum distillation. The dark residue was chromatographed on alumina. Elution with 75:25 hexane–benzene gave N-benzyl benzaldehyde phenylhydrazone and elution with 20:80 hexane–benzene afforded benzaldehyde phenylhydrazone. No bicumyl could be found in the hexane eluates.

Decomposition in Diphenylmethane.—At the end of the decomposition an aliquot of the final solution was subjected to glpc analysis using a column temperature of 160°. The chromatogram showed four peaks, three of which had retention times identical with those of benzene, toluene and diphenylmethane, respectively. The identity of the small fourth peak was not determined.

The remaining solution was carefully vacuum distilled to remove the solvent and other volatiles. The residue was then chromatographed on alumina in the same manner as for the decompositions in cumene and benzene. The only materials eluted which could be identified were N-benzyl benzaldehyde phenylhydrazone and benzaldehyde phenylhydrazone. In particular, no *sym*-tetraphenylethane could be isolated.

Identification of the Intermediate in the Decomposition of 1b in Benzene.—Part of a 0.20 *M* solution of **1b** in benzene was placed in an nmr tube and degassed, and the tube was sealed. The tube was heated at 55° and from time to time the nmr spectrum was recorded. The sharp singlet owing to the methylene group of **1b** at τ 5.75 decreased steadily in intensity and finally disappeared. During this time a sharp singlet began to appear at τ 4.92. This reached a maximum at about the time when the signal at τ 5.75 had completely disappeared and then subsequently itself disappeared (see Figure 1).

At the same time that the nmr experiment was being carried out, the remainder of the 0.20 *M* solution of **1b** in benzene, which had also been degassed, was also heated at 55°. When the nmr measurements indicated that the maximum amount of the intermediate with the singlet at τ 4.92 was present, heating of this second portion of the solution was terminated, the solution was frozen, and the benzene was removed from the frozen mixture under reduced pressure. Part of the residue which remained

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was dissolved in chloroform, and the infrared spectrum was recorded. A second weighed portion was dissolved in cyclohexane and the ultraviolet and visible spectra were determined. A third portion was redissolved in benzene and examined in the nmr. The singlet at τ 4.92 was still present, showing that removal of the benzene from the original solution did not cause any significant destruction of the intermediate.

In a separate experiment a 0.20 *M* solution of **1b** in benzene, containing a small but known amount of cyclohexane, was also examined in the nmr with time in the same fashion as in the earlier experiment. The integrated intensity of the singlet at τ 4.92 was compared with that of the added cyclohexane.

Kinetic Study of the Decomposition of 1b. Sulfur Dioxide Evolution Method.—The same apparatus and procedure used to follow the decomposition of **1c**[4] was employed.

Nmr Method.—A *ca.* 0.20 *M* solution of **1b** in benzene, to which 1 drop of cyclohexane per 1 ml of solution had been added to serve as an internal proton standard, was transferred to an nmr tube having a constricted neck. The solution was then deaerated, and the tube was finally sealed off under *ca.* 100 mm pressure of prepurified nitrogen. The tube was then transferred to the thermostated nmr probe and the relative intensities of the singlet at τ 5.75 and the cyclohexane standard were determined as a function of time by integration.

Rate of Free-Radical Production in the Decomposition of 1b.—This was followed, using the Koelsch radical[7] as the radical counting reagent, in the same way as for the decomposition of **1c** in the accompanying paper.[4]

Registry No.—1b, 23264-06-4.

The Reaction of Diborane and Bistriphenylmethyl Disulfide to Give a Carbon–Sulfur Bond Cleavage

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Diborane has been found to cleave the carbon–sulfur bond in bistriphenylmethyl disulfide to produce triphenylmethane, hydrogen, and $(HBS)_x$ polymer. Triphenylmethyl mercaptan reacted with diborane in benzene solution to yield the identical products. Hydrogen sulfide in benzene solution was found to react with diborane much more rapidly to form the $(HBS)_x$ polymer than previously reported for the vapor-phase reaction. The $(HBS)_x$ polymer prepared by these methods was a white, amorphous solid. No characteristic X-ray powder pattern could be obtained. The infrared spectrum corresponded to that reported in the literature. The elemental analysis and hydridic hydrogen determination confirm the stoichiometry. The ion fragments observed in the mass spectrum are consistent with the proposed formulation. The broad-line nmr of the solid indicated tetrahedral coordination of the boron.

Reactions of boron hydrides with elemental oxygen were studied soon after the discovery of the boron hydrides because of the spontaneous nature of the reaction.[1] This was followed by the study of the reactions with oxygen-containing compounds.[2] The study of the reactions with the analogous sulfur compounds, on the other hand, has lagged. For example, in Steinberg's comprehensive monograph,[3] boron–oxygen chemistry requires some 800 pages compared with 20 pages for boron–sulfur chemistry. Recently, however, interest in boron–sulfur chemistry has been increasing.[4–6]

In general, sulfur compounds do not react so fast as their oxygen analogs. Experience in our laboratories indicates that many organic disulfides are unreactive with diborane at −65°. Because of the relative stability of the sulfur–sulfur bond, it was felt that a preferential sulfur–carbon bond cleavage might be observed by properly selecting the carbon group. Furthermore, it was of interest to see whether the sulfur–sulfur bond might not be a sufficiently weak oxidizing agent that it could coexist in the same molecule with a boron–hydrogen bond.

Experimental Section

Reagents.—The benzene, toluene, and diethyl ether were reagent grade solvents stored in glass over calcium hydride. These were transferred by distillation into the vacuum line as needed.

Diborane.—The diborane was prepared by slowly adding 0.5 g of sodium borohydride to 20 ml of concentrated H_2SO_4. It was purified by distilling successively through a −111° trap and two −126° traps.

Triphenylmethyl Mercaptan.—The compound was used as obtained from the Aldrich Chemical Co.

Bistriphenylmethyl Disulfide.—The method of Vorlander and Mittag[7] which involves the treatment of triphenylmethyl mercaptan in alcoholic alkali solution with sulfuryl chloride was used. The sulfuryl chloride was purified by distilling the practical grade from Matheson Coleman and Bell into glass ampoules. These ampoules were sealed and not reopened until just prior to use.

The product obtained directly from the synthesis was a crystalline material, with mp 155–156°. Recrystallization of the disulfide from benzene, toluene–ethanol, and ether–benzene gave rise to some decomposition products and low recoveries. The disulfide used for all of these experiments was, therefore, unrecrystallized.

Bistriphenylmethyl Tetrasulfide.—The method described by Nakabayashi and coworkers[8] involving the reaction of triphenylmethyl mercaptan with sulfur monochloride was used. The product was recrystallized from chloroform–ethanol.

Reaction of Bistriphenylmethyl Disulfide with Diborane.—The reaction was carried out in an inverted U tube which could be sealed off under vacuum and which also contained a break-off so that it could be opened under vacuum. These tubes varied in size. The standard tubes, which were used for most of the experiments, had legs 300 mm long and 18 mm in diameter. The legs were *ca.* 80 mm apart. At the top, perpendicular to the plane of the inverted U, a 14/35 through joint with a 3-mm extension tube was attached. The volatile contents of the tube could be removed by breaking this 3-mm tube with a tube breaker. An accurately weighed amount of 0.3–0.5 g of bis-

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