

Free-Radical Elimination Reactions. The Reaction of Phenyl Radicals with *t*-Butyl Sulfide and Phenyl *t*-Butyl Sulfide¹

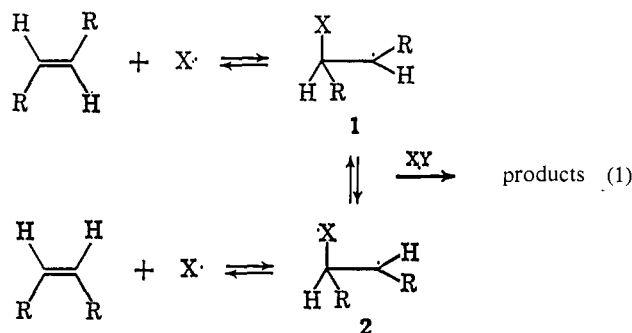
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Abstract: The reaction of phenyl radicals with *t*-butyl sulfide and phenyl *t*-butyl sulfide was carried out by decomposing phenylazotriphenylmethane in dilute solution in the sulfides. Reactions were run in the absence and in the presence of air. In the absence of air, benzene and isobutylene are formed in equivalent amounts, indicating quantitative, nonchain, free-radical elimination reactions. The leaving group in the *t*-butyl sulfide reaction, *t*-butyl thiyl radical, is trapped by radical scavengers in solution. The most important scavenger is triphenylmethyl formed from phenylazotriphenylmethane. The effect of air on the nature and yields of products is discussed in terms of the steady-state concentrations of triphenylmethyl and related radicals. Possible mechanisms for the elimination reactions are discussed. A simple rate-determining hydrogen abstraction followed by a rapid β elimination of thiyl radical is ruled out for *t*-butyl sulfide. Phenyl radical is shown to react at the *para*-position of triphenylmethyl at least three to four times more readily than at the central atom. This *para* coupling of phenyl and triphenylmethyl accounts for several unusual aspects of phenylazotriphenylmethane decompositions.

Ionic and cyclic multicenter elimination reactions have been studied in detail and the general features of these reactions are well understood.³ The existence of free-radical elimination reactions in solution is generally recognized, but systematic studies of olefin-forming processes have not been reported. This paper presents our observations on two simple elimination reactions, the reactions of phenyl radicals with *t*-butyl sulfide and phenyl *t*-butyl sulfide.

The isomerization of olefins by radicals is usually explained by an addition-rotation-elimination sequence⁴ (eq 1). Only certain radicals catalyze *cis-trans* interconversion under mild conditions; those found to be particularly effective are iodine and bromine atoms and thiyl radicals. Noyes and co-workers



demonstrated that halogen exchange accompanies the isomerization of dibromo- and diiodoethylenes by bromine and iodine atoms.^{5,6} The reversibility of thiyl radical additions to olefins is especially relevant to this

work and has been studied by Walling⁷ and Sivertz.⁸ In particular, Walling and Helmreich concluded that the rate constants for elimination from the intermediate radicals (1 and 2, R = CH₃, X = SCH₃) are 80 times (1) and 20 times (2) greater than the rate constant for the chain-transfer step with methyl mercaptan (XY). The reversibility of the addition of radicals to olefins has been studied in detail in the gas phase.⁹

Many radical reactions have been rationalized in terms of elimination of a substituent β to a free-radical center.¹⁰ Halogen atoms are the most common leaving groups; a recent example is the formation of significant amounts of *trans*-1,2-dichlorocyclopentane in the photochlorination of bromocyclopentane at 40°. ¹¹ Enol thioethers are formed by the reaction of *t*-butoxy radicals with dithioacetals.¹² If sufficiently provoked, alkyl substituents seem to be satisfactory leaving groups. Thus, the addition of carbon tetrachloride to β -pinene gives a ring-opened product.^{13,14} The elimination is apparently not concerted with the initial attack on the double bond since the addition of thiolacetic acid to β -pinene gives only normal products¹⁵ (*i.e.*, no ring opening). Similar results have recently been reported for radical additions to vinylcyclopropanes.¹⁶ Many pyrolytic decompositions have been studied in detail and appear to involve radical elimination steps.¹⁷⁻²¹

(1) Abstracted from the Ph.D. Thesis of R. P. Geer, and the M.S. Thesis of A. J. Meskin, University of Rochester, 1964.

(2) Esso Fellow, 1962-1963.

(3) Recent reviews are (a) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963; (b) W. H. Saunders, Jr., and A. Maccoll, Chapters 2 and 3, respectively, in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964; (c) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962); (d) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 302, 322.

(5) H. Steinmetz and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 4141 (1952).

(6) R. M. Noyes, R. G. Dickenson, and V. Schomaker, *ibid.*, **67**, 1319 (1945).

(7) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).

(8) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959), and earlier papers.

(9) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

(10) C. Walling, "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 7.

(11) G. A. Russell and A. Ito, *J. Am. Chem. Soc.*, **85**, 2983 (1963).

(12) A. B. Terent'ev and R. G. Petrova, *Bull. Acad. Sci. USSR Div. Chem. Sci. (English Transl.)*, 1984 (1963), and previous papers.

(13) D. M. Oldroyd, G. S. Fisher, and L. A. Goldblatt, *J. Am. Chem. Soc.*, **72**, 2407 (1950).

(14) G. Dupont, R. Dulous, and G. Clement, *Compt. Rend.*, **236**, 2512 (1953), and earlier references.

(15) F. G. Bordwell and A. W. Hewett, *J. Am. Chem. Soc.*, **79**, 2493 (1957).

(16) E. S. Huyser and L. R. Munson, *J. Org. Chem.*, **30**, 1437 (1965).

(17) D. H. R. Barton, A. J. Head, and R. J. Williams, *J. Chem. Soc.*, 352 (1952), and previous papers.

(18) A. Maccoll and P. J. Thomas, *ibid.*, 5033 (1957).

(19) S. W. Benson, *J. Chem. Phys.*, **38**, 1945 (1963).

(20) R. Simha, L. A. Wall, and P. J. Blatz, *J. Polymer Sci.*, **5**, 615 (1950).

Table I. Products of the Reaction of Phenyl Radicals with *t*-Butyl Sulfide

Conditions	Moles of product/mole of PAT ^a			
	Benzene	Isobutylene	<i>t</i> -Butylthiol	<i>t</i> -Butyl disulfide
Degassed	0.54 ± 0.04	0.56 ± 0.06	<0.001 ^b	Trace <0.03 ^b
Air	0.56 ± 0.06	0.73 ± 0.06	0.14 ± 0.06	0.14 ± 0.04

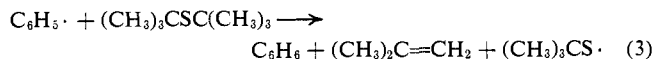
^a Reproducibility of measurements indicated as standard deviation. ^b Limit of detectability.

There is ample evidence, therefore, for a β -elimination reaction as a fundamental type of free-radical process. In many of the cases cited above, the elimination is in competition with an abstraction reaction. Such competition implicates an intermediate; these fragmentations are therefore best described as two-step eliminations. Very few of the results concerning elimination reactions in solution require a concerted formulation.²²

Because of the complicated, and often circumstantial, nature of much of the evidence, we sought a simple, free-radical elimination reaction which would be suitable for detailed study. The reaction of phenyl radicals with *t*-butyl sulfide was chosen for a number of reasons. Phenyl radicals are conveniently²³⁻²⁵ and efficiently²⁶ obtained by the thermal decomposition of phenylazotriphenylmethane (PAT) at moderate temperatures (eq 2). *t*-Butyl sulfide presents only two



possibilities for reaction, abstraction of one of the 18 equivalent β hydrogens or attack on the sulfur atom. Thiyl radicals efficiently isomerize olefins^{7,8} and, therefore, are good radical leaving groups. The expected stoichiometry of an elimination reaction initiated by the attack of a phenyl radical on one of the β hydrogens of *t*-butyl sulfide is indicated in eq 3. Benzene and iso-



butylene are the atom abstraction and olefinic fragments of the elimination reaction. *t*-Butylthiyl radical is the leaving group and might simply dimerize. Finally, the form of the reaction permits changes in the alkyl group, the leaving group, and the attacking radical. Premeditated variation of these parameters should lead to information about the detailed mechanism of free-radical elimination reactions.

Results

The reaction of phenyl radicals with *t*-butyl sulfide was accomplished by the thermal decomposition of phenylazotriphenylmethane in dilute solution ($4-5 \times 10^{-2} M$) in *t*-butyl sulfide. The reactions were carried out in sealed tubes at 76-79° for 2-3 hr. Some tubes were thoroughly degassed before being sealed, others were sealed in the presence of air. The yields of isobutylene, benzene, *t*-butylthiol, and *t*-butyl disulfide were determined by vpc using internal standard methods.

(21) N. Grassie and H. W. Melville, *Proc. Roy. Soc. (London)*, **199**, 14, 24, 29 (1949).

(22) S. W. Benson, D. M. Golden, and K. W. Egger, *J. Chem. Phys.*, **42**, 4265 (1965).

(23) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946, p 146 ff.

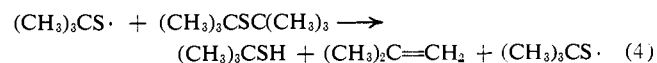
(24) H. Wieland, E. Popper, and H. Seefried, *Ber.*, **55**, 1816 (1922).

(25) R. Huisgen and J. Nakaten, *Ann.*, **586**, 70 (1954).

(26) J. F. Garst and R. S. Cole, *Tetrahedron Letters*, 679 (1963).

The average results of many runs are shown in Table I. *t*-Butyl sulfide is stable under the reaction conditions in the absence of PAT. The decomposition of PAT is known to give small amounts of benzene in the absence of any hydrogen source other than PAT.²⁶⁻²⁸ The amount of benzene usually produced in this manner is small (<0.05 mole/mole PAT). Since the decomposition of PAT gives triphenylmethyl radicals (eq 2), their reactivity toward *t*-butyl sulfide was tested. A solution of triphenylmethyl in benzene was prepared by the reaction of triphenylmethyl chloride with mercury²⁹ and introduced into a reaction tube containing *t*-butyl sulfide. The solution was heated for 4 hr at 76-79°. Small amounts of isobutylene (ca. 0.07 mole/mole of triphenylmethyl chloride) were detected. Therefore, the amount of isobutylene which might arise by reaction of triphenylmethyl with *t*-butyl sulfide is of the order of the uncertainty in our measurements. The preceding arguments clearly indicate that the products described in Table I are the result of the reaction of phenyl radicals with *t*-butyl sulfide.

In degassed tubes, the benzene and isobutylene yields are quantitatively in accord with the 1:1 stoichiometry of a simple, nonchain elimination reaction (3). In air tubes, the benzene yield no longer accounts for all of the isobutylene. The excess olefin, however, is accompanied by a corresponding amount of a new hydrogen abstraction product, *t*-butylthiol. Therefore, the equivalence of hydrogen abstraction product and olefin is maintained in both air and degassed tubes. A short-chain reaction involving *t*-butylthiyl radicals apparently occurs in the presence of air (eq 4). The fate of the



leaving group depends, in part, on the reaction conditions. Neither thiol nor disulfide is formed in significant amounts in the degassed tubes. In air tubes, *t*-butyl disulfide is obtained in 50% yield (based on the benzene yield). The disulfide gives clear evidence of the formation of thiyl radicals and qualitatively supports the elimination reactions described by eq 3 and 4.

Because of the absence of *t*-butylthiol and disulfide in the degassed tubes, we investigated some of the more complex reaction products. Estimates of the yields of the products identified are given in Table II.

The products in Table II are, in general, the result of radical-radical reactions involving phenyl, triphenylmethyl, and *t*-butylthiyl radicals. Tetraphenylmethane is a relatively unimportant product. The formation of large amounts of triphenylmethane might seem to be in

(27) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

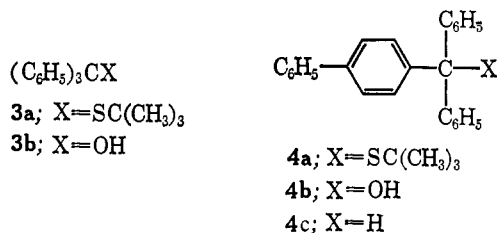
(28) W. A. Pryor and H. Guard, *ibid.*, **86**, 1150 (1964).

(29) G. S. Hammond, A. Ravve, and F. J. Modic, *Anal. Chem.*, **24**, 1373 (1952).

Table II. Complex Products from the Decomposition of PAT ($4.5 \times 10^{-2} M$) in *t*-Butyl Sulfide

Product	Moles of product/mole of PAT		
	Degassed	Air	Method ^a
Tetraphenylmethane	0.03	0.02	A
Triphenylmethane	0.37	...	B
	0.35	0.21	A
	0.26	0.22	A
3a, 3b^b	0.28	0.34	C
	0.39	0.47	D
4a, 4b^b	0.08	0.05	C
	0.11	0.06	D

^a A, vpc of the reaction mixture; B, isolation; C, vpc of the reaction mixture after reduction with HBr-HI (see text); D, visible spectrum of carbonium ion (see text). ^b The analytical methods did not distinguish between **3a** and **3b** or **4a** and **4b**. The results represent the sums of the two (see text).



contradiction to our conclusion that triphenylmethyl radical does not react readily with *t*-butyl sulfide. There are many previous examples, however, of the formation of significant amounts of triphenylmethane from the decomposition of PAT in the absence of any obvious hydrogen donor. The most striking of these is the report³⁰ that decomposition of PAT in carbon tetrachloride gives a 27% yield of triphenylmethane. The origin of the triphenylmethane will be discussed later. Phenyl *t*-butyl sulfide, which might have been formed by coupling of phenyl and *t*-butylthiyl radicals or by radical displacement by phenyl on the sulfur of *t*-butyl sulfide or *t*-butyl disulfide, could not be detected (<0.005 mole/mole of PAT).

Triphenylmethyl *t*-butyl sulfide (**3a**) and 4-biphenyldiphenylmethyl *t*-butyl sulfide (**4a**) are particularly important products since they account, in part, for the leaving group in the elimination reaction (*t*-butylthiyl radical). Authentic samples of these sulfides were prepared by the condensation of *t*-butylthiol with the appropriate arylmethyl chloride in pyridine solution. Both sulfides **3a** and **4a** were shown to be products of the PAT reaction by a comparison of R_f values for components of the reaction mixtures with those of the authentic sulfides under several substrate and solvent conditions. In addition, the two sulfides were collected separately from thin layer chromatograms and dissolved in 1:1 sulfuric acid-acetic acid. The sulfides from the reaction mixture gave the visible spectra of the appropriate ions, triphenylmethyl cation and 4-biphenyldiphenylmethyl cation.

Attempts to isolate or accurately determine the yields of the sulfides were frustrated by the complexity of the reaction mixtures and the lability of the sulfides under the work-up conditions. Vapor phase chromatography, as well as silica gel and alumina chromatography, led to extensive decomposition of the sulfides. The sulfides are converted, in part, to the corresponding

(30) D. H. Hey and J. Peters, *J. Chem. Soc.*, 79 (1960).

triarylcarbinols. Carbinols **3b** and **4b** were identified in the reaction mixture by isolation and thin layer chromatography, respectively. It is not known, however, if the carbinols are primary reaction products or if they are formed from the sulfides during work-up and analysis of the reaction mixtures. Because of these difficulties, two indirect methods of analysis were employed. Both methods give the sum of the yields of sulfide and carbinol of a given structural type. In the first procedure, the reaction mixtures were evaporated to dryness and the residues were dissolved in a known volume of 1:1 sulfuric acid-acetic acid. The absorbance at 405 $m\mu$ was taken to be indicative of the yield of precursors of the triphenylmethyl cation, *i.e.*, triphenylmethyl *t*-butyl sulfide (**3a**) and triphenylcarbinol (**3b**). The absorbance at 506 $m\mu$ was similarly used to estimate the yield of 4-biphenyldiphenylmethyl cation precursors, **4a** and **4b**. The second approach was based on the reduction of the carbinols and sulfides in the reaction mixture to the corresponding hydrocarbons with HBr-HI and gave results in approximate agreement with the spectral method. 4-Biphenyldiphenylmethane (**4c**) was isolated by vpc, confirming the presence of the 4-biphenyldiphenylmethyl structural system among the reaction products and supporting the R_f and spectral data mentioned earlier.

It is unfortunate that we were not able to accurately determine the yields of sulfides **3a** and **4a**. Nevertheless, it is difficult to see how carbinols **3b** and **4b** could be important primary products in degassed reaction mixtures. It is reasonable and consistent with the results to suggest that the sulfides are products in degassed tubes and that the carbinols are formed during work-up and analysis. If this is true, then the fate of the leaving group (*t*-butylthiyl radical) in degassed tubes becomes clear. In particular, the absence of *t*-butyl disulfide and -thiol in degassed tubes is due to the presence of radical scavengers in the reaction mixtures. Triphenylmethyl radicals are formed from PAT,^{24,25} are relatively unreactive toward *t*-butyl sulfide, and are known to be efficient scavengers of other radicals.^{27,31} The reaction of triphenylmethyl with *t*-butylthiyl radical gives triphenylmethyl *t*-butyl sulfide (**3a**). The products in Table II also indicate the presence of 4-biphenyldiphenylmethyl radicals. 4-Biphenyldiphenylmethyl scavenges *t*-butylthiyl radical giving sulfide **4a**.

The effect of oxygen on the reaction products is now understandable in terms of this scavenging process. Triphenylmethyl radicals react rapidly with oxygen.³² Therefore, the steady-state concentration of triphenylmethyl radicals in air tubes is less than in degassed tubes. The lower concentration of triphenylmethyl decreases the efficiency of the scavenging of *t*-butylthiyl radicals, leaving some free for other reactions such as attack on sulfide or dimerization. Oxygen undoubtedly has a similar effect on the concentration of the 4-biphenyldiphenylmethyl radical.

(31) (a) F. R. Mayo and R. A. Gregg, *J. Am. Chem. Soc.*, 70, 1284 (1948); (b) C. S. Marvel, J. Dec, and J. O. Corner, *ibid.*, 55, 3475 (1933); (c) J. B. Conant and B. F. Chow, *ibid.*, 55, 3475 (1933); (d) H. Wieland, K. Heymann, T. Tsatsas, D. Juchum, G. Varvoglis, G. Labriola, O. Döbelstein, and H. S. Boyd-Barrett, *Ann.*, 514, 145 (1934); (e) D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 110 (1965).

(32) M. Gomberg, *Chem. Rev.*, 1, 91 (1924).

In summary, we have accounted for two of the products of the elimination reaction, the atom abstraction and olefinic fragments, in a quantitative, stoichiometric fashion. The leaving group is accommodated by an internally consistent, albeit qualitative scheme. We conclude from the product studies described above that the process initiated by the attack of phenyl radicals on *t*-butyl sulfide in degassed tubes is a quantitative nonchain elimination reaction whose stoichiometry is described by eq 3. *In particular, the elimination reaction is sufficiently well defined to allow further detailed discussion and investigation.*

We have also studied the benzene and isobutylene yields for the reaction of phenyl radicals with phenyl *t*-butyl sulfide. The conditions of reaction were identical with those described earlier. Phenyl *t*-butyl sulfide is stable to the reaction conditions in the absence of PAT. The results shown in Table III are analogous to those obtained with *t*-butyl sulfide, indicating that phenyl *t*-butyl sulfide also undergoes a quantitative elimination reaction. We have not studied the other products of this reaction, although the low benzene yield presumably indicates that some of the phenyl radicals attack the aromatic ring of the sulfide.

Table III. Yields of Benzene and Isobutylene from the Decomposition of PAT in Phenyl *t*-Butyl Sulfide^a

Conditions	—Moles of product/mole of PAT—	
	Benzene	Isobutylene
Degassed	0.27 ± 0.03	0.28 ± 0.04
Air	0.28 ± 0.02	0.59 ± 0.13

^a Reproducibility of measurements indicated as standard deviation.

Discussion

Since this work began it has been found that the hydrogen atoms of *t*-butyl sulfide are surprisingly reactive toward free radicals. Pryor and Pickering³³ measured the chain-transfer constant of *t*-butyl sulfide for styrene polymerization (Table IV). Since the sulfur atoms of *t*-butyl disulfide should be more accessible and reactive than that of *t*-butyl sulfide,³⁴ the behavior of the latter compound must be attributed to the β hydrogens.

Table IV. Chain-Transfer Constants for Polymerization of Styrene at 60°

Compound	$C \times 10^4$
Heptane	0.42 ^a
<i>t</i> -Butyl disulfide	1.42 ^a
<i>n</i> -Butyl sulfide	21.8 ^b
Carbon tetrachloride	90 ^b
<i>t</i> -Butyl sulfide	250 ^a

^a Reference 33. ^b Reference 4, p 152.

Russell and co-workers measured the relative reactivity of the hydrogens of a number of compounds toward phenyl radicals (Table V).

(33) W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).

(34) Pryor and Pickering³³ suggested that unusual reactivity of *t*-butyl sulfide was due to a concerted, polystyryl radical initiated elimination reaction.

Table V. Reactivity Relative to Carbon Tetrachloride for the Reaction of Phenyl Radicals with Hydrogen Donors

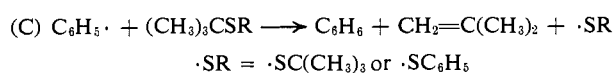
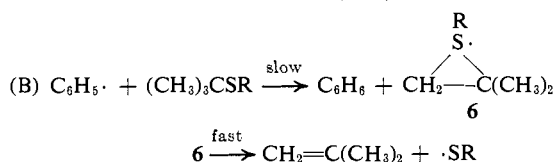
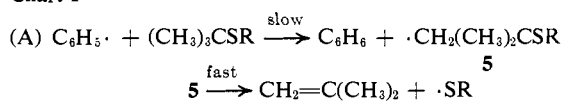
Compound	Relative reactivity $\times 10^{2a}$
Dimethylpropane	1.2 ^b
<i>t</i> -Butyl disulfide	1.4 ^c
Phenyl <i>t</i> -butyl sulfide	2.3 ^c
Thioanisole	13 ^b
<i>t</i> -Butyl sulfide	69 ^c
Diphenylmethane	69 ^c

^a At 60°. Relative reactivity is statistically corrected, *i.e.*, per reactive hydrogen. ^b Reference 27. ^c Private communication from G. A. Russell of unpublished results of Mr. J. D. Hunt.

The β hydrogens of *t*-butyl sulfide are approximately six times as reactive as the α hydrogens of thioanisole in which the developing radical center is adjacent to the sulfur atom. Therefore, a simple inductive effect of the sulfur cannot explain the reactivity of *t*-butyl sulfide. A β hydrogen in *t*-butyl sulfide is 30 times as reactive³⁵ as a corresponding hydrogen in phenyl *t*-butyl sulfide. The β hydrogens of the latter compound are only twice as reactive as those of 2,2-dimethylpropane.

Three reasonable mechanisms for the reaction of phenyl radicals with *t*-butyl sulfide and phenyl *t*-butyl sulfide are suggested in Chart I.

Chart I



If the rate-determining step were simple unassisted β -hydrogen abstraction as in (A), then the relative reactivities of the sulfides might be similar to that of 2,2-dimethylpropane. In fact, *t*-butyl sulfide is 57 times as reactive as the hydrocarbon. The equivalent yields of benzene and isobutylene in degassed tubes require that intermediate radical (**5**) fragment to olefin before it is appreciably scavenged by triphenylmethyl. The triphenylmethyl concentration is admittedly low, but high enough to give significant scavenging of phenyl leading to 4-biphenyldiphenylmethyl products.

Case B readily accounts for the unusual reactivity of *t*-butyl sulfide in terms of neighboring group participation by sulfur in the transition state for hydrogen abstraction. The difference in reactivity between *t*-butyl sulfide and phenyl *t*-butyl sulfide is more difficult to understand. In the classic work on neighboring group participation by sulfur in radical reactions, Benstrude and Martin³⁶ observed that *t*-

(35) G. A. Russell and R. F. Bridger, Abstracts of Papers, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 2C, have previously attributed the high reactivity of *t*-butyl sulfide to a concerted abstraction-elimination process wherein relief of steric strain was the major driving force.

(36) W. G. Benstrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

butyl (*o*-phenylthio)perbenzoate decomposed twice as fast as *t*-butyl (*o*-methylthio)perbenzoate. It is possible that electronic differences between the transition states for the reactions of the two sulfides are small, as suggested by the data of Bentrude and Martin. These small electronic differences may be swamped out by a steric acceleration of the reaction of *t*-butyl sulfide. Both cases B and C allow for a relief of steric strain in the transition state. Finally, the same scavenging argument indicated earlier restricts the lifetime of intermediate 6.

A concerted elimination reaction (case C) agrees with the absence of scavenging of an intermediate radical derived from the sulfides and with the high reactivity of *t*-butyl sulfide. However, since phenylthiyl radical should be a better leaving group than *t*-butylthiyl radical, the sulfide reactivities are reversed from what one might have predicted. As in case B, steric effects may be more important than electronic effects. It is not possible to make a clear choice between alternatives B and C. Case C, however, most easily explains the reactivity of *t*-butyl sulfide and the stoichiometric yields of benzene and isobutylene.

The steric differences between the two sulfides may lead to mechanistic differences. Zavitsas and Ehrenson³⁷ recently suggested a concerted mechanism for the reaction of *t*-butyl radical with the highly strained *t*-butylmethylcarbinyl hypochlorite to give *t*-butyl chloride, acetone, and a new *t*-butyl radical. In contrast, other hypochlorites clearly give intermediate alkoxy radicals and, therefore, do not react by a concerted elimination process.

Phenylazotriphenylmethane. As indicated in Table II, the decomposition of PAT in *t*-butyl sulfide gives significant amounts of triphenylmethane. Since triphenylmethyl does not react readily with the sulfide, there must be some unexpected hydrogen donor(s) in the reaction mixture.³⁰ Bridger and Russell²⁷ and Pryor and Guard²⁸ have noted that PAT in carbon tetrachloride gives small amounts of benzene. The benzene yield increases from 4.8 to 8.0% as the PAT concentration increases from 0.048 to 0.192 *M*;²⁷ benzene is apparently formed by both cage and non-cage processes.^{27, 38} In addition, the sum of the yields of benzene and chlorobenzene (*i.e.*, recovery of phenyl radicals) decreases as PAT concentration increases.²⁷ A similar effect of PAT concentration on the benzene and isobutylene yields in the sulfide reaction was observed in this work.

A logical explanation of (1) the formation of hydrogen donors in PAT decompositions and (2) the decrease in available phenyl radicals with increasing PAT concentration involves an appreciable steady-state concentration of triphenylmethyl radicals in the course of the PAT decomposition.³⁹

These triphenylmethyl radicals scavenge phenyls,

(37) A. A. Zavitsas and S. Ehrenson, *J. Am. Chem. Soc.*, **87**, 2841 (1965).

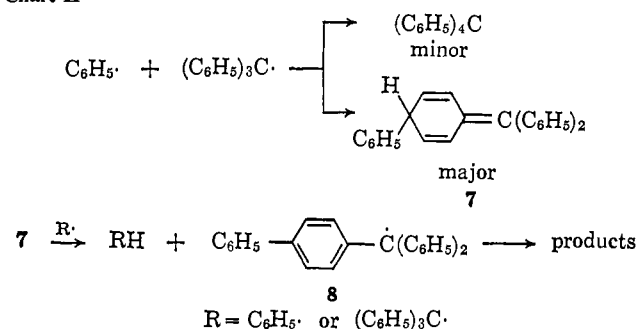
(38) W. A. Pryor, J. T. Echols, Jr., S. C. Stodola, and H. E. Guard, *ibid.*, in press.

(39) The attack of phenyl radicals on PAT^{27, 28} is inconsistent with the kinetic behavior of the azo compound:²⁵ G. L. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4397 (1956); J. F. Garst and G. S. Hammond, *J. Org. Chem.*, **23**, 98 (1958); S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953); M. G. Alder and J. E. Leffler, *ibid.*, **76**, 1425 (1954); S. Solomon, C. H. Wang, and S. G. Cohen, *ibid.*, **79**, 4104 (1957); J. E. Leffler and R. A. Hubbard, *J. Org. Chem.*, **19**, 1089 (1954).

thereby decreasing the total number available for abstraction reactions. The steady-state concentration of triphenylmethyl and, therefore, the number of phenyls destroyed by scavenging will increase with PAT concentration.

Tetraphenylmethane is the obvious product of the reaction of phenyl with triphenylmethyl. Tetraphenylmethane, however, is consistently a minor product (2–3% yield) of PAT decompositions.⁴⁰ The formation of products derived from the 4-biphenyldiphenylmethyl radical (8) indicates that *para* coupling of triphenylmethyl and phenyl is also important. From the yields of tetraphenylmethane and 4-biphenyldiphenylmethyl products quoted in Table II, phenyl couples at the *para* position of triphenylmethyl at least three to four times more readily than it couples at the central carbon atom. Since *para* coupling gives a hydroaromatic intermediate (7), the reaction accounts for both the disappearance of phenyls and for the formation of hydrogen donors. The relevant reactions are shown in Chart II. The yield of 7 depends on triphenylmethyl

Chart II



concentration (*i.e.*, PAT concentration) and hence the yield of benzene by reaction of phenyl with 7 will depend on PAT concentration. The scheme in Chart II, therefore, is completely consistent with the observed effects⁴¹ and is directly supported by the identification of products (4a and 4b) derived from the *para* coupling reaction.

Ambident reactivity of triphenylmethyl systems with radicals and nucleophiles has been observed previously.^{42–45} The factors determining the central *para* position reactivity have not been established. Bartlett and Lorand⁴⁶ have recently observed that triphenylmethyl and *t*-butoxy radicals give approximately equal amounts of *para* and central atom coupling. The ionic reaction of triphenylmethyl chloride with potassium *t*-butoxide in *t*-butyl alcohol–benzene gives α,α -diphenyl-*p*-tolyl *t*-butyl ether (9a) in 70% yield; *t*-butyl triphenylmethyl ether was formed in only minor amounts.⁴⁶ In contrast to these results, we have found that the reaction of triphenylmethyl chloride with *t*-

(40) (a) D. H. Hey and J. Peters, *J. Chem. Soc.*, 88 (1960); (b) D. H. Hey and C. J. M. Stirling, *ibid.*, 3963 (1955); (c) D. H. Hey, M. J. Perkins, and G. H. Williams, *ibid.*, 110 (1965).

(41) The scheme in Chart II is clearly not applicable to the formation of benzene by a cage process.

(42) F. Ullman and W. Borsum, *Ber.*, **35**, 2877 (1902).

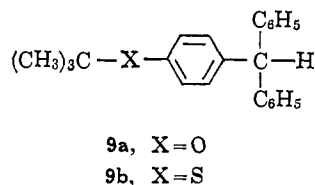
(43) H. Wieland and C. Muller, *Ann.*, **401**, 233 (1913).

(44) R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Letters*, No. 30, 2033 (1964).

(45) C. S. Schoepfle and S. G. Trepp, *J. Am. Chem. Soc.*, **58**, 791 (1936).

(46) J. P. Lorand, Ph.D. Thesis, Harvard University, 1964. We are indebted to Drs. Bartlett and Lorand for permission to quote their results.

butylthiol in pyridine gives central atom product, triphenylmethyl *t*-butyl sulfide (**3a**), in at least 70% yield. A small amount of material having a benzylic proton absorption corresponding to that of the *para* coupling product, α,α -diphenyl *p*-tolyl *t*-butyl sulfide (**9b**), was detected by nmr in <2% yield in the residue from the initial crystallization of the major product. The nmr absorption may not be due to **9b**, but nevertheless sets an upper limit on the yield of *para* coupling product.



Experimental Section

Melting points are corrected. Boiling points are uncorrected. Analyses are by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were taken on a Perkin-Elmer Model 421 recording spectrophotometer. Ultraviolet and visible spectra were taken on a Cary Model MS 11 recording spectrophotometer. Nuclear magnetic resonance spectra were taken on 60-Mc Varian A-60 and V-4300B instruments by Dr. L. D. Colebrook and Miss Sandra Didenko. Mass spectra of isobutylene were taken on a Consolidated Engineering Corp. mass spectrometer Type 21-620 by Mr. Carl Whiteman. Vapor fractometers used were Wilkin's Aerographs, A-90-P, A-90-P2, A-110-C, and Hy-Fi Model 600. The A-90-P, A-90-P2, and A-110-C instruments had thermal conductivity detectors and used helium as the carrier gas while the Hy-Fi Model 600 had an hydrogen flame-ionization detector and used prepurified nitrogen as the carrier gas. A number of different columns⁴⁷ were used.

Thin layer chromatography was performed on glass plates coated with Silica Gel G or Alumina G⁴⁸ to 0.25-mm thickness and activated at 105° for 30 min. Samples were applied by spotting 1–2 μ l of approximately a 2% solution in benzene. The chromatography was carried out by solvent ascension to a height of 10–15 cm and the materials were located with iodine vapor, concentrated sulfuric acid, or 1:1 (v/v) sulfuric-acetic acid.

Materials. Phenylazotriphenylmethane, prepared from triphenylmethyl chloride and phenylhydrazine with subsequent oxidation of the hydrazo compound with hydrogen peroxide,⁴⁷ was recrystallized by dissolving in a minimum amount of benzene and adding 1.25 volumes of *n*-pentane. The material crystallized as yellow needles: mp 110.5–111.8° dec (lit.⁴⁹ mp 111°), λ_{max} (cyclohexane) 418 m μ (ϵ 190), λ_{max} (*t*-butyl sulfide) 415 m μ (ϵ 210) (lit.⁵⁰ λ_{max} (hexane) 420.5 m μ (ϵ 180)). The absorption in *t*-butyl sulfide conforms to Beer's Law.

Commercial *t*-butyl sulfide was purified by distilling twice at atmospheric pressure through a 12-in. Vigreux column with a partial take-off head. Only the center third, bp 151° (lit.³³ bp 151°) was taken each time. Vpc showed that small amounts of *t*-butylthiol, isobutylene, and *t*-butyl isobutyl sulfide were present in about equal amounts and that the purity was >99.95%.

Phenyl *t*-butyl sulfide, prepared by the acid-catalyzed condensation of *t*-butyl alcohol with thiophenol,⁵¹ was distilled on a 16-in. spinning-band column to give material, bp 107° (26 mm) (lit.⁵¹ bp 73° (5 mm)), n_D^{20} 1.5312 (lit.⁵¹ n_D^{20} 1.5335). Phenyl *t*-butyl sulfide turns yellow if allowed to stand at room temperature in the presence of light. Isobutylene can be detected in these samples by

(47) (a) 15 ft \times 0.20 in 20% tricresyl phosphate on 30–60 mesh Chromosorb P; (b) 15 ft \times 0.25 in. 20% Dow Corning 11 Silicone on 30–60 mesh Chromosorb P; (c) 15 ft \times 0.25 in. 20% SF-96 on 30–60 mesh Chromosorb P; (d) 15 \times 0.25 in. 20% Apiezon L on 30–60 mesh Chromosorb P; (e) 15 ft \times 0.25 in. 20% Ucon Polar on 30–60 mesh Chromosorb P; (f) 10 ft \times 1/16 in. 20% tricresyl phosphate on 30–60 mesh Chromosorb P.

(48) Brinkmann Instruments, Inc., Great Neck, N. Y.

(49) M. Gomberg, *Ber.*, 30, 2043 (1897).

(50) A. Buroway, *J. Chem. Soc.*, 1865 (1937).

(51) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, 60, 2731 (1938).

vpc. The sulfide was stored in the dark and freshly distilled before each run; analyses by vpc^{47c} indicated less than 0.01% detectable impurities.

4-Biphenyldiphenylmethanol (4b), mp 135–137° (lit.⁵² mp 136°), was prepared by the reaction of phenylmagnesium bromide with methyl 4-biphenylcarboxylate.⁵²

4-Biphenyldiphenylmethane (4c), mp 110.5–112.5° (lit.⁵² mp 112–113°), was prepared by the reduction of the carbinol (**4b**) with zinc-acetic acid.⁵²

Triphenylmethyl *t*-Butyl Sulfide (3a). Chlorotriphenylmethane (2.79 g, 0.010 mole) and *t*-butylthiol (2.25 g, 0.025 mole) were added to 10 ml of pyridine. This solution was heated on a steam bath for 5 hr, cooled to room temperature, diluted with 10 ml of benzene, and filtered. The filtrate was washed six times with water and dried with sodium sulfate. Evaporation of volatile material yielded 3.21 g (97%) of a light yellow, gummy solid. Recrystallization from 95% ethanol yielded 2.31 g (70%) of triphenylmethyl *t*-butyl sulfide as white crystals, mp 102.5–104.0°.

Further recrystallization of a portion of triphenylmethyl *t*-butyl sulfide from 95% ethanol gave mp 104.5–105.5°. The infrared spectrum (CCl₄) shows no absorption above 3100 cm⁻¹, but has bands attributed to the *t*-butyl group at 2965 (s), 2920 (s), 2890 (s), 2860 (s), 1392 (s), and 1364 cm⁻¹ (s). The ultraviolet spectrum (95% ethanol) shows strong end absorption and slight shoulders at 248 m μ (ϵ 2.2 \times 10³), 256 (1.8 \times 10³), 262 (1.2 \times 10³), and 267 (6.1 \times 10²). The visible spectrum (1:1 H₂SO₄-HOAc by volume) shows λ_{max} 406 m μ (ϵ 3.03 \times 10⁴), λ_{max} 433 m μ (ϵ 3.00 \times 10⁴). The visible spectrum of triphenylcarbinol (1:1 H₂SO₄-HOAc) exhibits λ_{max} 406 m μ (ϵ 3.69 \times 10⁴), λ_{max} 433 m μ (ϵ 3.69 \times 10⁴); reported⁵³ visible spectrum of triphenylcarbinol (H₂SO₄) λ_{max} 408 m μ (ϵ 3.64 \times 10⁴), τ_{max} 431 m μ (ϵ 3.74 \times 10⁴). The extinction coefficients of triphenylcarbinol and triphenylmethyl *t*-butyl sulfide do not agree probably because of incomplete ionization of the sulfide. The nmr spectrum (CCl₄) of the sulfide shows a singlet at τ 9.05 and a multiplet at 2.64. *Anal.* Calcd for C₂₈H₂₄S: C, 83.07; H, 7.28. Found: C, 83.17; H, 7.27.

Evaporation of the solvent from the filtrate from the initial crystallization of triphenylmethyl *t*-butyl sulfide yielded 0.514 g of a yellow oil. The nmr spectrum (CCl₄) of this material exhibited a singlet at τ 4.55 which was attributed to the benzylic proton of the *para* reaction product, α,α -diphenyl-*p*-tolyl *t*-butyl sulfide (**9b**) (τ 4.52 in authentic material). Diphenylmethane (22.7 \times 10⁻³ g, 0.135 mmole) was added to the sample as an internal standard and the absorption areas at τ 4.55 and 6.22 (diphenylmethane) were carefully integrated. The ratio of the areas τ 4.55/ τ 6.22 was approximately 1/2, indicating a 1–2% yield of α,α -diphenyl-*p*-diphenyl-*p*-tolyl *t*-butyl sulfide.

4-Biphenyldiphenylmethyl *t*-Butyl Sulfide (4a). Chloro-4-biphenyldiphenylmethane,⁵² mp 144–146° (2.35 g, 6.67 mmoles), and *t*-butyl thiol (1.5 g, 16.7 mmoles) were dissolved in 10 ml of pyridine, and the solution was heated at about 100° for 20 hr. On cooling, a white precipitate was formed. The solution was decanted from the solid, diluted with 50 ml of benzene, washed four times with water, and dried with sodium sulfate, and the solvent was evaporated to yield 2.3 g (85% yield) of a gummy solid. Two recrystallizations from 95% ethanol yielded 1.3 g (37%) of 4-biphenyldiphenylmethyl *t*-butyl sulfide as white crystals, mp 133.5–135.5°. The infrared spectrum (CHCl₃) shows no bands above 3100 cm⁻¹ but exhibits bands attributed to the *t*-butyl group at 2970 (s), 2930 (m), 2900 (m), 2865 (m), 1450 (m), and 1370 cm⁻¹ (m); ultraviolet spectrum (95% ethanol) λ_{max} 261 m μ (ϵ 2.36 \times 10⁴), strong end absorption; visible spectrum (1:1 H₂SO₄-HOAc) λ_{max} 506 m μ (ϵ 2.9 \times 10⁴), λ_{max} 423 m μ (ϵ 1.6 \times 10⁴); nmr spectrum (CCl₄) τ 9.06 (singlet), 2.58 (multiplet). *Anal.* Calcd for C₂₈H₂₈S: C, 85.24; H, 6.91. Found: C, 85.34; H, 7.17.

α,α -Diphenyl-*p*-tolyl *t*-Butyl Sulfide (9b). (*p*-Thia-*t*-butyl)phenyldiphenylmethanol (0.412 g, 118 mmoles) was dissolved in 10 ml of glacial acetic acid with warming on a steam bath. The addition of 1.5 ml of 47% HBr and heating for 5 min produced a deep violet solution. The reduction was completed by addition of 1.5 ml of 47% HI and heating for 45 min on a steam bath. After cooling the solution, 1 g of sodium bisulfite in 20 ml of water was added, the excess acids were neutralized with sodium carbonate, and the solution was extracted twice with benzene. The benzene extracts were dried with sodium sulfate and evaporated to produce 0.355 g

(52) W. Schlenk, *Ann.*, 368, 295 (1909).

(53) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

(91% yield) of a light yellow oil. Chromatography on 10 g of neutral alumina and elution with pentane yielded 117 mg (30%) of α,α -diphenyl-*p*-tolyl *t*-butyl sulfide as a white solid, mp 86–89°. Two recrystallizations from ethanol–water raised the melting point to 88.5–90.0°. The infrared spectrum (CCl₄) showed no bands above 3100 cm⁻¹ but showed *t*-butyl bands at 2980 (s), 2965 (s), 2945 (m), 2925 (m), 2900 (m), 2865 (m), 1454 (m), and 1368 cm⁻¹ (s). The nmr spectrum (CCl₄) shows a multiplet between τ 2.5–3.1 (14.5 H), singlet at 4.52 (1.0 H), and a singlet at 8.74 (8.5 H). *Anal.* Calcd for C₂₃H₂₄S: C, 83.08; H, 7.28. Found: C, 82.87; H, 7.26.

Decomposition of PAT in *t*-Butyl Sulfide. General Procedure. Solutions of known concentrations of PAT in *t*-butyl sulfide were prepared by weighing a sample of PAT into a volumetric flask and diluting to the correct volume with sulfide or by making a nearly saturated solution of PAT in *t*-butyl sulfide and determining the concentration from the visible absorption maximum at 415 m μ . Known volumes of the solutions (ca. 1 ml) were transferred to Pyrex glass ampoules by means of a calibrated syringe. Some tubes were sealed directly with about 10 ml of air above the solution. Other tubes were degassed at 10⁻⁵–10⁻⁶ mm with three successive freezings and thawings and sealed under vacuum. The sealed tubes were heated in a refluxing ethyl acetate bath at 76–79° for 2–3 hr (greater than 10 half-lives of PAT). The tubes were cooled in Dry Ice–acetone and opened, and an internal standard for vpc analysis was added and closed with serum caps. These procedures were followed for all runs except as noted. PAT concentrations were usually 4–5 \times 10⁻² M.

Products. In order to isolate isobutylene, a decomposition of PAT in *t*-butyl sulfide was carried out in a tube fitted with a stopcock held in place by a high-pressure fitting. On completion of the decomposition, the contents of the tube was distilled on a high-vacuum line, and the isobutylene was separated from the reaction mixture by fractionally condensing the high-boiling material at -78° and the isobutylene at -196°. The mass spectrum of the isolated material was identical with that of known isobutylene except for a few small impurity peaks at mass numbers greater than 56. The product with retention time corresponding to benzene on two columns^{47a,b} was collected from the vpc and its ultraviolet spectrum (95% ethanol) was found to be correspond to that of authentic benzene. Relative peak heights (254 m μ = 1.00) for the two samples were identical at six wavelengths between 237 and 268 m μ . *t*-Butylthiol and *t*-butyl disulfide were shown to be reaction products in air tubes by comparison of vpc retention times with authentic materials on four columns.^{47a,c-e}

The isobutylene, benzene, *t*-butylthiol, and *t*-butyl disulfide yields were determined by vpc^{47a,f,g} using internal standard methods. Standard mixtures containing known amounts of the product(s) in question in *t*-butyl sulfide and the internal standard were prepared and analyzed concurrently with the reaction mixtures. *n*-Pentane, ether, or cyclopentane were used as standards for isobutylene. Solutions of known concentrations of isobutylene in *t*-butyl sulfide were prepared as follows. *t*-Butyl sulfide (10 ml) was placed in a small flask fitted with a vacuum adapter, frozen with a Dry Ice–acetone bath, and the flask evacuated with a water aspirator. A known volume (usually 5–10 ml, corrected to STP) of isobutylene was admitted to the flask from a calibrated gas buret. The solution was allowed to warm to room temperature with occasional swirling. The stopcock on the vacuum adapter was opened to equalize the pressure and quickly closed. The solvent was then swirled for a few more minutes to ensure dissolution of the isobutylene, the adapter was removed, the internal standard was added, and the flask was stoppered. *n*-Pentane, cyclopentane, or toluene were used as standards for the benzene determinations. Tetralin was used as a standard for *t*-butyl disulfide. Toluene served as a standard for *t*-butylthiol. Some of the results of the analyses are presented in Table VI. Not all of the runs are included, but the data have been chosen to illustrate the maximum spread in the results.

There are a number of possible sources of error in analyses of this type. Standard deviations between runs, between tubes in a given run, and between injections for a given tube were all comparable. Therefore, the results of all similar runs, tubes, and injections were averaged. Since the yield of available phenyl radicals depends on the initial PAT concentrations,^{27,28} only those tubes which were 4–5 \times 10⁻² M in PAT are included in the average. Data for air and degassed tubes were handled separately. Table I presents the averaged results and standard deviations obtained from the experiments indicated in Table VII.

The limits of detectability of *t*-butylthiol, *t*-butyl disulfide, and

Table VI

[PAT] \times 10 ²	Condi- tions ^a	10 ² of moles of product/mole of PAT ^b			
		C ₄ H ₈	C ₆ H ₆	<i>t</i> -Butyl- thiol	<i>t</i> -Butyl disulfide
4.54	D	a, 55, 55, 55	57, 57, 54
		b, 52, 48, 52	50, 49, 51
4.61	D	a, 46, 43, 47	54, 50, 53
		b, 44, 44, 40	49, 50,
1.02	D	a, 86, 94, 90	86, 87, 89
		b, 86, 84, 84	89, ..,
4.24	A	c, 98, 98, 96	90, ..,
		a, 81, 80, 80
4.86	A	b, 75, 67, 74
		a,	28, 31, 26	...
4.37	A	b,	23, 13, 14	...
		a,	5, 6, 5	...
4.98	A	b, ...	67, 64, 57	11, 11,
		a, ...	60, 58, 60	...	10, 9, 11
4.57	A	b,	9, 9, 11
		a,	15, 16, 18
4.71	O ₂	b,	18, 19, 18
		a, ...	57, 54, 54	...	18, 18, ..
		b, ...	49, 55, 48	...	15, 15, ..

^a D = degassed tube. A = air tube. O₂ = tube sealed under oxygen. ^b The small letters (a, b, c) designate individual tubes. Each number indicates the result of a single injection.

Table VII

Product	Condi- tions ^a	No. of runs	Total no. of tubes
C ₄ H ₈	D	5	14
C ₆ H ₆	D	7	11
C ₄ H ₈	A	3	10
C ₆ H ₆	A	3	12
<i>t</i> -Butylthiol	A	4	13
<i>t</i> -Butyl disulfide	A	5	18

^a D = degassed tube; A = air tube.

phenyl *t*-butyl sulfide by vpc were established by analysis of standard solutions of the materials in *t*-butyl sulfide.

Triphenylmethane and tetraphenylmethane were isolated and characterized from large-scale decompositions of PAT in *t*-butyl sulfide. Fifty milliliters of a solution of PAT in *t*-butyl sulfide (4.52 \times 10⁻² M) was sealed in a tube (air atmosphere) and heated for 3 hr at 82.5°. The solvent was evaporated, and the residue was chromatographed on 15 g of 200 mesh silica gel to give triphenylcarbinol, mp 161.5–163.0°, mmp 162–164°, tetraphenylmethane, mp 281–283°, mmp 280–283°, and triphenylmethane, mp 90–92°, mmp 91–93°.

Comparable treatment of a degassed reaction mixture (50 ml, 4.52 \times 10⁻² M) gave 203 mg (37% yield) of triphenylmethane, mp 91–93°, mmp 92–94°, and tetraphenylmethane, mp 282–283°, mmp 282–284°.

A degassed tube (18.5 ml of 4.50 \times 10⁻² M PAT in *t*-butyl sulfide) and an air tube (20.0 ml of 4.50 \times 10⁻² M PAT in *t*-butyl sulfide) were opened, and the volatile materials were evaporated. The residue from each was dissolved in 4 ml of benzene. Standard solutions of triphenylmethane and tetraphenylmethane were prepared by dissolving weighed amounts of material in 4 ml of benzene. The amounts of tri- and tetraphenylmethane in the unknowns were determined by comparison of the areas of their peaks in the vpc^{47c} curves with those of the standards using equi-volume injections. Results are shown in Table II.

Triphenylmethyl *t*-butyl sulfide (3a) and triphenylcarbinol (3b) were characterized as reaction products by a variety of techniques. As described previously, chromatography of the residue from a large-scale decomposition of PAT in an air tube gave triphenylcarbinol. Triphenylcarbinol was detected in degassed tubes by thin layer chromatography under two sets of conditions and vpc^{47c} behavior at column temperatures of 209 and 253°. Authentic triphenylcarbinol gave a major peak and a single satellite peak at 209° and a major peak and two satellite peaks at 253°. A degassed reaction mixture gave retention times and decomposition patterns similar to those of the authentic material.

Several unsuccessful attempts were made to devise methods for isolation of triphenylmethyl *t*-butyl sulfide. The sulfide was demonstrated to be present in degassed tubes by thin layer chromatography under four sets of conditions. R_f values for the sulfide in the reaction mixtures were identical with those observed for authentic sulfide. A single thin layer chromatogram of the residue from an air tube indicated a sulfide with the same R_f as authentic **3a**.

4-Biphenylyldiphenylmethyl *t*-butyl sulfide (4a) and **4-biphenylyldiphenylmethanol (4b)** were shown to be present in the reaction mixtures by thin layer chromatography. R_f values for sulfide **4a** in degassed mixtures and authentic **4a** were identical under six sets of conditions. A single thin layer chromatogram of the residue from an air tube indicated the presence of sulfide **4a** and carbinol **4b**. Two different thin layer chromatograms indicated the presence of carbinol **4b** in degassed tubes.

The sulfides **3a** and **4a** were further characterized as reaction products as follows. Two tubes of PAT in *t*-butyl sulfide were prepared and decomposed by the usual procedure. Each tube contained 2 ml of $4.50 \times 10^{-2} M$ solution; one was degassed, the other was sealed in air. The solvent was evaporated from each and each residue was dissolved in 100 μ l of benzene. Thin layer chromatography was performed on Alumina G with 6:1 pentane-carbon tetrachloride as solvent. On completion of chromatography, the plates were sprayed with 1:1 sulfuric acid-acetic acid to determine the locations of the spots. The spots corresponding to triphenylmethyl *t*-butyl sulfide and 4-biphenylyldiphenylmethyl *t*-butyl sulfide were scraped from the plates into small beakers. To the beaker containing triphenylmethyl *t*-butyl sulfide were added a few drops of water and a few milliliters of benzene. After thoroughly mixing the alumina with the benzene, the solvent was decanted into another flask and evaporated. Solutions for the visible spectra were made by adding about 5 ml of 1:1 H_2SO_4 -HOAc. The visible spectrum for the material isolated from the degassed tube exhibited bands at λ_{max} 405 $m\mu$ ($A = 1.04$), λ_{max} 431 $m\mu$ ($A = 1.04$). The visible spectrum for triphenylcarbinol under the same conditions shows: λ_{max} 406 $m\mu$ ($\epsilon 3.69 \times 10^4$), λ_{max} 433 $m\mu$ ($\epsilon 3.69 \times 10^4$). The plate from the air tube did not yield enough material for a spectrum.

To the beaker containing 4-biphenylyldiphenylmethyl *t*-butyl sulfide from the degassed tube was added about 5 ml of 1:1 H_2SO_4 -HOAc. This was filtered through a sintered-glass disk to yield a pink solution. The visible spectrum showed λ_{max} 506 $m\mu$ ($A = 1.85$), λ_{max} 412 $m\mu$ ($A = 1.59$). The visible spectrum for 4-biphenylyldiphenylmethanol under the same conditions shows λ_{max} 506 $m\mu$ ($\epsilon 3.58 \times 10^4$), λ_{max} 423 $m\mu$ ($\epsilon 1.99 \times 10^4$). The spectral solution was diluted with water, neutralized with sodium carbonate, and extracted once with benzene. The benzene extract was evaporated. To the residue was added 5 ml of 95% ethanol. The ultraviolet spectrum of this solution showed λ_{max} 253 $m\mu$. The ultraviolet spectrum of 4-biphenylyldiphenylmethanol (95% ethanol) shows λ_{max} 254 $m\mu$ ($\epsilon 2.38 \times 10^4$).

The remaining benzene solutions containing the crude solids: 88 μ l of 100 μ l from the air tube, 76 μ l of 100 μ l from the degassed tube were evaporated, and each residue was dissolved in 1:1 H_2SO_4 -HOAc to give 100 ml of solution. One milliliter of each of these solutions was diluted to 25 ml to give the solutions for visible spectra. The solution from the air tube showed λ_{max} 506 $m\mu$ ($A = 0.11$). The solution from the degassed tube showed λ_{max} 405 $m\mu$ ($A = 0.55$), λ_{max} 430 $m\mu$ ($A = 0.56$), λ_{max} 506 $m\mu$ ($A = 0.07$). Assuming that the peak at 405 $m\mu$ is indicative of the sum of triphenylmethyl *t*-butyl sulfide (**3a**) and triphenylcarbinol (**3b**), then the total yield from the air tube is 0.47 mole/mole of PAT and from the degassed tube is 0.39 mole/mole of PAT. Assuming that the peak at 506 $m\mu$ is indicative of the sum of the 4-biphenylyldiphenylmethyl *t*-butyl sulfide (**4a**) and 4-biphenylyldiphenylmethanol (**4b**), then the total yield from the air tube is 0.06 mole/mole of PAT and from the degassed tube is 0.11 mole/mole of PAT. No correction was made for the fact that the sulfides are not completely ionized in 1:1 H_2SO_4 -HOAc.

The yields of triphenylmethyl *t*-butyl sulfide and triphenylcarbinol, and 4-biphenylyldiphenylmethyl *t*-butyl sulfide and 4-biphenylyldiphenylmethanol were also determined by reduction to the respective hydrocarbons, triphenylmethane and 4-biphenylyldiphenylmethane. Control experiments showed the reductions to be nearly quantitative. To the residues from an air and a degassed tube was added 8 ml of acetic acid, and the mixtures were warmed on a steam bath to ensure solution. Two milliliters of 47% HBr was added, and the solutions were heated for 15 min. Two milliliters more of 47% HBr was added, and the solutions were heated for another 10 min. Six milliliters of 47% HI was added, and the

solutions were heated for 1 additional hr. After cooling the solutions to room temperature, an aqueous solution of 4 g of sodium bisulfite was added to each. The acids were neutralized with sodium carbonate, and the resultant solutions were extracted three times with benzene. The extracts were dried with sodium sulfate, and the solvent was evaporated. Each residue was dissolved in 10 ml of benzene for vpc analysis. Comparison of the vpc curves with those of standards using known injection volumes indicated 0.59 mole of triphenylmethane/mole of PAT in the degassed tube and a value of 0.57 for the air tube. After correcting the triphenylmethane for that amount which was present before reduction, the sum of yields of triphenylcarbinol and triphenylmethyl *t*-butyl sulfide is 0.23 mole/mole of PAT in the degassed tube and 0.34 mole/mole of PAT in the air tube. 4-Biphenylyldiphenylmethane (**4c**) could not be detected by vpc^{47c} in the reaction mixtures before reduction. The yields of 4-biphenylyldiphenylmethane after reduction were 0.08 mole/mole PAT in the degassed tube and 0.05 mole/mole of PAT in the air tube. These yields are presumably indicative of the sum of the yields of sulfide **4a** and carbinol **4b**. 4-Biphenylyldiphenylmethane (**4c**) was isolated by vpc^{47c} from a reduced reaction mixture and, after chromatography on alumina and crystallization from ethanol, had mp 109.5–111.5°, mmp 111.0–112°, λ_{max} ethanol 254 $m\mu$.

Decomposition of PAT in Phenyl-*t*-Butyl Sulfide. Reaction mixtures were prepared and analyzed essentially as described for *t*-butyl sulfide reactions. Results are shown in Table VIII. Not all of the data are recorded; the maximum and minimum values observed are given, however. The averaged results and standard deviations of all the data are presented in Table III. Eight degassed runs, one tube/run, were performed. Four air runs, one tube/run, were performed.

Table VIII

[PAT], $\times 10^2$	Condi- tions ^a	Time, hr	10 ² moles of product/mole of PAT ^b	
			C ₆ H ₆	C ₄ H ₈
4.25	D	2.5	33, 31	30, 27
4.71	D	2.5	22, 21	21, 22
4.50	D	11	25, 26, 26	26, 26, 26
4.24	D	11	28, 28, 27	32, 34, 34
4.42	A	2.5	26, 30	47, 51
4.16	A	2.5	26, 27, 27	67, 68, 68
4.10	A	11	26, 29, 31	71, 72, 76
4.31	O ₂	2.5	25, 22	87, 88

^a D = degassed tube; A = air tube; O₂ = oxygen bubbled through the tube before sealing. ^b Each number represents the results of a single injection.

Controls. *t*-Butyl Sulfide and Phenyl *t*-Butyl Sulfide. One milliliter samples of *t*-butyl sulfide and phenyl *t*-butyl sulfide were charged to a series of tubes which were sealed, heated in refluxing ethyl acetate for 3 hr, and opened. The sulfide samples were analyzed by vpc using injection volumes comparable to those normally used for quantitative analysis of PAT reaction mixtures. The degassed samples of *t*-butyl sulfide and phenyl *t*-butyl sulfide and the air samples of phenyl *t*-butyl sulfide showed no detectable change. The air samples of *t*-butyl sulfide showed traces of isobutylene, but no detectable *t*-butyl disulfide.

Reaction of Triphenylmethyl with *t*-Butyl Sulfide. The reaction was conducted in a Y-shaped apparatus. Each arm of the apparatus terminated in a male joint. The upper arm was interrupted by a stopcock and the right-hand arm contained a sintered glass filter disk just above the joint. Mercury (0.2 g, 10^{-3} mole) was placed on the sintered glass disk. A solution of 0.100 g (3.59×10^{-4} mole) of chlorotriphenylmethane in 2 ml of benzene was placed in a 5-ml flask with a magnetic stirrer, and the flask was attached to the left-hand arm. A reaction ampoule containing 1 ml of *t*-butyl sulfide was attached to the right-hand arm and the whole assembly thoroughly degassed. The stopcock was closed, the apparatus was detached from the vacuum line, and the mercury tipped into the benzene solution. The mixture was shielded with aluminum foil and stirred for 22 hr at room temperature.²⁸ At the end of this time, the deep orange solution of triphenylmethyl was filtered through the glass disk into the *t*-butyl sulfide. The ampoule was sealed off, heated for 4 hr in refluxing ethyl acetate, and opened, and a known volume of cyclopentane was added.

Analysis by vpc using cyclopentane as the internal standard indicated 0.07 mole of isobutylene/mole of chlorotriphenylmethane. The reaction mixture was then diluted to 10 ml with benzene and the triphenylmethane yield was determined by comparison with a standard solution using equivolume injections of standard and reaction mixture. The triphenylmethane yield was 0.24 mole/mole of chlorotriphenylmethane. A control experiment was identical with that just described except that the *t*-butyl sulfide was omitted. The control gave no isobutylene, but a triphenylmethane yield of 0.19 moles/mole of chlorotriphenylmethane.

Reduction of Triphenylcarbinol and Sulfides 3a and 4a.⁵⁴ Triphenylcarbinol (0.540 g, 2.0 mmole) was dissolved in 10 ml of acetic acid with warming on a steam bath. To this solution was added 1.5 ml of 47% HBr. After heating the solution on a steam

bath for 5 min, 1.5 ml of 47% HI was added and the solution was heated for 1 hr. After cooling the solution to room temperature, 1 g of sodium bisulfite in 10 ml of water was added, and the acids were neutralized by the addition of sodium carbonate. The solution was extracted twice with benzene. Drying of the benzene extracts with sodium sulfate followed by evaporation of the solvent yielded 0.500 g (98.5%) of triphenylmethane, mp 92–93.5°.

Similar treatment of a mixture of triphenylmethyl *t*-butyl sulfide (0.051 g, 0.153 mmole) and 4-biphenyldiphenylmethyl *t*-butyl sulfide (0.050 g, 0.123 mmole) gave 77 mg of reduction product which was dissolved in 4 ml of benzene. Comparison of the vpc of this solution with that of a standard solution using known injection volumes showed the yield of triphenylmethane was 89% and that of 4-biphenyldiphenylmethane was 100%.

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(54) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass, 1955, p. 81.

Reactions of α -Hydroxybenzyl Free Radicals. III.¹ Processes for α -Hydroxycyclopropylcarbinyl Radical Formation

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Abstract: The reactions of arylcyclopropylcarbinols with di-*t*-butyl peroxide and aryl cyclopropyl ketones with 2-butanol and di-*t*-butyl peroxide have been investigated. Factors influencing the stability of the free-radical intermediates have been evaluated. Mechanisms for the formation of α -hydroxybenzyl free radicals from the corresponding ketone have been studied. Direct hydrogen-atom transfer from an α -hydroxyalkyl radical to the aromatic ketone is proposed. Evidence concerning the nature of α -hydroxycyclopropylcarbinyl free radicals suggests that substituents on the cyclopropane ring affect the rate of formation of the radical but that the product composition is highly dependent on radical lifetime.

The cyclopropylcarbinyl free radical has generated neither the interest nor the controversy of its carbonium-ion counterpart. Although the cyclopropylcarbinyl free radical shows a tendency to undergo ring-opening rearrangement reactions, there is no evidence to favor a bicyclobutonium-type reaction intermediate. Whereas the cyclopropylcarbinyl carbonium ion tends to equilibrate with cyclobutyl and allylcarbinyl species, allylcarbinyl products only are most often observed when the radical is generated.³ Only one tentative report of cyclobutyl radical products from cyclopropylcarbinyl radical intermediates has appeared.⁴ Furthermore, although the cyclobutyl carbonium ion shows a tendency to equilibrate with the corresponding allylcarbinyl and cyclopropylcarbinyl structures, reactions of the cyclobutyl free radical generally lead only to unrearranged products.^{5,6}

In spite of the apparent lack of equilibration of the cyclopropylcarbinyl and allylcarbinyl free radicals with

the corresponding four-membered ring species, the ring strain associated with the cyclopropyl group adjacent to the radical site is sufficient to provide the cyclopropylcarbinyl radical with some unusual properties. For example, in almost every case ring opening of the cyclopropylcarbinyl radical to the allylcarbinyl radical occurs concomitant with an unusually large rate of formation of the species. Thus, in every known case the cyclopropylcarbinyl radical is more easily formed than sterically analogous species.^{7–12}

In an earlier communication⁹ we reported that α -hydroxycyclopropylcarbinyl free radicals underwent ring-opening rearrangement to give enolate radicals which, after chain transfer and tautomerization, gave straight-chain ketones. We now report these studies in detail and discuss their bearing on the problem of cyclopropylcarbinyl free-radical intermediates. Further, we report studies pertinent to the mechanism of the reaction of α -hydroxyalkyl radicals with aromatic ketones.

(1) Part II: D. C. Neckers, J. Hardy, and A. P. Schaap, *J. Org. Chem.*, **31**, 622 (1966).

(2) National Science Foundation Undergraduate Research Participant, 1965.

(3) (a) N. Demjanov, *Ber.*, **40**, 4393 (1907); (b) *ibid.*, 4961 (1907); (c) R. Skrabel, *Monatsch.*, **70**, 420 (1927); (d) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(4) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

(5) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(6) D. Schuster, Ph.D. Thesis, California Institute of Technology, 1960.

(7) C. G. Overberger and A. Lebovits, *J. Am. Chem. Soc.*, **76**, 2722 (1954).

(8) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).

(9) D. C. Neckers, *Tetrahedron Letters*, 1889 (1965).

(10) H. Hart, and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

(11) H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

(12) E. S. Huyser and D. H. Wang, *J. Org. Chem.*, **29**, 2720 (1964).