

converted to 1,2-dibromopropane to a small extent (less than 1%). The poor precision in the olefin analyses from the NaSC_2H_5 runs evident in Table III is believed due to this complication; the values listed are uncorrected.

Rate measurements were conducted as previously described.¹¹ The substrate concentration was 0.02–0.04 M. All concentrations listed in the tables have been corrected for thermal expansion of the solvent.

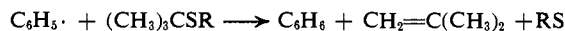
Free Radical Elimination Reactions. Reaction of Phenyl Radicals with Phenyl Amyl Sulfides

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Abstract: The reactions of phenyl radicals with the β hydrogens of *tert*-butyl, phenyl *tert*-butyl, and phenyl amyl sulfides initiate an elimination reaction. The reactivity profile, I:II:III:1:8.5:43, for phenyl radical with hydrogens β to sulfur is obtained from the observed yields of olefins formed from four phenyl amyl sulfides. Competition of *tert*-butyl sulfide against carbon tetrachloride for phenyl radicals gives $k_{\text{H}}/k_{\text{Cl}} = 0.26$. Both results show the reactivities of the β hydrogens of sulfides toward phenyl radicals to be the same as those of alkanes. These results indicate a simple, unassisted hydrogen abstraction and are inconsistent with significant bridging by sulfur or double bond character in the transition state for hydrogen abstraction. The elimination reaction, therefore, is described by a simple two-step process involving a β -thioalkyl radical intermediate.

The preceding paper² described a free radical elimination reaction initiated by attack by phenyl radicals on the β hydrogens of *tert*-butyl and phenyl *tert*-butyl sulfides.

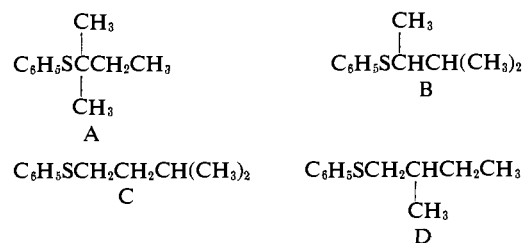


Hydrogen abstraction product and olefin are formed in equivalent yields; intermediate radicals from the sulfides, if present, must therefore fragment more rapidly than they are scavenged by other radicals in the reaction mixture. Other data^{3,4} indicated that the β hydrogens of *tert*-butyl sulfide are appreciably more reactive than comparable primary hydrogens in alkanes. Several mechanisms for the elimination reaction were discussed; the combination of stoichiometric elimination and enhanced reactivity of *tert*-butyl sulfide seemed best accommodated by a concerted $\text{E}_{\text{H}2}$ mechanism. The present work makes use of competitive elimination reactions to study the relative reactivities of the β hydrogens in several *tert*-butyl and amyl sulfides. In addition, the primary β hydrogens of *tert*-butyl sulfide are pitted against carbon tetrachloride for phenyl radicals. In contrast to previous results, both competitions show that the reactivities of these hydrogens β to sulfur to phenyl radicals are the same as the reactivities of hydrogens β to carbon.

Results and Discussion

Four phenyl amyl sulfides (A–D) were prepared and allowed to react with phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane

(PAT) at 77°. The sulfides were used as solvents and the reaction mixtures were carefully deoxygenated. The reaction of phenyl radical with phenyl *tert*-amyl sulfide (A) provides an intramolecular competition between primary and secondary β -hydrogen abstraction to give 2-methylbutene-1 and 2-methylbutene-2, respectively. Since the previous work² established a 1:1 correspondence of H abstraction to olefin, the statistically corrected ratio of the yields of olefins gives the relative reactivities of the β hydrogens. Phenyl *sec*-isoamyl sulfide (B) provides primary/tertiary competition to give 3-methylbutene-1 and 2-methylbutene-2. Mixtures of phenyl isoamyl (C) and phenyl *act*-amyl sulfide (D) as substrates for phenyl radical give 3-methylbutene-1 and 2-methylbutene-1, respectively, and the relative reactivity of secondary to tertiary β hydrogens. In the latter experiments, the ratio of sulfides, C/D, was varied. The reactivity ratio was calculated from the appropriate expression for competitive reactions, $k_{\text{sec}}/k_{\text{tert}} = [3\text{-methylbutene-1}][\text{D}]/[2\text{-methylbutene-1}][\text{C}]$.



All of these sulfides, A–D, are also susceptible to attack at α , γ , and δ hydrogens to give radicals whose fate is unknown. These side reactions affect the absolute yields of olefins (mol of olefin/mol of PAT) as well as the benzene/olefin ratio. They should not, however, perturb the relative yields of olefins which form the basis of the reactivity comparisons. The olefins and benzene were identified by mass spectral

(1) From the Ph.D. Thesis of J. T. Hepinstall, Jr., University of Rochester, 1971.

(2) J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1257 (1966).

(3) W. A. Pryor and T. L. Pickering, *ibid.*, **84**, 2705 (1962).

(4) Private communication from G. A. Russell of unpublished results of J. D. Hunt, Ph.D. Thesis, Iowa State University, 1966; G. A. Russell and R. F. Bridger, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 2C.

Table IV. Reaction of Phenyl Radicals with Mixtures of *tert*-Butyl and Phenyl *tert*-Amyl Sulfide^{a-c}

Sulfide ratio ^d	(CH ₃) ₂ C=CH ₂	CH ₂ =C(CH ₃)C ₂ H ₅	(k _b /k _a) ^e
0.105	0.406	0.0162	0.88
0.237	0.350	0.088	0.96
0.948	0.197	0.636	0.98
2.845	0.082	0.082	0.94
6.007	0.050	0.0903	1.11
8.536	0.034	0.0884	1.08

^a [PAT] $\cong 5 \times 10^{-2}$ M; $T = 77^\circ$. ^b The yields of 2-methylbutene-1 and 2-methylbutene-2 gave an intramolecular reactivity of the β hydrogens of phenyl *tert*-amyl sulfide, $k_{\text{prim}}/k_{\text{sec}}$, identical with that reported in Table I. ^c Each entry is the average of three gc analyses of a single reaction mixture. ^d [Phenyl *tert*-amyl sulfide]/[*tert*-butyl sulfide]. ^e Statistically corrected ratio of rates of abstraction of β -methyl hydrogens of *tert*-butyl sulfide to abstraction of β -methyl hydrogens of phenyl *tert*-amyl sulfide.

shown in Table IV. *tert*-Butyl sulfide and carbon tetrachloride were allowed to compete for phenyl radicals according to the technique of Bridger and Russell.⁵ The yields of benzene and carbon tetrachloride were monitored; the results are shown in Table V.

Table V. Reaction of Phenyl Radicals with *tert*-Butyl Sulfide and Carbon Tetrachloride^a

CCl ₄ /(<i>t</i> -Bu) ₂ S	Mol/mol of PAT ^b		$k_{\text{H}}/k_{\text{Cl}}$ ^c	
	C ₆ H ₆	C ₆ H ₅ Cl	Uncor ^d	Cor ^e
1.837	0.133	0.576	0.360	0.223
0.967	0.168	0.468	0.346	0.257
0.211	0.366	0.238	0.325	0.288
0.048	0.483	0.080	0.292	0.266
∞ ^f	0.043	0.776		

^a [PAT] $\cong 6 \times 10^{-2}$ M; $T = 77^\circ$. ^b Each entry is the average of three gc determinations. ^c Relative reactivity of *tert*-butyl sulfide to carbon tetrachloride on a per molecule basis. ^d Uncorrected for benzene formed from the decomposition of PAT in pure CCl₄. ^e Corrected for the benzene formed from the decomposition of PAT in pure CCl₄; ⁵ cf. W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966); W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967). ^f Pure CCl₄; data are the average of three gc analyses of each of three separate reactions.

Although there is a small experimental trend in the relative reactivities of the β -methyl hydrogens of *tert*-butyl sulfide and phenyl *tert*-amyl sulfide, the data in Table IV clearly show comparable reactivities. The competition between *tert*-butyl sulfide and carbon tetrachloride is a direct measure of the reactivity of the β hydrogens of the sulfide and does not depend in any way on the elimination reaction. This experiment gives an average $k_{\text{H}}/k_{\text{Cl}}$ of 0.26 which is to be compared with the $k_{\text{H}}/k_{\text{Cl}}$ of 2,2,3,3-tetramethylbutane⁵ (18 primary methyl hydrogens) of 0.21. These independent experiments lead to the same conclusion; there is no special reactivity to phenyl radicals of the β hydrogens of *tert*-butyl sulfide. The apparent high reactivity of *tert*-butyl sulfide in previous experiments^{3,4} is presumably due to contamination by *tert*-butyl mercaptan. Both $k_{\text{H}}/k_{\text{Cl}}$ ⁴ and chain transfer³ results would be distorted by the presence of mercaptan.

The preceding data clearly indicate that the primary : secondary : tertiary reactivity profile for phenyl radicals for hydrogens β to sulfur is the same as that for hydrogens β to carbon. The absolute reactivities, as

judged by competitions against carbon tetrachloride, are also the same, ruling out a situation where the profile is identical, but all hydrogens β to sulfur are more reactive than alkane hydrogens. Because the strength of the C-S bond and the stabilities of the olefins to be formed vary from sulfide to sulfide, these reactivity data are not compatible with a concerted EH2 elimination reaction with appreciable double bond character in the transition state. The data also rule out any important assistance to hydrogen abstraction by bridging sulfur.^{6,7} We conclude, therefore, that the elimination reaction involves simple, unassisted hydrogen abstraction to give an intermediate β -thioalkyl radical which fragments rapidly to olefin and a thiyl radical.⁸ In retrospect, the reaction of phenyl radicals with sulfides may not have been a very good candidate for an EH2 mechanism. A combination of a less reactive, more selective attacking radical and a weaker carbon-leaving group bond may be necessary.⁹ At the present time, however, the concerted EH2 mechanism remains unknown.

Experimental Section

Melting points are corrected and boiling points are uncorrected. Nuclear magnetic resonance (nmr) spectra were recorded on a Jeolco Model C60-HL (60 MHz) spectrometer in CCl₄ with tetramethylsilane as an internal standard. Mass spectra were recorded at 70 eV on an Hitachi Perkin-Elmer Model RMU-6E mass spectrometer by Mrs. Eloise Rohner. Distillations were carried out on an 18-in. vacuum-jacketed Nester-Faust annular spinning band column fitted with a stainless steel band and a vacuum take off. Gas chromatographic (gc) analyses were made on an F&M Model 700 dual column instrument equipped with a flame ionization detector, and an F&M Model 720 dual column instrument equipped with a thermal conductivity detector. The following gc columns were used: $\frac{1}{8}$ in. \times 20 ft di-*n*-decyl phthalate on 60-80 mesh Chromosorb A; $\frac{1}{8}$ in. \times 1 m, 10% di-*n*-propyl tetrachlorophthalate on 60-80 mesh Chromosorb A; $\frac{1}{8}$ in. \times 2 m, 20% β , β' -oxydipropionitrile on 60-80 mesh Chromosorb A; $\frac{1}{8}$ in. \times 20 ft, 20% dimethylsulfolane on 60-80 mesh Chromosorb A; $\frac{1}{8}$ in. \times 20 ft, 20% ethylene glycol saturated with AgNO₃ on 60-80 mesh Chromosorb A; $\frac{1}{8}$ in. \times 10 ft, 15% FFAP on 60-80 mesh Chromosorb P; $\frac{1}{8}$ in. \times 14 ft, 10% Carbowax 20M on 60-80 mesh Chromosorb A.

Chemicals. 2-Methylbutene-1, 2-methylbutene-2, 3-methylbutene-1, and cyclopentane were Phillips 66 Pure grade (99+ %), and were used as received. Isobutylene (Matheson, CP grade), was used as received. Benzene (Mallinckrodt, analytical AR grade), was used as received. Chlorobenzene (Fisher, certified pure grade), was determined to be 99+ % pure by gc on a di-*n*-butyl tetrachlorophthalate column in tandem with the β , β' -oxydipropionitrile column at 70°, and was used as received.

Carbon tetrachloride (Baker, Spectrograde, "Baker Analyzed"), was used as received. No impurities (<0.1 %) were detected on the di-*n*-propyl tetrachlorophthalate column in tandem with the β , β' -oxydipropionitrile column.

Preparation of Sulfides. Phenyl *tert*-amyl sulfide was prepared by the acid-catalyzed reaction of *tert*-amyl alcohol with thiophenol.¹⁰ The crude sulfide was distilled on a spinning band column: bp 43° (0.1 mm); n_{D}^{25} 1.5353 [lit.¹⁰ bp 88° (3.5 mm), n_{D}^{25} 1.5351]; nmr (CCl₄) δ 1.2 (complex multiplet, 11 H), 7.2 (complex multiplet, 5 H). Phenyl *tert*-amyl sulfide of maximum purity by distillation showed three groups of peaks by gc on a 14 ft \times $\frac{1}{8}$ in. 10% Carbowax 20M column at 215°. The first peak was a sharp spike consistent with olefin retention time. The second was a multiplet with five or more components. The third and major peak was phenyl *tert*-amyl sul-

(6) P. S. Skell, *Chem. Soc., Spec. Publ.*, No. 19, 131 (1965).

(7) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); A. Ohno and Y. Ohnishi, *Tetrahedron Lett.*, 339 (1972).

(8) C. Walling and W. Helms, *J. Amer. Chem. Soc.*, **81**, 1144 (1959).

(9) F. R. Jensen and H. E. Guard, *ibid.*, **90**, 3250 (1968).

(10) V. N. Ipatieff, H. Pines, and B. S. Friedman, *ibid.*, **60**, 2731 (1938).

fide which was overlapped by a much smaller peak at slightly greater retention time. The latter peak was identified as phenyl *sec*-isoamyl sulfide by coinjection. Estimates from relative peak areas indicated the sulfide to be 99+ % pure. Repeated attempts to separate the impurities by distillation were unsuccessful.

Phenyl *sec*-isoamyl sulfide was prepared by the free radical addition of thiophenol to 2-methylbutene-2. Thiophenol, 22 g (2.02 mol), was placed in a flask equipped with a condenser, magnetic stirrer, and an addition funnel. A small amount of phenylazotriphenylmethane was added. 2-Methylbutene-2, 115 g (2.15 mol), was added dropwise over 1.5 hr. The mixture was irradiated for several hours with a sun lamp. The crude mixture was distilled through a Vigreux column at reduced pressure and finally distilled on the spinning band column: bp 92° (5.5 mm) [lit.¹⁶ bp 83.5–86° (3.5 mm), 99–100° (5 mm)]; nmr (CCl₄) δ 0.93 (doublet, *J* = 6.75 Hz, 6 H), 1.13 (doublet, *J* = 4.5 Hz, 3 H), 1.8 (complex multiplet, 1 H), 3.05 (octet, *J*_{H,H} = 6.75, *J*_{H,Me} = 4.5 Hz, 1 H), 7.1 (complex multiplet, 5 H). Gc analysis on Carbowax 20M and FFAP columns at 140° showed traces of pentenes and phenyl *tert*-amyl sulfide; the phenyl *tert*-amyl sulfide concentration was reduced to 0.6% by distillation. Phenyl isoamyl and *act*-amyl sulfides were not detected.

Phenyl isoamyl sulfide was prepared by the free radical addition of thiophenol to 3-methylbutene-1 using the procedure described for the preparation of phenyl *sec*-isoamyl sulfide. The crude product was distilled from copper powder on a spinning band column: bp 99° (5 mm) [lit.¹⁰ bp 100–100.5° (6 mm)]; nmr (CCl₄) δ 0.85 (doublet, 6 H), 1.5 (complex multiplet, 3 H), 2.8 (triplet, 2 H), 7.1 (complex multiplet, 5 H).

Phenyl *act*-amyl sulfide was prepared by the free radical addition of thiophenol to 2-methylbutene-1 using the procedure described for the preparation of phenyl *sec*-isoamyl sulfide. The product was distilled from copper powder on a spinning band column: bp 97° (3 mm) [lit.¹⁰ 99–101° (4 mm)]; nmr (CCl₄) δ 0.9, 1.4 (overlapping multiplets, 9 H), 2.7 (octet, 2 H), 7.1 (complex multiplet, 5 H).

Phenyl *act*-amyl sulfide and phenyl isoamyl sulfide were not separable by gc. Examination on a di-*n*-decyl phthalate column showed that each of these isomers contained small quantities of all three isoamylenes and a very small peak that corresponded to benzene. On the FFAP column at 140° only one additional impurity was detected in each case. The phenyl *act*-amyl sulfide contained a small amount (less than 1%) of phenyl *tert*-amyl sulfide and the phenyl isoamyl sulfide contained a small amount (less than 1%) of phenyl *sec*-isoamyl sulfide. While it could not be determined that phenyl *act*-amyl sulfide and phenyl isoamyl sulfide were not mutual contaminants, decomposition of PAT in the neat sulfides showed an increase in only the olefin expected from β elimination in the respective sulfide. Phenyl *act*-amyl sulfide showed a significant production of 2-methylbutene-1 and, qualitatively, no increase in 2-methylbutene-2 or 3-methylbutene-1 while phenyl isoamyl sulfide showed a significant production of 3-methylbutene-1 and qualitatively no increase in the amount of 2-methylbutene-1 or 2-methylbutene-2 already present as contaminants.

Di-*tert*-butyl Sulfide. Several distillations of commercial di-*tert*-butyl sulfide on a spinning band column were required to obtain sulfide of acceptable purity: bp 153° [lit.⁹ 151°]; nmr (CCl₄) δ 1.34 (singlet). Examination on a tandem column (di-*n*-propyl tetrachlorophthalate, β,β'-oxydipropionitrile) showed peaks corresponding to isobutylene and *tert*-butyl mercaptan, as well as a small peak corresponding in retention time to benzene, and a cluster of peaks just ahead of di-*tert*-butyl sulfide. Samples used in reactions were determined to be 99+ % pure by measuring peak areas. In a typical sample, mercaptan was found to be 0.02 mol % of the sample. The impurity with the same retention time as benzene was often completely removed; when present, the benzene yield was corrected by a blank.

Phenylazotriphenylmethane (PAT). *N*-Phenyl-*N'*-tritylhydrazine is prepared by the reaction of trityl chloride with phenylhydrazine in absolute ether.¹¹ The crude product, mp 104–110°, is dissolved in 50 ml of chloroform, the solution filtered, and methanol added to initiate crystallization. The recovered material (73% recovery), mp 111–112°, contains only phenylazotriphenylmethane (PAT) as an impurity when examined by tlc on silica gel with 50:50 hexane-benzene and iodine development (*R*_f 0.65 for PAT and 0.75 for the hydrazo compound).

Crude hydrazo compound, 4.9 g (0.014 mol), is dissolved in ap-

proximately 125 ml of ether and placed in a Parr shaker under 30 psi of oxygen. After 45 min no hydrazo compound is detected by tlc; other impurities are present at the origin. The ether is removed and the crude PAT dissolved in benzene. Petroleum ether (bp 30–60°) is added. Refrigeration and filtration yields 2.2 g of yellow needles, mp 106–108° (cor). Tlc as described above shows only the spot corresponding to PAT. The remaining mother liquor is evaporated to dryness at 25° and the residue dissolved in chloroform. Methanol is added; cooling yields a second crop, 1.7 g, mp 108–110° (cor). Tlc shows only one spot and a clean origin. The total yield of PAT is 80%. Methanol-chloroform is the solvent system of choice since benzene tends to adhere to the PAT crystals. Both of the above crops of PAT were stored overnight under vacuum: first crop, mp 111–111.5°; second crop, mp 108–109.5°. The first and second crops showed λ_{max} (cyclohexane) 421 nm, ε 201 and 192, respectively. Two further recrystallizations from chloroform-methanol give mp 113.5–115.0°, ε⁴²¹ (cyclohexane) 204.

Decomposition of PAT in Various Mixtures. Solutions of known concentrations of PAT in either pure solvents or mixtures of solvents (of known mole ratio) were prepared by standard volumetric and gravimetric techniques. Samples of these solutions were transferred to glass reaction tubes, degassed by three freeze-pump-thaw cycles at <0.05 mm, sealed, and heated in a refluxing ethyl acetate bath (77 ± 3°) for 2.5–3.5 hr. The contents of the tubes were frozen, the tubes were opened, and a known amount of internal standard for gc was added.

Qualitative Determination of Products. The olefin products and benzene from PAT-sulfide reactions were collected from the gc with a 0.25-in. di-*n*-decyl phthalate column.

Mass spectra of the collected olefin products gave parent peaks at *m/e* 70 and fragmentation patterns consistent with the mass spectra of authentic olefins which were measured at the same time and under the same operating conditions. The parent peak at *m/e* 70 establishes the formula of these compounds to be C₈H₁₀. However, many of the C₈H₁₀ isomers have very similar fragmentation patterns.¹² Only cyclopentane, ethylcyclopropane, and 1-pentene can be clearly distinguished from the others since these isomers have their base peak at *m/e* 42 rather than 55 which the other isomers have as a common base peak.

Gc of the reaction mixtures on three columns did, however, clearly distinguish among the three olefins as well as the other C₈H₁₀ isomers. Reaction mixtures were injected on each of the three columns, and the retention time of the olefin product(s) for each sulfide agreed with the retention time of authentic material. The reaction mixtures were then coinjected with authentic olefins and benzene in turn and smooth increases (no shoulders or new peaks) in the appropriate product peaks were observed. Coinjections were made only on di-*n*-decyl phthalate (DMD) and dimethylsulfolane (DMS). Retention times alone were measured on the silver nitrate column (AGN).

The AGN column, as reported by Ohlson,¹³ retains even low boiling olefins while relatively high boiling paraffins are eluted first. Only phenyl *tert*-amyl sulfide reaction mixtures produced a peak which eluted before olefin products. This was identified as isopentane (see below). On this basis, all cyclic C₈H₁₀ isomers can be ruled out as products from the sulfides.

It is therefore established that the products designated as olefins are of the formula C₈H₁₀ and can only be 2-methylbutene-1, 2-methylbutene-2, 3-methylbutene-1, and *cis-trans* pentene-2; cyclic hydrocarbons and pentene-1 are excluded.

All three gc columns clearly distinguish 2-methylbutene-2 from the other isomers under consideration. 2-Methylbutene-1 is distinguished from 3-methylbutene-1 and 2-methylbutene-2 on DND and DMS, and from *cis-trans* pentene-2 on AGN. 3-Methylbutene-1 is also well separated from all other possibilities on all three columns. The mass spectral evidence which eliminated 1-pentene is confirmed by all three columns.

A large scale decomposition of PAT in phenyl *tert*-amyl sulfide (200 ml) was run (3.7 g in 200 cc). The olefin reaction products were distilled from solvent on a vacuum line and collected from a DND column. 2-Methylbutene-2 and 2-methylbutene-1 were collected. The ir spectra (CCl₄) in the C–H stretching region of the authentic olefins were superimposable with those of the respective collected products.

(12) "Catalog of Mass Spectral Data," American Petroleum Institute Research Project No. 44, National Bureau of Standards, 1949, Spectra No. 29-34, 116, 738, 926, 972.

(13) B. Smith and R. Ohlson, *Acta Chem. Scand.*, **16**, 351 (1962).

(11) S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **77**, 3628 (1955).

The minor product (<5% of the benzene yield) in the phenyl *tert*-amyl reaction mixtures eluted from AGN before any olefin. The product was examined on a vpc-mass spectrum tandem arrangement with a DND column. Mass spectra were recorded at several different points as the gc peak increased and decreased in intensity. The differences in intensities between different spectra at each value of *m/e* cancel the background and give an indication of the relative intensities of the peaks to be attributed to material being eluted. The latter values were then normalized in the usual way. A strong parent peak appears at *m/e* 72 and the fragmentation pattern is consistent with the published spectra of isopentane.¹² Excluding heteroatoms, the parent peak at *m/e* 72 requires C₅H₁₂, namely, *n*-pentane, isopentane, and neopentane. Pentane, isopentane, and the product all have a base peak at *m/e* 43 (C₃H₇⁺), whereas neopentane has a base peak at *m/e* 57 and only a very small peak (1.7%) at *m/e* 43.¹² *n*-Pentane and isopentane are readily separable on DND and DMS and isopentane coinjects with the product peak on both of these columns.

The benzene collected from the reaction of PAT with each individual sulfide gave mass spectra characteristic of benzene by comparison with that of authentic benzene.

Benzene and chlorobenzene from a reaction mixture of PAT, carbon tetrachloride, and di-*tert*-butyl sulfide were collected by gc from a 0.25 in. di-*n*-decyl phthalate column; mass spectra and retention times agreed with those of authentic material.

Quantitative Analysis of Reaction Products. The olefins and benzene from the reactions of the phenyl amyl sulfides and *tert*-butyl sulfides were measured quantitatively on a 20 ft × 1/8 in., 20% di-*n*-decyl phthalate column on an F & M Model 700 gas chromatograph equipped with a flame detector. Cyclopentane was used as an internal standard. Triplicate injections were made for each sample. Peak areas were measured by planimeter or triangulation.

Standards solutions of the products in the appropriate sulfide were generally prepared along with each set of reaction tubes and response factors determined. However, this was not always the case; since the response factors were reasonably consistent from run to run, an average value for each product was calculated from all the values obtained, and this value was used for each reaction tube.

Since some samples of sulfide contained small amounts of product olefins, corrections were sometimes necessary. A blank tube (1.0 ml of sulfide, degassed and heated with reaction tubes) was doped with a known amount of cyclopentane and analyzed to determine correction factors.

The benzene and chlorobenzene produced by the decomposition of PAT in *tert*-butyl sulfide-carbon tetrachloride mixtures were measured on a 1/8 in. × 1 m, 10% di-*n*-propyl tetrachlorophthalate

column in tandem with a 1/8 in. × 2 m, 20% β,β'-oxydipropionitrile column at 70°. *tert*-Butylbenzene was used as an internal standard. Response factors were calculated from the gc analysis of solutions of known composition.

Effect of Added Olefin on Product Yields in the Decomposition of PAT in Phenyl *tert*-Amyl Sulfide. A control experiment was run to verify the assumption that the olefins formed in the elimination reaction are not consumed by subsequent secondary reactions. Two stock solutions were prepared. One was a solution of PAT (0.05 M) in phenyl *tert*-amyl sulfide. The other was prepared by adding small amounts of 2-methylbutene-1 and 2-methylbutene-2 via microliter syringe to a sample of phenyl *tert*-amyl sulfide to give a solution which was approximately the same in respective olefin concentrations as the phenyl *tert*-amyl sulfide-PAT solutions after decomposition.

Five reaction tubes were then prepared. Each of the first two contained a 1-ml aliquot of the PAT solution. Each of the second two contained a 1-ml aliquot of the PAT solution and a 1-ml aliquot of the olefin solution. The fifth tube contained a 1-ml aliquot of the olefin solution. The tubes were degassed, sealed, and heated in a refluxing ethyl acetate bath, opened, and analyzed by gc. The analyses are presented in Table VI. Averaged values are reported.

Table VI. Stability of Product Olefins to the Reaction Conditions

Sample	Mol × 10 ⁶ /tube	
	CH ₂ =C(CH ₃)C ₂ H ₅	(CH ₃) ₂ C=CHCH ₃
PAT ^a	5.60	12.75
Olefin ^b	4.69	12.95
PAT + olefin ^c	10.63	26.15

^a PAT in phenyl *tert*-amyl sulfide. ^b Olefin in the sulfide. ^c Olefin + PAT in the sulfide.

The total yield of olefins in the tube containing PAT + olefin in the sulfide should equal the sum of the olefins in the "PAT tube" and the "olefin tube," if the olefins are stable to the reaction conditions. The results show this to be the case; replicate experiments gave comparable results.

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Photolysis of a Charge Transfer Complex. Triphenylsulfonium Iodide

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Abstract: A charge transfer absorption is identified for triphenylsulfonium iodide in chloroform. Selective irradiation of the complex at the wavelength of the CT transition gives stoichiometric conversion of the sulfonium salt to diphenyl sulfide with a quantum yield of 0.35. The phenyl group lost is quantitatively accounted for as iodobenzene and benzene. Triiodide ion is also formed. The ratio iodobenzene/diphenyl sulfide is about 0.6 and is not significantly dependent on conversion from 0.05 to 70% reaction. Accordingly, the formation of phenyl products is rationalized by nondiffusive (C₆H₅I) and diffusive (C₆H₆) pathways.

The role of excited charge transfer (CT) complexes in photochemical processes is receiving increasing recognition. These excited states can be formed by

(1) From the Ph.D. Thesis of S. L. N., University of Rochester, 1970.

irradiation of ground state CT complexes in the CT absorption band or, possibly, by interaction of an excited state with a ground state molecule. Excited CT complexes show a wide range of chemical behavior. For example, irradiation of the CT band of the ben-