Either added oleic acid or the hydroaromatic itself might function as the hydrogen acceptor. Guaiene has a particularly favorable structure for this role. It is also possible that the final aromatic compound under some conditions might be a hydrogen acceptor.

A third reaction of the selenol might consist of homolytic cleavage of the C—Se bond followed by radical disproportionation to form aromatic product:

$$2\text{VI} \longrightarrow 2\text{HSe}\cdot + \text{phenanthrene} + \text{IV}$$

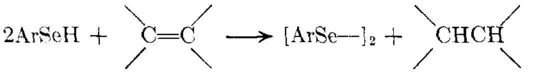
Other reaction paths that produce the hydrocarbon radical could similarly lead to disproportionations.

Aryl Diselenides.—The dehydrogenation of guaiene by β,β'-dinaphthyl diselenide at lower temperatures may proceed by dissociation of the diselenide to organoselenium radicals:

$$\text{ArSeSeAr} \overset{\Delta}{\rightleftharpoons} 2\text{ArSe}\cdot$$

The radicals in the presence of a hydrogen donor (guaiene) abstract hydrogen to give the selenol. Regeneration of the diselenide may occur by reaction of the selenol with the external double bond of guaiene and guaiazulene is finally produced by radical disproportionation:

$$\text{ArSe}\cdot + \text{guaiene} \longrightarrow \text{ArSeH} + \text{R}\cdot$$



$$2\text{ArSeH} + {>}\text{C}{=}\text{C}{<} \longrightarrow [\text{ArSe—}]_2 + {>}\text{CHCH}{<}$$

$$2\text{R}\cdot \longrightarrow \text{saturate} + \text{aromatic}$$

At higher temperatures (290°), the dehydrogenation of guaiene with the diselenide was essentially similar to that observed with elemental selenium. Presumably, the aryl diselenide decomposes to elemental selenium and monoselenide.

Thermal decomposition of diphenyl diselenide alone at the same temperature gives diphenyl monoselenide and what appears to be an impure new compound which may be a diphenyl triselenide, since it readily decomposes to elemental selenium and diphenyl diselenide:

$$\begin{tikzcd}\text{ArSeSeAr} \arrow[r, shift left, "\Delta"] & \text{ArSe}_3\text{Ar} + \text{ArSeAr} \arrow[l, shift left] \arrow[d, shift right] \\ & \text{ArSeSeAr} + \text{Se} \arrow[u, shift right]\end{tikzcd}$$

Heating stoichiometric amounts of diphenyl monoselenide and elemental selenium, as well as diphenyl diselenide and elemental selenium to 280–300° gave the same mixture believed to contain the triselenide. Diphenyl diselenide has been prepared by heating diphenyl monoselenide with selenium, and diphenyl diselenide gives diphenyl monoselenide on heating,[10] so apparently all the reactions are reversible. Since at about 290° elemental selenium, mono-, di-, and triselenide coexist, the similarity in the dehydrogenations of guaiene with elemental selenium and with the aryl diselenide is not unexpected. Although other diaryl triselenides are known,[11] diphenyl triselenide has not been prepared. Our compound, presumed to be impure diphenyl triselenide, apparently exists in two forms. The unstable form (yellow) is prepared by irradiating the stable form (red) with ultraviolet light. Although we have no basis on which to propose structures at this time, it is possible that the red and yellow forms of the triselenide represent a cyclic and open chain structure, respectively.

Acknowledgment.—The authors wish to thank the National Science Foundation for a grant (NSF-G-14459) which made this work possible.

[10] H. Bauer, *Ber.*, **46**, 92 (1913).

[11] H. Rheinboldt and E. Giesbrecht, *ibid.*, **88**, 1 (1955).

Preparation and Reactions of Some Phosphobetaines[1]

DONALD B. DENNEY AND LOIS CHRISBACHER SMITH[2]

The School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey

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Triphenylphosphine has been allowed to react with chloroacetic acid, β-chloropropionic acid, and γ-chlorobutyric acid. In each case the carboxyalkyltriphenylphosphonium salt was obtained. The salt from chloroacetic acid decarboxylated on heating or on treatment with base. The two other salts on treatment with base gave stable phosphobetaines. The chemistry of these materials is discussed. Triphenylphosphine and bromoacetic acid reacted, under several sets of conditions, to give triphenylphosphine oxide and acetyl bromide.

There have been several reports concerning the preparation of phosphobetaines, I, $n = 1$.[3] The data concerning these substances was quite sparse and there was reason for doubting the structural assignments.

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[1] A preliminary account appeared in *Chem. Ind.* (London), 290 (1961).

[2] National Science Foundation Coöperative Graduate Fellow, 1959–1960.

[3] (a) A. Michaelis and H. v Gimborn, *Ber.*, **27**, 272 (1894); (b) D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 2933 (1930); (c) A. Michaelis, *Ann.*, **293**, 288 (1896); (d) A. H. Meyer, *Ber.*, **4**, 734 (1871).

$$R_3\overset{+}{P}—(CH_2)_n—CO_2^- \quad n \geqslant 1$$
$$\text{I}$$

It was the purpose of the work now being reported to synthesize phosphobetaines where R in I is phenyl and $n = 1,2,3$.

Results

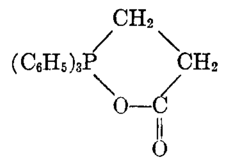
The appropriate ω-chloro acids were allowed to react with triphenylphosphine to afford the carboxyphosphonium salts, II–IV.

$$(C_6H_5)_3P + Cl—(CH_2)_n\text{-}CO_2H \longrightarrow (C_6H_5)_3\overset{+}{P}—(CH_2)_n—CO_2H + Cl^-$$
$$\text{II.}\ n = 1;\ \text{III.}\ n = 2;\ \text{IV.}\ n = 3$$

The salt, II, loses carbon dioxide at 180° to give triphenylmethylphosphonium chloride and carbon dioxide. Treatment of an ethanolic solution of II with aqueous sodium carbonate followed by isolation under mild conditions gave only triphenylmethylphosphonium chloride. Treatment of II with aqueous sodium bicarbonate followed by isolation under as mild conditions as possible gave a solid material which contained chloride ion and which effervesced on the addition of mineral acid. Pyrolysis of this solid yielded carbon dioxide, diphenylmethylphosphine oxide, and triphenylmethylphosphonium chloride.

When III was treated with a slight excess of aqueous sodium bicarbonate an 87% yield of the phosphobetaine, V, was obtained. This material was soluble in water and ethanol, did not contain chloride ion and was relatively high-melting, 169–170°. Its infrared spectrum in chloroform showed a strong absorption band at 6.3 μ which is characteristic of a carboxylate anion.[4] The phosphorus n.m.r. spectrum in methanol had a shift of −23 p.p.m. relative to 85% phosphoric acid.[5] This shift is characteristic of a triphenylalkylphosphonium salt. For example McKelvie[5] reports for triphenylmethylphosphonium iodide, −20 p.p.m. and triphenylethylphosphonium iodide, −26 p.p.m. Both spectra were obtained in methanol. On the other hand the few known compounds with pentacovalent phosphorus show positive shifts relative to 85% phosphoric acid.[6] These data are entirely consistent with V and lend no support to the possible alternative, VI.

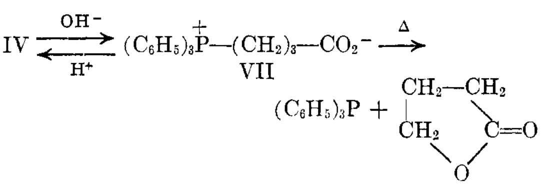
$$\text{III} \underset{H^+}{\overset{HCO_3^-}{\rightleftarrows}} \underset{\text{V}}{(C_6H_5)_3\overset{+}{P}—CH_2—CH_2—CO_2^-} \xrightarrow{\Delta} (C_6H_5)_3P + CH_2{=}CHCO_2H$$



VI

Treatment of V with hydrochloric acid reconstituted the starting material (III). Pyrolysis of V at 200° yielded triphenylphosphine and acrylic acid.

Treatment of IV with aqueous sodium hydroxide gave VII whose properties were very similar to those found for V. In accordance with these observations the zwitterionic structure is proposed. Pyrolysis of VII gave triphenylphosphine and γ-butyrolactone.



In the early phases of this investigation bromoacetic acid was allowed to react with triphenylphosphine with the object of preparing the bromo analog of II, *i.e.* IIa. Reaction in benzene or in the absence of solvent afforded triphenylphosphine oxide as the major phosphorus-containing compound. The other major product is most probably acetyl bromide. It was never isolated but its presence has been inferred by the formation of acetanilide and aniline hydrobromide. In ether at room temperature triphenylphosphine and bromoacetic acid reacted to give a mixture of triphenylphosphine oxide and what is assumed to be IIa.

Discussion

Earlier attempts to prepare phosphobetaines (I, $n = 1$) have all involved treatment of esters, VIII, with base.[3] It is quite apparent now that these conditions lead to the production of phosphoranes.[7] Careful inspection of the experimental details of the earlier attempts[3] suggests that phosphoranes were formed in these reactions.

$$\underset{\text{VIII}}{R_3\overset{+}{P}—CH_2CO_2R'} + X^- \xrightarrow{B} \underset{\text{IX}}{R_3P{=}CHCO_2R'}$$

The results obtained in this work suggest that phosphobetaines $n = 1$ are quite unstable. The results obtained on treating II with base are readily interpretable in terms of the transient formation of the phosphobetaine, X, which loses carbon dioxide rapidly to give the phosphorane, XI. Subsequent reaction yields a phosphonium salt.

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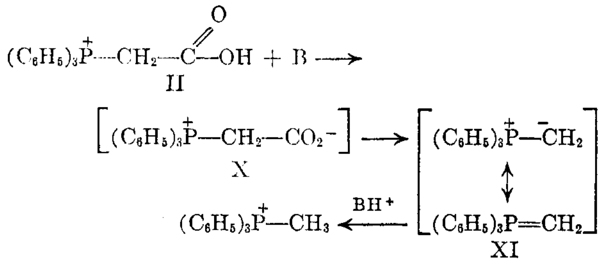
[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, New York, N. Y., 1958, p. 174.

[5] Obtained through the courtesy of Dr. Neil McKelvie, American Cyanamid Co., Stamford, Connecticut.

[6] R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, **74**, 60 (1962).

[7] O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).



Rapid decarboxylation of X is not unexpected because of the stability of XI.[8,9]

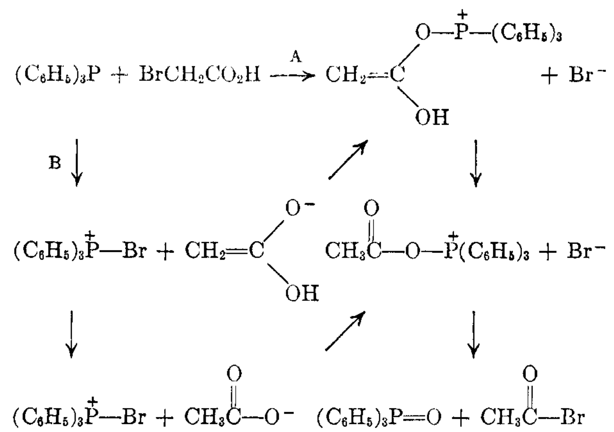
The formation of diphenylmethylphosphine oxide on pyrolysis of material obtained from II and aqueous bicarbonate can be explained by the assumption that a triphenylmethylphosphonium carbonate and/or bicarbonate was present along with triphenylmethylphosphonium chloride. Pyrolysis of basic phosphonium salts yields phosphine oxides and hydrocarbons[10]; in this case benzene would be the other product.

The assignment of the "open" structures to V and VII is of some interest because of the possibility that one or both might exist in the "closed" structure, an example being VI. Ring closure would result in a pentacovalent phosphorus, a state which is generally of higher energy than the tetracovalent state.[11] Ring formation would also result in the loss of resonance energy associated with the carboxylate anion. Apparently there are no special factors which overcome these barriers to ring formation in these particular examples.

The pyrolytic reactions of V and VII are not unusual. Decomposition of V occurs, in all probability, by a β-elimination in which a carboxylate anion may act as the base. Decomposition of VII appears to be an intramolecular S_N2 reaction with the carboxylate group performing as the nucleophile.

The reaction of triphenylphosphine with bromoacetic acid[12] is of some theoretical interest. One possible explanation for the formation of triphenylphosphine oxide and acetyl bromide involves decomposition of IIa. This route is not considered likely because IIa appeared to be stable when formed in ether and more importantly treatment of II with bromide ion did not yield triphenylphosphine oxide and acetyl bromide.

Two other alternative paths deserve consideration. They are A and B. Both involve nucleophilic displacement by triphenylphosphine on either oxygen (A) or bromine (B). Although no definite evidence can be offered to establish which one is correct, path A is favored because the first pair of ions formed should be of lower energy than those formed from path B and because of the economy of steps required to arrive at the products. Furthermore, path B requires the formation of acetate ion in the presence of bromoacetic acid. If this occurred one might expect the ultimate formation of bromoacetyl bromide as well as acetyl bromide.



Similar S_N2' displacements on oxygen by phosphorus containing nucleophiles have been observed.[13] Apparently this mode of reaction is not unusual in these systems.

Experimental[14]

Preparation of II.—A solution of 26.2 g. (0.100 mole) of triphenylphosphine and 11.3 g. (0.120 mole) of chloroacetic acid in 700 ml. of methanol was heated at 40° for 24 hr. Removal of solvent followed by extraction of the residue with ether afforded a white solid which was crystallized four times from absolute ethanol–ether to give 7.9 g. (21.8%) of white needles, m.p. 221–223°. The infrared spectrum of this material had carbonyl absorption at 5.7 μ and was otherwise commensurate with the assigned structure. The phosphorus n.m.r. spectrum in chloroform had a shift of −20 p.p.m. relative to 85% phosphoric acid.[5]

Anal. Calcd. for $C_{20}H_{18}O_2PCl$: C, 67.32; H, 5.08; Cl, 9.94. Found: C, 67.56; H, 5.37; Cl, 10.2.

Thermal Decomposition of II.—Heating of 0.20 g. (0.00056 mole) of II in a stream of nitrogen led to the formation of carbon dioxide (determined by conversion to barium carbonate) at *ca.* 120°. The temperature was gradually increased to 180° and held there for 1 hr. Crystallization of the residue from ethyl acetate–petroleum ether (b.p. 30–60°) gave 0.16 g. (91.5%) of triphenylmethylphosphonium chloride, m.p. 218–221° (lit.,[15] 212–213°). The infrared spectrum was identical to that of an authentic sample, m.p. 222–224°, prepared from triphenylphosphine and methyl chloride. In many instances, it was noted that samples of triphenylmethylphosphonium chloride partially melted at *ca.* 110°, resolidified and then melted at 222–224°. This is in accord with the observation of Michaelis and Soden[15] that the salt forms a hydrate which loses water between 100–110°.

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[8] W. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

[9] The possibility of arresting the reaction at XI was investigated in a few preliminary experiments without success. Prof. C. E. Griffin has informed us that he is investigating this further.

[10] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

[11] J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, pp. 70–76.

[12] G. Aksnes, *Acta Chem. Scand.*, **15**, 438 (1961), has also reported that triphenylphosphine and bromoacetic acid give triphenylphosphine oxide and acetyl bromide when heated at 80°.

[13] (a) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 2976 (1960); (b) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 1960), and references contained therein.

[14] Melting points are corrected. Analyses by G. Robertson, Florham Park, New Jersey, unless otherwise stated.

[15] A. Michaelis and H. V. Soden, *Ann.*, **229**, 310 (1885).

A quantitative yield of barium carbonate (0.11 g.) was also obtained.

Reaction of II with Aqueous Sodium Carbonate.—To a solution of 0.5 g. (0.00140 mole) of II in 5 ml. of 95% ethanol was added a 2% solution of aqueous sodium carbonate to a phenolphthalein end point. The solvents were removed at reduced pressure and a bath temperature of 45°. The residue was dried *in vacuo* over phosphorus pentoxide. The resulting solid was extracted with absolute ethanol, filtered from 0.1 g. of insoluble material (presumably sodium chloride), and the filtrate was evaporated *in vacuo*. The gummy residue was treated with dry acetone to give 0.23 g. (52%) of triphenylmethylphosphonium chloride, m.p. 216–220°. Further purification by crystallization from ethanol–ether and then from acetone–hexane raised the melting point to 221–222°. The infrared spectrum was identical to that of an authentic sample of triphenylmethylphosphonium chloride.

Reaction of II with Aqueous Sodium Bicarbonate.—A solution of 0.475 g. (0.00566 mole) of sodium bicarbonate in 7 ml. of water was added to 2.00 g. (0.00560 mole) of II in 15 ml. of 95% ethanol. Removal of the solvent at reduced pressure, bath temperature 40°, was followed by drying of the solid residue *in vacuo* over phosphorus pentoxide. The dried residue was extracted with absolute ethanol, filtered from 0.30 g. of solid, and the solvent was removed *in vacuo*. The yellowish, gummy residue on treatment with acetone–hexane afforded 1.50 g. of fine white crystals, m.p. *ca.* 110–170° with effervescence *ca.* 110–120°. The infrared spectrum was very similar to that of triphenylmethylphosphonium chloride.

A portion of the solid, 0.5 g., was heated in a nitrogen stream at 90° for 1 hr. The effluent gas stream was passed through barium hydroxide solution. Barium carbonate, 0.15 g. (0.00076 mole), was formed. The residue from the pyrolysis was extracted with ether. The insoluble material was crystallized from ethanol–ether to give 0.19 g. (33%) of triphenylmethylphosphonium chloride, m.p. 222–223.5°. The infrared spectrum was identical to that of an authentic sample.

Concentration of the ether extract gave 0.10 g. (25%) of material, m.p. 113–115°. This material had an infrared spectrum identical to that of an authentic sample of diphenylmethylphosphine oxide, m.p. 112.5–114.5°.

Anal. Calcd. for $C_{13}H_{13}OP$: C, 72.20; H, 6.06. Found: C, 71.51; H, 6.02.

Preparation of III.—A mixture of 13.1 g. (0.050 mole) of triphenylphosphine and 5.4 g. (0.0500 mole) of 3-chloropropionic acid was heated at 145–150° for 2 hr. The resulting crystalline mass was dissolved in absolute ethanol, dry ether was added, and the solution was cooled. White granular crystals, 12.5 g. (67%) of III, m.p. 196–198.5°, were obtained. The infrared spectrum had carbonyl absorption at 5.75 μ. The n.m.r. spectrum in methanol had a shift of −24 p.p.m. relative to 85% phosphoric acid.[5]

Anal. Calcd. for $C_{21}H_{20}O_2PCl$: C, 68.02; H, 5.44. Found: C, 68.08; H, 5.53.

Reaction of III with Aqueous Sodium Bicarbonate.—A solution of 3.52 g. (0.042 mole) of sodium bicarbonate in 25 ml. of water was added with stirring to 14.8 g. (0.040 mole) of III in 95% ethanol. After removal of the solvents at reduced pressure, the white solid residue was dried and extracted with absolute ethanol. The resulting solution was filtered and diluted with dry ether. White crystals, 11.6 g. (87%), m.p. 169–170° (lit.,[12] 186°), were obtained. The material had carbonyl absorption at 6.3 μ. The n.m.r. spectrum in methanol had a shift of −23 p.p.m. relative to 85% phosphoric acid. The material was soluble in ethanol and water.

Anal.[16] Calcd. for $C_{21}H_{19}O_2P \cdot H_2O$: C, 71.57; H, 6.01; P, 8.79. Found: C, 71.39; H, 5.98; P, 8.92.

Anal.[16] Calcd. for $C_{21}H_{19}O_2P$: C, 75.44; H, 5.73; P, 9.26. Found: C, 75.43; H, 5.40; P, 9.16.

Pyrolysis of V.—The hydrate of V, 4.00 g. (0.0114 mole), was heated in a stream of nitrogen for 2.5 hr. at 200°. The residue was crystallized from 95% ethanol to give 2.40 g. (80%) of triphenylphosphine, m.p. 80–82°. A mixed melting point determination with an authentic sample showed no depression. The infrared spectrum was identical to that of a known sample.

During the pyrolysis 1.00 g. of liquid was collected. The infrared spectrum was very similar to that of acrylic acid. Titration of the liquid indicated it contained 63% acrylic acid. The aqueous solution from the titration was evaporated to dryness. The residue was dissolved in 8 ml. of 1:1 ethanol–water and treated with 0.20 g. of *p*-nitrobenzyl bromide. The mixture was heated under reflux for 1 hr. cooled and filtered. The resulting solid was crystallized from ethanol–water to give 0.1 g. of *p*-nitrobenzyl acrylate, m.p. 52–53°. A mixed melting point determination with an authentic sample, m.p. 52–54°, showed no depression. Their respective infrared spectra were identical.

Treatment of V with Aqueous Hydrochloric Acid.—V, 0.25 g., was dissolved in 10 ml. of dilute hydrochloric acid. The solution was evaporated to dryness and the residue was dried *in vacuo* over phosphorus pentoxide. The dried material was crystallized from absolute ethanol–ether to give 0.1 g. of III, m.p. 195–198°. The infrared spectrum was identical to that of an authentic sample.

Preparation of IV.—A mixture of 26.2 g. (0.100 mole) of triphenyl phosphine and 12.2 g. (0.100 mole) of γ-chlorobutyric acid was heated at 140° for *ca.* 20 hr. The cooled solid was washed with dry ether and crystallized four times from ethanol–ether to give 16.2 g. (42%) of needles, m.p. 234–237°. The infrared spectrum had carbonyl absorption at 5.7 μ. The n.m.r. spectrum in chloroform–methanol was shifted −23 p.p.m. relative to 85% phosphoric acid.

Anal. Calcd. for $C_{22}H_{22}O_2PCl$: C, 68.66; H, 5.76; Cl, 9.21. Found: C, 68.04; H, 6.06; Cl, 9.00.

Reaction of IV with Aqueous Sodium Hydroxide.—A 5% aqueous solution of sodium hydroxide was added in small portions to 11.5 g. (0.030 mole) of IV in 35 ml. of 95% ethanol to a phenolphthalein end point. The solvents were removed at 45° (bath) *in vacuo*. The residue was washed twice with dry benzene and dried *in vacuo*. The residue was taken up in absolute ethanol, filtered to remove insolubles, and concentrated. Addition of ether and chilling caused an oil to form. Considerable difficulty was encountered in crystallizing this material. Finally the solvents were removed and the residue was taken up in acetone followed by the addition of dry hexane. In this manner 4.6 g. of material, m.p. 134–137°, was obtained. This material was crystallized from absolute ethanol–ether to give 4.00 g. (38%) of VII. The melting point behavior of this material indicated that it probably was a hydrate. It melted at 227–230° only if the temperature was increased slowly from room temperature to the melting point. If the sample was introduced at *ca.* 150°, it melted completely resolidified and melted again at *ca.* 210°. The analytical sample was dried at room temperature and 0.05 mm. for 24 hr. It melted at 227°.

Anal.[16] Calcd. for $C_{22}H_{21}O_2P \cdot H_2O$: C, 72.11, H, 6.33. Found: C, 72.45; H, 6.94.

The product was soluble in water and ethanol and did not contain chloride ion. The infrared spectrum had an absorption band at 6.3 μ.

Treatment of VII with Hydrochloric Acid.—To 10 ml. of dilute hydrochloric acid was added 0.25 g. of VII. The solution was evaporated to dryness and dried *in vacuo* over phosphorus pentoxide. The residue was crystallized from absolute ethanol–ether to give 0.1 g. of IV, m.p. 235–238°. The infrared spectrum was identical to that of IV prepared from triphenylphosphine and γ-chlorobutyric acid.

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(16) Analyses were carried out at the microanalytical laboratories of Hoffman-LaRoche, Inc., Nutley, New Jersey. The first sample was dried at room temperature and 0.04 mm. for 6 hr. The second sample was dried at 110° and 0.05 mm. for 18 hr.

Pyrolysis of VII.—A. 2.70-g. sample (0.00775 mole) of V, previously dried at 110° and 0.1 mm. for 5 hr. over phosphorus pentoxide, was heated at *ca.* 225° and 14 mm. for 1.5 hr. The temperature was then reduced to *ca.* 200° and continued for 3 hr. The pyrolysis residue was cooled and crystallized from absolute ethanol to afford 1.20 g. (69%) of triphenylphosphine, m.p. 80–81°. This material had an infrared spectrum identical to that of an authentic sample of triphenylphosphine and the mixed melting point was not depressed.

The distillate from the pyrolysis, 0.41 g. (62%), had an infrared spectrum identical to that of γ-butyrolactone. It was further characterized by heating with 0.60 g. of phenylhydrazine on a steam bath for 1.5 hr. After cooling and washing with 10 ml. of dry ether, the resulting solid was crystallized from chloroform to give 0.43 g. (46%) of γ-hydroxybutyric acid phenylhydrazide, m.p. 93–95°. The infrared spectrum was identical to a known sample and there was no depression on mixed melting point determination.

Reaction of Triphenylphosphine with Bromoacetic Acid in Benzene.—A slow stream of nitrogen was passed through a refluxing mixture of 5.24 g. (0.020 mole) of triphenylphosphine and 2.78 g. (0.020 mole) of bromoacetic acid in 80 ml. of dry benzene. The effluent gas stream was passed through two traps each containing 4.6 g. (0.050 mole) of aniline and then through 50 ml. of saturated barium hydroxide solution. The reaction mixture was heated for 48 hr. It contained a small amount of tan solid which was not characterized.

The barium hydroxide solution was filtered and the barium carbonate was weighed, 0.15 g. (3.5%).

The xylene–aniline mixtures were filtered to yield 1.00 g. (29%) of solid, m.p. 284–286°. The infrared spectrum was identical to that of an authentic sample of aniline hydrobromide. No depression of melting point with an authentic sample was observed.

The benzene was distilled from the reaction mixture. The benzene distillate was added to the xylene–aniline filtrate. There was formed 0.45 g. (12%) of aniline hydrobromide, m.p. 285°. The total yield of aniline hydrobromide was 42%.

Distillation of the benzene–xylene–aniline solution yielded a brown, liquid residue which was dissolved in 3 *N* hydrochloric acid. The acidic solution was extracted with ether. The ether extract was stirred with anhydrous potassium carbonate, filtered, and distilled. A tan, solid residue, 0.50 g. (18%), m.p. 106–111°, was obtained. Crystallization of this material from water yielded 0.35 g. (13%) of acetanilide, m.p. 114–116°. This material had an infrared spectrum identical to that of an authentic sample, and the mixed melting point was not depressed.

The residue from the benzene solution was dissolved in 70 ml. of dry benzene and filtered to remove 0.40 g. of insoluble material. Distillation of the benzene afforded 5.6 g. of residue, m.p. 144–152°, which was crystallized from acetone–hexane to give 4.3 g. (77%) of triphenylphosphine oxide, m.p. 155–157°. The infrared spectrum was identical to that of a known sample, and the mixed melting point was not depressed.

Reaction of Triphenylphosphine with Bromoacetic Acid.—A mixture of 1.31 g. (0.0050 mole) of triphenylphosphine and 0.69 g. (0.0050 mole), of bromoacetic acid were heated on a steam bath in a slow stream of nitrogen for 16 hr. The sweep gas was passed through 25 ml. of water. After 16 hr. titration of the solution with standard sodium hydroxide showed the presence of 0.00879 mole of acid. The neutralized solution was evaporated and the residue was dried, 0.57 g. Halide determination by the Mohr method indicated 42% bromide ion. Treatment of 0.20 g. of the residue with 0.20 g. of *p*-nitrobenzyl bromide in refluxing aqueous ethanol gave *p*-nitrobenzyl acetate, 0.5 g., which was crystallized from 95% ethanol, m.p. 76–77°. The infrared spectrum was identical to that of an authentic sample and the mixed melting point was not depressed.

The residue in the reaction flask was treated with dry acetone and filtered. The acetone was removed and the residue was extracted with boiling hexane. Cooling of the hexane extracts afforded 0.77 g. (55%) of triphenylphosphine oxide, m.p. 156–158°. The material gave no melting point depression with an authentic sample.

Reaction of Triphenylphosphine with Bromoacetic Acid in a Sealed Tube.—A mixture of 2.62 g. (0.010 mole) of triphenylphosphine and 1.39 g. (0.010 mole) of bromoacetic acid were heated in a sealed tube at 90° for 18.5 hr. The resulting brown, semisolid product was treated with a solution of 2.8 g. (0.03 mole) of aniline in 45 ml. of dry benzene. The reaction mixture was filtered to give 1.60 g. of material m.p. 270–280°. This material was crystallized from absolute ethanol and sublimed at 145° (20 mm.) to give 1.05 g. (60%) of aniline hydrobromide, m.p. 285–288°. The infrared spectrum was identical to that of an authentic sample of aniline hydrobromide.

The benzene was evaporated to give a gummy oil which was extracted with ether. The ether extract was washed with dilute hydrochloric acid, dried over potassium carbonate, and distilled. The residue was washed with hexane yielding 2.68 g. of material, m.p. 99–108°. Sublimation at 135° (25 mm.) gave 0.8 g. of sublimate, m.p. 110–114°, which was resublimed to give 0.66 g. (48%) of acetanilide, m.p. 112–114°. The infrared spectrum was identical to that of an authentic sample of acetanilide.

The residue from the sublimation weighed 1.73 g. (62%), m.p. 155–157°. Its infrared spectrum was identical to that of an authentic sample of triphenylphosphine oxide.

Reaction of Triphenylphosphine with Bromoacetic Acid in Ether.—A solution of 2.78 g. (0.020 mole) of bromoacetic acid and 5.24 g. (0.020 mole) of triphenylphosphine in 40 ml. of ether was stirred at room temperature for 19 hr. The resulting suspension was chilled and filtered to give 4.5 g. of product. This material melted from 123–147° with slow effervescence which became vigorous at *ca.* 144°. It was partially soluble in water and readily soluble in ethanol and chloroform. An aqueous ethanolic solution was acidic. The infrared spectrum had carbonyl absorption at 5.7 μ and was generally similar but not identical to that of II.

Thermal decomposition of 0.5 g. at 160° in a stream of nitrogen gave carbon dioxide. Crystallization of the pyrolysis residue from ethanol–ether afforded 0.1 g. of material, m.p. 228–232°. A mixed melting point determination with an authentic sample of triphenylmethylphosphonium bromide, m.p. 229–231°, was not depressed.

Reaction of II with Sodium Bromide in Water.—A solution of 0.10 g. (0.0028 mole) of II and 0.50 g. (0.0049 mole) of sodium bromide in 5 ml. of water was heated at 75–80° for 18 hr. Removal of the water afforded 0.60 g. of ether–insoluble residue whose infrared spectrum was identical to that of triphenylmethylphosphonium chloride.

Reaction of II with Tetrabutylphosphonium Bromide in Bromoacetic Acid.—A solution of 0.059 g. of II and 0.30 g. of tetrabutylphosphonium bromide in 1.0 g. of bromoacetic acid was heated for 22 hr. on a steam bath. The reaction mixture was completely soluble in 7 ml. of water.