raised by external heating from 25° at the start of the reaction to about 70° at the end. Filtration of the mixture through Celite yielded a colorless filtrate which was concentrated *in vacuo*, under nitrogen to yield a colorless gum. A benzene solution of this material was adsorbed on 100 g. of silica gel in a chromatographic column. Elution of the column with a 10% solution of ether in benzene yielded 1.31 g. (41.4%), m.p. 131–134°, of 1,3,-4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline. The analytical sample, m.p. 132.5–133.5°, was prepared by recrystallizing some of this material from methanol–water. This material could also be crystallized from ether, ether–Skellysolve B, and benzene–Skellysolve B. The white, crystalline compound turned dark when exposed to air and light for several days. The ultraviolet spectrum (ethanol) had λ_{max} 227, 277, 290, and 299 mμ (ϵ 33,650, 6600, 5950, and 6050, respectively).

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.11; H, 6.18; N, 17.32.

Further elution of the silica gel column with ether yielded 0.386 g. (11.3%), m.p. 134–136°, of 4-aminoindol-3-ylacetonitrile. The analytical sample, m.p. 135–136°, was prepared by recrystallizing a portion of this material from ethyl acetate–Skellysolve B. The ultraviolet spectrum (ethanol) had λ_{max} 225, 273, and 295 mμ (ϵ 45,300, 7100, and 5000, respectively) with an inflection at 288 mμ (ϵ 5300). The infrared spectrum (Nujol) showed NH, 3400, 3350, 3330, and 3240 cm.$^{-1}$; and $-C{\equiv}N$, 2250 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_9N_3$: C, 70.15; H, 5.30; N, 24.55. Found: C, 70.39; H, 5.45; N, 24.24.

5-Formyl-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline (XI).—Formic acetic anhydride was prepared by mixing 9.45 ml. of acetic anhydride with 3.98 ml. of 98% formic acid. To 3 ml. (21.4 mmoles) of this solution, cooled in an ice bath, was added slowly 1.54 g. (9.73 mmoles) of the amine (II). The resulting solution was allowed to stand at room temperature for 5 hr. Ether was added and the solution was allowed to stand for 18 hr. It then was washed successively with water, dilute ammonium hydroxide, and brine. The resulting ether solution was dried over anhydrous sodium sulfate and concentrated *in vacuo* under nitrogen. Crystallization of the residue from ethyl acetate–Skellysolve B yielded 1.55 g., m.p. 138–139°, and 0.173 g., m.p. 128–132° (95.1%), of the N-formyl derivative. The analytical sample, m.p. 131–134°, was prepared by recrystallizing this material from ethyl acetate–Skellysolve B. The ultraviolet spectrum (ethanol) had λ_{max} 225 and 294 mμ (ϵ 31,750 and 9300, respectively) with an inflection at 288 mμ (ϵ 9500). The infrared spectrum (Nujol) showed NH, 3250 cm.$^{-1}$; and C=O, 1663 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41. Found: C, 70.83; H, 5.04.

5-Methyl-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline (X).—To an ice-cold mixture of 1.5 g. of powdered lithium aluminum hydride in 200 ml. of dry tetrahydrofuran was added 1.69 g. (9.08 mmoles) of the amide (XI). The resulting mixture was allowed to stir at room temperature under nitrogen for 20 hr. After the mixture had been allowed to reflux for 1 hr., it was cooled in an ice bath and treated successively with 1.5 ml. of water, 1.5 ml. of 15% sodium hydroxide, and 4.5 ml. of water. The inorganic salts were collected by vacuum filtration through Celite and washed with ether. Concentration of the combined filtrates under nitrogen and reduced pressure yielded an oil which was dissolved in benzene and chromatographed on silica gel with 2% ether–benzene to yield 1.39 g. (89.3%) of 5-methyl-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline, m.p. 119–121°. The analytical sample, m.p. 121–123°, was prepared by recrystallizing this material from benzene–Skellysolve B. The ultraviolet spectrum (ethanol) had λ_{max} 227, 282, and 299 mμ (ϵ 33,850, 7250, and 7900, respectively). The infrared and n.m.r. spectra supported the proposed structure.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.74; H, 7.39; N, 15.96.

1-Methyl-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline Hydrochloride (XII).—To a stirred solution of 2.00 g. (12.7 mmoles) of the amine (II) in 150 ml. of dry dimethylformamide was added, under nitrogen, 600 mg. (13.3 mmoles) of a 53.2% mineral oil suspension of sodium hydride. After 1.5 hr., methyl iodide (0.828 ml., 13.3 mmoles) was added to the mixture; the resulting solution was allowed to stand at room temperature for 2 hr. It then was poured into about 1 l. of water, and the resulting mixture was saturated with sodium chloride and extracted with ether. The ether extract was washed with brine, dried over anhydrous potassium carbonate, and concentrated to yield, after preliminary silica gel chromatography, 2.06 g. of a mixture of product and starting material. Careful chromatography of this material on silica gel with 0.5% ether–benzene resulted in a pure product which was converted to the hydrochloride and crystallized from methanol–ethyl acetate to yield 1.05 g. (39.7%), m.p. >200° dec., of 1-methyl-1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]-quinoline hydrochloride. A sample of this material was recrystallized three times from methanol–ethyl acetate for analysis and had m.p. 220–235° (sublimation and decomposition in a sealed capillary). The ultraviolet spectrum (ethanol) had λ_{max} 228, 284, and 310 mμ (ϵ 32,900, 5700, and 7050, respectively) with an inflection at 303 mμ (ϵ 6500). The infrared spectrum supported the proposed structure.

Anal. Calcd. for $C_{11}H_{13}ClN_2$: C, 63.31; H, 6.28; Cl, 16.99; N, 13.43. Found: C, 63.46; H, 6.39; Cl, 17.08; N, 13.42.

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A Search for the Sulfonium Radical Intermediate

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The existence of a sulfonium and sulfonium-type radical intermediate in some free-radical reactions of phenyl sulfide has been studied. It has been found that the *t*-butoxy radical with phenyl sulfide gives phenyl sulfoxide and the *t*-butyl radical; these could form *via* a sulfonium-type radical intermediate. The cumyloxy radical and benzophenone triplet were apparently not reactive enough to give the intermediate, and alkyl radicals gave indefinite products.

Recent work by Walling and Rabinowitz[2] has offered substantial evidence that the phosphorus atom undergoes an expansion of its valence shell to accommodate nine electrons under certain free-radical reaction conditions. This state was described as an intermediate consisting of four groups bonded to and a free electron associated with the central phosphorus atom.

Research both by Price and Zomlefer[3] on free-radical additions to vinyl sulfides and Martin and Bentrude[4] on the rates of decomposition of *o*-methylthiophenyl peresters indicates that a d-orbital of a sulfur atom might also be capable of accepting an unpaired electron, thus elevating its octet to a nonet. The resulting transient intermediate, with three alkyl or aryl groups and an un-

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[1] (a) IBM Research Laboratory, San Jose 14, Calif.; to whom inquiries should be sent; (b) from the M.S. thesis of D. J. C., June, 1963.

[2] C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959).

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[4] W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

TABLE I

Reactants	Conditions	Products
Ph_2S and $(CH_3)_3CBr$	Ultraviolet	Polyisobutylene and a solid, m.p. 182–185°, which contained no S or Br
	Heat, 60°	N.r.[b]
Ph_2S and CH_3I	Ultraviolet	Solids, m.p. 150–153° and 143–147°, neither containing S or I
$Ph_2S + Ph_2C{=}O$	Ultraviolet	N.r.
	Heat, 170°	N.r.
$Ph_2S + (CH_3)_3COOC(CH_3)_3$	Heat, 150°	Phenyl sulfoxide (1%), phenyl tolyl sulfide,[a] acetone (0.75%)
Ph_2S	Heat, 150°	N.r.
$Ph_2S + (CH_3)_3COCl$	Spontaneous	Phenyl sulfoxide (28%), *t*-butyl chloride, and acetone
	Ultraviolet	Phenyl sulfoxide (46%)
	Dark	Phenyl sulfoxide after a 4-min. induction period
$Ph_2S + PhC(CH_3)_2OOC(CH_3)_2Ph$	Heat, 135°	Acetophenone, phenyl tolyl sulfide,[a] and no phenyl sulfoxide
$Ph_2S + Ph(CH_3)_2COCl$	Ultraviolet	Acetophenone, no sulfoxide

[a] Tentative identification. [b] N.r. = no reaction.

paired electron about the sulfur atom, would be the sulfonium radical.

This study was conducted in an effort to investigate and substantiate the existence of the postulated sulfonium and sulfonium-type radical intermediates. Proof for such intermediates could assist in explaining other free-radical reactions with organic sulfur compounds, *i.e.*, the breakdown of sulfur containing amino acids,[5] disulfides,[6] thiosulfones,[7] and arylsulfenyl chlorides.[8] In contrast, Pryor[9] has indicated that radicals may cleave disulfides at the S–S bond by a reaction that could be a direct displacement.

The free-radical forming reagents used were selected on the basis of the reaction conditions which would be necessary to obtain homolytic bond scission of the reagent, and on the feasibility of obtaining and investigating the products from the decomposition of the proposed sulfonium radical intermediate.

Results and Discussion

Phenyl sulfide was selected as the sulfur compound for this investigation for two reasons. First, the homolysis of the phenyl–sulfur bond in the postulated sulfonium radical, as described in eq. 1, would not be expected to

$$Ph_2\dot{S}\text{–}R \longrightarrow PhS\text{–}R + Ph\cdot \qquad (1)$$

occur, because the phenyl radical is too unstable. Second, it has been found that phenyl sulfide does not undergo autoxidation with molecular oxygen, even when the oxidation is catalyzed by peroxides.[10] This absence of the autoxidation of phenyl sulfide was confirmed.

Evidence for a sulfonium-type radical intermediate is available from the studies done with peroxide. The following sequence summarizes a possible mechanism for phenyl sulfide–*t*-butyl peroxide reactions (Table I).

$$((CH_3)_3CO)_2 \longrightarrow 2(CH_3)_3CO\cdot \qquad (2)$$

$$(CH_3)_3CO\cdot + Ph_2S \longrightarrow Ph_2\text{–}\dot{S}\text{–}O\text{–}C(CH_3)_3 \qquad (3)$$

$$Ph_2\dot{S}\text{–}O\text{–}C(CH_3)_3 \longrightarrow Ph_2SO + (CH_3)_3C\cdot \qquad (4)$$

$$(CH_3)_3C\cdot \longrightarrow \text{dimer, isobutylene, and other hydrocarbon products} \qquad (5)$$

Phenyl sulfoxide and acetone were the compounds identified from a number of products formed in the thermally initiated reaction. The other products (minor amounts) were probably formed by the abstraction, disproportionation, and addition reactions of the alkoxy and alkyl radicals. Gas chromatography gave evidence for the formation of phenyl tolyl sulfide, undoubtedly from the attack of the methyl radical on the sulfide.

The formation of acetone indicates that the *t*-butyl peroxide was reacting by a free-radical mechanism. It would be difficult to explain the formation of acetone by an ionic mechanism proceeding through either the alkoxonium cation, RO^+, or the alkoxide anion, RO^-, since the formation of the latter two species usually requires extensive solvation and the presence of a strong Lewis base or Lewis acid, respectively. Thus, the identified products and the conditions employed strongly support the existence of a sulfonium-type radical intermediate in this reaction.

t-Butyl hypochlorite and phenyl sulfide (Table I) reacted exothermically at a rapid rate to produce a number of products: phenyl sulfoxide, *t*-butyl chloride, and acetone, but no phenyl sulfone. A proposed radical mechanism to explain these results is as described above, plus the following reaction.

$$(CH_3)_3C\cdot + (CH_3)_3COCl \longrightarrow (CH_3)_3CCl + (CH_3)_3CO\cdot \qquad (6)$$

Support for a radical mechanism may be derived from the work of Walling and Thaler,[11] and Greene and coworkers,[12] from the large increase in the rate of reaction in the presence of light, and from the formation of both *t*-butyl chloride and acetone.

Cumyl peroxide–phenyl sulfide and the cumyl hypochlorite–phenyl sulfide reactions (Table I) were carried out under the same conditions in order to obtain additional information concerning the sulfonium-type radical, and to compare the reactions of the electrophilic cumyloxy radical with those of the electrophilic *t*-butoxy radical. The proposed mechanism for the cumyl peroxide–phenyl sulfide reactions involves a sequence like that above. Acetophenone from the decomposition of the cumyl radical was identified as a reaction product in both the cumyl peroxide and cumyl hypochlorite reactions with phenyl sulfide. However, phenyl sulfoxide was *not* identified as a reaction product in either case.

The absence of phenyl sulfoxide suggests that the sulfonium-type radical intermediate, $Ph(CH_3)_2CO\dot{S}$-

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[9] W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962); See also **85**, 1496 (1963).

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[12] F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963).

Ph_2, was not formed under the reaction conditions. A possible explanation for the failure of the electrophilic cumyloxy radical and phenyl sulfide to react and form the intermediate lies in the stability of the cumyloxy radical. The *t*-butoxy radical, which apparently forms a sulfonium-type radical intermediate, has a reactivity comparable to that of a chlorine atom,[13,14] while the cumyloxy radical, which does not give the intermediate, is the only alkoxy radical which is known to dimerize.[15] Thus, from a comparison of the two oxy radicals, the cumyloxy radical appears to be stable in this type of reaction in relation to the very reactive *t*-butoxy radical.

The studies with alkyl halides and benzophenone (Table I) did not afford evidence for the intermediate. Neither *t*-butyl bromide nor methyl iodide gave sulfonium halide, which would have to form by subsequent electron transfer from the intermediate to the halogen atom as depicted in reaction 7. The polyisobutylene isolated came from isobutylene, undoubtedly formed

$$\mathrm{Ph_2\dot{S}{-}R + X\cdot \longrightarrow Ph_2S{-}R + X^-} \qquad (7)$$

by the photolytic dehydrohalogenation of the halide. Benzophenone when photolytically activated to its triplet state[16] did not give rise to the expected phenyl sulfoxide and the diphenylmethyl diradical (eq. 8).

$$\mathrm{Ph_2\dot{C}{-}O{-}\dot{S}Ph_2 \longrightarrow Ph_2\dot{C}\cdot + Ph_2SO} \qquad (8)$$

The latter also did not form in a thermal reaction similar to one by Poshkus and Herweh[17] with phenylphosphine.

The results of this investigation suggest that the formation of the sulfonium radical with phenyl sulfide requires a reactive, electrophilic radical. This might be explained by stating that the *t*-butoxy radical, in comparison to the cumyloxy radical and benzophenone triplet, is the only free radical of the three which has the necessary reactivity to supply the energy required to reach a transition state with phenyl sulfide. This transition state would be expected to be closer to the products than to the reactants. The absence of reaction with the alkyl radical is probably due to the polar effect.[13] The polar effect would also readily explain why no sulfone was formed, even in the reactions in which large amounts of sulfoxide was produced.

Experimental

Reagents.—These two were used without purification: benzophenone (Paragon Testing Laboratories, m.p. 48–49°) and dicumyl peroxide (Hercules Powder Co., m.p. 38°). The following were distilled through an 18-in. column equipped with glass helices: *t*-butyl bromide (Eastman Kodak Co., White Label, b.p. 42°, $n^{21}\mathrm{D}$ 1.5291), and all the solvents that were used for column and thin layer chromatography. Phenyl sulfide (Eastman Kodak Co., White Label, b.p. 76–77° at 0.08 mm.) was distilled through a 6-in. column equipped with a tantalum-wire spiral. Purity of the phenyl sulfide was checked by gas chromatography before use. *t*-Butyl peroxide (Lucidol Corp., $n^{20}\mathrm{D}$ 1.3889) was distilled through a 14-in. column equipped with a tantalum-wire spiral.

Ultraviolet-Initiated Reaction of Phenyl Sulfide and *t*-Butyl Bromide.—A solution of *t*-butyl bromide (0.54 mole, 73.6 g.) and phenyl sulfide (0.54 mole, 100.0 g.) was placed in a Kharasch-Friedlander type of ultraviolet irradiation vessel and illuminated for 24 hr. at 40–60°. Distillation gave about 5 g. of residue. Chromatography gave a number of oils and tars, but no solid product.

Heat-Initiated Reaction of Phenyl Sulfide and *t*-Butyl Bromide.—A control reaction of *t*-butyl bromide (0.054 mole, 7.36 g.) and phenyl sulfide (0.054 mole, 10.0 g.) was conducted at 60° with stirring for 24 hr. The temperature was maintained with a Thermocap relay. Distillation of the reaction mixture yielded only the starting components.

Ultraviolet-Initiated Reaction in Benzene Solvent.—When the reaction above was run in benzene, distillation gave a sublimate, m.p. 73.5°. The residue was chromatographed to give a solid B, m.p. 182–185°. Compounds A and B both gave negative tests for ionic halogen and sulfur. Compound A was shown to be polyisobutylene by its infrared spectrum.

Ultraviolet-Initiated Reaction of Phenyl Sulfide and Iodomethane.—Phenyl sulfide (0.54 mole, 100.0 g.), iodomethane (0.54 mole, 76.29 g.), and benzene (350 ml.) were placed in an ultraviolet chamber and irradiated for a 24-hr. period. Work-up by chromatography gave two compounds, A and B. Compound A, m.p. 150–153°, was recrystallized from petroleum ether (b.p. 60–80°), and compound B, m.p. 143–147°, from ethanol. A silver nitrate test for halogen and a sodium fusion analysis for sulfur and halogen were negative for both compounds.

Phenyl Sulfide and Benzophenone.—Phenyl sulfide and benzophenone in various solvents and with cyclohexene both present and absent were heated at 170° for 72 hr. or irradiated at room temperature with different ultraviolet sources for varying lengths of time. Analysis of the mixtures by thin layer and gas chromatography (5-ft. 5% Carbowax column, 215°, 20 lb. He) indicated the presence of starting compounds plus a small amount of unknown materials.

Phenyl Sulfide and *t*-Butyl Peroxide (A).—A mixture of phenyl sulfide (0.054 mole, 10.0 g.) and *t*-butyl peroxide (0.009 mole, 1.31 g.) was placed in a steel bomb fitted with a Pyrex liner and heated for 2 hr. at 150°. The resultant mixture was analyzed by gas chromatography (10-ft. silicone column, 235°, 16 lb. He), to yield peaks corresponding to phenyl sulfide at 4.8 min. and phenyl sulfoxide at 10.2 min. The phenyl sulfoxide peak was sharp and uniform and remained so even when phenyl sulfoxide was added and the height of the phenyl sulfoxide peak of the reaction mixture changed correspondingly with each addition. A peak immediately following the phenyl sulfide peak (5.0 min.) was tentatively identified as phenyl tolyl sulfide. Acetone was also identified as a reaction product by gas chromatography (10-ft. Ucon Polar column, 106°, 4 lb. He at 4.4 min.). Acetone to sulfoxide molar ratio was 0.74:1 and sulfide to sulfoxide molar ratio was 800:1.

Phenyl Sulfide without Peroxide.—A reaction of phenyl sulfide (0.054 mole, 10.0 g.) was carried out under the same conditions as stated above except no peroxide was present. The resultant liquid was analyzed under exactly the same conditions as previously stated, but no phenyl sulfoxide was observed.

Phenyl Sulfide and *t*-Butyl Peroxide (B).—Phenyl sulfide (0.027 mole, 5.0 g.), *t*-butyl peroxide (0.0135 mole, 1.98 g.), and benzene (10 ml.) were placed in a glass ampoule which was cooled to −80°, flushed with nitrogen, sealed, and heated at 160° for 4 hr. Thin layer analysis using a solution of 3% glacial acetic acid, 20% benzene, and ligroin as solvent showed the presence of phenyl sulfoxide (blue color when sprayed with sulfuric acid followed by heating). The mixture was analyzed by gas chromatography (5-ft. 5% Carbowax column, 210°, 10 lb. He), and the peaks at 5.4 min. and 18.2 min. corresponded to a prepared mixture of the phenyl sulfide and phenyl sulfoxide, respectively. The apparent phenyl tolyl sulfide peak was also present. Acetone was also identified as a reaction product by gas chromatography (10-ft. Ucon Polar column, 106°, and 4 lb. He at 4.4 min.).

Phenyl Sulfide and *t*-Butyl Hypochlorite (A).—A mixture of phenyl sulfide (0.054 mole, 10.0 g.) and benzene (150 ml.) was placed in a flask fitted with a condenser, dropping funnel, magnetic stirrer, and gas inlet and outlet tubes. The system was flushed with nitrogen for several minutes. *t*-Butyl hypochlorite (0.054 mole, 5.9 g.), prepared by the method of Teeter and Bell,[18] was added slowly through the dropping funnel. Approximately 1 min. after the addition of the *t*-butyl hypochlorite an exothermic reaction took place. After approximately 5 min.

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[17] A. C. Poshkus and J. E. Herweh, Abstracts of Paper, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 17O.

[18] H. M. Teeter and E. W. Bell, *Org. Syn.*, **32**, 20 (1952).

the reaction subsided and the system had reached room temperature. The reaction mixture was worked up by distillation and trituration with ligroin to give a crystalline solid. The recrystallized product, m.p. 69°, 3.1 g., was obtained in 28% yield. The infrared spectrum of the solid coincided with that of the prepared phenyl sulfoxide. Mixture melting technique gave no depression.

Analysis of the reaction mixture, prior to distillation, by gas chromatography (10-ft. silicone column, 125°, 4 lb. He) showed the presence of *t*-butyl chloride at 3.4 min. and a trace amount of acetone at 3 min. Each of the peaks were raised by successive additions of pure samples. Gas and thin layer chromatography also verified the presence of phenyl sulfide and possibly phenyl tolyl sulfide, but no phenyl sulfone.

Phenyl Sulfide and *t*-Butyl Hypochlorite (B).—A solution of phenyl sulfide (0.054 mole, 10.0 g.) and benzene (150 ml.) was treated exactly the same as in A. The *t*-butyl hypochlorite was added slowly, and the reaction was allowed to proceed for a period of 24 hr. with an ultraviolet light source placed outside of the reaction vessel. The yield of phenyl sulfoxide was 5.15 g., 46%.

Phenyl Sulfide and *t*-Butyl Hypochlorite (C).—The reaction of phenyl sulfide and *t*-butyl hypochlorite was carried out in the dark under a nitrogen atmosphere. The reactants, in the same molar ratio as above but on smaller scale, were placed in a dark room for a period of 30 min. before the addition of the *t*-butyl hypochlorite to the solution of phenyl sulfide in benzene. The *t*-butyl hypochlorite was added and a 4-min. induction period was recorded before the exothermic reaction took place. Thin layer analysis showed the presence of phenyl sulfoxide and phenyl sulfide.

Phenyl Sulfide and Cumyl Peroxide (A).—Phenyl sulfide (0.027 mole, 5.0 g.), cumyl peroxide (0.0135 mole, 3.64 g.), and dry benzene (10 ml.) were placed in a glass ampoule which cooled to −80°, flushed with nitrogen, sealed, and heated at 135° for 8 hr. Thin layer chromatography using a 3% glacial acetic acid, 20% benzene, and ligroin solvent mixture showed the presence of phenyl sulfide and a tar which diffused over the plate. Gas chromatography (5-ft. 5% Carbowax column, 210°, 10 lb. He) indicated the presence of various products, *i.e.* phenyl tolyl sulfide, but the presence of the phenyl sulfoxide or phenyl sulfone was not detected.

Phenyl Sulfide and Cumyl Peroxide (B and C).—The reactants were as stated above in A with a change in reaction conditions. An ultraviolet light source was placed 1 in. from the flask, and the reaction was allowed to proceed for a period of 24 hr. under a nitrogen atmosphere. The analysis of the reaction mixture was carried out as stated above, but neither phenyl sulfoxide nor phenyl sulfone was detected. In reaction C, acetophenone was definitely shown to be present by gas chromatography.

Phenyl Sulfide and Cumyl Hypochlorite.—Phenyl sulfide (0.054 mole, 10.0 g.) was dissolved in benzene (150 ml.) and placed in a flask equipped with a magnetic stirrer and a condenser. The system was flushed with nitrogen. Cumyl hypochlorite (0.054 mole, 9.2 g.) prepared in a manner similar to the *t*-butyl hypochlorite, b.p. 20° (1 mm.), 90% yield, was added and the mixture was irradiated externally. Samples of the reaction mixture were removed after 14 and 24 hr. Gas chromatography (5-ft. 5% Carbowax column, 180–210°, 4–20 lb. He; 10-ft. silicone column, 214–240°, 4–20 lb. He) on two columns showed the presence of a number of products, but the phenyl sulfoxide and phenyl sulfone were not detected. Gas chromatography (10-ft. silicone column, 125°, 10 lb. He) showed the presence of acetophenone at 10.6 min. The size of the acetophenone peak, in comparison with the other products, indicated that it was one of the major products of the reaction. The peak was identified by additions of pure sample as described in previous portions of the experimental section.

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Free-Radical Reactions of Pyrroles

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The free radical resulting from hydrogen atom abstraction from the methyl group of N-methylpyrrole has been shown to dimerize, forming 1,1′-ethylenedipyrrole, and to attack the diene system of N-methylpyrrole, giving 1-methyl-3-(1-pyrrolylmethyl)pyrrole after radical chain transfer. Pyrrole under similar conditions gave 2,2′-(1′-pyrrolinyl)pyrrole. The structure of the latter product indicates that hydrogen atom abstraction occurs at the 2-position of pyrrole and that the pyrrole ring acts as an effective free-radical trap. In addition, the reactivities toward free-radical attack of a number of related compounds have been established and shown to lie in the order N-methylpyrrole > toluene > 4-picoline > benzene for the compounds examined.

Much research has been done to determine the position of attack of a free radical on organic molecules; these studies have included both addition and abstraction reactions.[2] For example, the benzene aromatics have been studied extensively in terms of addition reactions and to a limited degree in terms of abstraction reactions. In comparison, the free-radical chemistry of heterocyclic aromatics had been investigated only sparsely, with most of this work being done on pyridine. The radical addition and abstraction reactions of pyrrole have been studied to a lesser extent and, therefore, offer a fertile field for investigation.

Most of the free-radical research which has been published on pyrrole has dealt with the reactions of the pyrrole ring under thermal cleavage conditions. In 1958, Jacobsen, Heady, and Dinneen[3] studied the kinetics of the decomposition of N-methylpyrrole to a variety of products in the temperature range 477–745°. These workers suggested no mechanism for the pyrolysis reactions. Subsequent work by Patterson, Brasch, and Drenchko,[4] who repeated the experiments and extended them, implied that the pyrolyses were radical in nature. The latter workers used cycloalkyl pyrroles as illustrated, where $n = 3, 4$, and 5. The cycloalkyl pyrroles were assumed to undergo homolytic thermal cleavage of a carbon to nitrogen bond; resulting radicals were thought to follow these reaction paths (p. 1164). The same type of cleavage occurs with N-butylpyrrole as shown by Jacobsen and Jensen.[5]

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