0.00020 mol, 52%), mp 124° (lit.[13] mp 128, 127, 125–126, and 127–128°). A picrate was obtained, mp 158° (lit.[29] mp 158°).

Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71; mol wt, 158.2. Found: C, 75.96; H, 6.22; N, 17.81; mol wt (benzene), 165.

Ultraviolet spectrum: 251 nm (ϵ 15,600) (CH_3OH); 248 nm (ϵ 9200) ($CHCl_3$). Infrared spectrum (KBr): 3170 (m), 3120 (m), 3075 (m), 3000 (m), 2920 (m), 2840 (m), 1595 (m), 1580 (m), 1520 (m), 1500 (m, doublet), 1465 (m), 1410 (w), 1380 (w), 1320 (m), 1295 (m), 1275 (m), 1205 (m), 1155 (w), 1130 (w), 1100 (w), 1080 (m), 1060 (w), 1030 (m), 1015 (w), 965 (m), 915 (w), 870 (m), 840 (w), 795 (w), 760 (s), 715 (m), 690 (s) cm^{-1}. The 60MHz proton nmr spectrum was run in deuteriochloroform and in carbon tetrachloride: δ 12.66 ($CDCl_3$), 13.50 (CCl_4) [singlet ($CDCl_3$), broad (CCl_4), 1 H, –NH–]; 7.43 ($CDCl_3$), 7.40 (CCl_4) (complex, 5 H, C_6H_5); 6.24 ($CDCl_3$), 6.15 (CCl_4) (singlet, 1 H, –C=CH–); 2.12 ($CDCl_3$), 2.15 (CCl_4) (singlet, 3 H, CH_3). Mass spectrum:[18] *m/e* 55 (1.37), 77 (0.99), 78 (0.76), 81 (0.76), 90 (1.52), 91 (0.46), 102 (0.38), 103 (1.75), 104 (0.91), 115 (0.91), 116 (0.61), 117 (2.81), 118 (0.61), 127 (0.38), 128 (1.37), 129 (1.60), 130 (2.81), 131 (0.53), 143 (2.05), 157 (16.4), 158 (100), 159 (11.6), 160 (0.76).

Pyrolysis of 4-*p*-Methoxyphenyl-6-thia-2,3-diazabicyclo[3.2.0]-hept-2-ene 6,6-Dioxide.—4-*p*-Methoxyphenyl-6-thia-2,3-diazabicyclo[3.2.0]hept-2-ene 6,6-dioxide (**1a**, R = *p*-$CH_3OC_6H_4$–; R′ = H) (0.22 g, 0.00089 mol) was heated in a sublimator at 125° (5 mm) for 30 min. A white solid sublimed, mp 108°; two more sublimations produced an analytical sample of 3(5)-methyl-5-(3)-*p*-methoxyphenylpyrazole (**3**, Ar = *p*-CH_3O-C_6H_5) 0.060 g, 0.00032 mol, 36%), mp 111°.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88; mol wt, 188.2. Found: C, 70.40; H, 6.62; N, 14.87; mol wt (chloroform), 206.

Ultraviolet spectrum ($CHCl_3$): 261 nm (ϵ 18,600). Infrared spectrum (KBr): 3100 (m), 3000 (m), 2850 (m), 1620 (w), 1580 (w), 1525 (m), 1460 (m), 1440 (m), 1300 (w, sh), 1275 (m), 1250 (s), 1210 (w, sh), 1180 (m), 1160 (m), 1115 (w), 1070 (w), 1025 (m), 1010 (m), 960 (w), 840 (m, sh), 830 (m), 810 (w), 790 (m, sh), 780 (m), 685 (w) cm^{-1}. The 60-MHz proton nmr spectrum was run in deuteriochloroform: δ 12.07 (singlet, 1 H, NH), 7.18 (quartet, 4 H, C_6H_4), 6.20 (singlet, 1 H, –C=CH), 3.76 (singlet, 3 H, CH_3O), 2.20 (singlet, 3 H, CH_3C=C). Mass spectrum (70 V, indirect inlet): *m/e* 90 (4.17), 91 (14.9), 92 (3.57), 94 (8.63), 102 (4.75), 103 (3.57), 104 (3.57), 115 (19.1), 116 (8.64), 117 (6.55), 145 (39.2), 146 (5.06), 159 (4.76), 173 (66.0), 174 (8.94), 188 (100), 189 (13.4).

5,5-Diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-Dioxide. Reduction with Raney Nickel.—A solution of 5,5-diphenyl-2-thiabicyclo[2.1.0]pentane 2,2-dioxide (**2**, R = R′ = C_6H_5) (0.108 g, 0.00040 mol) in 40 ml of warm ethanol was added to a suspension of W-4 Raney nickel,[30] prepared from 10 g of nickel–aluminum alloy (K & K Laboratories, Jamaica, N. Y.) in 75 ml of 95% ethanol. The mixture was refluxed for 16 hr and the metal was removed by filtration from the hot solvent. Evaporation of ethanol left 3,3-diphenyltetrahydrothiophene 1,1-dioxide (0.052 g, 0.00019 mol, 47%) as a white solid, mp 135°. Two recrystallizations from ether produced an analytical sample of colorless crystals, mp 144–145°.

Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.58; H, 5.92; S, 11.75; mol wt, 272.3. Found: C, 70.78; H, 5.92; S, 11.69; mol wt (chloroform), 269.

Ultraviolet spectrum ($CHCl_3$): 253 nm (ϵ 208), 260 (238), 270 (ϵ 168). Infrared spectrum (KBr): 3010 (w), 2950 (w), 1600 (w), 1490 (m), 1450 (m), 1410 (w), 1400 (w), 1300 (s), 1240 (w), 1220 (s), 1180 (w), 1125 (s), 1090 (w), 1070 (w), 1030 (w), 1005 (w), 980 (w), 955 (w), 915 (w), 910 (w), 875 (w), 860 (w), 805 (w), 795 (w), 775 (m), 745 (s), and 700 (s), cm^{-1}. The 60 MHz proton nmr spectrum was run in dimethyl sulfoxide-d_6: δ 7.35 [complex, 10 H, $(C_6H_5)_2C$–], 3.89 (complex, 4 H, $CH_2SO_2CH_2$), 3.05 (triplet, 2 H, –$CH_2CH_2SO_2$–). Mass spectrum (20 V, indirect inlet):[18] *m/e* 91 (9.10), 117 (8.44), 129 (16.7), 165 (10.4), 167 (48.9), 168 (6.75), 179 (8.60), 180 (100), 181 (15.8), 193 (42.1), 194 (6.85), 207 (25.2), 208 (6.24), 272 (9.70).

Registry No.—Thiete sulfone, 7285-32-7; 7-thia-2,3-diazobicyclo[3.2.0]hept-2-ene 7,7-dioxide, 23263-85-6; 3,3-diphenyltetrahydrothiophene 1,1-dioxide, 23263-97-0; **1a** (R = C_6H_5; R′ = H), 23263-86-7; **1a** (R = *p*-$CH_3OC_6H_4$; R′ = H), 23263-87-8; **1a** (R = CH_3; R′ = H), 23263-88-9; **1a** (R = C_6H_5; R′ = D), 23263-89-0; **1a** (R = R′ = C_6H_5), 23282-27-1; **1a** (R = C_6H_5; R′ = CH_3), 23263-90-3; **1b** (R = R′ = CH_3), 23263-91-4; **1c**, 23263-92-5; **2** (R = R′ = C_6H_5), 23263-93-6; **2** (R = C_6H_5; R′ = CH_3), 23263-94-7; **3** (Ar = C_6H_5), 3440-06-0; **3** (Ar = *p*-$CH_3OC_6H_4$), 23263-96-9.

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[29] I. I. Grandberg and A. N. Kost, *Zh, Obshch. Khim.*, **28**, 3071 (1958); *Chem. Abstr.*, **53**, 10188 (1959).

[30] A. A. Pavlic and H. Adkins, *J. Amer. Chem. Soc.*, **68**, 1471 (1946).

The Thermal Decomposition of Benzenediazo Sulfones. I. Methyl Benzenediazo Sulfone[1]

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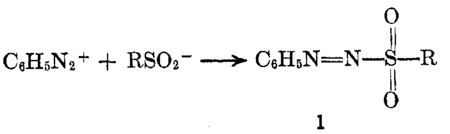
The thermal decomposition of methyl benzenediazo sulfone (**1c**) has been investigated in four different solvents. In three nonpolar solvents, benzene, cumene, and diphenylmethane, the principal identifiable decomposition products (Table I) are all ones that can be most easily interpreted as arising *via* a mechanism involving initial homolytic dissociation of **1c** and free-radical intermediates. The involvement of radical intermediates in the decomposition under these conditions is also shown by the results of experiments using a stable free radical (**2**) to scavenge the radicals formed by decomposition of **1c**. In the polar, aprotic solvent acetonitrile, on the other hand, the principal decomposition product, acetanilide, is thought to arise *via* an initial heterolytic dissociation of **1c** into a sulfinate and a benzenediazonium ion and reaction of the latter with the solvent in the manner shown in eq 10.

Benzenediazo sulfones (**1**) are an intriguing and little studied class of compounds which can be easily prepared by the reaction of a benzenediazonium salt with the salt of a sulfinic acid (eq 1). Although one reference work[2] claims that their thermal decomposition in nonpolar solvents leads to the formation of the sulfone $C_6H_5SO_2R$ and nitrogen, a study of the decomposition of phenyl



$$C_6H_5N_2^+ + RSO_2^- \longrightarrow C_6H_5N{=}N{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R \qquad (1)$$

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

[2] Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 334.

TABLE I

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

Products, mol/mol of **1c**	Benzene	Benzene + suspended CaO	Cumene	Ph_2CH_2
SO_2	0.14	0.14	0.03	0.11
Biphenyl	0.26	0.32	...	...
Azobenzene	0.14	0.03	...	...
Benzene	(Solvent)	(Solvent)	0.24	0.23
$CH_3SO_3C_6H_5$	0.07	0.00	0.07	0.00
Bis(methanesulfonyl)-phenylhydrazine (**4a** or **4b**)	0.05	...	...	...
p-Phenylazobenzene	0.00	0.02	...	...
Benzhydryl methyl sulfone	...	...	...	0.11
sym-Tetraphenylethane	...	....	...	0.065
o- and *p*-Phenyldiphenyl methane	...	...	...	0.08
Bicumyl	...	...	0.12	...

[a] All data for 80°, initial concentration of **1c**, 0.10–0.13 *M*.

benzenediazo sulfone (**1a**, R = C_6H_5) by Overberger and Rosenthal[3] has shown that this is certainly not true for this diazo sulfone at least. In benzene as solvent they found that the principal products of the thermal decomposition of **1a** were biphenyl, nitrogen, and benzenesulfinic acid, only 5% of diphenyl sulfone being formed.

Our own interest in the thermal decomposition of benzenediazo sulfones was first aroused when we happened to prepare benzyl benzenediazo sulfone (**1b**, R = $C_6H_5CH_2$) and discovered[4] that its decomposition in benzene gave products entirely different from those given by **1a**. We felt that our efforts to understand the complex behavior of the benzyl compound might be materially improved if we had available knowledge about the thermal decomposition of a simpler alkyl benzenediazo sulfone (**1c**, R = CH_3). Such information, for example, would tell us whether all alkyl benzenediazo sulfones behave very differently on thermal decomposition than their aryl counterparts, or whether, alternatively, there is something special about the decomposition of **1b**.

The present paper describes the results of our investigation of the thermal decomposition of **1c**. These show that its behavior is basically similar to that of the aryl compound[3] **1a** and that it is the decomposition of the benzyl compound **1b** which behaves in an unusual manner.

Results

Products of the Thermal Decomposition of 1c in Nonpolar Solvents.—Samples of methyl benzenediazo sulfone (**1c**) were decomposed at 80° in three different nonpolar solvents—benzene, cumene, and diphenylmethane. The decompositions were carried out under a nitrogen atmosphere, and a slow stream of nitrogen was passed through the solution during the decomposition in order to remove any sulfur dioxide which might be liberated in the decomposition as rapidly as it was formed.

In studying the kinetics of the decomposition of **1a**, Overberger and Rosenthal[3] observed that the rate tended to accelerate with time, and that this acceleration was apparently due to autocatalysis by an acidic material formed in the decomposition, since the acceleration could be eliminated by suspending a small amount of calcium oxide in the solvent. We have also observed (*vide infra*) a similar but much less pronounced phenomenon in the decomposition of **1c**. Because of this we determined the nature of the decomposition products of **1c** in benzene for runs both in the presence and absence of suspended calcium oxide. The results of these and the runs in the other two solvents (no calcium oxide was added here) are summarized in Table I. Besides the reaction products listed, there was formed in all runs a large amount of intractable, tarry material, which, in our hands at least, did not prove amenable to chromatographic separation into identifiable components. Infrared spectra of the tarry material indicated that it contained NH, sulfonyl, and phenyl groups.

In benzene we see that the principal identifiable product is biphenyl and that a significant amount of sulfur dioxide is also formed. In the absence of suspended calcium oxide a good bit of azobenzene is formed, but the yield of this product drops to almost nothing when CaO is present. In cumene and diphenylmethane we find quite large amounts of benzene and significant amounts of the coupling products from solvent-derived radicals—bicumyl and *sym*-tetraphenylethane. In diphenylmethane we also find a significant amount of benzhydryl methyl sulfone, a product which could arise from coupling of a $CH_3SO_2\cdot$ radical with a solvent-derived diphenylmethyl radical, and small amounts of both *o*- and *p*-$C_6H_5C_6H_4CH_2C_6H_5$, products that would result from attack of phenyl radicals on the aromatic rings of diphenylmethane.

One curious product which was isolated in significant yield from the decompositions of **1c** in both benzene and cumene, although not from the decomposition in benzene in the presence of calcium oxide, is phenyl methanesulfonate. Another, bis(methanesulfonyl)-phenylhydrazine, isolated from the decomposition of **1c** in benzene, presumably results from the addition of the elements of methanesulfinic acid across the nitrogen–nitrogen double bond of **1c**.

Products of Thermal Decomposition of 1c in Acetonitrile.—We also investigated the decomposition of **1c** in the polar, aprotic solvent acetonitrile at 80°. On chromatographic work-up, only one organic product, acetanilide (0.71 mol/mol of **1c**), was isolated. Only

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(3) C. G. 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**, 1010 (1970).

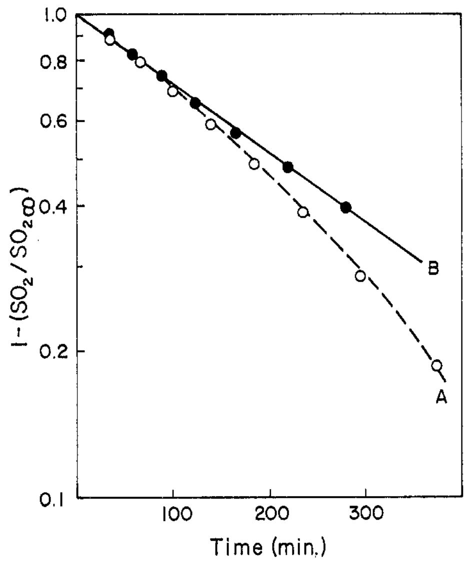

Figure 1.—Plot of log (1 − $SO_2/SO_{2\infty}$) *vs.* time for the decomposition of 0.10 *M* **1c** in benzene at 80°: curve A, ○, absence of suspended CaO; curve B, ●, presence of CaO.

0.03 mol of SO_2 was evolved. Clearly, in polar, aprotic solvents the decomposition of **1c** takes a very different course than it does in nonpolar solvents like benzene.

Rate of Decomposition of 1c in Benzene.—Because alkyl benzenediazo sulfones have a weak, but well-defined, absorption maximum in the visible region of the spectrum, we originally hoped to follow the disappearance of **1c** by observing the change in the visible absorption of the solution with time. However, because the solution turns from yellow-orange to a deep red during the course of the decomposition, apparently owing mainly to the formation of some of the products later isolated as intractable, tarry material, this turns out not to be feasible. An alternate approach was accordingly used.

We have seen that some sulfur dioxide (0.14 mol/mol of **1c**) is evolved in the decomposition of **1c** in benzene. The rate at which this gas is evolved can be followed by sweeping it out of the reaction vessel as it is formed and observing the time required for the reduction of an aliquot of standard iodine solution in a trap attached to the reaction vessel. Figure 1 shows a plot of log (1 − $SO_2/SO_{2\infty}$) *vs.* time for the decomposition of a 0.01 *M* solution of **1c** in benzene at 80° both in the absence (curve A) and the presence (curve B) of suspended calcium oxide. One sees that suspending CaO in the solution stops the gradual acceleration of the rate otherwise observed during the decomposition. This acceleration is similar to, although considerably less pronounced than, that observed in the decomposition of **1a**.[3] The first-order rate constant, k_d, for the disappearance of **1c** at 80° in benzene, as estimated from the slope of curve B, is 5.5×10^{-5} sec^{-1}.

Rate of Free-Radical Production in the Decomposition of 1c.—A common procedure for measuring the rate at which free radicals are produced in a given system is to add a known quantity of some reagent which is known to be extremely effective at scavenging free radicals and then to measure the rate at which this radical scavenger is consumed.[5,6] If the initial concentrations are chosen such that the concentration of the scavenger is much smaller than that of the radical source, and if the scavenger is highly effective at capturing all radical intermediates produced before they can undergo bimolecular radical termination, then the disappearance of the scavenger will follow zero-order kinetics and the experimental zero-order rate constant will be equal to the rate of radical production.[5] We have employed this type of technique to measure the rate of radical production during the decomposition of **1c**.

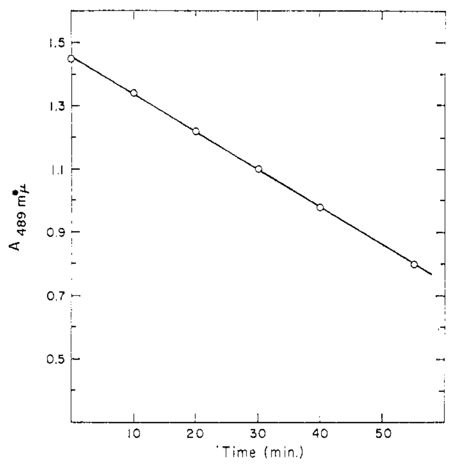

Figure 2.—Plot of optical density at 489 mμ *vs.* time for the decomposition at **1c** (5.3×10^{-4} *M*) in the presence of **2** (5×10^{-5} *M*) in benzene at 70°.

The radical scavenger used in the present work was the stable free radical α,γ-bis(biphenylene)-β-phenylallyl[7] (**2**), the so-called Koelsch radical. This has been used successfully on several occasions in the past for this purpose.[6] Experiments were carried out in benzene as solvent at temperatures of 55–80° using initial concentrations of **1c** and **2** of 5×10^{-4} *M* and 5×10^{-5} *M*, respectively. As can be seen from Figure 2, the disappearance of the Koelsch radical follows good zero-order kinetics under these conditions. The results of these runs are summarized in Table II.

Table II

Decomposition of Methyl Benzenediazo Sulfone in the Presence of 2 in Benzene

[**1c**] × 10⁴, *M*	[**2**] × 10⁴, *M*	Temp, °C	$k_0 \times 10^9$, *M* sec^{-1} [a]	$k_i \times 10^5$, sec^{-1} [b]
5.0	0.51	80.0	19	1.9
		70.0	7.3	0.73
		59.9	1.9	0.19
		54.8	0.86	0.086

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

The first-order rate constant for dissociation of **1c** into pairs of scavengable free radicals, k_i, is calculated from the zero-order rate constant for disappearance of **2**, k_0, by assuming[5,6] that $k_0 = 2k_i[\mathbf{1c}]$. Comparing k_i at 80° with k_d, the overall rate of disappearance of **1c** at this temperature, as measured by the rate of evolu-

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(5) (a) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955); (b) C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56**, 815 (1960); (c) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962); (d) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

(6) (a) R. C. Lamb, J. G. Pacifici, and P. W. Ayres, *ibid.*, **87**, 3928 (1965); (b) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

(7) C. F. Koelsch, *ibid.*, **79**, 4439 (1957).

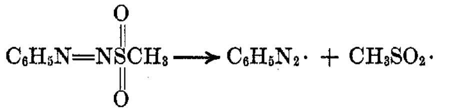
tion of sulfur dioxide, one sees that $k_i/k_d = 0.35$ (at 80° in benzene).

Discussion

Decomposition of Methyl Benzenediazo Sulfone (1c) in Nonpolar Solvents. Evidence for Radical Intermediates.—The experiments using the stable free radical **2** as a radical scavenger show that the decomposition of **1c** in nonpolar solvents leads to the production of free-radical intermediates, although the rate of radical production, k_i, as measured by these experiments, seems to be only about 35% of k_d, the overall rate of decomposition of **1c** under these conditions.

Deferring for the moment discussion of possible reasons for this difference between k_i and k_d, we will first point out that the principal identifiable decomposition products in such solvents are all ones that seem most easily accounted for in terms of reactions involving free-radical intermediates, and we will indicate the manner in which we believe they are formed.

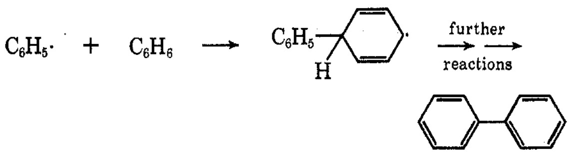
Homolytic dissociation of **1c** would presumably lead initially to the formation of a $CH_3SO_2\cdot$ radical and a $C_6H_5N_2\cdot$ radical (eq 2). Loss of nitrogen from the latter yields a phenyl radical (eq 3).



$$C_6H_5N{=}N\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}CH_3 \longrightarrow C_6H_5N_2\cdot + CH_3SO_2\cdot \qquad (2)$$

$$C_6H_5N_2\cdot \longrightarrow C_6H_5\cdot + N_2 \qquad (3)$$

Phenyl radicals are known[8] to react with benzene to give biphenyl (eq 4) *via* a reaction sequence which is initiated by addition of the phenyl radical to the aromatic ring.

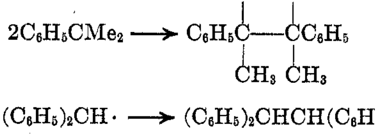


(4)

The yield of biphenyl (0.32 mol/mol of **1c**) from the decomposition of **1c** in benzene is *ca.* 70% of the amount (0.45 mol/mol of **1a**) formed in the decomposition of **1a** under the same conditions.

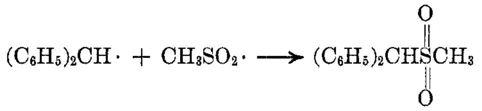
Both cumene and diphenylmethane possess hydrogen atoms that can be easily abstracted by phenyl radicals (eq 5). This presumably accounts for the considerable yield of benzene (0.25 mol/mol of **1c**) from the decomposition in these two solvents. Coupling (eq 6) of the cumyl (or diphenylmethyl) radicals produced in eq 5 accounts for the bicumyl (or *sym*-tetraphenylethane) isolated. In diphenylmethane we also apparently have some radical coupling between the solvent-derived radical and $CH_3SO_2\cdot$ (eq 7), since an appreciable amount of benzhydryl methyl sulfone (**3**), 0.11 mol/mol **1c**, was found to be one of the products in that solvent.

$$C_6H_5\cdot + \begin{array}{c} C_6H_5CHMe_2 \\ \text{or} \\ (C_6H_5)_2CH_2 \end{array} \longrightarrow C_6H_6 + \begin{array}{c} C_6H_5\dot{C}Me_2 \\ \text{or} \\ (C_6H_5)_2CH\cdot \end{array} \qquad (5)$$



$$2C_6H_5\dot{C}Me_2 \longrightarrow C_6H_5\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}C_6H_5 \qquad (6a)$$

$$2(C_6H_5)_2CH\cdot \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \qquad (6b)$$



$$(C_6H_5)_2CH\cdot + CH_3SO_2\cdot \longrightarrow (C_6H_5)_2CH\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}CH_3 \qquad (7)$$

3

The fate of most of the $CH_3SO_2\cdot$ radicals formed in the initial homolysis of **1c** shown in eq 2 is not obvious. Some presumably desulfonylate (eq 8), thereby accounting for the sulfur dioxide evolved in the decomposition. In diphenylmethane others obviously react as shown in eq 7. Others probably abstract hydrogen atoms from one source or another, thereby being converted into methanesulfinic acid, CH_3SO_2H. We noted in the Results section that the bis(methanesulfonyl)-phenylhydrazine formed in the decomposition in benzene is a product which could well result from the addition of CH_3SO_2H across the nitrogen–nitrogen double bond of **1c**. However, what happens to any CH_3SO_2H formed under other conditions is not clear. Alkanesulfinic acids are generally considered[9] to be less stable than their aryl counterparts, and it could be that CH_3SO_2H once formed would itself decompose under the reaction conditions employed. (We did not, however, find any methyl methanethiolsulfonate, $CH_3SO_2SCH_3$, a product frequently formed on decomposition of the sulfinic acid.) Perhaps any CH_3SO_2H formed is simply lost during the chromatographic work-up procedure normally employed. However, according to the experience of Overberger and Rosenthal[3] it should have been isolable from the calcium salts recovered from the decomposition in the presence of suspended CaO if any had been there.

$$CH_3SO_2\cdot \longrightarrow CH_3\cdot + SO_2 \qquad (8)$$

From the infrared spectra of the intractable, tarry residues always found as one of the major components of the decomposition products of **1c** it is clear that at least some of the original CH_3SO_2 groups of **1c** are contained therein, although in what form we do not know. In general, the large amount and the as yet unknown structures of the compounds in the intractable, tarry residue makes it unwarranted to conduct any further discussion of the origin of the products of the decomposition of **1c** in nonpolar solvents.

Possible Origins of the Difference between k_d and k_i.—We noted earlier that the apparent rate of radical production, k_i, as measured by scavenging experiments with **2**, was only about 35% of k_d, the overall rate of disappearance of **1c** under the same conditions. *A priori*, one can suggest three possible causes for this behavior for further consideration: (1) cage recombination of some of the initial radical pairs to give products before the radicals can diffuse away and be scavenged by **2**; (2) induced decomposition of some **1c** by attack of radicals on it, resulting in more than one molecule of **1c** disappearing for each initial homolytic act represented by eq 2; (3) a competing nonradical decomposition pathway.

Of these three, cage recombination is not apparently an important source of the difference between k_d and k_i, since no appreciable yield of any plausible cage recom-

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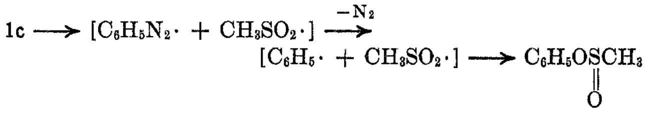
[8] D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **80**, 4742 (1958).

[9] See ref 2, pp 289–298.

bination product is found among the products. Although it is possible that the phenyl methanesulfonate isolated under certain conditions could arise from oxidation of initially formed phenyl methanesulfinate, and that the latter compound could be the product of a cage recombination reaction, *i.e.*



$$\mathbf{1c} \longrightarrow [C_6H_5N_2\cdot + CH_3SO_2\cdot] \xrightarrow{-N_2} [C_6H_5\cdot + CH_3SO_2\cdot] \longrightarrow C_6H_5O\underset{\underset{O}{\|}}{S}CH_3$$

this could only account for a small part of the difference between k_d and k_i.

On the other hand, if attack of different radicals on **1c** can lead to that complex product mixture which we have isolated only as an intractable, tarry residue, then clearly induced decomposition of **1c** remains a strong possibility for the source of the difference in rate between k_d and k_i.

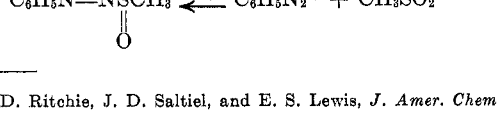
However, the fact (*vide infra*) that decomposition of **1c** in polar aprotic solvents like acetonitrile obviously occurs by a nonradical route and the evidence that, in the absence of suspended calcium oxide, part of the decomposition in benzene apparently occurs by an acid-catalyzed, and presumably nonradical, pathway mean that one also cannot rule out the third alternative—a competing nonhomolytic pathway—as a potentially important source of a significant part of the difference between k_d and k_i.

The evidence presently at hand is simply not adequate to allow one to decide whether induced decomposition or the competing nonradical decomposition of **1c** is principally responsible for the fact that k_i/k_d is only 0.35, and for this reason any further speculation on this point is unjustified.

The important point to stress is that, whatever the origin of the difference between k_d and k_i, the decomposition of **1c** in nonpolar solvents *does occur to* at least *a sizeable extent via a radical mechanism* and that the products and other aspects of the reaction bear a considerable resemblance to the behavior[3] of the aryl benzenediazo sulfone **1a** under the same conditions. As will be seen in the accompanying paper,[4] the behavior of the aralkyl benzenediazo sulfone $C_6H_5CH_2SO_2N{=}NPh$ is different from that of either **1a** or **1c**.

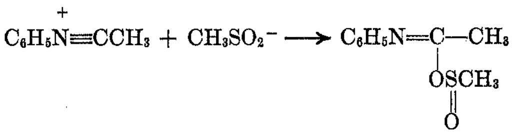
Decomposition of Methyl Benzenediazo Sulfone (1c) in a Polar, Aprotic Solvent, Acetonitrile.—In acetonitrile the decomposition of **1c** takes an entirely different course than it does in nonpolar solvents, and the only organic product which was isolated on chromatographic work-up on alumina was acetanilide (0.71 moles/mole of **1c**).

Ritchie, Saltiel, and Lewis[10] have demonstrated that in the polar solvent methanol aryl benzenediazo sulfones are in equilibrium with the corresponding sulfinate and diazonium ions (eq 9). Since Makarova and Nesmeyanov[11] have found that decomposition of benzenediazonium fluoroborate in acetonitrile also results in the formation of acetanilide, it seems reasonable to suggest the mechanism shown in eq 9–12 for the decomposition of **1c** in acetonitrile. (No specific mechanism is implied for eq 10.)

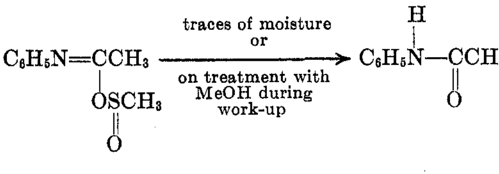


$$C_6H_5N{=}N\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}CH_3 \rightleftarrows C_6H_5N_2^+ + CH_3SO_2^- \qquad (9)$$

$$C_6H_5N_2^+ + CH_3C{\equiv}N \longrightarrow C_6H_5\overset{+}{N}{\equiv}CCH_3 + N_2 \qquad (10)$$

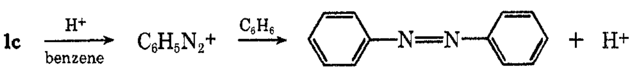


$$C_6H_5\overset{+}{N}{\equiv}CCH_3 + CH_3SO_2^- \longrightarrow C_6H_5N{=}\underset{\underset{\underset{\underset{O}{\|}}{OSCH_3}}{|}}{C}{-}CH_3 \qquad (11)$$



$$\underset{\underset{\underset{\underset{O}{\|}}{OSCH_3}}{|}}{C_6H_5N{=}CCH_3} \xrightarrow[\text{on treatment with MeOH during work-up}]{\text{traces of moisture or}} C_6H_5\overset{\overset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}CH_3 \qquad (12)$$

Table I shows that decomposition of **1c** in the absence of suspended CaO in benzene, conditions where presumably part of the decomposition involves an acid-catalyzed pathway, gave an appreciable amount of azobenzene, while practically no azobenzene was formed in the presence of suspended calcium oxide in that solvent. Given the results in acetonitrile, we speculate that the acid-catalyzed decomposition in benzene may also lead to the formation of the benzenediazonium ion from **1c**, and that this then reacts with the solvent to give azobenzene, *i.e.*



Experimental Section

Synthesis of 1c.—Benzenediazonium fluoroborate (3.64 g, 19.1 mmol) in 50 ml of water was added dropwise to a stirred cold solution of sodium methanesulfinate (2.42 g, 19.1 mmol) in 40 ml of water. The solution was stirred in the ice bath for an additional 15 min. The crystals which had formed were filtered off and washed with 100 ml of cold water. The yellow crystals of the diazo sulfone were dissolved in 30 ml of warm benzene, and the solution was filtered through anhydrous magnesium sulfate. Two volumes of hexane were added slowly to the benzene solution, and the solution was placed in the refrigerator overnight. The yellow needles of the diazo sulfone were filtered off, washed with cold hexane, and dried, giving 1.60 g (46%) of methyl benzenediazo sulfone (**1c**), mp 73–74.5° (lit.[12] mp 70–71°).

Purification of Solvents.—Reagent-grade benzene and cumene were refluxed over lithium aluminum hydride and then fractionally distilled through a 60-cm, glass helices packed column. Diphenylmethane was fractionally distilled twice under vacuum through a 40-cm Nester–Faust spinning-band column. Reagent grade acetonitrile was refluxed over calcium oxide for 24 hr, then fractionally distilled through a 60-cm, glass helices packed column. The distillate was then refluxed over and distilled from phosphorus pentoxide through the same column.

Thermal Decomposition of 1c. Product Studies.—The decompositions were carried out in an apparatus of the type previously described by Kice, Parham, and Simons.[13] The desired amount of diazo sulfone was placed in the decomposition flask, the solvent was pipetted in, and the vessel was covered with aluminum foil to prevent any photodecomposition of the diazo sulfone. The solution was then deaerated by passing a stream of nitrogen through it for 1 hr at room temperature, after which the vessel was immersed in a bath kept at 80° and left there until decomposition was complete. A slow stream of nitrogen was passed through the solution during the decomposi-

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[10] C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961).

[11] L. G. Makarova and A. N. Nesmeyanov, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 1019 (1954); *Chem. Abstr.*, **50**, 241a (1965).

[12] P. K. Dutt, *J. Chem. Soc.*, **125**, 1463 (1924).

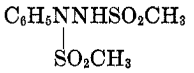
[13] J. L. Kice, F. M. Parham, and R. M. Simons, *J. Amer. Chem. Soc.*, **82**, 834 (1960).

tion in order to remove sulfur dioxide as it was formed and the nitrogen stream was subsequently passed through a trap containing standard iodine solution where the sulfur dioxide was absorbed.

Decomposition in Benzene.—To the final solution from the decomposition was added 1.5 times its volume of hexane, the mixture was cooled, and the crystals which formed were filtered off. The crystals were dissolved in benzene, treated with decolorizing charcoal, and filtered hot, and the benzene was removed under reduced pressure. Recrystallization of the residue from benzene–hexane gave light tan crystals, mp 155–156°. The spectral properties of the substance are consistent with either of the two possible bis(methanesulfonyl)phenylhydrazines (**4a** and **4b**).

$C_6H_5NHN(SO_2CH_3)_2$

4a



$C_6H_5\underset{SO_2CH_3}{\underset{|}{N}}NHSO_2CH_3$

4b

Anal. Calcd for $C_8H_{12}N_2O_4S_2$: C, 36.35; H, 4.58; N, 10.60; mol wt, 264. Found: C, 36.57; H, 4.49; N, 10.68; mol wt, 267 ± 3.

The hexane–benzene filtrate was evaporated down under reduced pressure and the tarry residue was chromatographed on alumina. Elution with pure hexane gave a mixture of biphenyl and azobenzene. The amount of azobenzene was determined by dissolving this mixture in 95% ethanol, measuring the optical density at 315 mμ, and calculating the amount of azobenzene present from the known extinction coefficient of azobenzene at this wavelength.[14] The rest of the fraction was assumed to consist of biphenyl. Recrystallization of a portion of the fraction gave a pure sample of biphenyl, mp 69–71°, mixture melting point undepressed on admixture with a known sample.

Elution with 2:1 ether–methanol gave phenyl methanesulfonate, identified by its melting point, 60–61°, and its mixture melting point with a known sample.[15] The infrared spectra of the material isolated from the decomposition and the known sample were also identical.

Decomposition in Benzene with Suspended Calcium Oxide.—In the decomposition of **1c** in the presence of suspended calcium oxide (1.8 mol/mol **1c**) the final solution after the decomposition was complete was filtered, and the calcium salts on the filter were washed with small portions of benzene until colorless. After being dried overnight at room temperature, the calcium salts were dissolved in the minimum amount of dilute hydrochloric acid, and the pH of the solution was adjusted to 6 by the addition of sodium bicarbonate solution. The solution was then cooled in an ice bath and aqueous benzenediazonium fluoroborate was added. A yellow solution resulted, but there was no precipitate of **1c**, indicating that there could not have been very much calcium methanesulfinate in the recovered calcium salts.

The benzene filtrate was evaporated down and the residue was chromatographed on alumina. Elution with hexane gave biphenyl, this time free from any azobenzene, the latter being eluted with 80:20 hexane–benzene. Elution with 50:50 hexane–benzene gave a small amount of a product tentatively identified as *p*-phenylazobenzene on the basis of its infrared spectrum and melting point, 148–150° (lit.[16] mp 154–155°). No phenyl methanesulfonate was found on elution of the column with ether–methanol.

Decomposition in Cumene.—After the decomposition was complete, an aliquot of the reaction mixture was withdrawn and subjected to glpc on a 15-ft XF-1150 (15% on firebrick) column. The chromatogram showed two peaks with retention times identical with the retention times of known samples of benzene and cumene.

The remainder of the final solution was carefully fractionally distilled under vacuum to remove cumene and other volatiles. The tarry residue was chromatographed on alumina. Elution with hexane gave white crystals, whose infrared spectrum indicated that they were bicumyl (2,3-dimethyl-2,3-diphenylbutane), mp 117–118° (lit.[17] mp 119–120°). Elution with 2:1 ether–methanol gave some phenyl methanesulfonate.

Decomposition in Diphenylmethane.—At the end of the decomposition an aliquot was withdrawn and subjected to glpc in the same manner as for the decomposition in cumene. The chromatogram showed two peaks with retention times identical with those of known samples of benzene and diphenylmethane.

The remaining solution was carefully fractionally distilled under reduced pressure to remove the solvent and other volatiles and the tarry residue was chromatographed on alumina. Elution with hexane gave *o*-phenyldiphenylmethane, mp 55–56° (lit.[18] mp 54–56°). Elution with 95:5 hexane–benzene gave *p*-phenyldiphenylmethane, mp 85–86°, identified by infrared and mixture melting point comparison with a known sample.[19] Elution with 80:20 hexane–benzene gave *sym*-tetraphenylethane, mp 210–212°, identical in all respects with a known sample.[13] Elution with 80:20 benzene–ether afforded benzhydryl methyl sulfone (**3**), mp 129–133°, identical in all respects with a synthetic sample.[20]

Decomposition in Acetonitrile.—After decomposition was complete an aliquot of the solution was removed and subjected to glpc. No benzene was present.

The remaining solution was evaporated under reduced pressure to remove the acetonitrile and the residue was dissolved in a small amount of methanol. Alumina was added to the methanol solution, and the methanol was then evaporated. The coated alumina was placed on the top of a regular alumina chromatographic column and then the column was eluted with various solvents and solvent mixtures. Elution with 80:20 benzene–ether afforded acetanilide, mp 112–113°, identified by spectral and mixture melting point comparison with a known sample.

Kinetic Study of the Decomposition of 1c.—The same apparatus and procedure used for the product studies was employed. The rate of evolution of sulfur dioxide was followed in the manner described by Kice, Parham, and Simons.[13]

Rate of Free-Radical Production in the Decomposition of 1c.—The Koelsch radical **2** was prepared by the method used by Koelsch,[7] with two slight modifications: (1) 9-benzylidenefluorene was prepared by the improved procedure described by Kice,[21] and (2) α,γ-bis(diphenylene)-β-phenylallyl alcohol was prepared by the method used by Nelsen and Bartlett.[22] The crude radical was recrystallized from 95% ethanol, giving lustrous green plates, mp 186–188°. The visible spectrum in benzene showed a λ_{max} at 489 mμ (ϵ 2.71 × 10^4).

The rate at which **1c** decomposed to give radicals scavenged by **2** was measured by the method of Bartlett and Funahashi[5c] in a self-contained reaction cell of the type described by Kice and Pawlowski.[23] In a typical run 2.0 ml of a solution of **2** in benzene was placed in compartment B of the apparatus, and 2.0 ml of a solution of **1c** in benzene was placed in compartment A. The apparatus was connected to the vacuum line through D. The solutions in the two compartments were frozen, and the system was degassed in the usual way three times. After the third freeze–pump–thaw cycle, *ca* 400 mm of nitrogen pressure was introduced into the cell and the system was closed and disconnected from the vacuum system. The solutions in A and B were then mixed together and the resulting final solution was poured into cell C. The absorbance of the solution in C was then measured at 489 mμ. Cell C was then immersed in a thermostated oil bath and withdrawn after a suitable period of time. It was quickly cooled to room temperature, any bath oil was carefully rinsed off the outside of the cell, and the absorbance at 489 mμ was remeasured. Care was taken to ensure that cell C was always at the same temperature when the absorbance measurements were made. The process was repeated a number of times until the Koelsch radical had been consumed. In the absence of **1c** the Koelsch radical is indefinitely stable in benzene under the conditions employed.

Registry No.—**1c**, 23265-32-9.

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[14] R. M. Silverstein and G. C. Bassler, "Spectrophotometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 177.

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[16] W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

[17] A. Klages, *Chem. Ber.*, **35**, 2633 (1902).

[18] J. P. Freeman, *J. Amer. Chem. Soc.*, **80**, 1926 (1958).

[19] V. S. Etlis and G. A. Razuvaev, *Zh. Obshch. Khim.*, **38**, 1225 (1958).

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[21] J. L. Kice, *ibid.*, **80**, 348 (1958).

[22] S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

[23] J. L. Kice and N. E. Pawlowski, *ibid.*, **86**, 4898 (1964).