

# Photolysis and Thermolysis of Pentaphenylantimony in Benzene

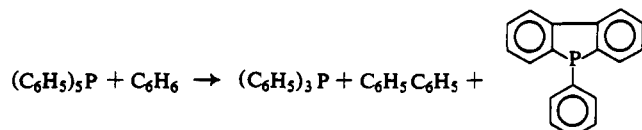
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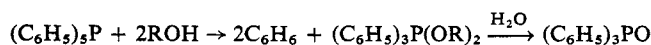
**Abstract:** The photolysis and thermolysis reactions of pentaphenylantimony (PPA) in benzene solution have been studied by use of C<sup>14</sup> tracer experiments and mass spectral analyses. Following the photolysis of PPA in benzene, triphenylantimony, biphenyl, and *p*-quaterphenyl were isolated. Based on the results of the C<sup>14</sup> tracer studies, it was concluded that the reaction mechanism is complex; however, free phenyl radicals are produced and undergo reactions which account for many of the products. It was noteworthy that the percentage of biphenyl which resulted from attack of phenyl radicals on solvent benzene was found to be strongly wavelength dependent. In the case of the thermolysis of PPA, triphenylstibine and biphenyl were the only products obtained. The C<sup>14</sup> tracer studies showed that this is an intramolecular process, not involving free phenyl radicals.

A review of the structures of pentacoordinate compounds of group V elements has recently been published.<sup>2a</sup> Although such compounds have been known for several years,<sup>2b</sup> relatively few detailed studies of their reactions have been made.<sup>3a</sup>

Razuvaev and coworkers<sup>3b</sup> have investigated the reactions of pentaphenylphosphorus (PPP) with different solvents. They found that PPP can react with various solvents in both a homolytic and a heterolytic manner, depending on the nature of the solvent. For example, carbon-14 labeled PPP reacts with benzene at 80° to give biphenyl in which 5–6% of the phenyl groups are derived from the solvent.<sup>3c</sup> It was concluded that the decom-



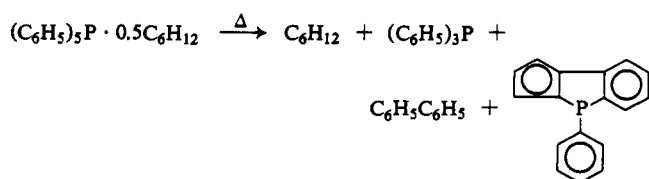
position takes place with the formation of phenyl radicals. It was also suggested that the reaction of PPP with alcohol to give benzene and triphenylphosphine oxide involves a heterolytic cleavage of the carbon-phosphorus bonds.



(1) (a) University of Massachusetts; (b) Brookhaven National Laboratory.

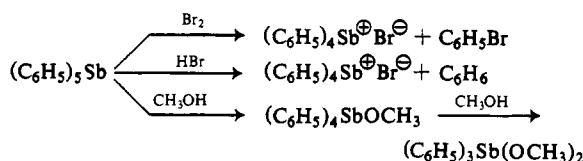
(2) (a) E. L. Muetterties and K. A. Schum, *Quart. Rev. (London)*, **20**, 245 (1966); (b) G. Wittig, *Bull. Soc. Chim. France*, 1162 (1966), and references cited therein; G. Wittig and P. Hellwinkel, *Angew. Chem. Intern. Ed. Engl.*, **1**, 53 (1962).

(3) (a) A review of free-radical reactions of trivalent organic compounds of group V elements has been published: N. J. Friswell and B. G. Gowenlock, "Advances in Free-Radical Chemistry 2," G. H. Williams, Ed., Academic Press, New York, N.Y., 1967, Chapter 1; (b) G. A. Razuvaev, G. G. Petukhov, and N. A. Osanova, *J. Gen. Chem. USSR*, **31**, 2190 (1961), and references cited therein; (c) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953). These workers first reported that the initial products of the thermolysis of PPP initiate the polymerization of styrene.



Even though several pentaarylsarsines<sup>4</sup> have been synthesized, there have been no reports of free-radical reactions of these compounds.

Pentaaryl- and pentaalkylantimony compounds<sup>5</sup> were first reported in 1952 by Wittig and coworkers. Since then, several reactions involving both heterolytic and homolytic cleavage of antimony-carbon bonds have been observed. As examples of reactions involving heterolytic bond cleavage, pentaphenylantimony (PPA) can react with halogens or with hydrogen bromide to give rise to tetraphenylstibonium halides. It has also been observed<sup>6</sup> that pentaphenylantimony can undergo a solvolysis reaction with methanol to give first methoxytetraphenylantimony



and then dimethoxytriphenylantimony. Recently, however, Razuvaev, *et al.*,<sup>7</sup> have found that the reaction of PPA with carbon tetrachloride gives tetraphenylstibonium chloride, benzene, and chlorobenzene. A similar reaction occurs with chloroform. The free-radical nature of these reactions was indicated by the change in color of  $\alpha,\alpha'$ -diphenyl- $\beta$ -(2,4,6-trinitrophenyl)hydrazyl added to the reaction mixtures, and, in the case of the reaction with carbon tetrachloride, by the capture of the radicals by mercury. Yet another similar reaction<sup>8</sup> was observed to

(4) W. R. Cullen, *Advan. Organometal. Chem.*, **4**, 145 (1966).

(5) G. Wittig and K. Clauss, *Ann.*, **577**, 26 (1952); G. Wittig and K. Torssell, *Acta Chim. Scand.*, **7**, 1293 (1953).

(6) (a) G. H. Briles and W. E. McEwen, *Tetrahedron Letters*, 5191 (1966); (b) G. H. Briles, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1966. (c) Both methoxytetraphenylantimony and dimethoxytriphenylantimony adopt trigonal-bipyramidal configurations in the crystalline state which is in contrast to the structure of PPA, which approximates a square-pyramidal configuration: K. Shen, W. E. McEwen, S. J. La Placa, W. C. Hamilton, and A. P. Wolf, *J. Am. Chem. Soc.*, **90**, 1718 (1968); P. J. Wheatly, *J. Chem. Soc.*, 3718 (1964). A X-ray crystallographic study of the molecular structure of PPA has been reinvestigated by F. A. Cotton and coworkers (submitted for publication).

(7) G. A. Razuvaev, N. A. Osanova, N. P. Shulaev, and B. Tsigin, *J. Gen. Chem., USSR*, **30**, 3203 (1960).

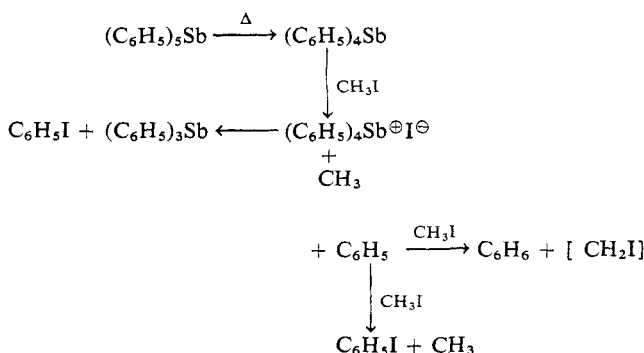
(8) G. A. Razuvaev, N. A. Osanova, and Yu. A. Sangalov, *Zh. Obshch. Khim.*, **37**, 37 (1967).

Table I. Isotopic Analysis of Photolysis<sup>a</sup> of Pentaphenylantimony (PPA) in Benzene

Expt no.	Reactants					Products										
	Structure	PPA		C <sub>6</sub> H <sub>6</sub> Amt, g	Exptl condition	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb			Biphenyl		C <sub>6</sub> H <sub>6</sub>			<i>p</i> -Quaterphenyl		
		Amt, g	Sp act. <sup>b</sup>			Amt, g	Sp act.	Ar <sup>c</sup>	Amt, g	Sp act.	Ar	Sp act.	Act, % <sup>d</sup>	Amt, g	Sp act.	Ar
1 <sup>f</sup>	PPA-C <sup>14</sup>	6.12	0.883	96.25	Quartz, <i>in vacuo</i> , 19 hr	1.8	0.857	0.97	1.0	0.598	0.677	0.0054	13	0.05	0.446	0.51
2 <sup>f</sup>	PPA-C <sup>14</sup>	6.11	1.89	96.25	Quartz, <i>in vacuo</i> , 7 hr	1.8	1.92	1.02	1.1	1.28	0.677	0.0101	11	0.05	0.917	0.49
3	PPA-C <sup>14</sup>	6.11	0.883	96.25	Pyrex, <i>in vacuo</i> , 3.5 hr	2.0	0.880	1.00	1.1	0.535	0.606	0.0043	10	0.05	0.445	0.50
4	PPA-C <sup>14</sup>	6.11	0.883	96.25	Pyrex, in air, 3.5 hr	2.2	0.874	0.99	1.1	0.540	0.612	0.0042	10	0.05	0.450	0.51
5	PPA-1-C <sup>14</sup>	6.11	1.78	96.25	Pyrex, in air, 3.5 hr	2.2	1.77	0.99	1.1	1.08	0.607	0.0080	9	0.05	0.900	0.50
6	PPA-C <sup>14</sup>	3.01	1.89	96.25	Pyrex, in air, 3.5 hr				0.4	1.13	0.598					
7	PPA-C <sup>14</sup>	8.19	1.89	96.25	Quartz, in air, 3.5 hr					1.24	0.657					
8 <sup>e</sup>	PPA-C <sup>14</sup>	3.88	1.89	61.46	Quartz, in air, 9 hr					1.33	0.704					
9 <sup>e</sup>	PPA-C <sup>14</sup>	0.60	1.89	96.25	Quartz, in air, 9 hr					1.25	0.661					
10	PPA-C <sup>14</sup>	0.60	1.89	96.25	Pyrex, in air, 3.5 hr					1.08	0.571					

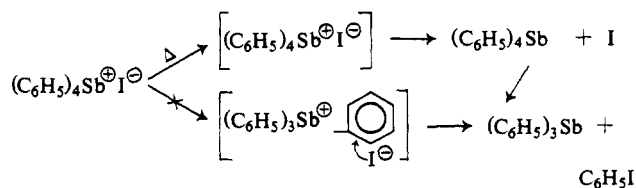
<sup>a</sup> The light source was a Hanovia mercury lamp, No. 673A, 550 W. <sup>b</sup> Specific activity in terms of nCi/mg of C. <sup>c</sup> Ratio of specific activity of this product to that of PPA. <sup>d</sup> Percentage of total activity of starting material (PPA) in benzene after photolysis. <sup>e</sup> A Hanovia mercury low-pressure resonance lamp (2537 Å) was used as the light source in this experiment. <sup>f</sup> The extent of the reaction was not monitored by ir in this run.

take place between PPA and methyl iodide.<sup>9</sup>



In this paper, we wish to report the results of the photolysis and thermolysis of PPA in benzene solution.<sup>10-12</sup>

(9) No mechanism for the formation of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb and CH<sub>3</sub>I from (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Sb<sup>+</sup>I<sup>-</sup> was suggested. We believe that this is a free-radical reaction rather than an ionic displacement reaction.



There is evidence available that free-radical reactions are involved in the thermal decomposition of tetraphenylstibonium hydroxide: F. Chupka, and W. E. McEwen, unpublished results.

(10) H. A. Skinner, *Advan. Organometal. Chem.*, **2**, 49 (1964).  $\bar{D}(\text{P}-\text{C}_6\text{H}_5) = 71.9 \pm 2.3$ ,  $\bar{D}(\text{As}-\text{C}_6\text{H}_5) = 63.8 \pm 2.3$ ;  $\bar{D}(\text{Sb}-\text{C}_6\text{H}_5) = 58.3 \pm 2.3$ ,  $\bar{D}(\text{Bi}-\text{C}_6\text{H}_5) = 42.2 \pm 2.3$  kcal/mole for compounds of the type (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>M. The energies of Sb-C bonds in pentavalent antimony compounds are unknown.

(11) For a discussion of factors which may be of importance regarding the feasibility of a photochemical process, see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 58. Although both triphenylphosphine<sup>12a</sup> and triphenylbismuthine<sup>12b,c</sup> can

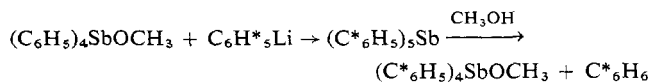
## Results and Discussion

**Photolysis of PPA in Benzene.** PPA-1-C<sup>14</sup>, prepared by reaction of triphenylantimony dichloride with phenyllithium-1-C<sup>14</sup>, was dissolved in benzene and photolyzed under various conditions. The results are summarized in Table I. Let us first consider expt no. 5 (Table I), in which PPA (0.11 mole/l.) was photolyzed with use of a Pyrex filter, and the extent of the photolysis was monitored by observation of the characteristic ir absorption<sup>13a</sup> peak at 1052 cm<sup>-1</sup> of PPA. After 3.5 hr of irradiation this peak had completely disappeared; thus, it was concluded that the use of a quartz vessel was not necessary to effect the

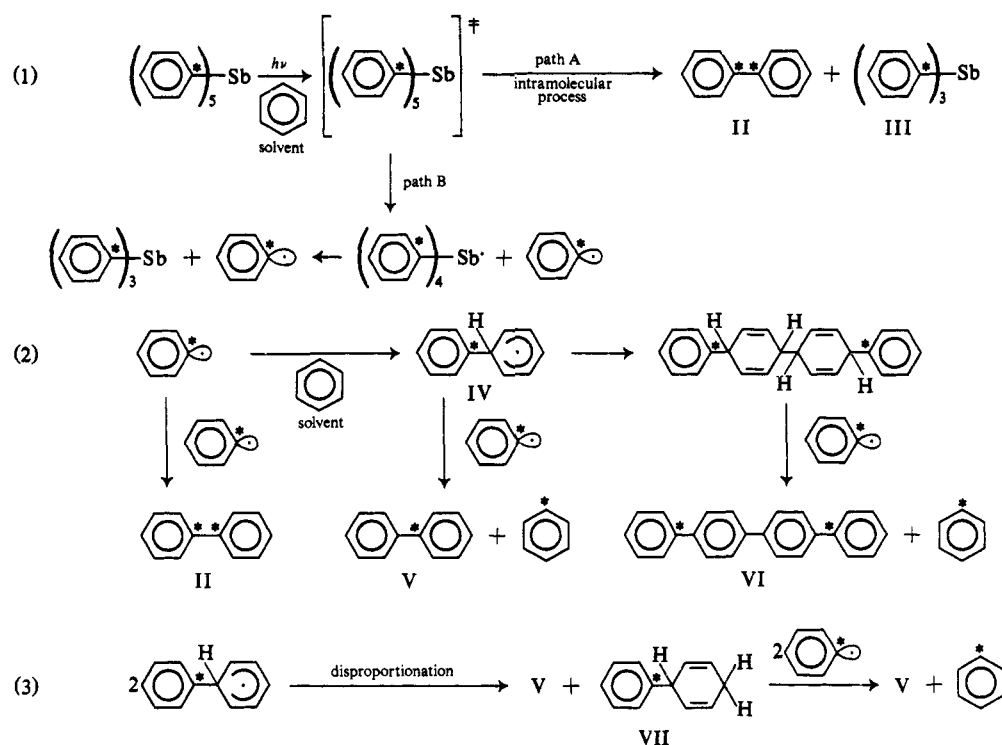
undergo photo-initiated reactions, we have found that triphenylstibine is almost completely stable to uv irradiation.

(12) (a) M. L. Kaufman and C. E. Griffin, *Tetrahedron Letters*, 769 (1965); (b) D. H. Hey, D. A. Shingleton, and G. H. Williams, *J. Chem. Soc.*, 5612 (1963). (c) For the reaction of triphenylbismuthine with benzene, see G. A. Razuvaev, G. G. Petukhov, V. A. Titov, and O. N. Druzhkov, *J. Gen. Chem. USSR*, **35**, 479 (1965).

(13) (a) For assignments of ir peaks of PPA, see K. M. MacKay, D. S. Sowerby, and W. C. Young, *Spectrochim. Acta*, **A24**, 611 (1968). (b) It has been suggested that PPA in solution might undergo rapid transformation between trigonal-bipyramidal and square-pyramidal conformations: D. Hellwinkel, *Angew. Chem. Intern. Ed. Engl.*, **5**, 725 (1966). We have completed a tracer study of the following pair of reactions to explore whether stereospecific reactions can occur.



It was found that the specific activities (nanocuries/milligram of C) of methoxytetraphenylantimony and benzene produced were identical. This indicates that the five phenyl groups in PPA are chemically equivalent at least with respect to methanolysis. However, we cannot claim a complete understanding of the situation since we do not know the detailed mechanism of the formation of PPA by the reaction of C<sup>\*</sup>H<sub>5</sub>Li with methoxytetraphenylantimony, which, in the crystalline state, has the configuration of a trigonal bipyramid (see ref 6c). A preliminary kinetics study indicated that methanolysis of PPA is second order over-all, first order with respect to PPA and first order with respect to methanol concentrations (rate constant = 2.95 × 10<sup>-3</sup> l. mole<sup>-1</sup> sec<sup>-1</sup> at 53° in dioxane).

Scheme I<sup>a</sup>

<sup>a</sup> An asterisk (\*) signifies carbon-14. Two asterisks are used in structures such as II because the 1 and 1' positions are indistinguishable by virtue of symmetry. The presence of two asterisks in such structures is not meant to indicate a double label. The sign  $\ddagger$  signifies an excited state.

photolysis. There is no conclusive evidence<sup>13b</sup> available that the five phenyl groups of PPA are chemically equivalent; however, insofar as radioactivity considerations are concerned, they can be considered to be equivalent inasmuch as the method of preparation of PPA employed in our work involves the use of an intermediate which is completely symmetrical, *i.e.*, lithium hexaphenylantimonate.

Triphenylstibine, biphenyl, *p*-quaterphenyl, and a resinous material were obtained. Based on the carbon-14 distribution in the products, the following gross mechanism (Scheme I) of the over-all reaction can be proposed.<sup>14</sup> The specific activity of triphenylstibine is the same as that of the starting material, PPA-1-C<sup>14</sup>, indicating that no exchange occurs between the phenyl groups attached to antimony and the solvent benzene. The biphenyl isolated was oxidized to benzoic acid using chromium trioxide.<sup>15</sup> The specific activity of the benzoic acid indicated that the carbon-14 label was located in the 1 and 1' positions of the biphenyl; thus no apparent attack of phenyl radicals on PPA or the tetraphenylantimony radical with subsequent cleavage of the phenylated products and hydrogen migration had taken place under

photolytic conditions.<sup>16</sup> This result eliminates conclusively the otherwise conceivable reaction paths of the types shown in Scheme II.

Based on the specific activity of PPA-1-C<sup>14</sup> and biphenyl, it can be calculated that the relative amounts of biphenyl-1,1'-C<sup>14</sup> (II) and biphenyl-1-C<sup>14</sup> (V)<sup>17</sup> are 21.3 and 78.7%, respectively (Pyrex filter). This is in good agreement with the results of another experiment in which the photolysis of PPA was carried out in benzene-H<sub>2</sub><sup>6</sup> under the same conditions as was used in the carbon-14 tracer studies. There was obtained C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub> (21.7%), C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>D<sub>5</sub> (75.2%), and C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>D<sub>7</sub> (3.1%),<sup>17</sup> no significant amount of C<sub>6</sub>D<sub>5</sub>C<sub>6</sub>D<sub>5</sub> being found (<0.1%, if any, based on mass spectral analysis of the isolated biphenyl). The presence of an impurity (presumably attributable to the presence of C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>D<sub>7</sub> (3.1%)) shows up in the mass spectrum of the biphenyl and strongly suggests that disproportionation of the phenylcyclohexadienyl free

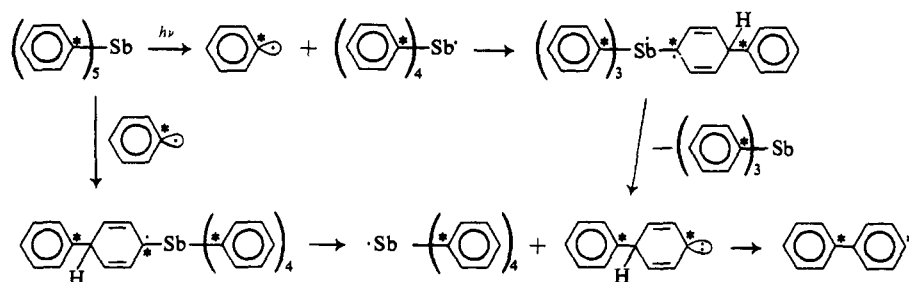
(14) This mechanism is analogous to that which has been proposed for the thermal decomposition of benzoyl peroxide in benzene. For reviews of studies of the mechanisms of the reaction between benzoyl peroxide and aromatic solvents, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 482; E. L. Eliel, S. Meyerson, Z. Welvert, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960); W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapter 16; "Advances in Free-Radical Chemistry 2," ref 3a, Chapter 2.

(15) H. Wynberg and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 3308 (1963).

(16) (a) Experimental data and MO considerations are in agreement that the unpaired electron in the ground state of a phenyl radical remains in the  $sp^2$  orbital of the carbon atoms at which bond scission has taken place to give the  $\sigma$  radical: G. Porter and B. Ward, *Proc. Roy. Soc. (London)*, **A287**, 457 (1965); J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965). (b) It is of interest to note that the thermolysis of PPA is analogous to the photolysis of benzoyl peroxide in benzene in which no solvent participates in the formation of biphenyl. It has been found that there is no hydrogen migration either in the thermal or photolytic decomposition of benzoyl peroxide in benzene: G. A. Razuvaev and B. G. Zateev, *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **138**, 120 (1963).

(17) Since C<sup>14</sup> assay cannot differentiate biphenyl-1-C<sup>14</sup> and dihydrobiphenyl-1-C<sup>14</sup> (as impurity), the 78.7% yield should be the sum of the yields of these two compounds; this result is in good agreement with that obtained by the mass spectral analysis 78.3% (75.2 + 3.1%).

Scheme II



radical (IV) to biphenyl and dihydrobiphenyl (VII)<sup>18,19</sup> has taken place. Furthermore, when PPA was photolyzed in benzene-H<sub>2</sub>, the mass spectra of the isolated biphenyl indicated the relative mole percentages of the following compounds to be C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>, 30.38%; C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>D, 69.23%; and C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>3</sub>D<sub>2</sub>, 0.78%. The presence of C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>3</sub>D<sub>2</sub> further indicates that disproportionation of the phenylcyclohexadienyl free radical and subsequent dehydrogenation of dihydrobiphenyl have taken place. The calculated "apparent isotope effect"<sup>19b</sup> is 1.33. This small, but significant, isotope effect again suggests that a side reaction (*i.e.*, disproportionation) of the intermediate (IV) formed by the addition of the phenyl radical to benzene<sup>19c</sup> has occurred.

It is noteworthy that the ratio of II/V is wavelength dependent. As shown in Table I, the ratio of specific activities of biphenyl to PPA was ~0.600 (expt 3–6, corresponding to 21% of II and 79% of V when a Pyrex filter and a high-pressure mercury lamp were used (*i.e.*,  $\lambda > \sim 3000$  Å). This value increased to ~0.660 (expt no. 1, 2, 7, corresponding to 32% of II and 68% of V when no Pyrex filter was used (*i.e.*,  $\lambda < 3000$  Å). It further increased to ~0.704 (expt no. 8, corresponding to 40% of II and 60% of V when a low-pressure mercury resonance lamp was used<sup>20</sup> (*i.e.*,  $\lambda \approx 2537$  Å).

Expt no.	(II)	(V)	PPA concn, M
5	21%	79%	0.11
8	40%	60%	0.11
9	32%	68%	0.01

When the concentration of PPA was decreased from

(18) DeTar and Long have isolated 1,4-dihydrobiphenyl together with a small amount of 1,2-dihydrobiphenyl from the thermal decomposition of benzoyl peroxide in benzene at low concentration: D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

(19) (a) For a brief discussion of the relative stabilities and identification of the various dihydrobiphenyl isomers prepared by other methods, see P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. R. Williams, *J. Org. Chem.*, **33**, 1916 (1968). (b) These values are each the average of two measurements. Eliel and coworkers<sup>14</sup> found that the reaction of benzoyl peroxide with benzene-H<sub>2</sub> does not give rise to an observable isotope effect if the ratio of benzoyl peroxide to benzene-H<sub>2</sub> is 1:42; however, there is an observable isotope effect of 2.6 if this ratio is 1:420 (the isotope effect is calculated for a reaction conforming to the hypothetical equation  $R\cdot + C_6H_6 \rightarrow RC_6H_5 + H\cdot$ ). Our results are in good agreement with this observation (PPA: benzene-H<sub>2</sub> = 1:103, isotope effect 1.33). (c) H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964).

(20) The uv spectrum of PPA has broad absorption bands (log  $\epsilon$  in parentheses):  $\lambda_{\max}^{\text{hexane}}$  253 m $\mu$  (log  $\epsilon$  3.64), 260 (3.66), 265 (3.66), and 275 (sh 3.63).

0.11 (expt no. 8) to 0.01 M (expt no. 9), the ratio II/V was changed from 40/60 to 32/68. This shows that there is a concentration effect on the ratio of II/V produced (*i.e.*, intermolecular coupling of labeled phenyl radicals represents one source of II). This concentration effect then suggests the possibility that the observed wavelength dependence of the ratio II/V might have been attributable to a variation in light intensity (different light source in expt no. 5 and no. 8, 9) or to a difference in extinction coefficients. If this were true, however, one would expect that a shorter irradiation time would have been needed in order to effect complete disappearance of PPA in expt no. 8 as compared to expt no. 5 in order to explain the change of ratio from 21/79 (expt no. 5) to 40/60 (expt no. 8). Actually an irradiation time of 8 hr was necessary in expt no. 8 and 9 as compared to 3.5 hr in order to bring about complete disappearance of PPA, and this indicates that, in addition to path B, another reaction pathway (*i.e.*, path A, a direct intramolecular process) is also operative. These results can best be explained in terms of excited states of PPA. At long wavelength, it is probable that direct excitation of PPA gives singlet (S<sub>1</sub>) PPA which, in turn, gives rise to a tetraphenylantimony radical and a phenyl radical by rupture of one Sb–C bond. At short wavelengths (*i.e.*,  $\lambda$  2537 Å), however, the population of the higher vibrational states of the singlet is increased which presumably gives rise to more II by rupture of two Sb–C bonds in the same molecule.<sup>21</sup>

*p*-Quaterphenyl (VI) was also isolated from the photolysis mixture. Its specific activity was exactly one-half that of PPA-1-C<sup>14</sup>, thus demonstrating that this compound results by dimerization of phenylcyclohexadienyl radicals; these, in turn, result from attack of radioactive phenyl radicals derived from PPA-1-C<sup>14</sup> on the "dead" solvent molecules.

Based on the specific activity of the benzene recovered after photolysis, it was found that about 9.3% (expt 5) of the initial total activity of the PPA-1-C<sup>14</sup> was transferred to benzene. Obviously, this results from hydrogen abstraction by radioactive phenyl radicals from phenyl-

(21) An alternative explanation for this wavelength dependence involves the solvent benzene acting as a sensitizer. At short wavelength (*i.e.*,  $\lambda$  2537 Å), benzene has absorbed the major fraction of light (86%, for example, in expt 5), and the first triplet benzene (85 kcal/mole) by energy transfer gives triplet PPA, which presumably leads to formation of more II than does singlet PPA. The triplet energy of triphenylarsine is known to be 73 kcal/mole: D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). We think that the energy of the first triplet state of PPA is probably of this magnitude. As pointed out by one of the referees, we have no conclusive evidence for either of these mechanisms at this stage; however, we believe that the wavelength dependence is evidence of intramolecular process. A detailed photochemical study involving the measurement of quantum yield and the use of proper sensitizers will be the subject of a further study. We wish to thank Dr. Ernest Lam for his suggestions with regard to this problem.

Table II. Isotopic Analysis of Thermolysis of Pentaphenylantimony (PPA) in Benzene

Expt no.	Reactants					Products							
	Structure	PPA		C <sub>6</sub> H <sub>6</sub> Amt, g	Exptl condition	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb			Biphenyl		C <sub>6</sub> H <sub>6</sub>		
		Amt, g	Sp act. <sup>a</sup>			Amt.	Sp act.	Ar <sup>b</sup>	Amt, g	Sp act.	Ar	Sp act.	Act, % <sup>c</sup>
1	PPA-C <sup>14</sup>	3.98	0.883	5.25	Evacuated ampoule, 250°, 3 hr	2.1	0.859	0.97	1.1	0.874	0.99	0.006	1
2	PPA-C <sup>14</sup>	4.43	1.89	6.13	Evacuated ampoule, 220°, 3 hr	2.6	1.91	1.01	1.4	1.89	1.00	0.010	1
3	PPA-1-C <sup>14</sup>	4.22	1.78	6.13	Evacuated ampoule, 220°, 3 hr	2.5	1.78	1.00	1.2	1.77	0.99	0.010	1

<sup>a</sup> Specific activity in terms of nCi/mg of C. <sup>b</sup> Ratio of specific activity of this product to that of PPA. <sup>c</sup> Percentage of total activity of starting material (PPA) in benzene after thermolysis.

cyclohexadienyl radicals, tetrahydro-*p*-quaterphenyls, and dihydrobiphenyls. Furthermore, if it is assumed that two-fifths of the total activity [(C<sub>6</sub>H<sub>5</sub>)<sub>5</sub>Sb → (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb + 2C<sub>6</sub>H<sub>5</sub>·] of PPA participates in the reactions leading to formation of biphenyl and *p*-quaterphenyl, and that one radioactive phenyl radical reacts with one molecule of solvent while another radioactive phenyl radical subsequently abstracts a hydrogen atom to give either biphenyl or *p*-quaterphenyl,<sup>22</sup> then 17.2% rather than the observed 9% of total activity should end up in the benzene. This discrepancy can be rationalized by the following facts.

(1) Some phenyl radicals react with benzene to form resinous substances.

(2) Some dihydrobiphenyl is formed and does not undergo further reaction.

(3) Dihydrobiphenyl may be oxidized to biphenyl by oxygen.

(4) Oxygen may react with phenylcyclohexadienyl radicals<sup>23</sup> to bring about the formation of biphenyl.

**Thermolysis of PPA-1-C<sup>14</sup> in Benzene.** PPA-1-C<sup>14</sup> and benzene<sup>24</sup> were sealed in an ampoule (see Table II) and heated in an autoclave to 220° for 3 hr (no reaction at 175°). Triphenylstibine<sup>25</sup> and biphenyl were the only products formed. Both compounds were found to have the same specific activity as the starting material, and this result demonstrates that only an intramolecular reaction is operative. Benzene recovered after thermolysis was found to have almost no radioactivity, as expected for a strictly intramolecular process. The specific activity of benzoic acid obtained by oxidation of biphenyl again indicated that all C<sup>14</sup> remained at the 1 position, and thus eliminated the possibility of mechanisms of the type shown in Scheme II.<sup>16b</sup>

A summary of related studies is given in Table III.

## Experimental Section

### Pentaphenylantimony-1-C<sup>14</sup>.<sup>5a</sup> Bromobenzene-1-C<sup>14</sup> (3.56 nCi/

(22) Corrections for the formation of II have been made in the calculations.

(23) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2239 (1962).

(24) It has been claimed (see ref 7) that an intramolecular splitting of PPA occurs in a thermolysis reaction with labeled benzene, but no details were given.

(25) It is of interest to note that in contrast to the behavior of pentaphenylphosphorus no Sb-phenyl biphenylenestibine was isolated (see ref 3c). The detailed mechanism of the formation of 9-phenylphosphaphluorene from PPP is not clear. It is known that the reaction of methyl-lithium with tetraphenylphosphonium bromide gives 9-phenylphosphaphluorene by a mechanism in which the lithium reagent abstracts an *ortho* proton: D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3467 (1965). A similar reaction was observed for the arsenic analog: D. Hellwinkel and G. Kilthaw, *Chem. Ber.*, **101**, 121 (1968).

mg of C) was prepared<sup>26,27</sup> in ca. 40% yield from benzoic acid-1-C<sup>14</sup> (Mallinckrodt/Nuclear) by use of a Hunsdiecker reaction. To 300 ml of anhydrous ether in which lithium shavings (2.95 g, 0.425 g-atom) were suspended, bromobenzene-1-C<sup>14</sup> (33 g, 0.21 mole) was added over a period of 40 min, a nitrogen atmosphere being maintained over the reaction mixture. After the lithium had been consumed, the mixture was filtered, the filtrate being collected in a flask under nitrogen. The concentration of this solution was determined to be ca. 0.775 *M* by titration with hydrochloric acid. Into a three-necked flask equipped with a condenser and a nitrogen inlet tube was introduced triphenylantimony dichloride (27 g, 0.06 mole) and 200 ml of anhydrous ether, with stirring. The phenyllithium solution was added slowly by the use of a syringe. After 2.80 ml of the phenyllithium solution had been added, the solution was stirred for an additional hour at room temperature, filtered, and washed with a small amount of anhydrous ether. The white precipitate which had formed (lithium hexaphenylantimonate) was collected and decomposed with water to give PPA-1-C<sup>14</sup> and benzene. The PPA-1-C<sup>14</sup> obtained in this manner was recrystallized from acetonitrile to give PPA-1-C<sup>14</sup>, mp 162° (27 g, 90%).<sup>28</sup>

*Anal.* Calcd activity for C<sub>30</sub>H<sub>24</sub>Sb: 1.78 nCi/mg of C. Found: 1.78 nCi/mg of C.

**Photolysis of PPA-1-C<sup>14</sup> in Benzene.** These experiments were carried out in a 125-ml cylindrical quartz vessel fitted with a water-cooled jacket. The light source was a Hanovia high-pressure mercury lamp, No. 673A, 550 W, or a Hanovia mercury low-pressure resonance lamp. In expt no. 7, for example, PPA-1-C<sup>14</sup> (6.11 g, 0.012 mole, 1.78 nCi/mg of C) was dissolved in benzene (96.25 g, 1.23 moles) in the vessel. A Pyrex filter was inserted between the lamp and vessel. After 3.5 hr of irradiation, the yellow solution was transferred to a distillation flask, and the benzene was removed under reduced pressure (ca. 600 mm) on a steam bath. The benzene was converted to *m*-dinitrobenzene by the action of sulfuric acid and fuming nitric acid. Recrystallization from methanol gave pure *m*-dinitrobenzene, mp 89–90°.

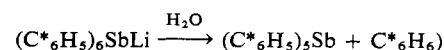
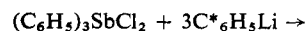
*Anal.* Found activity of C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: 0.007 nCi/mg of C, 0.009 nCi/mg of C.

The red oily residue was subjected to steam distillation to give biphenyl (1.1 g). Extraction of the aqueous solution with ether, evaporation of the ether, and sublimation of the residue gave pure biphenyl, mp 70°.

(26) W. G. Dauben and H. Tilles, *J. Am. Chem. Soc.*, **72**, 3185 (1950).

(27) The position of C<sup>14</sup> was determined by converting the bromobenzene to biphenyl (Ullman reaction, yield 16%) and degrading the latter compound to benzoic acid. The specific activity of biphenyl and benzoic acid indicates that the carbon-14 is at the 1 position.

(28) (a) The C<sup>14</sup> assay was obtained by measuring the activity of C<sup>14</sup>O<sub>2</sub> with a gas proportional counter: D. R. Christman and A. P. Wolf, *Anal. Chem.*, **27**, 1939 (1955). The precision of each measurement is 2%. (b) The specific activity of PPA



is exactly one-half of that of the phenyllithium, indicating that the formation of (C<sup>\*</sup>H<sub>5</sub>)<sub>6</sub>SbLi is not reversible. A recent report based on a T-labeling study contained a statement of the same conclusion: H. Daniel and J. Paetsch, *Chem. Ber.*, **101**, 1451 (1968).

Table III. Summary of Present and Related Studies

Substrate	Condition	Solvent	Biphenyl, <sup>a</sup> %	Ref
(C <sup>*</sup> <sub>6</sub> H <sub>5</sub> ) <sub>5</sub> P	100°, 20 hr	Benzene	5-6 <sup>b</sup>	
(C <sup>*</sup> <sub>6</sub> H <sub>5</sub> ) <sub>5</sub> Sb	220°, 3 hr	Benzene	0	
	<i>hν</i> (Pyrex)	Benzene	40 <sup>c</sup>	
	<i>hν</i> (2537 Å)	Benzene	30 <sup>c</sup>	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Bi	260-270°	Benzene-C <sup>14</sup>	40	12c
(C <sup>*</sup> <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub> O	80°	Benzene	41	16b

<sup>a</sup> Percentage of phenyl group originating from the solvent in the isolated biphenyl. <sup>b</sup> 1.1 mole/l. of PPP. <sup>c</sup> 0.11 mole/l. of PPA.

*Anal.* Found activity of C<sub>12</sub>H<sub>10</sub>: 1.07 nCi/mg of C, 1.08 nCi/mg of C.

Calculation of relative amount of II and V in isolated biphenyl equals

$$\frac{1.78X + (1 - X)1.78/2}{X + (1 - X)} = 1.08$$

$$100X = 21.3\% \text{ II}$$

$$100(1 - X) = 78.7\% \text{ V}$$

$X$  = fraction of II in isolated biphenyl,  $1 - X$  = fraction of V in isolated biphenyl, specific activity of PPA and II = 1.78, specific activity of V = 1.78/2, and specific activity of isolated biphenyl = 1.08.

The red oily residue from the steam distillation was extracted with ether. *p*-Quaterphenyl separated as a suspension in the ether solution and was collected by filtration. There was obtained 0.05 g of *p*-quaterphenyl. After sublimation it had mp 305-307°.

*Anal.* Calcd for C<sub>24</sub>H<sub>18</sub>: C, 94.09; H, 5.91. Found: C, 94.38; H, 5.8. Found activity: 0.90 nCi/mg of C.

The ether filtrate was evaporated and the residue was vacuum distilled (210-230° at 10 mm). Triphenylstibine (light yellow) was obtained. Crystallization from petroleum ether gave 2.2 g of colorless triphenylstibine, mp 50-52°.

*Anal.* Found activity of C<sub>18</sub>H<sub>15</sub>Sb: 1.77 nCi/mg of C.

**Oxidation of Biphenyl-1,1'-C<sup>14</sup> with Chromium Trioxide.** Biphenyl (0.85 g, 0.0055 mole, 1.08 nCi/mg of C) was dissolved in 50 ml of acetic acid and 0.5 ml of acetic anhydride with stirring. Chromium trioxide (3.43 g, 0.034 mole) was added in four portions over 30 min. The temperature was maintained at about 30-35°. After having been stirred for 4 hr at room temperature, the mixture was poured into 150 ml of water saturated with sodium chloride. This was extracted with four 60-ml portions of benzene. The benzene solution was then extracted with sodium hydroxide solution (5%) which, after acidification, was extracted with four 60-ml portions of benzene. The benzene solution was evaporated on the steam bath. The light brown residue was subjected to sublimation. The benzoic acid (mp 120-121°, 0.3 g, 50%) obtained was repeatedly crystallized from hot water and resublimed.

*Anal.* Calcd activity for C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>: 1.85 nCi/mg of C (based on all C<sup>14</sup> at the 1 position). Found: 1.80, 1.82 nCi/mg of C.

**Photolysis of PPA in Benzene-H<sup>2</sup><sub>6</sub> and Benzene-H<sup>2</sup><sub>1</sub>.** The photolysis experiments were carried out under the identical conditions as those described above. Nearly pure benzene-H<sup>2</sup><sub>6</sub> (D, 99.5%) was purchased from Merck and Co., Ltd. Benzene-H<sup>2</sup><sub>1</sub> was prepared by a modification<sup>14</sup> of a known method. The biphenyl isolated was analyzed by mass spectrometry at reduced ionizing voltage.<sup>29</sup>

**Thermolysis of PPA-1-C<sup>14</sup> in Benzene.** PPA-1-C<sup>14</sup> (4.22 g, 0.0083 mole, 1.78 nCi/mg of C) was suspended in benzene (6.13 g, 0.078 mole, thiophene free). The mixture was placed in a thick-walled glass tube which was sealed under vacuum. The ampoule was placed in an autoclave, with a small amount of water (to balance the pressure inside the ampoule) and heated for 3 hr at 220°. The

procedure for isolation of products was the same as that described for the photolysis reaction mixture. *m*-Dinitrobenzene (mp 90°), biphenyl (1.1 g, 90%), triphenylstibine (2.6 g, 89%, mp 51-52°), and benzoic acid, mp 121-122° (from oxidation of biphenyl), were obtained.

*Anal.* Found activity for C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: 0.010 nCi/mg of C. Calcd activity for C<sub>12</sub>H<sub>10</sub>: 1.78 nCi/mg of C (based on an intramolecular process). Found: 1.77 nCi/mg of C. Calcd activity for C<sub>18</sub>H<sub>15</sub>Sb: 1.78 nCi/mg of C. Found: 1.78 nCi/mg of C. Calcd activity for C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>: 3.05 nCi/mg of C. Found: 3.00 nCi/mg of C.

**Reaction of Methoxytetraphenylantimony with Phenyllithium-C<sup>14</sup>** Methoxytetraphenylantimony (3.7 g, 0.008 mole) was dissolved in ca. 200 ml of anhydrous ether. The solution was filtered under nitrogen to remove an insoluble precipitate (decomposed methoxytetraphenylantimony). Phenyllithium 18.7 ml (ca. 0.38 mole/l., specific activity 1.72 nCi/mg of C) was added rapidly with stirring. After 10 sec, a mixture of water and methanol was added. After separation of the ether layer from the aqueous layer, ether was evaporated by heating the mixture on the steam bath; the residue was repeatedly crystallized from cyclohexane and acetonitrile. There was obtained 2.0 g (50%) of PPA. It was found that the yield was independent of the temperature (-60 to 25°) at which the reactions were carried out and also independent of the reaction time, indicating that this is an extremely fast reaction.

*Anal.* Calcd activity for C<sub>36</sub>H<sub>25</sub>Sb: 0.342 nCi/mg of C. Found: 0.325 nCi/mg of C.

**Methanolysis of PPA-C<sup>14</sup>.** PPA-C<sup>14</sup> (1.5 g, 0.003 mole) was placed in a 25-ml pear-shaped flask fitted with a condenser and nitrogen inlet tube. Anhydrous methanol (3.5-4 ml) was distilled into this flask. The solution was refluxed under nitrogen for 7 hr and became a light yellow, clear solution. The flask containing the solution was then evacuated. Methanol and benzene were trapped by use of a spiral trap immersed in Dry Ice-acetone. A colorless crystalline solid remained in the flask. The methanol-benzene mixture was separated on an F and M gas chromatograph (aluminum column packed with silicone on Fluoropak 80). Benzene (retention time 16 min, flow rate 22 ml/min) was readily separated from methanol (retention time 3 min, oven temperature 65°). The benzene was collected in a trap immersed in Dry Ice-acetone solution. After a second chromatographic separation, the benzene was transferred via a vacuum line to two quartz capillaries and sealed for radioactivity assay.

*Anal.* Calcd activity for C<sub>6</sub>H<sub>6</sub>: 0.325 nCi/mg of C. Found: 0.325, 0.325 nCi/mg of C.

The colorless crystalline methoxytetraphenylantimony (1 g, 70%) was dissolved in anhydrous petroleum ether (in a nitrogen atmosphere) and filtered; pure methoxytetraphenylantimony, mp 132°, was obtained by cooling the solution.

*Anal.* Calcd activity for C<sub>25</sub>H<sub>23</sub>OSb: 0.312 nCi/mg of C. Found: 0.315 nCi/mg of C.

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(29) We want to thank Miss Parmakovich of Columbia University for obtaining the mass spectra.