

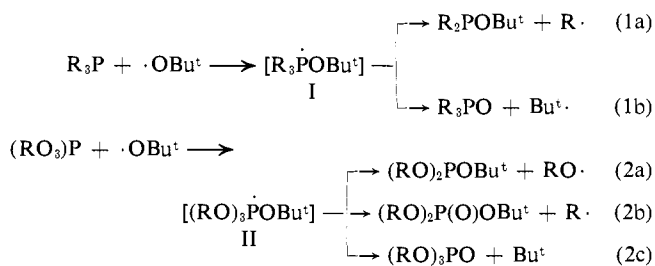
Electron Spin Resonance Spectra and Structures of Phosphoranyl Radicals in Solution¹

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Contribution No. 1882 from the Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, and Contribution No. 2101 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received December 6, 1971

Abstract: The esr spectra of the phosphorus-centered transient radicals which result from the reaction between photolytically generated *tert*-butoxy radical and various phosphines and phosphites in inert liquid media are reported. The lower phosphines (*e.g.*, PH₃, CH₃PH₂, (CH₃)₂PH, and (CH₃)₃P) give rise to two types of phosphoranyl radicals: the simple adduct R₃POBu[•] (R = H, alkyl) and a second species which is identified as the dialkoxyphosphoranyl radical R₂P(OBu[•])₂ (R = H, alkyl). The latter are the only phosphorus-centered radicals which can be detected with the higher phosphines (R = ethyl or higher). Trialkyl phosphites (RO)₃P, on the other hand, give rise only to the adduct radicals (RO)₃POBu[•]. All of these phosphoranyl radicals have well-resolved proton hyperfine structures and are characterized by phosphorus isotropic hyperfine splittings in excess of 600 G. The esr data are interpreted in terms of trigonal bipyramidal structures in which the sp³ hybrid orbital containing the unpaired electron occupies an equatorial position. The mechanistic implications of these results on the free-radical chemistry of organophosphorus compounds are discussed.

Recently we presented direct esr evidence for the formation of a variety of alkyl radicals when organophosphines and phosphites were allowed to react with photolytically generated *tert*-butoxy and thiyl radicals.³ These esr observations were interpreted as a series of homolytic substitution reactions proceeding *via* metastable phosphoranyl radicals⁴ I and II. The subsequent fragmentation of these intermediates (eq 1 and 2) is consistent with a vast amount of chemical



information relating to homolytic reactions of organophosphorus compounds.⁵

The direct observation of the phosphoranyl intermediate is crucial to this mechanistic formulation. Indeed, the esr spectrum of a phosphorus-centered radical was observed in the reaction of trimethylphosphine and *tert*-butoxy radicals, to which the structure of the phosphoranyl adduct (CH₃)₃POBu[•] was assigned.³ Phos-

phine, methylphosphine, and dimethylphosphine showed similar behavior. We rationalized our failure to uniformly observe analogous paramagnetic intermediates from other organophosphines to their short lifetimes when alkyl groups more readily cleaved than methyl radical were available in I or II. Since it is possible that separate mechanisms are operative in the latter cases, we carefully reexamined the same reacting systems to scrutinize for phosphoranyl radicals more unstable than the methyl analogs.

In this report we present our studies of a variety of phosphoranyl radicals formed as intermediates in the reactions of organophosphines and phosphites with *tert*-butoxy and thiyl radicals. The multiplicity of adducts which we find indicates that they are indeed ubiquitous species in these reactions.⁶ We shall describe the esr spectra and discuss the geometry of two kinds of phosphoranyl radicals: those formed by initial addition of a *tert*-butoxy radical to the trivalent organophosphorus compound (radicals of the type I and II) and those formed in subsequent reactions with additional *tert*-butoxy radicals.

The phosphorus atom in these radicals achieves quinquevalency (counting the electron as a substituent) and most likely a trigonal bipyramidal orbital geometry through participation of its 3d orbitals in the electronic structure. Distorted trigonal bipyramidal structures have also been presented for the related tetrahalophosphoranyl radicals ·PF₄⁷ and ·PCl₄⁸ formed by addition of a halogen atom to the corresponding phosphine. These radicals exhibit larger phosphorus splittings (1330° and 1210 G,⁸ respectively) than those we report

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(2) (a) Central Research Department, E. I. du Pont Co. (b) Department of Chemistry, Indiana University.

(3) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969).

(4) Phosphoranyl radical refers to a phosphorus species having four covalent bonds and nine electrons in its valence shell: F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957).

(5) For reviews see (a) C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, **3**, 1 (1966); (b) J. I. G. Cadogan, *Advan. Free Radical Chem.*, **2**, 203 (1967); (c) R. F. Hudson, "Structure and Mechanism of Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 291 ff; (d) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1967, p 116 ff; (e) W. G. Bentrude, *Annu. Rev. Phys. Chem.*, **18**, 237 (1967); (f) R. S. Davidson, "Organophosphorus Chemistry, Vol. I and II," Chemical Society, London, 1969 and 1970.

(6) Our earlier conclusion³ was partly due to inconsistency in employing wider sweeps of the magnetic field required to observe the phosphorus splitting.

(7) (a) J. R. Morton, *Can. J. Phys.*, **41**, 706 (1963); (b) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964); (c) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966); (d) W. Nelson, G. Jackel, and W. Gordy, *ibid.*, **52**, 4572 (1970); (e) *cf.* also the structure of SF₄⁺ (ref 7c) and SF₄ [W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 119 (1962)].

(8) G. F. Kokoszka and F. E. Brinckman, *Chem. Commun.*, 349 (1968); *J. Amer. Chem. Soc.*, **92**, 1199 (1970).

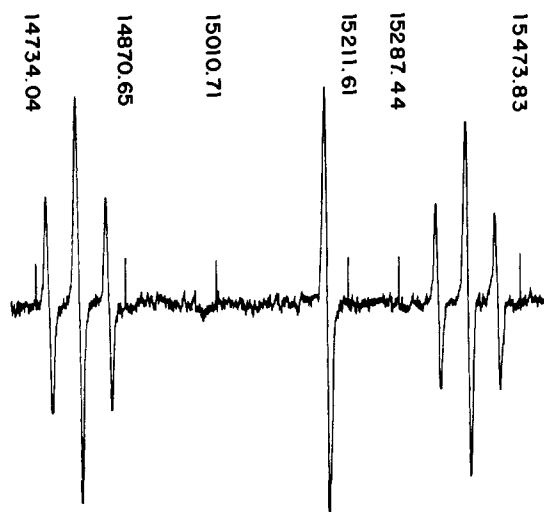


Figure 1. High-field half of the esr spectrum obtained by photolysis of di-*tert*-butyl peroxide in PH_3 at -95° . The two triplets separated by 139.6 G represent the proton hyperfine structure associated with the adduct radical tert-BuOPH_3 in which two of the three protons are equivalent. The central line is associated with a phosphorus-centered radical formed from a reaction product (see text). The proton nmr field markers are in kHz (4.25776 kHz/G).

for the alkyl and alkoxy phosphoranyl radicals (600–900 G). They also possess two pairs of equivalent halogen nuclei of widely different coupling constants. Higuchi⁹ has recently made a thorough theoretical analysis of the bonding in the $\cdot\text{PF}_4$ radical. He proposes a distorted trigonal bipyramidal structure having the half-occupied hybrid orbital in the equatorial plane and the pair of fluorine atoms with the *larger* coupling near the axial positions. Furthermore, by considering the properties of five spd orthonormal hybrid orbitals on phosphorus, he showed that relatively small changes in the two FPF bond angles can produce large changes in the s character of the half-occupied orbital and hence in the isotropic hyperfine splitting of the phosphorus nucleus. Despite greatly diminished phosphorus splittings and the different nature of the ligands, we consider the phosphoranyl radicals described in this paper to be structurally analogous to the $\cdot\text{PF}_4$ radical, differing primarily in the magnitude of the bond angle between the equatorial ligands.

Experimental Section

The esr instrumentation with its auxiliary equipment, the source of ultraviolet radiation, and the optical system employed in this study are described in detail elsewhere.^{10a}

Since most compounds used are volatile, toxic, and air sensitive, sample preparation was carried out on a high-vacuum system. Approximately 0.1 ml each of di-*tert*-butyl peroxide, the phosphorus compound, and an "inert" low melting solvent (cyclopropane, ethane, ethylene) were condensed in a fused silica tube ("Suprasil," quartz, 5-mm o.d., 4-mm i.d.) provided with a small bulb at the upper end to facilitate stirring of the contents. After thorough degassing by freeze-pump-thaw cycling and with the contents frozen at liquid nitrogen temperature, the tube was sealed with a torch and placed in a -78° bath (or colder if ethane or ethylene were used as

diluents). The contents were stirred by several inversions of the tube in the cold bath. With the tube upside down in the bath a collet was placed at the appropriate height and the bottom part of the tube was cleaned and dried. The tube was then quickly inserted in the unsilvered dewar insert ("Suprasil" quartz) of the cavity kept at the desired low temperature by a stream of dry nitrogen cooled by passage through a heat exchanger in liquid nitrogen. The temperature was varied simply by changing the flow rate of the nitrogen gas.

The compounds employed in this study were either commercial samples or were synthesized by standard methods. $(\text{CH}_3)_2\text{PD}$ was made by treating dimethylphosphine with D_2O .

Results

The esr spectra of phosphoranyl radicals examined in this study are presented and discussed in the order of increasing number and complexity of alkyl substituents.

Phosphine [PH_3]. Ultraviolet photolysis of a mixture of phosphine and di-*tert*-butyl peroxide in cyclopropane solution directly in the cavity of the spectrometer produces an esr spectrum of two radical species exhibiting unusually large doublet splittings (626.7 and 672.5 G at -100°) which must be attributed to isotropic hyperfine interactions with phosphorus nuclei. The high-field half of the spectrum is shown in Figure 1. The species with the smaller phosphorus splitting exhibits in addition a large doublet of 139.6 G further split into 1:3:1 triplets of 10.8 G. The line widths of about 1.2 G for these radicals are substantially broader than those observed for alkyl radicals (typically 0.1 G) in our previous studies.¹¹ We could not resolve any further structure for the species with the larger phosphorus splitting. However, under conditions leading to highest resolution (low microwave power, low modulation amplitudes, and slow sweep), the line shape of the central line in Figure 1 displayed unresolved shoulders on each side of the line which seemed to indicate the presence of a small (~ 0.6 G) triplet splitting. After

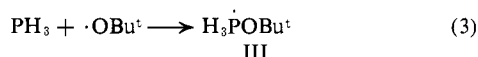
(9) J. Higuchi, *J. Chem. Phys.*, **50**, 1001 (1969).

(10) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); (b) A. R. Stiles, F. F. Rust, and W. E. Vaughan, *ibid.*, **74**, 3282 (1952); M. M. Rauhat, H. A. Currier, A. M. Semel, and V. P. Wystrach, *J. Org. Chem.*, **26**, 5138 (1961).

(11) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

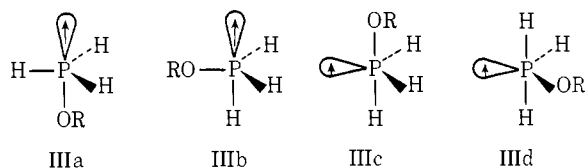
correction for the different second-order downfield shifts, the g factors of the two radicals are nearly identical and are close to those of alkyl radicals. The esr absorptions of both species decay immediately on shuttering the ultraviolet light. Their relative intensities, however, are strongly dependent on the temperature. At -170° , the lowest temperature which could be reached without crystallization (using ethylene as solvent), the central line of Figure 1 could just barely be detected. At temperatures above -100° , on the other hand, the central line predominated, and with further increase in temperature (up to -70°) it went strongly off scale. Another important difference is that the spectrum corresponding to the doublet-of-triplets (Figure 1) appears immediately upon irradiating the sample, while the central line develops its full strength only after several minutes of irradiation.

We identify the paramagnetic species displaying the doublet-of-triplets hyperfine structure (in addition to the phosphorus doublet splitting) as the phosphoranyl radical III resulting by addition of a *tert*-butoxy radical



to phosphine. In this radical, one of the protons interacts much more strongly (139.6 G) with the unpaired electron than the remaining pair of equivalent protons (10.8 G). These proton hyperfine splittings are, furthermore, quite insensitive to changes in the temperature. In the temperature interval from -90 to -160° the larger coupling constant changes by 0.3 G while the smaller only by 0.1 G. We attribute this small temperature dependence of the hyperfine splittings to considerable structural rigidity of the phosphoranyl radical species.^{11a}

By comparison with $\cdot\text{PF}_4$ we choose a trigonal bipyramidal structure (possibly distorted) which allows four different stereoisomers. Of these structures only IIIa with three equivalent protons is rigorously excluded



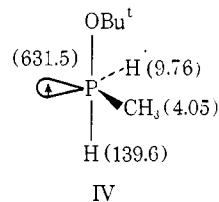
by the esr observations. We resort again to a comparison with $\cdot\text{PF}_4$. Higuchi's theoretical study⁹ assigned the pair of fluorine atoms with the larger hyperfine constant to the (nearly) axial positions and placed the unpaired electron in an equatorial hybrid orbital. Extension of these conclusions to our situation allows us to choose structure IIIc as the most probable for the phosphoranyl radical. This structure, with an apical *tert*-butoxy group, is also favored by the generalizations pertinent to pentacoordinate phosphorus compounds according to which the more electronegative ligand tends to assume the axial position in trigonal bipyramids.¹²

(11a) NOTE ADDED IN PROOF. We have found recently that the line shapes associated with this radical are strongly temperature dependent in the range -80 to $+40^\circ$. These line shape effects are interpreted in terms of a rapid rearrangement process in which the hydrogens directly bonded to the phosphorus are permuted. A density matrix treatment gives a free energy of activation for this process of about $5.3 \text{ kcal mol}^{-1}$: P. J. Krusic and P. Meakin, submitted for publication.

The identity of the second paramagnetic species exhibiting only a large phosphorus doublet will be discussed after the data for the more highly substituted phosphines are presented. Suffice it to say at this point that the temperature dependence of the spectral intensity and the slow growth of the signal after the start of the irradiation strongly suggest a second generation radical species arising from a product of photolysis.

It is noteworthy that we obtained no evidence for the phosphinyl radical $\cdot\text{PH}_2$ which could arise by hydrogen atom abstraction. We also failed to observe the adduct radical $\text{PH}_2\text{CH}_2\text{CH}_2\cdot$ which should have been formed by addition of such phosphinyl radicals to ethylene,^{10b} in analogy with the behavior of thiyl radicals. For example, thiyl radicals are not detected in inert solvents but are readily trapped by olefins to yield the corresponding β -alkylmercaptoalkyl adducts.¹⁰

Methylphosphine [CH_3PH_2]. Two paramagnetic species with different phosphorus splittings (631.5 and 703.3 G at -85°) are also formed when *tert*-butoxy radicals react with methylphosphine in cyclopropane solutions. The species with the smaller a_P has an additional hyperfine structure consisting of a large proton doublet of 139.6 G further split into doublets (9.76 G) of quartets (4.05 G). By internal consistency with phosphine, the spectrum must be attributed to the phosphoranyl adduct IV in which the methyl group occupies an equatorial position.



The second radical species with the larger phosphorus doublet splitting also possesses additional hyperfine structure of at least six nearly equidistant lines. From the relative intensities in this multiplet, the splitting cannot be attributed to five equivalent protons. Insight gained from the behavior of the higher homologs (*vide infra*) indicated that the multiplet should be interpreted as a doublet of overlapping quartets. Indeed, a systematic computer synthesis of the spectrum as a function of the ratio $k = a$ (doublet): a (quartet) led to a very good fit with $k = 2.17$. Normalization of the computed spectra to the experimental width of the multiplet gave 6.84 G for the doublet and 3.15 G for the quartet splitting. The structure of this phosphorus-centered radical will also be deferred (see Discussion).

Dimethylphosphine [$(\text{CH}_3)_2\text{PH}$]. The spectrum obtained from dimethylphosphine on reaction with *tert*-butoxy radicals in a cyclopropane solution is shown in Figure 2. Two types of phosphorus-centered radicals are again obtained. The phosphoranyl radical V displays a phosphorus doublet splitting of 631.4 G, a large doublet of 142.9 G due to the apical proton, and a septet of 3.45 G for the six equivalent protons of the equatorial methyl groups.

(12) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, J. K. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963); *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967); (d) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); (e) K. Mislow, *ibid.*, **3**, 321 (1970); (f) F. H. Westheimer, *ibid.*, **1**, 70 (1968); (g) F. Ramirez, *ibid.*, **1**, 168 (1968).

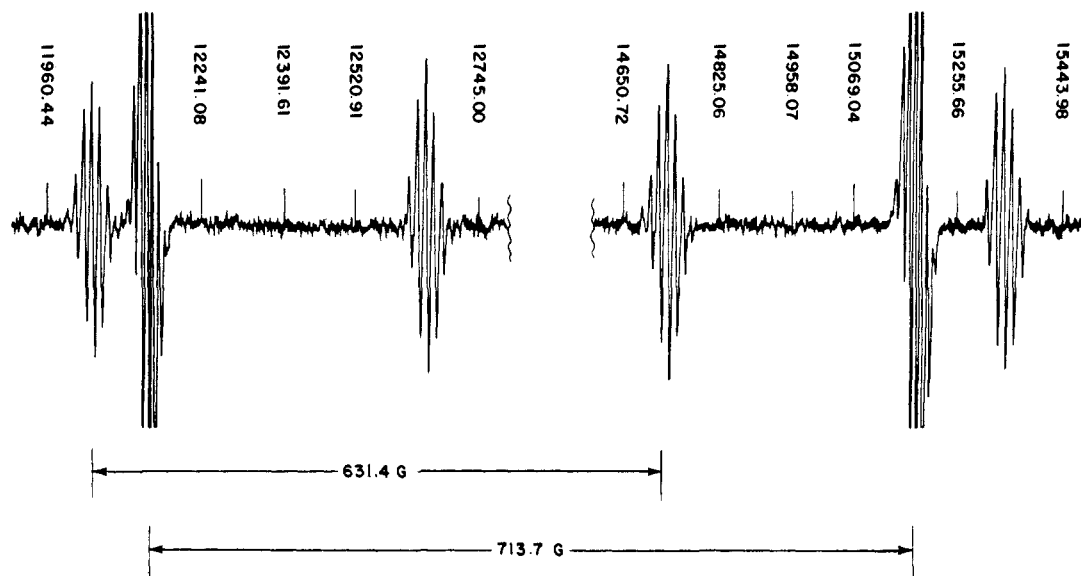
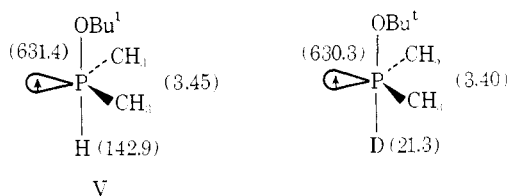


Figure 2. ESR spectrum obtained by reaction of *tert*-butoxy radicals with $(\text{CH}_3)_2\text{PH}$ at -65° . The species with a phosphorus splitting of 631.4 G is identified as the primary adduct *tert*-BuOPH $(\text{CH}_3)_2$. The species with $a_{\text{P}} = 713.7$ G and a proton hyperfine structure consisting of septets (truncated) is formed from a reaction product (see text). The two species have nearly identical g values. The different relative positions of the multiplets in the two halves of the spectrum are caused by different second-order shifts.



The paramagnetic species with the larger phosphorus splitting (713.7 G) exhibits a fine structure consisting of a binomial septet of 2.5 G (Figure 2). This phosphorus-centered radical is analogous to the species of similar phosphorus splittings obtained from phosphine and methylphosphine. Thus, the signal due to this species is still very weak after 5 min of irradiation of a fresh sample at -100° , but it steadily grows in intensity as the irradiation continues. The relative intensities for the two spectra are again temperature dependent with the second generation spectrum predominating at higher temperatures. In contrast to the behavior of the simple phosphoranyl adduct V, the signal of the second species decays with a time constant of about 0.5 min.

We have also carried out a photolysis experiment in isobutylene as solvent hoping to trap the phosphinyl radical $\cdot\text{PR}_2$ (for which there was no evidence in inert solvents) as an adduct to isobutylene, *i.e.*, $\text{PR}_2\text{CH}_2\text{-}\dot{\text{C}}(\text{CH}_3)_2$, since the latter, being a tertiary alkyl radical, should be relatively stable. However, no substituted alkyl radicals, methyl radical, or 2-methylallyl radical¹³ could be detected near the $g = 2$ region of the magnetic field, although the solution had a milky appearance after photolysis in contrast to similar photolyses in cyclopropane.

The value of 142.9 G is unusually large for a proton hyperfine coupling constant. Only the formyl radical¹⁴

has a proton isotropic splitting of a comparable magnitude (137 G). It was of interest therefore to confirm the assignment by examining $(\text{CH}_3)_2\text{PD}$ under the same conditions used for the protonated species. Indeed, the large doublet splitting is replaced by a 1:1:1 triplet of 21.3 G while the other hyperfine splittings remain essentially unchanged ($a_{\text{P}} = 630.3$ G, $a_{\text{CH}_3} = 3.40$ G, at -98°). The deuteron coupling constant can be compared with the proton splitting found earlier. However, multiplication of 21.3 G by the proton-deuteron moment ratio $\mu_{\text{H}}/\mu_{\text{D}} = 6.514$ yields only 138 instead of the expected 142.9 G. The latter implies a substantial vibrational contribution to the hyperfine coupling constant of the apical proton which is not in agreement, at first glance, with its very small temperature dependence¹⁵ (*vide supra*). We do not understand this apparent anomaly at present, although it must be mentioned that the measurement of a_{D} may be less precise than that of a_{H} due to a spectrum of poorer quality for the partially (70%) deuterated species.

The spectrum of the second species derived from the deuterated dimethylphosphine, on the other hand, bears no sign of its deuterium label. The splittings and general behavior are the same as those of the corresponding spectrum from ordinary dimethylphosphine ($a_{\text{P}} = 711.7$ G, $A_{\text{H}} = 2.5$ G (septet) at -98°).

Trimethylphosphine [$(\text{CH}_3)_3\text{P}$]. Trimethylphosphine is the simplest organophosphine for which we could detect a spectrum of the displaced ligand (methyl radicals) in addition to the two types of phosphoranyl radicals previously described. The spectra of the latter are shown in Figure 3. By comparison with the lower phosphines, it was clear that the complex pattern of the spectrum with the smaller phosphorus splitting (618.7 G at -81°) should be interpreted as an overlapping quartet

(13) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

(14) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

(15) J. K. Kochi, and P. J. Krusic, to be submitted for publication.

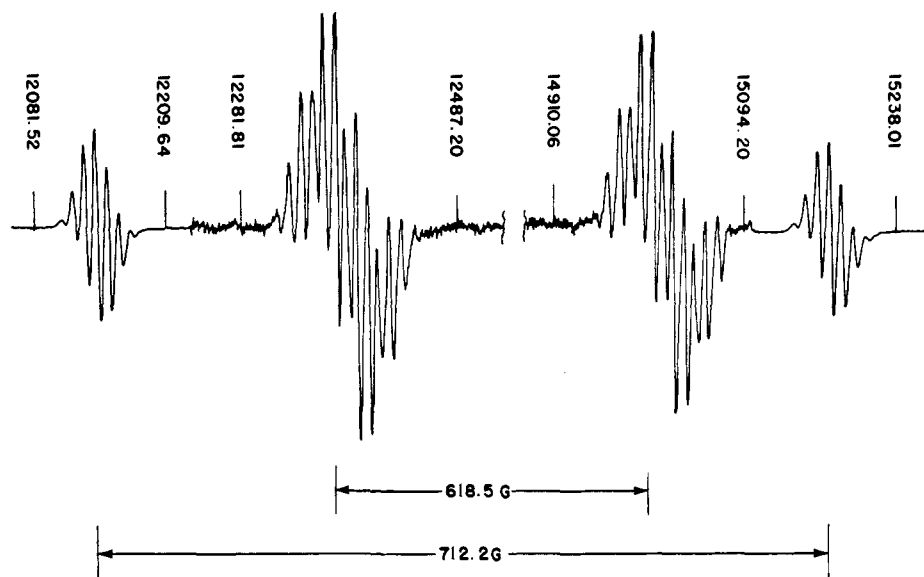
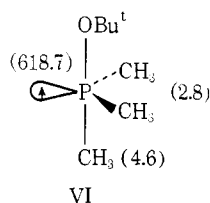


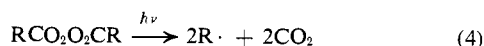
Figure 3. ESR spectrum obtained by photolysis of di-*tert*-butyl peroxide in trimethylphosphine at -81° . The spectrum with a phosphorus splitting of 618.5 G is assigned to the primary adduct *tert*-BuOP(CH₃)₃. Its complex proton hyperfine structure is interpreted as an overlapping quartet-of-septets by computer simulation of the spectrum. The wing septets separated by 712.2 G have been recorded at reduced gain (10-fold) and belong to a more stable species formed from a reaction product (see text).

of septets. A systematic computer analysis of the line shape produced a good fit with the value of 1.642 for the ratio a (quartet): a (septet) and a peak-to-peak line width of 1.25 G. Normalization to the experimental width gave a (quartet) = 4.6 G and a (septet) = 2.8 G. The spectrum is assigned to the phosphoranyl radical VI.

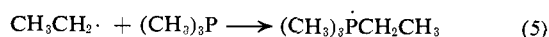


The spectrum of the other phosphorus-centered radical species also grows in intensity with the time of irradiation and decays more slowly on shuttering the light like the second generation radicals from phosphine, methylphosphine, and dimethylphosphine. Significantly the esr spectrum is indistinguishable from that of the second generation radical obtained from dimethylphosphine ($a_P = 712.4$ G, $a_H(\text{septet}) = 2.5$ G).

The addition of *alkyl* radicals to organophosphines was investigated by utilizing the photolysis of diacyl peroxides as an efficient method for the production of



alkyl radicals for esr study.¹⁶ However, irradiation of a cyclopropane solution of trimethylphosphine and di-propionyl peroxide affords only an esr spectrum of the ethyl radical. The absence of any evidence of the



methyl radical and a phosphorus-centered species in-

dicates that alkyl radicals do not add as readily to the phosphorus center as alkoxy radicals add. The ready addition of alkoxy radicals to phosphorus is consistent with the stability of the phosphorus-oxygen bond and may also reflect the lower steric requirements of an alkoxy substituent. It should be noted, however, that the solution became rather milky on mixing the components and suggests that the diacyl peroxide may have reacted heterolytically¹⁷ with trimethylphosphine prior to irradiation. Insoluble products were also formed on mixing phosphine with propionyl peroxide and also trifluorophosphine with di-*tert*-butyl peroxide.

Tris(trifluoromethyl)phosphine [(CF₃)₃P]. In contrast to the weak spectrum of methyl radicals obtained from trimethylphosphine, the reaction of *tert*-butoxy radicals with P(CF₃)₃ gives rise to a strong spectrum of trifluoromethyl radicals¹⁸ (Figure 4, $a_F = 143.8$ G at -80°). This observation supports our conclusion that the stability of the phosphoranyl adduct is in part related to the degree of crowding around the phosphorus atom. Interestingly, we could not detect any phosphorus-centered radical in this system.

Higher Tertiary Phosphines [R₃P]. Reaction of *tert*-butoxy radicals with triethylphosphine produces the spectrum of ethyl radicals as was already reported,¹ in addition to a very intense spectrum of only *one* phosphorus-centered radical (Figure 5) with a phosphorus splitting of 713.9 G (at 101°). Each line of the phosphorus doublet is further split into a partially resolved binomial quintet. A computer analysis of this multiplet gives a coupling constant of 2.3 G for *four* equivalent protons. This spectrum grows in intensity with the duration of irradiation and decays within several minutes after shuttering the ultraviolet light. The

(17) R. Hiatt, "Organic Peroxides," Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, p 875 ff.

(18) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(16) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).



Figure 4. ESR spectrum of the trifluoromethyl radical from $P(CF_3)_3$ in a cyclopropane solution at -80° . The central lines of the quartet are split by second-order effects.

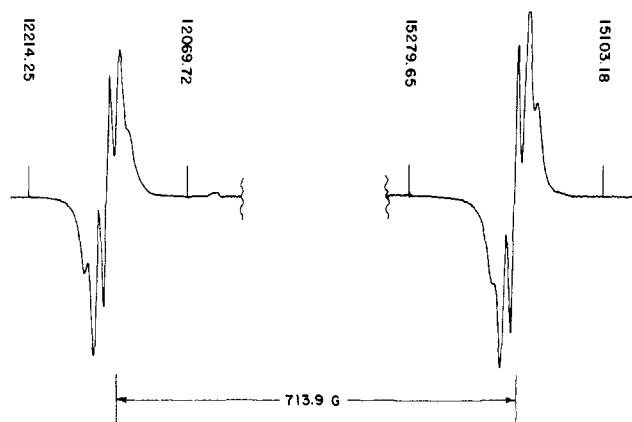


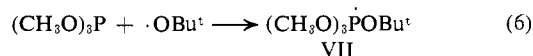
Figure 5. ESR spectrum of the phosphorus-centered radical obtained by photolysis of di-*tert*-butyl peroxide in triethylphosphine at -101° .

paramagnetic species giving rise to this spectrum is clearly analogous to the radicals with the larger phosphorus coupling constants obtained from the lower phosphines. In sharp contrast to the latter, however, the primary phosphoranyl adduct *tert*-BuOPEt₃ can no longer be detected since the ready expulsion of the ethyl radical (eq 1a) presumably shortens its lifetime.

An entirely similar behavior is observed with triisopropylphosphine which, in addition to the spectrum of isopropyl radicals,¹ gives rise to an intense spectrum of a phosphorus-centered species with $a_P = 714.6$ G (at -90°) and $a_H = 1.7$ G (triplet).

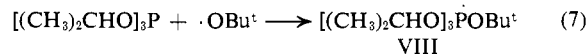
Trialkyl Phosphites [(RO)₃P]. We have also reexamined the reaction of *tert*-butoxy radicals with trimethyl phosphite in a cyclopropane solution. For this system we previously reported the detection of *tert*-butyl radicals as a consequence of an oxygen atom transfer from the *tert*-butoxy radical to phosphorus (eq 2c).³ Guided by the foregoing results we swept the magnetic field over a wider interval and discovered the presence of two intense lines without resolvable structure ($\Delta H = 1.4$ G) separated by 903.7 G at -90° . On interruption of the irradiation these lines decay within the response time of the instrument. To second order, the g factor of this radical species is essentially that of the *tert*-butyl radical ($\Delta g = 0.0001$). We attribute this doublet to the often invoked⁵ tetraalkoxyphos-

phoranyl radical VII in which the unpaired electron



interacts primarily with only the phosphorus nucleus.

A similar doublet ($a_P = 919.0$ G at -90°) was also observed with triisopropyl phosphite and is assigned to the homologous radical VIII resulting from the addi-

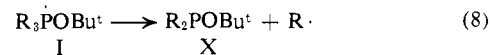


tion of the *tert*-butoxy radical to the phosphite. The wider line widths of these lines ($\Delta H = 2.1$ G) compared to those of the phosphoranyl radical from trimethyl phosphite are probably due to unresolved hyperfine structure.

Discussion

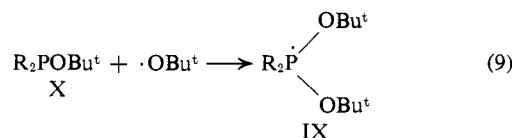
The ESR spectra of three types of paramagnetic species are generally observed during the reaction of *tert*-butoxy radicals with organophosphines. They are associated with an alkyl radical and two phosphorus-centered species I and IX (*vide infra*). The relative importance of the spectrum of each of these radicals depends on at least three factors: (a) the structure of the alkyl group, (b) the temperature, and (c) the duration of irradiation. For example, the spectrum of the displaced alkyl radical (eq 1a) is the most intense with trialkylphosphines. In this situation the spectrum of the phosphorus radical I is correspondingly the weakest and, in fact, only observed with trimethylphosphine. We relate the instability of this primary adduct I to steric crowding around the phosphorus nucleus as a result of replacing methyl with groups more readily cleaved.

A buildup of a substitution product X, a dialkyl-*tert*-butoxyphosphine, is a consequence of such an easy departure of an alkyl radical (*cf.* eq 1 and 8). We pro-



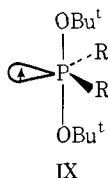
pose that the second paramagnetic species with phosphorus splittings of about 700 G has the structure IX and is derived from a secondary reaction involving further addition of *tert*-butoxy radical to the alkoxy-

phosphine X. Such a formulation is consistent with



the higher temperatures and longer times for irradiation often required to optimize the spectrum of IX.

From the magnitude of the hyperfine coupling constants we judge that the di-*tert*-butoxyphosphoranyl species IX is structurally analogous to the mono-

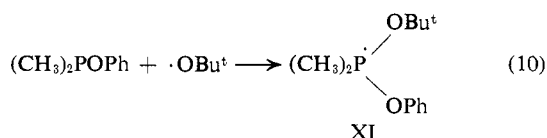


alkoxy precursor I. According to the empirical polarity rule,¹² the two *tert*-butoxy groups should occupy axial positions with the alkyl groups lying in the equatorial plane. The equivalence of the alkyl groups is borne out, of course, by the hyperfine splittings due to the protons (*i.e.*, septet from trimethylphosphine, quintet from triethylphosphine, and triplet from triisopropylphosphine). An analogous structure pertains to radicals XI, XII, and XIII derived from dimethylphenoxyphosphine described below.

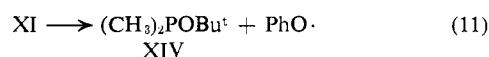
The structural assignment of IX receives further support from experiments with dimethylphenoxyphosphine. Thus, photolysis of a cyclopropane solution of this compound in the presence of di-*tert*-butyl peroxide produces the spectra of three phosphorus-centered radicals of different phosphorus splittings (XI = 752 G, XII = 715 G, and XIII = 779 G)¹⁹ and identical proton hyperfine structures, all consisting of septets with $a_{\text{H}} = 2.5$ G.

The relative intensities of these multiplets are remarkably temperature dependent (Figure 6). At low temperatures ($< -70^\circ$) the species with $a_{\text{P}} = 752$ G predominates and the least intense species is that with $a_{\text{P}} = 715$ G. The latter is barely detectable at -107° . At higher temperatures ($> -50^\circ$) the major species is that with $a_{\text{P}} = 779$ G which is the only species detected at -16° . At this temperature the signal disappears immediately upon interruption of the irradiation. At -107° , on the other hand, the same signal decays with a time constant of about 0.25 min whereas the signal with $a_{\text{P}} = 752$ (the strongest signal at this temperature) decays with a time constant of about 0.05 min.

We associate the strongest signal at the lowest temperature with the initially formed adduct XI. Such a



phosphoranyl radical will readily expel (eq 11) a phen-



(19) These phosphorus splittings may be somewhat in error since the high-field hyperfine structures partially overlap due to different second-order downfield shifts for the three species.

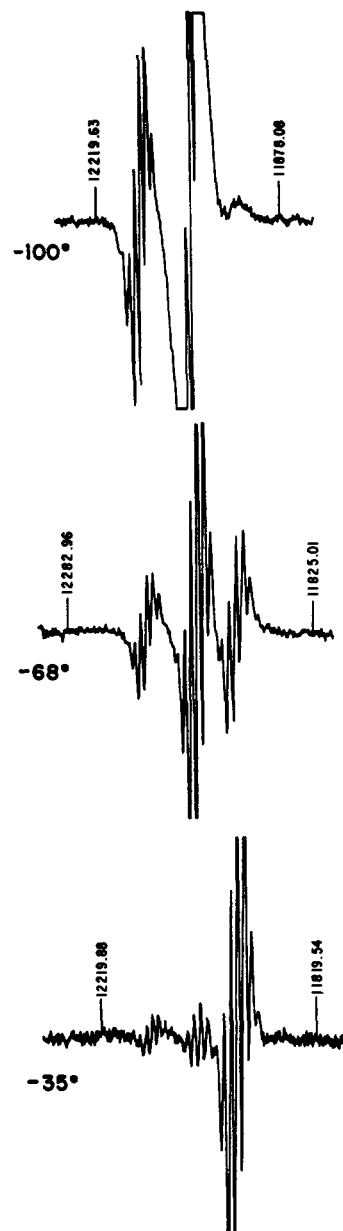
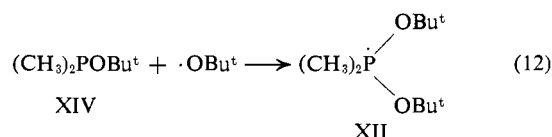


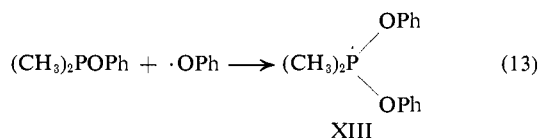
Figure 6. Low-field half of the esr spectrum obtained by photolysis of di-*tert*-butyl peroxide in a cyclopropane solution of dimethylphenoxyphosphine as a function of temperature.

oxy radical as described earlier (*cf.* eq 2a).³ Addition of another *tert*-butoxy radical to the diamagnetic product XIV affords a second phosphorus-centered



radical XII which is identical with that produced earlier from trimethylphosphine as a second generation species.²⁰ Finally, the phenoxy radical liberated from the original adduct (eq 11) can react with another molecule of the starting compound to form the adduct XIII (eq 13) to which we attribute the largest phosphorus splitting (779 G) and the greatest stability.

(20) We attribute the small discrepancy in their phosphorus splittings (715 *vs.* 712.4 G) to the experimental error arising from overlap of the high-field multiplets from phenoxydimethylphosphine (*cf.* ref 19).



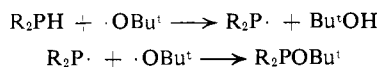
We wish to comment next on the second generation species obtained from phosphine and methyl- and dimethylphosphines. In comparing the spectral results for these phosphines (Table I), one is struck by the absence

Table I. Hyperfine Coupling Constants for Phosphoranyl Radicals Formed by Addition of *tert*-Butoxy Radicals (R = *tert*-Butyl) to Phosphines

Phosphine	T, °C	Radicals and coupling constants, ^a G	
PH ₃	-100		
CH ₃ PH ₂	-85		
(CH ₃) ₂ PH	-65		
(CH ₃) ₃ P	-81		
(C ₂ H ₅) ₃ P	-101		
(<i>i</i> -C ₄ H ₉) ₃ P	-80		

^ad = doublet, t = triplet, q = quartet, p = quintet, and s = septet.

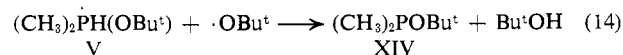
in the spectra of the second generation species of the large doublet splittings assigned to the axial proton in the primary adducts I. Furthermore, the deuterium label is also lost in the case of the deuterated dimethylphosphine. The splitting pattern and the magnitude of the coupling constants suggest that these radicals are closely related to the dialkoxyphosphoranyl radicals IX discussed above. We propose that these radicals also arise from a secondary reaction, in which a proton (deuteron) is initially abstracted from the primary adduct.²¹ For example, the primary adduct V formed



from dimethylphosphine reacts further with *tert*-butoxy

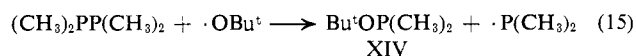
(21) (a) It is unlikely that a hydrogen atom (not observed) is unimolecularly ejected from the primary adduct, especially in preference to the cleavage of methyl radical [cf. the decomposition of alkoxy radicals, P. Gray, R. Shaw, and J. Thynne, *Progr. React. Kinet.*, **4**, 68 (1968)]. (b) It is also possible that XIV is formed by addition of *tert*-butoxy radical to V to form a five coordinate (CH₃)₂PH(OBu)₂, followed by abstraction of an hydrogen atom in a subsequent step. Alternatively, abstraction of hydrogen from these lower phosphines may also constitute the initial step, followed by further reaction of the phosphinyl intermediate with *tert*-butoxy radicals to form the diamagnetic XIV.

radicals to afford the diamagnetic dimethyl-*tert*-butoxyphosphine (XIV), which is described earlier as an inter-

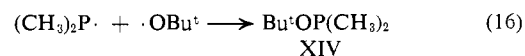


mediate in the reactions of trimethylphosphine (eq 8, R = CH₃) and dimethylphenoxyphosphine (eq 11). Ready addition of *tert*-butoxy radicals to XIV affords the second generation species XII (eq 12). Therefore, it is not surprising that the *same phosphoranyl radical XII is formed as a second generation species from trimethylphosphine and dimethylphenoxyphosphine as well as dimethylphosphine.*

The di-*tert*-butoxyphosphoranyl radical XII can also be generated by a fourth pathway. Thus, photolysis of di-*tert*-butyl peroxide in a cyclopropane solution of tetramethyldiphosphine yields the spectrum of *only one* paramagnetic species whose general behavior and spectral parameters ($a_P = 714.7$ G and a_H (septet) = 2.5 G at -50°) make it indistinguishable from the di-*tert*-butoxydimethylphosphoranyl radical XII. We propose that a *tert*-butoxy radical initially displaces the dimethylphosphinyl radical (CH₃)₂P· to form a molecule of *tert*-butoxydimethylphosphine (XIV, eq 15). The phosphinyl radical is not detected (*vide*

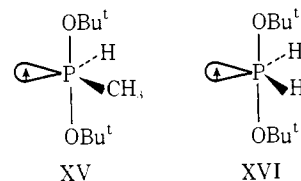


supra), because it either couples readily with *tert*-butoxy radicals or it effectively induces the decomposition of di-*tert*-butyl peroxide to form another molecule of XIV (eq 16). Both reactions are followed by



addition of *tert*-butoxy radical to generate the dialkoxyphosphoranyl radical XII (eq 12).

Methylphosphine and phosphine by similar processes would lead to the radicals XV and XVI, respectively.



It is noteworthy that the proton hyperfine splitting for radical XVI is much smaller than those observed for equatorial protons in the other species. Similarly, the phosphorus splitting is also unusually small compared to other dialkoxyphosphoranyl radicals. Such changes are consistent with the trend established in the series shown in Table I, but a quantitative interpretation is pending a theoretical analysis of the bonding in these radicals.

The absence of a resolvable proton hyperfine splitting in the spectra of tetraalkoxyphosphoranyl radicals does not allow for a distinction among alkoxy groups. The magnitude of the phosphorus splitting is the largest among the phosphoranyl radicals examined. It follows from the trend established by the successive addition of alkoxy ligands (Table I) and may be expected from a qualitative picture of the bonding.^{12,22} We in-

(22) Cf. also F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961); R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, **22**, 231 (1968).

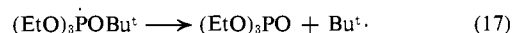
fer from the foregoing results that the tetraalkoxyphosphoranyl radicals also have a distorted trigonal-bipyramidal structure. The latter is consistent with the elegant chemical experiments which recently showed the retention of stereochemistry and nonequivalency of the alkoxy groups in these radicals.²³

Finally, these esr results only reveal the steady-state concentration of various radicals extant in solution. Nonetheless, by utilizing different substrates and varying conditions, the importance of various homolytic processes can be inferred by the appearance and absence of certain paramagnetic species. As a result, a consistent picture is derived for homolytic substitution on phosphorus involving an addition-elimination mechanism.²⁴ Competitive esr spectroscopy and time intermittency can be used to make such studies quantitative, and recent studies²⁵ have shown that fragmen-

(23) W. G. Bentrude and R. A. Wielessek, *J. Amer. Chem. Soc.*, **91**, 2406 (1969); W. G. Bentrude, P. E. Rusek, Jr., and J. H. Hargis, *Chem. Commun.*, 296 (1969); W. G. Bentrude and T. B. Min, private communication.

(24) These experiments, of course, do not rule out the participation of direct displacement processes.

tation (eq 17) of a phosphoranyl intermediate can pro-



ceed with a rate constant of at least $1.3 \times 10^6 \text{ sec}^{-1}$ at 30°.

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(25) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971). Additional kinetic esr studies on phosphoranyl radicals are in progress (A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin 2*, in press; G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, in press). Professor Davies and collaborators have recently prepared Et_2POEt and thence $\text{Et}_2\text{P}(\text{OEt})\text{OBu}^\cdot$, which shows $a(\text{P}) = 707 \text{ G}$, supporting our identification of the second generation radicals as dialkoxyphosphoranyl.

Photochemistry of Stilbenes. VI.¹ Steric Effects on the Photocyclizations of Some Meta-Substituted Stilbenes²

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Abstract: The isomer ratios of the 2- and 4-substituted phenanthrenes produced by the photocyclization in the presence of iodine of a series of meta-substituted stilbenes were determined to assess the importance of steric effects on these photoreactions. The irradiations of *m*-methyl-, *m*-chloro-, and *m*-trifluoromethylstilbene each gave product ratios near unity. From these results and other arguments it is concluded that the more crowded 4-substituted product and the less crowded 2-substituted product are formed at almost identical rates in each case, implying an early transition state for cyclization. The photocyclization of *m,m'*-dimethylstilbene revealed a modest steric hindrance to the formation of one of the three products, 4,5-dimethylphenanthrene; analogous behavior was found for the sterically related 2-(*m*-methylstyryl)naphthalene. In addition, the relative amount of 4,5-dimethylphenanthrene produced from *m,m'*-dimethylstilbene varied from 0 to 18% depending on the iodine concentration, indicating that thermal ring opening of the dihydrophenanthrene precursor is competitive with its oxidative trapping.

The formation of phenanthrenes and related polynuclear aromatic molecules by the ultraviolet irradiation of stilbenes or stilbene derivatives in solutions containing an oxidant like iodine or oxygen has been extensively studied, and many aspects of the scope, mechanism, and preparative utility of this photocyclization are known.³ Only a brief summary of portions of

this knowledge⁴ will be given here, using the parent system as an example (see Scheme I). Thus, ultraviolet irradiation of solutions⁵ of either *trans*-stilbene (1) or *cis*-stilbene (2) in the absence of an oxidant leads to the establishment of a photostationary mixture containing the two stilbenes together with the isomeric 4a,4b-

(1) For Part V, see F. B. Mallory and C. S. Wood, *Tetrahedron Lett.*, 2643 (1965).

(2) Presented in part at the First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 3, 1966, and also at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., Apr 1-5, 1968, Abstract P-217.

(3) For reviews, see (a) F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 247-282; (b) M. Scholz, F. Dietz, and M. Mühstätt, *Z. Chem.*, **7**, 329 (1967); (c) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **87**, 687 (1968); and (d) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

(4) (a) H. Stegemeyer, *Z. Naturforsch., B*, **17**, 153 (1962); (b) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, **84**, 4361 (1962); (c) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 829 (1963); (d) F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3094 (1964); (e) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964); (f) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965); (g) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967); (h) J. Saltiel, *J. Amer. Chem. Soc.*, **90**, 6394 (1968); (i) A. Bylina and Z. R. Grabowski, *Trans. Faraday Soc.*, **65**, 458 (1969).

(5) Concentrations less than about 0.05 M are generally used to avoid the formation of tetraphenylcyclobutanes by photodimerization.