addition to methylacetylene is slightly higher than that for addition to propylene, the activation energy for the dissociation of radical II ($E_{k_{-2}}$) should be at least 3 kcal/mole greater than the corresponding $E_{k_{-1}}$. Furthermore, radical II, being a vinylic radical, is more reactive than the secondary radical I and thus it is expected that $k_{d_2} > k_{d_1}$. Both conditions require that the rato M_1/M_2 would increase with the increase of the disulfide concentration. This was indeed observed.

In conclusion, the synthetic utility of the free radical addition of disulfides to acetylenes does not derive from any greater reactivity of acetylenes, but rather from the limited reversibility of the initial addition step and the greater reactivity of the vinyl radical intermediate.

Experimental Section

General Procedure for the Addition of Disulfides to Acetylenes.—In a typical experimental run, a mixture of disulfide (0.3 mole) and acetylene (0.1 mole) was transferred into a quartz ampoule fitted with a ground joint. The mixture was flushed with nitrogen then connected to a vacuum line, cooled to −78°, evacuated to remove traces of oxygen, and the sealed while on the vacuum line. When methylacetylene was used, the exact volume was condensed while the ampoule was connected to the vacuum line. Each ampoule was placed in a constant-temperature water bath (20 ± 2°) and irradiated with ultraviolet light from a Hanovia ultraviolet 200-w lamp. When *t*-butyl peroxide was used as initiator, the reaction mixture was sealed in a thick-walled Pyrex ampoule and heated in a constant-temperature oil bath at 120 ± 2°. In most runs the reaction was carried out for 24 hr. The reaction mixture was distilled and the different fractions were analyzed by gas chromatography using a 10-ft column of 10% Carbowax (20M) on Chromosorb P. Helium was used as a carrier gas and a temperature increase of 11°/min was programmed over the range of 80–225°. In all the runs side reactions were negligible. Products corresponding to thiol–acetylene 1:1 adduct were less than 2% and the undistillable residues were less than 10% (by weight) of all the reaction products. The per cent yield of the *cis* and *trans* 1:1 adducts was determined by vpc and the value obtained was found to be consistent with that obtained by nmr analysis of the crude reaction mixture prior to distillation.

Determination of the Relative Reactivity of Propylene and Methylacetylene toward the Addition of Methyl Disulfide.—Each of several solutions of various concentrations of methyl disulfide (1–8 *M*) in benzene was transferred into a quartz ampoule, flushed with nitrogen, cooled at −78°, and evacuated on a vacuum system. Equimolar quantities of propylene and methylacetylene (0.5 *M* each) were condensed and the ampoule was sealed under vacuum. The ampoules were placed in a constant-temperature water bath at 20 ± 2° and irradiated with a 200-w ultraviolet lamp. The runs at each methyl disulfide concentration were carried out in triplicate. The irradiation was continued until about 10% conversion took place (based on the disappearance of methyl disulfide). The radiation time varied from about 4 hr at the higher disulfide concentrations to about 18 hr at the lower concentrations. Each reaction mixture was analyzed by vpc (10-ft Carbowax column) and the ratios of the 1:1 adducts from the addition of methyl disulfide to propylene (M_1) and to methylacetylene (M_2) at various methyl disulfide concentrations were plotted in Figure 1.

Determination of the Reactivity of Propylene and Methylacetylene toward the Addition of Methyl Thiyl Radicals.—Equimolar amounts of propylene and methylacetylene (0.5 *M* each) were mixed with various concentrations of methanethiol in benzene (4, 6, and 7 *M*) applying the above-described technique. The runs at each methanethiol concentration were carried out in duplicate and irradiated with ultraviolet light until the reaction proceeded to about 10% conversion (based on the appearance of the products). The irradiation time varied from 10 to 30 min depending on the concentration of the methanethiol used. The major reaction products were 1-methylthiopropane, 1-methylthiopropene, and small amounts of 1,2-bismethylthiopropane resulting from the addition of two molecules of methanethiol to methylacetylene. The ratio of M_1/M_2 in Figure 1 represents the mole % of methanethiol–propylene 1:1 adduct relative to methanethiol–methylacetylene 1:1 adduct correcting for the fraction of the 1:1 adduct in the 2:1 adduct.

The Effect of Structure on the Rates of Thermal Decomposition of Solid Benzyldimethylsulfonium Salts[1a]

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The rates of thermal decomposition of 22 different benzyldimethylsulfonium salts have been measured. Counterion, substituent, particle size, and temperature effects have been studied. It is concluded that particle size and crystal lattice energy may be as important as chemical structure in determining reaction rates for these salts.

The rates of decomposition of neutral sulfonium salts in solution have been widely studied. In particular it is known that trimethylsulfonium salts undergo a second-order displacement reaction when the anion is a good nucleophile such as halide ion[2] (eq 1),

$$(CH_3)_3SX \longrightarrow (CH_3)_2S + CH_3X \qquad (1)$$

but that the competing, pseudo-first-order solvolysis (eq 2) dominates when the anion is a poor nucleophile, such as arenesulfonate.[3] With benzyldimethylsulfonium compounds the benzyl group is preferentially displaced (eq 3), permitting a systematic study of substituent effects.

$$(CH_3)_3S^+ + H_2O \longrightarrow (CH_3)_2S + CH_3OH + H^+ \qquad (2)$$

$$C_6H_5CH_2S(CH_3)_2X \longrightarrow (CH_3)_2S + C_6H_5CH_2X \qquad (3)$$

These reactions give curved Hammett plots and where hydroxide is the anion the Hammett plot displays a minimum, indicative of a change in mechanism from a process involving bond making to one involving bond breaking.[4] In the interest of learning whether the thermal decomposition of solid sulfonium salts shows the same dependence on the counterion and substituents, we have prepared 22 different benzyldimethylsulfonium salts and have

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[1] (a) Presented in part before the Division of Organic Chemistry of the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967; (b) National Academy of Sciences–National Research Council Senior Visiting Scientist, 1966–1967.

[2] C. G. Swain and L. E. Kaiser, *J. Am. Chem. Soc.*, **80**, 4089 (1958).

[3] (a) E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. Ind.* (London), 1282 (1959); (b) C. G. Swain and W. D. Burrows, unpublished results.

[4] (a) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961); (b) C. G. Swain, T. Rees, and L. J. Taylor, *ibid.*, **28**, 2903 (1963); (c) K. B. J. Schowen, Ph.D. Thesis, Massachusetts Institute of Technology, April, 1964.

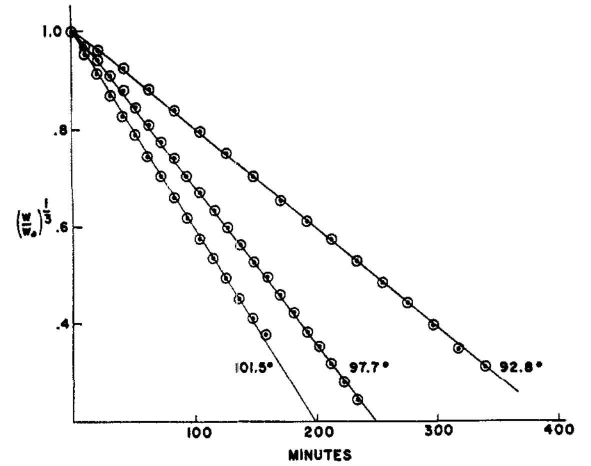


Figure 1.—The pyrolysis of *p*-nitrobenzyldimethylsulfonium bromide.

pyrolyzed them under reduced pressure in a thermogravimetric analyzer at 60–190°.

Kinetics

Insofar as decomposition of a solid is a process in which quantity but not concentration is changing, one would anticipate first-order kinetics regardless of the mechanism involved. The rates we observed vary from first to zero order over-all, but most commonly either first-order or two-thirds-order kinetics are obeyed. The latter is to be expected of reactions wherein the substrate is a diminishing cube or sphere, or a uniform aggregate of cubes or spheres, and decomposition takes place primarily at the surface[5] (eq 4, 5). This is best

$$A \propto w^{2/3} \tag{4}$$

illustrated by the decomposition of *p*-nitrobenzyldimethylsulfonium bromide, for which the cube root of the weight is a linear function of time for more than 95% of the reaction (Figure 1).

$$\frac{dw}{dt} = kw^{2/3} \tag{5}$$

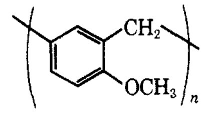
Counterion Effects

In Table I are presented the rates of decomposition of 22 benzyldimethylsulfonium salts relative to the unsubstituted chloride, arbitrarily based on the first half-life of weight loss after thermal equilibrium is established. The counterion effects are normal. As would be expected of reactions in solution, iodides decompose faster than bromides or chlorides and many times faster than methanesulfonates. *p*-Methoxybenzyldimethylsulfonium methanesulfonate decomposes at a rate comparable with that of the chloride, but the product is a glassy polymer for which we propose a linear structure.

TABLE I
RELATIVE RATES OF DECOMPOSITION OF $RC_6H_4CH_2S(CH_3)_2X$ AT 98°

	X			
R	Cl	Br	I	CH_3SO_3
p-CH_3O	2.1[a]	5.5[a]	11[a]	2.3
p-CH_3	2.7	1.6	12	
H	1.0[b]	2.5	3.2	0.03[c]
p-Cl	1.1	2.7	12	
m-NO_2	0.8	1.0	3.6	$<10^{-6}$
p-NO_2	1.6	1.7	6.8	10^{-6} [d]

[a] Rates are relative to *p*-$CH_3C_6H_4CH_2S(CH_3)_2I$ at 70° for the iodide, 90° for the bromide, and 85° for the chloride. [b] Actual first half-life is 109 min. [c] Extrapolated from 107°. [d] Extrapolated from 154°.



Substituent Effects

One might anticipate that substituent effects would also parallel those for reactions in solution, but even in a qualitative sense the discrepancies are substantial. Whether or not one assumes a nonlinear Hammett relation, it would not be expected that the *p*-chloro substituent would be so effective in promoting decomposition of the iodide. Further, the *p*-nitro group has the expected large retarding effect on reaction of the methanesulfonate, but accelerates reaction of the chloride more than the bromide and almost as much as the iodide.

Perhaps the electronic effect of a substituent depends on its orientation and environment within the crystal; or it may be that the principal effect is on the crystal lattice energy. Since sulfonium salt decomposition proceeds with charge destruction, it will be retarded in media of high dielectric constant. It seems likely that, in a system of such high charge density, the electrostatic free energy of activation will be disproportionately large and may depend as much on crystal geometry as on the nature of the substituent.

Effect of Particle Size

The rates in Table I were determined using uniformly pulverized samples, except for the chlorides, which are too hygroscopic to powder effectively in most cases. Pulverizing a sample would be expected to bring about a rate increase by increasing the surface area, but this is not necessarily the case (Table II). Decomposition rates of iodides are increased substantially by pulverizing, as much as 75-fold for the *p*-methyl derivative. Reactions of bromides are accelerated up to sixfold by pulverizing, but the over-all rates of chloride decomposition are nearly unchanged, even starting with large crystals. This is most readily understood in terms of a two-step reaction mechanism. In the first step

TABLE II
RATE RATIO OF PULVERIZED *vs.* UNPULVERIZED SAMPLE OF $RC_6H_4CH_2S(CH_3)_2X$

	X		
R	Cl	Br	I
p-CH_3O		2.3	
p-CH_3			76
H		1.8	1-1.6
p-Cl	1.2	5.7	44
m-NO_2	1	1.2	3.1
p-NO_2	1	1.2	4.6

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[5] Applying the same considerations a needle with square or circular cross section, which diminishes in weight but not in length in the course of reaction, should obey half-order kinetics and a thin wafer should give zero-order kinetics since it decomposes with constant surface area.

(eq 6) the salt is considered to dissociate reversibly to

$$[C_6H_5CH_2S(CH_3)_2X]_{crystal} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [C_6H_5CH_2X + (CH_3)_2S]_{crystal} \quad (6)$$

the benzyl halide or ester and dimethyl sulfide. In the second step (eq 7) the products diffuse irreversibly from

$$[C_6H_5CH_2X + (CH_3)_2S]_{crystal} \xrightarrow{k_2} C_6H_5CH_2X + (CH_3)_2S \quad (7)$$

the crystal lattice. Reformation of the sulfonium salt is more probable for benzyl iodide than for the chloride and diffusion of benzyl chloride is probably faster. Thus pulverizing the crystal greatly increases k_2/k_{-1} for the iodide, but this ratio is not rate limiting for the chloride.[6]

Effect of Added Materials

Addition of an inert material has a moderate effect on the pyrolysis of salts which show a large particle size dependence. Thus a sample of the *p*-methyl iodide pulverized 1:1 with tin oxide disappears at twice the rate of an unadulterated sample. In contrast addition of a stoichiometric quantity of sodium iodide to the highly stable *p*-nitrobenzyldimethylsulfonium methanesulfonate results in decomposition of the organic material at a rate about the same as that of the sulfonium iodide (Figure 2), as would be expected of the same reaction in solution.

Effect of Temperature

Activation energies were determined over a 10° range except for *p*-methylbenzyldimethylsulfonium iodide, which gaves a fairly linear Arrhenius plot over a 30° range (Table III). There certainly is no obvious correlation with structure and, although the actual values are probably not reliable to better than +10%, the large differences in activation energies give warning that conclusions based on relative rates of decomposition at 98° may have to be modified at much higher or lower temperatures. The limited number of cases we have studied suggest that pulverizing a sample significantly reduces the activation energy for decomposition of iodides but not bromides.

TABLE III

ACTIVATION ENERGIES FOR DECOMPOSITION OF $RC_6H_4CH_2S(CH_3)_2X$, (KILOCALORIES PER MOLE)

	X			
R	Cl	Br	I	CH_3SO_3
p-CH_3O	34	52	35	
p-CH_3	25	24	21	
H	34	48 (42)[a]	28 (52)[a]	35
p-Cl	25	48	23	
m-NO_2	36	26	27	
p-NO_2	37	26 (28)[a]	22 (41)[a]	55

[a] Values in parentheses are for unpulverized samples.

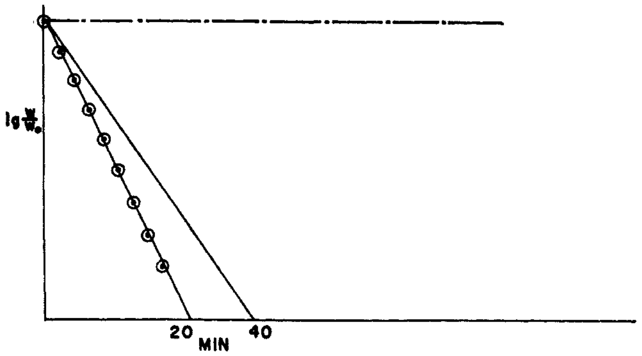

Figure 2.—The pyrolyses of *p*-nitrobenzyldimethylsulfonium methanesulfonate (— - —), *p*-nitrobenzyldimethylsulfonium iodide (———), and *p*-nitrobenzyldimethylsulfonium methanesulfonate with added sodium iodide (⊙—⊙—), all at 112°.

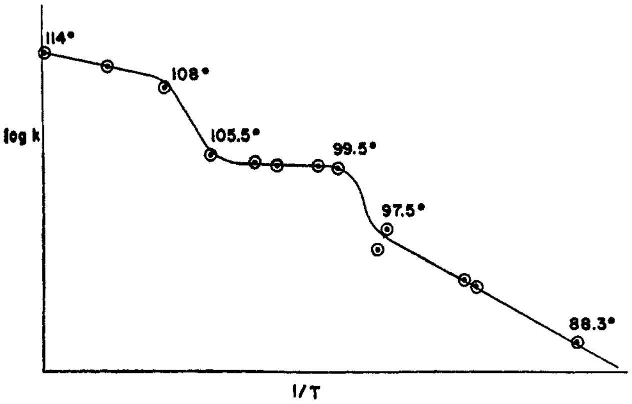

Figure 3.—Arrhenius plot for the pyrolysis of benzyldimethylsulfonium bromide.

Pyrolysis rates increase sharply as the melting point is approached, indicating again the importance of lattice energy. A few salts decompose much faster at atmospheric presuure than under vacuum, apparently because accumulation of products depresses the melting point. The effect of temperature on the rate of decomposition of the unsubstituted bromide extending well above its melting point is illustrated in Figure 3. The plot is initially linear, then there is a rapid increase in rate as the melting point is approached, and at higher temperatures the plot is again linear. We are unable to explain the plateau in the middle of the curve other than to suggest that our system is not in thermal equilibrium and that the thermocouple is not measuring the temperature of the sample. Decomposition is quite rapid in this region and it may be that evaporation of the products is cooling the sample. Anyway, throughout most of the reaction there is still some solid present as much as 5° above the normal (atmospheric) melting point.

Products

Decomposition of an unpulverized sample of benzyldimethylsulfonium iodide leaves a considerable residue (as much as 5%) of trimethylsulfonium iodide. Thus displacement at the methyl carbon forms methyl iodide

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[6] One might reasonably ask why, since it so closely obeys two-thirds-order kinetics, the decomposition of *p*-nitrobenzyldimethylsulfonium bromide is so little accelerated by pulverizing. One possible answer is that decomposition does not take place exclusively at the surface, but can be initiated within the crystal, perhaps at defects. Another is that large crystals may be unstable at the decomposition temperatures. We have frequently observed an induction period in the pyrolysis of unpulverized salts, apparently corresponding to the break-up of larger crystals. This shattering process, which can be quite vigorous, is most noticeable for chlorides and bromides. For this reason, and in the absence of information on the particle size distribution, we would advise caution in interpreting the kinetic behavior of this and any solid-state decomposition process.

(eq 8) which reacts with dimethyl sulfide formed by normal displacement. If the starting iodide is pulverized

$$C_6H_5CH_2S(CH_3)_2I \dashrightarrow C_6H_5CH_2SCH_3 + CH_3I \quad (8)$$

before pyrolysis, the residence time of methyl iodide in the crystal lattice is greatly reduced and almost no trimethylsulfonium iodide is formed. Complete product analyses show that the statistically adjusted ratio of benzyl to methyl displacement varies from 6 to 1 for nitro derivatives to more than 100 to 1 for methoxy derivatives (Table IV), somewhat lower on the average than obtained by Taylor for reactions in solution.[7] Taylor was able to show that most of the benzyl methyl sulfide he isolated was produced by displacement of a methyl group from the sulfonium salt by dimethyl sulfide (eq 9). However, this reaction is not important

$$ArCH_2S(CH_3)_2^+ + (CH_3)_2S \dashrightarrow ArCH_2SCH_3 + (CH_3)_3S^+ \quad (9)$$

for the pyrolysis of solid benzyldimethylsulfonium salts since pulverizing the sample does not substantially alter the ratio of benzyl to methyl displacement, even in the case where pulverizing brings about a 75-fold rate increase.

TABLE IV

RATIO[a] OF BENZYL TO METHYL DISPLACEMENT FOR $RC_6H_4CH_2S(CH_3)_2X$

	X			
R	Cl	Br	I	CH_3SO_3
p-CH_3O	20	65	130	
p-CH_3		15	25 (20)[b]	
H	13	14	11	13–25[c]
p-Cl	15	13	17	
m-NO_2	7	6	8	
p-NO_2		7	8	

[a] Statistically adjusted. [b] Value for unpulverized sample in parentheses. [c] Product mostly polymeric.

TABLE V

PROPERTIES OF BENZYLDIMETHYLSULFONIUM SALTS

			Calcd, %			Found, %		
Compound	Mp,[a] °C (lit.[b])	Solvent	C	H	N	C	H	N
$C_6H_5CH_2S(CH_3)_2Cl \cdot {}^1/_2H_2O$[c]	105–110	2-Propanol–ether	54.59	7.14		54.50	7.48	
$C_6H_5CH_2S(CH_3)_2Br$	99–100 (99–99.5)	Ethanol–ether	46.36	5.62		46.50	5.80	
$C_6H_5CH_2S(CH_3)_2I$	102–104	2-Propanol–ether	38.58	4.68		38.70	4.73	
$C_6H_5CH_2S(CH_3)_2O_3SCH_3$	124–126	2-Propanol–ether	48.34	6.50		48.60	6.50	
p-$CH_3C_6H_4CH_2S(CH_3)_2Cl$[c]	109–110	2-Propanol–ether	59.24	7.46		58.90	7.46	
p-$CH_3C_6H_4CH_2S(CH_3)_2Br$	115–116 (109–110)	2-Propanol–ether	48.58	6.12		48.80	6.48	
p-$CH_3C_6H_4CH_2S(CH_3)_2I$	127–129	Methanol–ether	40.82	5.14		41.08	5.17	
p-$ClC_6H_4CH_2S(CH_3)_2Cl$	115–117	2-Propanol–ether	48.44	5.42		48.20	5.72	
p-$ClC_6H_4CH_2S(CH_3)_2Br$	124–125 (124)	2-Propanol–ether	40.39	4.52		40.45	4.67	
p-$ClC_6H_4CH_2S(CH_3)_2I$	127–129	Methanol–ether	34.36	3.85		34.38	3.89	
p-$CH_3OC_6H_4CH_2S(CH_3)_2Cl \cdot {}^1/_4H_2O$[c]	88–90 (93–95)	*t*-Butyl alcohol–ether	53.80	7.00		54.00	7.25	
p-$CH_3OC_6H_4CH_2S(CH_3)_2Br$	93–95	2-Propanol–ether	45.63	5.74		45.43	5.74	
p-$CH_3OC_6H_4CH_2S(CH_3)_2I$	74–77	Acetone–ether	38.72	4.86		38.70	5.05	
p-$CH_3OC_6H_4CH_2S(CH_3)_2O_3SCH_3$	105–108	2-Propanol–ether	47.46	6.52		47.50	6.66	
p-$NO_2C_6H_4CH_2S(CH_3)_2Cl$	131–132	2-Propanol–ether	46.25	5.18	5.99	45.95	5.00	5.95
p-$NO_2C_6H_4CH_2S(CH_3)_2Br$	114–116 (112–113)	Methanol–ether	38.86	4.35	5.04	39.00	4.60	4.87
p-$NO_2C_6H_4CH_2S(CH_3)_2I$	112–114	Methanol–ether	33.24	3.72	4.31	33.40	3.36	4.30
p-$NO_2C_6H_4CH_2S(CH_3)_2O_3SCH_3$	192–193	2-Propanol–ether	40.92	5.16	4.78	41.10	5.42	5.18
m-$NO_2C_6H_4CH_2S(CH_3)_2Cl$	138–140	2-Propanol–ether	46.25	5.18	5.99	45.95	5.38	5.99
m-$NO_2C_6H_4CH_2S(CH_3)_2Br$	130–132 (137–138)	Methanol–ether	38.86	4.35	5.04	38.80	4.50	5.04
m-$NO_2C_6H_4CH_2S(CH_3)_2I$	120–122	Methanol–ether	33.24	3.72	4.31	33.30	3.80	4.32
m-$NO_2C_6H_4CH_2S(CH_3)_2O_3SCH_3$	116–118	2-Propanol–ether	40.92	5.16	4.78	40.80	5.26	4.72

[a] Corrected. Vigorous decomposition accompanied melting for all salts except the *m*-nitro methanesulfonate. [b] P. Mamalis, *J. Chem. Soc.*, 4747 (1960). [c] Hygroscopic.

Experimental Section

Preparation of Sulfonium Salts.—Sulfonium bromides were prepared by treating the corresponding benzyl bromide with excess dimethyl sulfide for 12–72 hr at 25°. (To prepare the *p*-chloro derivatives, *p*-chlorobenzyl chloride was treated with dimethyl sulfide for 4 weeks.) To obtain salts with other anions, the sulfonium hydroxide, prepared by treating an aqueous solution of the bromide with silver oxide, was added to a stoichiometric solution of the appropriate acid and lyophilized. Properties of the salts are listed in Table V. Benzyl halides were commercial preparations except for *p*-methoxybenzyl bromide, which was prepared from the alcohol.[8]

Rate Studies.—A sample of sulfonium salt (10–15 mg, recrystallized to analytical purity) was placed in the platinum pan of a DuPont Model 900 thermogravimetric analyzer and evacuated to 0.1–0.5 mm. The sample oven was heated and measurements were begun after the temperature had stabilized at the desired value and 20–40% of the initial sample had decomposed. At the end of the run the remaining sample was heated above its melting point for several minutes in order to complete pyrolysis and obtain the infinite time weight. Rates were reproducible to ±10%. In the case of the unsubstituted bromide, at least, further recrystallization did not substantially alter the rate of decomposition.

Samples were pulverized in a Wig-L-Bug (dental amalgam mixer) for 30 sec, since it was established that the rate of decomposition of *p*-methylbenzyldimethylsulfonium iodide (most dependent on particle size) reaches its maximum with this amount of pulverizing.

Product Analyses.—A 0.5–1.0-g sample of salt was pyrolyzed below its melting point at reduced pressure in a micro distillation apparatus, the receiver of which contained 5–10 ml of 5% sodium methoxide in methanol, chilled in Dry Ice-acetone. When decomposition was complete, the receiver was removed and heated under reflux for 1 hr. Water was then added and the sample was extracted with ether. The ratio of benzyl methyl sulfide to benzyl methyl ether in the product was established by vapor phase chromatography. A 6 ft × 0.25 in. column, GE SE-30 10% on Chromosorb W, was used. For the *p*-nitro compounds sodium methoxide could not be used because of the rapid formation of colored materials; for these salts the pyrolysis products were heated to reflux in methanol for 10 hr and the solvolysis

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[7] L. J. Taylor, Ph.D. Thesis, Massachusetts Institute of Technology, Feb 1963, p 63.

[8] A. Lapworth and J. B. Shoesmith, *J. Chem. Soc.*, **121**, 1397 (1922).

products (containing some benzyl halide) were analyzed as before.

Registry No.—$RC_6H_4CH_2S(CH_3)_2X$: R = p-CH_3O, X = Cl, 14181-51-2; R = p-CH_3O, X = Br, 14181-52-3; R = p-CH_3O, X = I, 14181-53-4; R = p-CH_3O, X = CH_3SO_3, 14264-68-7; R = p-CH_3, X = Cl, 14182-11-7; R = p-CH_3, X = Br, 14182-12-8; R = p-CH_3, X = I, 14182-13-9; R = H, X = Cl, 14182-14-0; R = H, X = Br, 14182-15-1; R = H, X = I, 14182-82-2; R = H, X = CH_3SO_3, 14182-17-3; R = p-Cl, X = Cl, 14182-18-4; R = p-Cl, X = Br, 14182-19-5; R = p-Cl, X = I, 14182-20-8; R = m-NO_2, X = Cl, 14182-21-9; R = m-NO_2, X = Br, 14182-22-0; R = m-NO_2, X = I, 14182-23-1; R = m-NO_2, X = CH_3SO_3, 14182-24-2; R = p-NO_2, X = Cl, 14182-25-3; R = p-NO_2, X = Br, 14182-26-4; R = p-NO_2, X = I, 14182-27-5; R = p-NO_2, X = CH_3SO_3, 14182-28-6.

The Mechanism of the Copper-Induced Pschorr Cyclization. A New Phenol Synthesis Involving Hydroxylation of the Intermediate Radical by Cupric Ion[1]

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The copper-catalyzed decomposition of aryl diazonium salts at low temperatures has been shown to yield an aryl radical and has been utilized to effect essentially unidirectional (a) Pschorr cyclizations, (b) hydroxylations, and (c) reductions. Excellent yields of the following products are obtained when the cuprous oxide catalyzed decompositions of 2-diazobenzophenone tetrafluoroborate are carried out under the conditions specified: (a) fluorenone, in dilute aqueous acid; (b) 2-hydroxybenzophenone, in dilute acid in the presence of a large excess of aquated cupric ion; and (c) benzophenone, in dioxane. Analogous results are obtained in decompositions of 2-(o-diazobenzoyl)naphthalene tetrafluoroborate; α-ring closure to give benzo[c]fluorenone exceeds β-ring closure to give benzo[b]fluorenone in a 9:1 ratio at low temperatures. These results are discussed in terms of the mechanism of the copper-catalyzed reaction which, contrary to suggestions in the literature, does not involve a cationic component. The oxidation by cupric ions of aryl radicals generated by diazonium ion decomposition constitutes a promising new method for the introduction of hydroxyl groups into aromatic nuclei. This method leads to high yields of phenols and no "diazo resins" which accompany the thermal production of phenols from diazonium salts. Phenols which could not be previously prepared from the corresponding amines are accessible by this new procedure. Evidence is presented that this reaction does not involve a phenyl cation intermediate but instead proceeds by transfer of $H_2O^{+\cdot}$ from the hydration shell of the cupric ion to the aryl radical (ligand radical transfer).

Among reactions of aromatic diazonium salts,[2] Pschorr cyclizations[3,4] (for example, **1** → **5** and **8** → **9** + **10**) are perhaps the most enigmatic. They are plagued with side reactions such as reduction which produces arenes, reductive coupling which yields symmetrical biaryls and azoarenes, halogenation, and phenol formation.[2,3] Furthermore, a survey of the very considerable literature on the subject helps very little in allowing a prediction as to the best reaction conditions for a given case. In fact, Pschorr cyclizations have been attempted under a wide variety of conditions: the diazonium salt is sometimes suspended in the medium, but more often it is in a solution which is usually acidic (basic solutions have also been used); the reaction is conducted in the presence or absence of catalysts, usually copper metal, but sometimes other copper compounds are used; the temperature is usually 50° or higher but there are many examples of decomposition at room temperature. In very few, if any, cases have the reaction conditions been chosen on a rational basis; frequently analogies are used but one can almost always find other analogies suggesting different conditions. At present, one of the major dilemmas is whether or not a copper catalyst should be used. In his review, Leake concludes, "In spite of its recorded effectiveness, the usefulness of copper cannot be predicted."[4]

Advances during the last decade in our understanding of the mechanisms of diazonium decomposition, especially with regard to the catalyzed reaction, have now provided the basis for a reevaluation of these problems. It has long been suspected that thermal decomposition of diazonium salts in acidic solution produces phenyl cations and this now appears to be well established, especially when the anion is not a good reducing agent (*e.g.*, fluoroborate and similar ions are the best choices, whereas chloride could cause a radical reaction).[2,3,5–7] On the other hand, decompositions in alkaline solution[8] are radical in character as are those in acid solution which are catalyzed by copper metal or cuprous compounds.[5,7,8b,9–13]

Since intramolecular arylations can be executed in either a radical or an electrophilic fashion, the choice of a radical or cationic decomposition rests with an

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