and 17–21, 52.9 mg (17.8%) of a mixture of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one and a trace of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one. The *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one from fractions 7–11 was crystallized from hexane–methylene chloride to give 41.5 mg (13.9%), mp 157.5–159°. The recovered starting material from fractions 13–16 was crystallized from hexane–methylene chloride to give 123 mg (41.3%), mp 157–158.5°.

Another photolysis, starting with 223 mg of *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, for 8.75 hr gave 27 mg (12.1%) of *cis,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 158–160°, and 135 mg (60.6%) of recovered starting material, mp 157–159°.

**Photolysis of *trans,trans*-4,5,6-Triphenylbicyclo[3.1.0]hexan-2-one.** Using the standard procedure, 786 mg (2.43 mmol) of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one was photolyzed in 110 ml of 3:1 *t*-butyl alcohol–benzene for 13.25 hr with a Pyrex filter. The solvent was removed *in vacuo* giving 853 mg of a glassy solid that was chromatographed on a 3.5 × 95 cm column, slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 5% ether–hexane. The column was eluted with 12 l. of 8% ether–hexane and 1.5 l. of 15% ether–hexane and 500-ml fractions were collected: fractions 1–3, 10 mg of aliphatic solvent residues; 4–13, nil; 14–22, 559 mg (71.1%) of starting material, *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one; 23, 19 mg of overlap; 24–31, 192 mg (24.4%) of a mixture of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and a new photoketone.

The *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one from fractions 14–22 was recrystallized from hexane–methylene chloride to give 496 mg (63.1%), mp 138–139°, and a nmr spectrum of the material remaining in the mother liquors showed no other compound. The material from fractions 24–31 was crystallized from ether to give 90 mg (11.5%) of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one, mp 188–191°. Nmr and infrared spectra of the material remaining in the mother liquors (102 mg) showed it to consist of *ca.* 30% *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and *ca.* 70% of a new photoketone (not *cis,trans*-, *trans,trans*-, or *cis,cis*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one) having a 5.81-$\mu$ carbonyl band in the infrared. Attempts to isolate the new photoketone by fractional crystallization and liquid–liquid partition chromatography were unsuccessful.

In another run, the irradiation of 105 mg of *trans,trans*-4,5,6-triphenylbicyclo[3.1.0]hexan-2-one for 2.5 hr gave 64.1 mg (61.0%) of starting material, mp 138.5–140.5°, and 16.4 mg (15.6%) of a mixture of *cis*-3,4,5-triphenyl-2-cyclohexen-1-one and the new photoketone.

**Acknowledgment.** Support of this research by the National Science Foundation, National Institutes of Health Grant GM-07487, and the Wisconsin Alumni Research Foundation is gratefully acknowledged.

---

# Studies in Mass Spectrometry. XXIV.[1] A Study of the Reactions Induced in Triphenylphosphine, Triphenylphosphine Oxide, and Related Substances upon Electron Impact

**Dudley H. Williams, Robert S. Ward, and R. Graham Cooks**

*Contribution from the University Chemical Laboratory, Cambridge, United Kingdom.*
*Received September 5, 1967*

**Abstract:** Some reactions induced by electron impact in triphenylphosphine, triphenylphosphine oxide, methylenetriphenylphosphorane, and triphenylphosphine sulfide have been studied by means of deuterium labeling. Evidence is presented to support the view that the main decomposition pathways occur with the formation of bridged phosphafluorenyl ions (containing trivalent or pentacovalent phosphorus). Some reactions proceed with hydrogen–deuterium scrambling within labeled phenyl rings, while others proceed without randomization.

As part of a program[2,3] to evaluate deuterium–hydrogen scrambling in deuterium-labeled phenyl rings, the reactions induced by electron impact on triphenylphosphine (**1a**), triphenylphosphine oxide (**2a**), methylenetriphenylphosphorane (**3a**, generated within the ion source by pyrolysis of methyltriphenylphosphonium bromide), and triphenylphosphine sulfide (**4a**) have been studied.

| $(C_6H_5)_3P$ | $(C_6H_5)_3P{=}O$ | $(C_6H_5)_3P{=}CH_2$ | $(C_6H_5)_3P{=}S$ |
|---|---|---|---|
| **1a** | **2a** | **3a** | **4a** |

To permit detailed and secure analysis of the mass spectra, a number of deuterated analogs of **1a–4a** have been synthesized. Bromination of benzene-$d_6$ gave bromobenzene-$d_5$ which was converted to the Grignard reagent and treated with phosphorus trichloride[4] to furnish triphenylphosphine-$d_{15}$ (**1d**). This material upon oxidation gave triphenylphosphine-$d_{15}$ oxide (**2d**), or upon quaternization with methyl bromide followed by pyrolysis within the source at $10^{-6}$ mm gave methylenetriphenylphosphorane-$d_{15}$ (**3b**). Analogous sequences starting from bromobenzene-2,4,6-$d_3$[5] afforded the triphenylphosphine-$d_9$ **1b**, the triphenylphosphine-$d_9$ oxide **2b**, and the methylenetriphenylphosphorane-$d_9$ **3c**. Alternatively, treatment of **1b** with sulfur in benzene[6] at room temperature furnished the triphenylphosphine-$d_9$ sulfide **4b**. Reaction of dichlorophenylphosphine with the Grignard reagent derived from bromobenzene-$d_5$ gave the triphenylphosphine-$d_{10}$ **1c** which on oxidation led to the triphenylphosphine-$d_{10}$ oxide **2c**.

The mass spectra of the unlabeled compounds and those of the deuterated derivatives are summarized in Figures 1a–d, 2a–d, 3a and b, and 4. The isotopic purities of the labeled triphenylphosphines **1b**, **1c**, and **1d** are summarized in Table I; these have been

---

[1] Part XXIII: I. Howe and D. H. Williams, *J. Chem. Soc.*, in press.

[2] R. G. Cooks, R. S. Ward, and D. H. Williams, *Chem. Commun.*, 850 (1967).

[3] D. H. Williams, S. W. Tam, and R. G. Cooks, *J. Amer. Chem. Soc.*, in press.

[4] J. Dodonov and H. Medoks, *Chem. Ber.*, **61**, 907 (1928).

[5] R. G. Cooks, R. S. Ward, D. H. Williams, M. A. Shaw, and J. C. Tebby, *Tetrahedron*, in press.

[6] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, **78**, 3179 (1956).

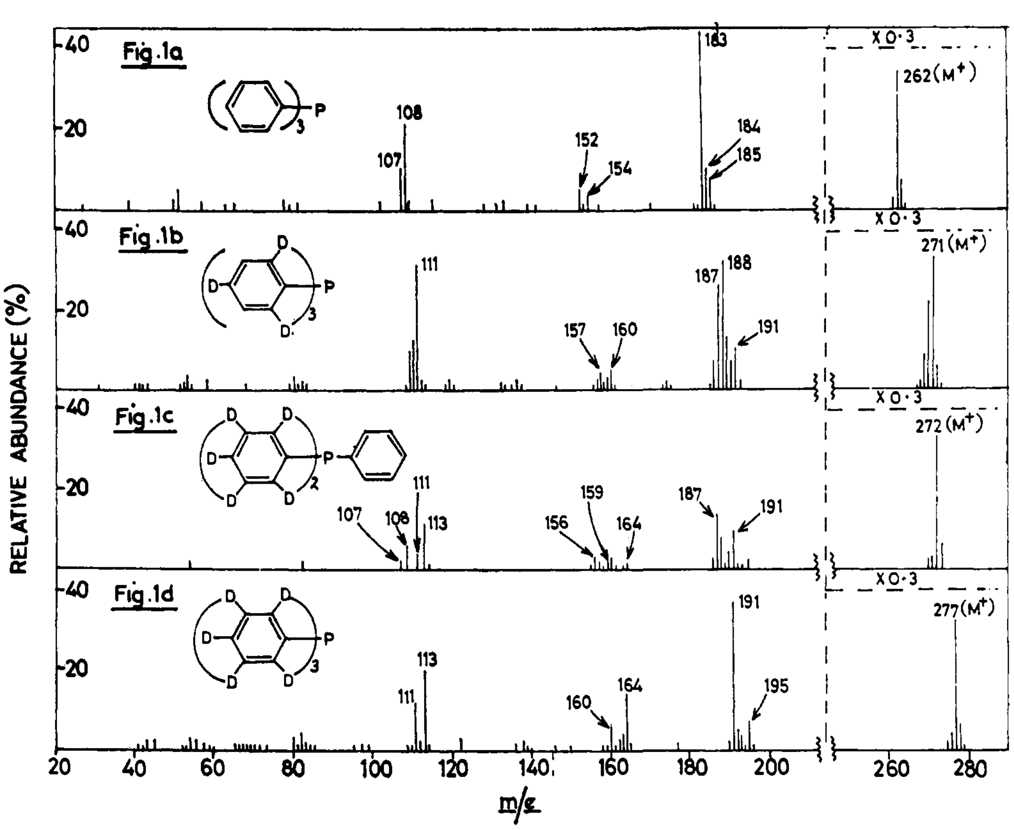
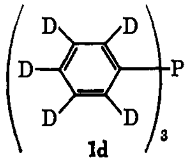
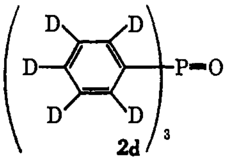
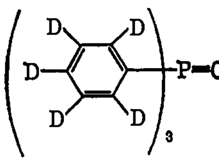
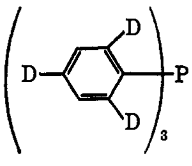


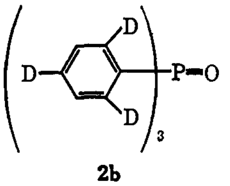
Figure 1. Mass spectra of triphenylphosphine and deuterated analogs.

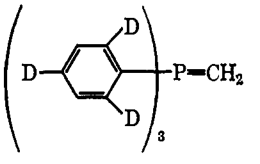

**1d**

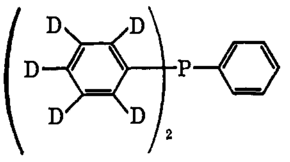

**2d**

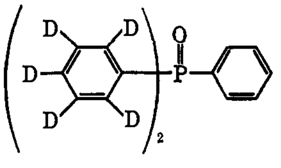

**3b**

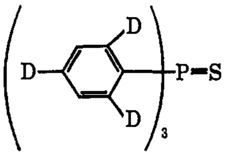

**1b**


**2b**


**3c**


**1c**


**2c**


**4b**

calculated from low-voltage spectra in which triphenylphosphine itself shows no M − 1 peak.[7] Since the labeled derivatives which contain phosphorus in the higher oxidation state give spectra in which the appearance potential of the M − 1 peak is very close to the ionization potential of the molecule, independent calculations of the isotopic purities of these materials are not possible. These substances are therefore assumed to have the same isotopic purities as the precursor triphenylphosphines (Table I).

Table I. Isotopic Purities (%) of Triphenylphosphine-$d_9$ (**1b**), Triphenylphosphine-$d_{10}$ (**1c**), and Triphenylphosphine-$d_{15}$ (**1d**)

| Compd | $d_6$ | $d_7$ | $d_8$ | $d_9$ |
|---|---|---|---|---|
| **1b** | 2.0 | 11.5 | 36.5 | 50.5 |
| | $d_7$ | $d_8$ | $d_9$ | $d_{10}$ |
| **1c** | 0 | 0 | 4.0 | 96.0 |
| | $d_{12}$ | $d_{13}$ | $d_{14}$ | $d_{15}$ |
| **1d** | 0 | 1.0 | 13.0 | 86.0 |

Four decomposition reactions of triphenylphosphine which are induced by electron impact have been reported by Miller.[8] Decomposition pathways which account for all the abundant ions and metastable ions in the spectra are summarized in Scheme I. Evidence supporting the assigned structures will be presented in conjunction with the discussion of the spectra of the labeled analogs. The assignments of the metastable peaks to the transitions indicated by asterisks are con-

---

[7] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 213.

[8] J. M. Miller, *J. Chem. Soc., Sect. A*, 828 (1967).

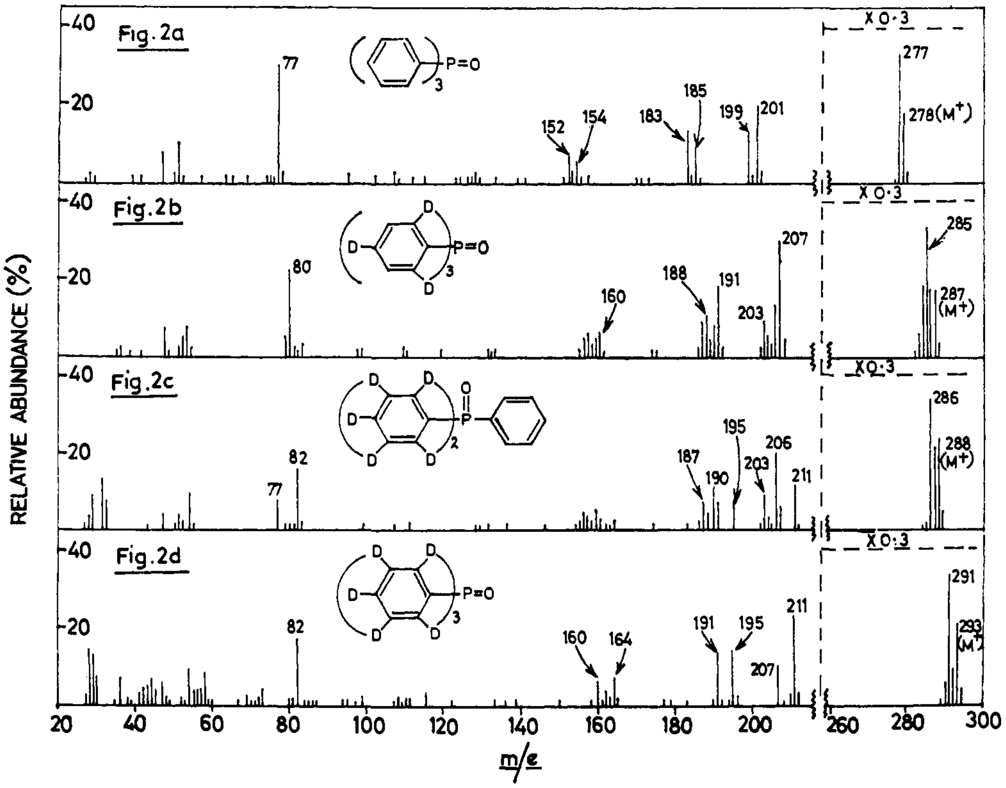
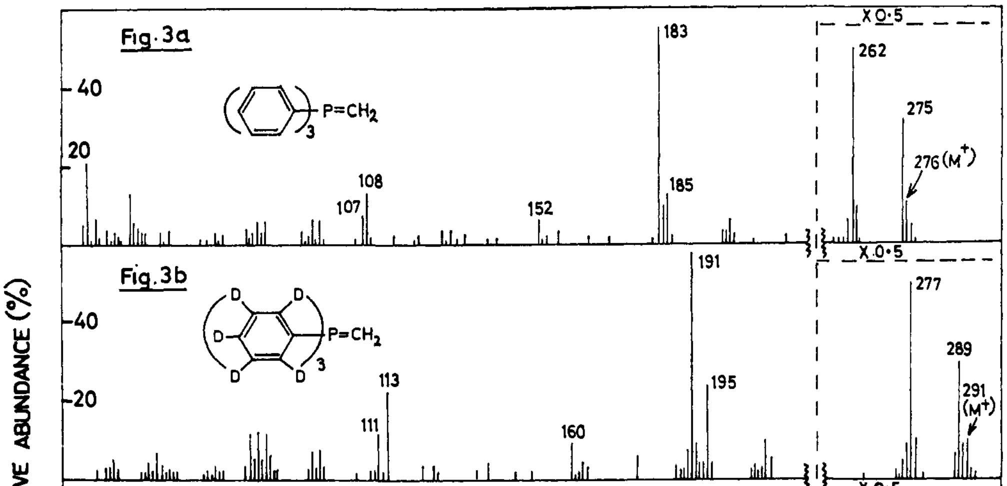


Figure 2. Mass spectra of triphenylphosphine oxide and labeled analogs.



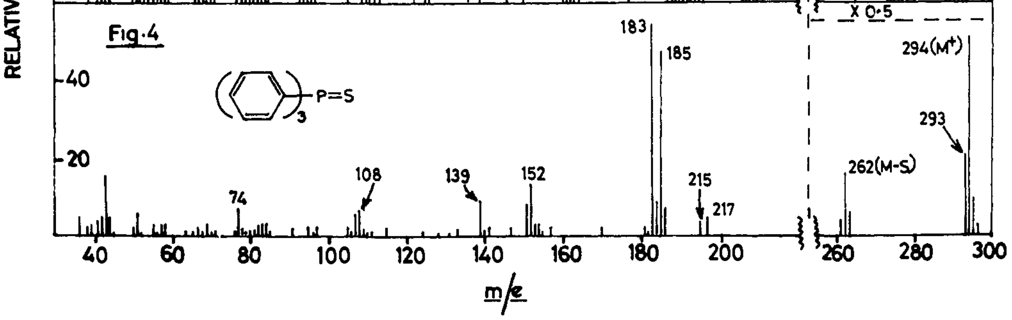
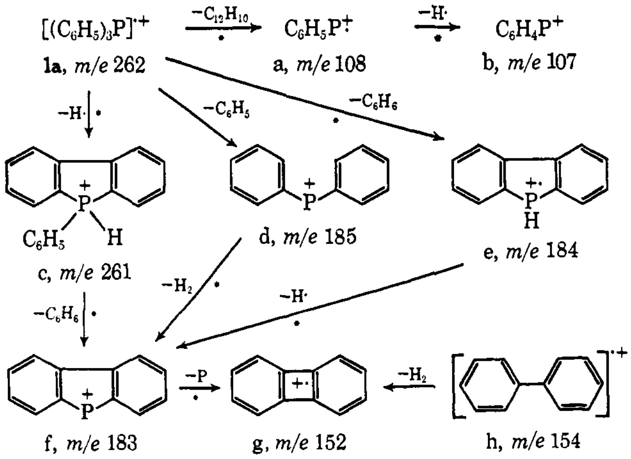


Figure 3. Mass spectra obtained by pyrolysis of methyltriphenylphosphonium bromide and its $d_9$ analog within the ion source.
Figure 4. Mass spectrum of triphenylphosphine sulfide.

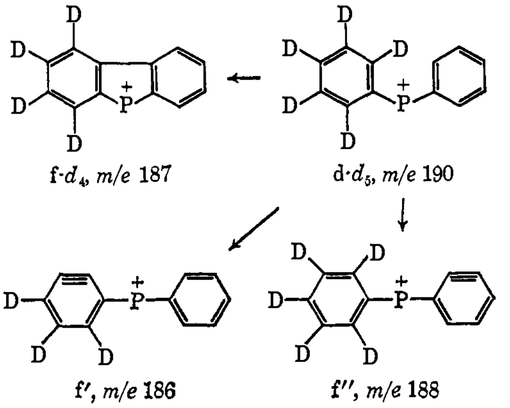
firmed by appropriate shifts in the spectra of the deuterated derivatives **1b–d**.

The spectrum (Figure 1c) of **1c**, which is completely deuterated in two of the three phenyl rings, establishes that randomization of hydrogen and deuterium atoms between the phenyl rings does not occur. For example, *m/e* 113 (a-$d_5$) and *m/e* 108 (a) are formed from **1c** in the ratio of approximately 2:1 and decompose

Scheme I



specifically by loss of a deuterium atom and a hydrogen atom, respectively (Figure 1c). The *m/e* 180–200 region of Figure 1c is of considerable interest and therefore is expanded in Figure 5. Fragmentation of **1c** by loss of a phenyl radical gives d-$d_{10}$ (*m/e* 195) which loses a deuterium molecule (or two deuterium atoms) to give *m/e* 191 (f-$d_8$). Loss of benzene-$d_1$ from the molecular ion of **1c** gives e-$d_9$ (*m/e* 193). This analysis accounts for all the peaks in the *m/e* 191–196 region, those at *m/e* 192 and 196 being merely $^{13}C$ isotope peaks from the ions occurring at *m/e* values one unit lower. As expected, *m/e* 190 (d-$d_5$) is formed with approximately twice the abundance of *m/e* 195. Since there is no evidence for deuterium–hydrogen scrambling between rings, a bridging reaction will be characterized by the formation of f-$d_4$ (*m/e* 187—see d-$d_5$ → f-$d_4$), while reaction without bridging will be characterized by the formation of $d_3$ (*m/e* 186) and $d_5$ (*m/e* 188) species (see, for example, f′ and f′′ which are illustrative structures only).



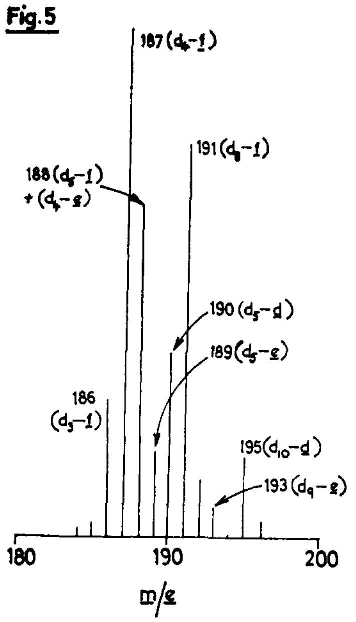


Figure 5. The *m/e* 180–200 region of the mass spectrum of the triphenylphosphine-$d_{10}$ **1c**.

If the *m/e* 188 peak is "corrected" for the $^{13}C$ contribution from *m/e* 187 and the contribution from e-$d_4$ (which should be the same abundance as the e-$d_5$ species), the ratio of the *m/e* 186, 187, 188 peaks is 1.0:3.8:1.6, *i.e.*, the reactions leading to formation of *m/e* 183 in the mass spectrum of triphenylphosphine predominantly ((3.8/6.4) × $10^2 \simeq 60\%$) involve loss of a phenyl group and one hydrogen atom from *each* of the other rings. The *m/e* 183 ion therefore most probably corresponds to the bridged 9-phosphafluorenyl ion f, in accord with a recent speculation.[9] However, the loss of a phenyl group and two hydrogens from one of the remaining rings occurs to a minor extent (~40%) as a competing process. The greater abundance of *m/e* 188 relative to *m/e* 186 is in accord with a smaller activation energy to break two C–H bonds relative to two C–D bonds.

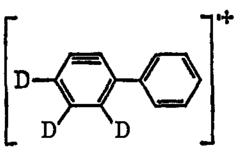
Support for the formulation of 60% of *m/e* 183 as the 9-phosphafluorenyl ion f is found in the further decomposition of *m/e* 183 by loss of a phosphorus atom to $C_{12}H_8{}^{\cdot+}$ (possibly ionized *o*-biphenylene g). Therefore bond formation between the rings must have occurred in *m/e* 183 or during the transition *m/e* 183 → 152. A second route to *m/e* 152, namely $C_{12}H_{10}{}^{\cdot+} \rightarrow C_{12}H_8{}^{\cdot+}$ *via* loss of $H_2$, is established by an appropriate metastable peak. The $C_{12}H_{10}{}^{\cdot+}$ ion probably corresponds to ionized biphenyl (h, *m/e* 154, Scheme I); analogous ions occur in Figure 1c at *m/e* 164 (h-$d_{10}$) and *m/e* 159 (h-$d_5$). If f is very largely the precursor of g, then the intensity distribution in Figure 1c among *m/e* 155, 156, 157, should be the same as that among *m/e* 186, 187, 188, as indeed it is. If on the other hand the pathway h → g is of similar importance to f → g, or even dominant, the observed peak distribution of *m/e* 155, 156, 157 in Figure 1c would follow only if (i) loss on $H_2$ from *one* phenyl ring competed with the bridging reaction h → g to give structures such as i, g-$d_4$, and i′ in the same (or similar) ratio as f′, f-$d_4$, f′′, or (ii) randomization of hydrogen and deuterium occurs *between* phenyl rings in h-$d_5$ (*m/e* 159) so that even a specific bridging reaction to an ionized *o*-biphenylene would result in a (statistical) loss of $H_2$, HD, and $D_2$ to give *m/e* 155, 156, 157 in the ratio 1:2.5:1 (in the absence of an isotope effect, and with a slight preference for loss of hydrogen over deuterium in the presence of an isotope effect).

Although the mass spectra of a large number of deuterated biphenyls have been analyzed[10] with the

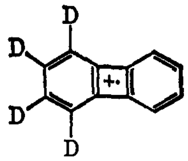
---

(9) A. N. Hughes and M. Woods, *Tetrahedron*, **23**, 2937 (1967).

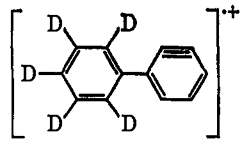
(10) J. G. Burr, J. M. Scarborough, and R. H. Shudde, *J. Phys. Chem.* **64**, 1359 (1960); see also S. Facchetti, *Chim. Ind.* (Milan), **47**, 966 (1965).



i, $m/e$ 155



g-$d_4$, $m/e$ 156



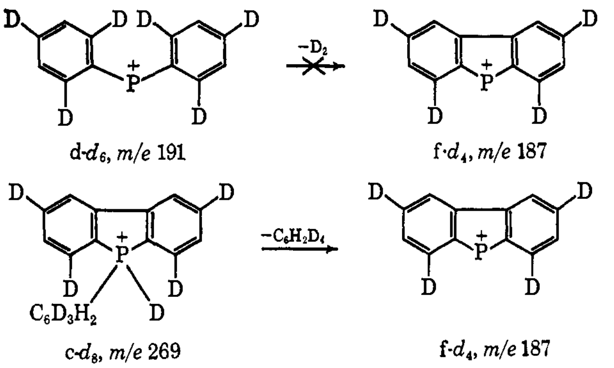
i′, $m/e$ 157

conclusion that "prior to separation of the carbon-containing fragments from the several molecular ions, the C–H and C–D bonds have all become structurally equivalent," all the deuterated biphenyls were symmetrical about the central C–C bond and it is not possible to securely deduce whether randomization occurs within one phenyl ring or over both rings.

With the analysis based on complete labeling with deuterium of two out of three phenyl rings a background, it is instructive to consider the spectrum (Figure 1b) of the symmetrically labeled triphenylphosphine-$d_9$ (**1b**). After subtracting out isotopic impurities in the $M^+$ region of Figure 1b it is apparent that the M − 1 ion of triphenylphosphine is replaced in the spectrum of the triphenylphosphine-$d_9$ **1c** almost completely (90%) by an M − 2 ion. Thus in that form of the molecular ion of **1c** undergoing this reaction (i) there is no randomization of hydrogen and deuteriums in the phenyl rings and (ii) the reaction involves loss of an *o*- or *p*-deuterium atom. Clearly the former possibility is more plausible, and presumably the M − 1 ion from triphenylphosphine is formed with loss of an *o*-hydrogen atom and rearrangement of a second *o*-hydrogen to phosphorus with associated bridging (**1a** → c, Scheme I). The further decomposition of the M − 1 ion by loss of benzene (Scheme I) is in reasonable accord with the structure c. The peak distribution in the $m/e$ 187–191 region of the spectrum of the triphenylphosphine-$d_9$ **1c** after correction for isotopic contaminants and removal of the $^{13}C$ contributions is given as follows (($m/e$) relative abundance (in arbitrary units)): (187) 26, (188) 56, (189) 25, (190) 3, (191) 20. To correct for isotopic contaminants, the percentage of deuterium incorporation in each phenyl ring had to be calculated ($d_1$, 1%; $d_2$, 18%; $d_3$, 81%) and hence the isotopic distribution corresponding to two phenyl rings calculated ($d_4$, 4%; $d_5$, 30%; $d_6$, 66%).

From the peak distribution data given above, it is apparent that the $m/e$ 183 ion of Figure 1a is shifted very largely to $m/e$ 188. This means that the major portion of the bridged ion f of Scheme I is not formed by over-all loss of ($C_6D_3H_2$ + $D_2$) from **1c** to give f-$d_4$, but rather by over-all loss of ($C_6D_3H_2$ + HD). The observation is compatible with hydrogen scrambling within the phenyl rings of that form of the labeled triphenylphosphine molecular ion which is the predominant precursor of $m/e$ 183 (f, Scheme I). For example, in a bridging reaction d-$d_6$ ($m/e$ 191, Scheme II) would be anticipated to lose exclusively deuterium to give f-$d_4$ ($m/e$ 187, Scheme II); however, deuterium-hydrogen scrambling in d-$d_6$ prior to bridging would result in the loss of $H_2$:HD:$D_2$ in the ratio 4:12:9.

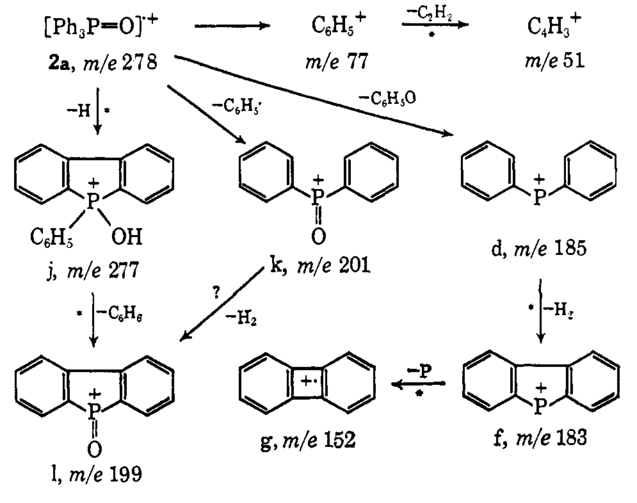
Scheme II



The relative abundances of $m/e$ 187, 188, and 189 shown above are sufficiently close to those corresponding to deuterium–hydrogen scrambling within phenyl rings prior to the formation of these ions[11] that it is reasonable to enquire whether all pathways leading to the phosphafluorenyl ion f ($m/e$ 183, Scheme I) are preceded by scrambling. To this question, it can only be replied that it seems likely that the M − 1 ion (c-$d_8$, Scheme II) from **1c** (which is formed *without* hydrogen–deuterium scrambling) will specifically lose benzene-$d_4$ to give $m/e$ 187 (f-$d_4$, Scheme II). If this is true (and strong supporting evidence is given subsequently from the analogous case of triphenylphosphine oxide), then it must be concluded that c → f (Scheme I) is not a major pathway to $m/e$ 183.

An interpretation of the spectrum (Figure 2a) of triphenylphosphine oxide (**2a**) is summarized in Scheme III. Although it is possible that k ($m/e$ 201) may lose hydrogen to give l ($m/e$ 199), there is no metastable peak to support this transition. In addition, the formation of d ($m/e$ 185) may not occur *via* a one-step process.

Scheme III

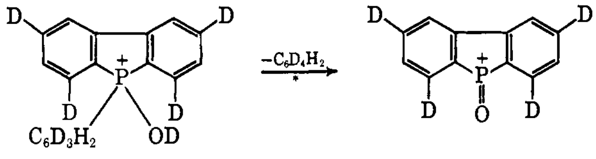


The evidence that the base peak M − 1 ion corresponds to the bridged ion j (Scheme III) is very strong. First, there must obviously be an energetically favorable structure for the M − 1 species since it accounts for no less than 34% of the total ion current ($\Sigma_{30}$) at 70 eV,

---

[11] There is the additional complication of loss of 2 H from *one* phenyl ring as a minor process (~40%, *vide supra*), which after scrambling in the labeled compound would lead to contributing $m/e$ 187, 188, and 189 ions in the ratio 3:6:1.

even though its genesis requires breaking an aromatic C–H bond with loss of a hydrogen radical. Second, the formation of this ion proceeds with almost complete specificity (~93%) by loss of a deuterium atom from $Ph_3PO$-$d_9$ (**2b**) (Figure 6 summarizes relevant regions of the spectrum of **2b** after correction for isotopic contaminants and $^{13}C$ isotope contributions). The M − D ion is therefore formulated as j-$d_8$ (*m/e* 285) and a strong metastable peak at *m/e* 144.7 establishes the decomposition of this intermediate by loss of benzene-$d_4$ to l-$d_4$ (*m/e* 203).



j-$d_8$, *m/e* 285 l-$d_4$, *m/e* 203

The small peaks at *m/e* 204 and 205 in Figure 6 suggest a minor contribution of the reaction k (*m/e* 201) → l (*m/e* 199) (Scheme III), preceded by hydrogen scrambling. In contrast, *m/e* 183 in Figure 2a is from metastable peak evidence formed exclusively from *m/e* 185 and since d-$d_6$ (*m/e* 191, Figure 6) randomly loses $H_2$, HD, and $D_2$ (to *m/e* 187, 188, and 189), hydrogen scrambling precedes the formation of *m/e* 183 from triphenylphosphine oxide.

The arguments for formulating *m/e* 185 → 183 (Figure 2a) as a bridging reaction will not be outlined at length here, since they are analogous to those already discussed for triphenylphosphine. However, it can briefly be stated that d-$d_5$ (*m/e* 190) predominantly loses HD (*i.e.*, hydrogen from one ring and deuterium from the other) to give f-$d_4$ (*m/e* 187) in the spectrum (Figure 2c) of triphenylphosphine-$d_{10}$ oxide (**2c**). The small satellite peaks (*m/e* 202 and 204) at either side of *m/e* 203 (l-$d_4$, Scheme III) in Figure 2c suggest a minor loss of $H_2$ from within one phenyl ring of k (*m/e* 201, Scheme III).

It is also noteworthy that the hydrogens of $C_6H_5^+$ (*m/e* 77) from triphenylphosphine oxide (**2a**) are randomized prior to the further decomposition of $C_6H_5^+$ to $C_4H_3^+$ (*m/e* 51) by loss of acetylene. This follows since the *m/e* 80 ion ($C_6D_3H_2^+$) from the triphenylphosphine-$d_9$ oxide **2b** (see Figure 2b) decomposes by statistical loss of $C_2H_2$, $C_2HD$, and $C_2D_2$ as evidenced by metastable peaks for these processes at *m/e* 36.4, 35.1, and 33.8 (in the intensity ratios of 1:6:3). The relative intensities of *m/e* 77:51:33.8 (the last value corresponding to the metastable peak for the transition 77 → 51) are recorded in Table II, as are also the corresponding intensities observed in the spectrum of diphenyl ether (both spectra recorded at 70 eV); the recorded values represent the average of five determinations in each case. The ratios are sufficiently similar to warrant the conclusion that common $C_6H_5^+$ species are generated from the two substances.[12]

**Table II.** Relative Abundances of *m/e* 77, 51, and 33.8 in the Mass Spectra of Triphenylphosphine Oxide and Diphenyl Ether

| Compd | [*m/e* 77] × $10^{-2}$ | [*m/e* 51] × $10^{-2}$ | [*m/e* 33.8] |
|---|---|---|---|
| $(C_6H_5)_3P{=}O$ | 5.80 ± 0.90 | 3.53 ± 0.40 | 1.00 |
| $(C_6H_5)_2O$ | 5.62 ± 0.40 | 3.90 ± 0.40 | 1.00 |

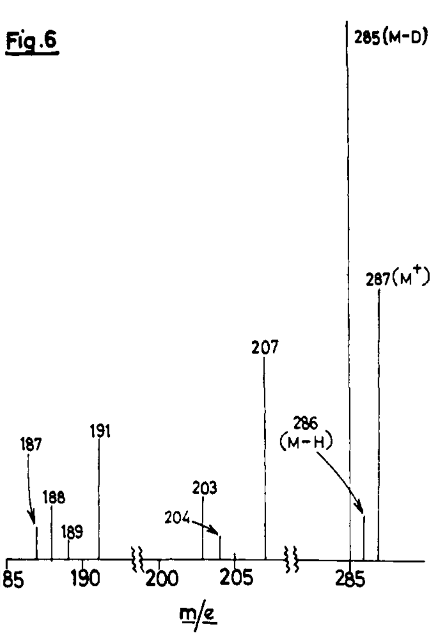
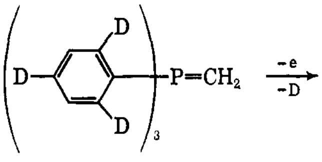


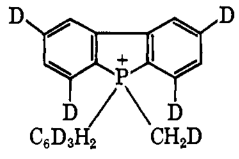
Figure 6. The *m/e* 185–193, 200–208, and 283–288 regions of the mass spectrum of the triphenylphosphine-$d_9$ oxide **2b** after correction for isotopic impurities and $^{13}C$ contributions.

Since the $C_6H_5^+$ ion generated from diphenyl ether at its appearance potential is not the phenyl ion,[13] it may be concluded that $C_6H_5^+$ from triphenylphosphine oxide is also not the phenyl ion and is probably linear.

The behavior of methylenetriphenylphosphorane (**3a**) upon electron impact is so similar as not to warrant a detailed description. Particularly noteworthy is the pronounced loss of a hydrogen atom from *m/e* 276 to give *m/e* 275 (Figure 3a, metastable peak at *m/e* 274.0).[14] The *m/e* 275 peak is shifted to *m/e* 289 in Figure 3b and therefore the loss of a hydrogen atom has been replaced by loss of a deuterium atom. A methylenetriphenylphosphorane-$d_9$ (**3c**) has also been prepared; its spectrum (not reported in detail) establishes ionized **3c** to decompose specifically (~94%) by loss of a deuterium atom and the product is formulated as m (*m/e* 283).



**3c**



m, *m/e* 283

$(C_6H_5)_3P{=}C{=}C{=}O$

**6**

Similarly, the spectrum (Figure 4a) of triphenylsulfide (**4a**) contains an abundant M − 1 peak, but

---

(12) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, 88, 5021 (1966).

(13) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 69, 2943 (1965).

(14) The spectrum reproduced in Figure 3a probably contains peaks due to triphenylphosphine (*m/e* 262) and its associated fragments which arise due to thermal (rather than electron impact) production of triphenylphosphine.

this is replaced by an M − 2 peak in the spectrum (not reproduced) of tri(phenyl-2,4,6-$d_3$)phosphine sulfide (**4b**). This type of behavior seems so general in adducts of triphenylphosphine containing pentacovalent phosphorus that it was possible to predict that the novel phosphorane **6**, recently synthesized,[15] would yield an abundant M − 1 ion; in fact the base peak in the spectrum of **6** is due to the M − 1 ion.

In summary, the evidence for the formation of bridged ions in the spectra of the compounds studied lies in (i) the formation of very abundant M − 1 ions from those compounds containing pentacovalent phosphorus, (ii) the specific loss of an *o*- or *p*-hydrogen atom (assumed to be in fact an *o*-hydrogen atom) in the formation of the M − 1 ions, (iii) the predominant loss of one hydrogen from each ring in the genesis of the *m/e* 183 ion, and (iv) the further loss of a phosphorus atom from *m/e* 183 to give $C_{12}H_{10}\cdot^+$. One of the most interesting facts uncovered in the study is that the M − 1 ions are formed without hydrogen scrambling in the phenyl rings, and that the further loss of benzene from the M − 1 ion of triphenylphosphine oxide proceeds completely (or largely) without hydrogen scrambling. In contrast, the major pathways to *m/e* 183 in the spectra are preceded by hydrogen scrambling. One possible explanation for these observations is that those forms of the molecular ions from which, for example, d (*m/e* 185) is generated have been excited to electronic states which simulate the reactions of benzene rings which have been photochemically excited. Photochemically excited benzene rings are thought to be in reversible equilibrium with isomeric structures as prismanes and benzvalenes;[16] these reversible reactions result in 1,2 and 1,3 shifts in the benzene rings. Analogous intermediates in excited states produced by electron impact[17] would result in hydrogen–deuterium randomization in labeled phenyl rings, as observed for some reactions in the present study. In the same way, common intermediates could be generated from *ortho*-, *meta*-, and *para*-disubstituted benzenes, as has indeed been observed for some electron impact induced reactions.[18] In contrast, the forms of the molecular ions which furnish the M − 1 ions may not be in, or have passed through, the excited states which result in hydrogen scrambling within a given phenyl ring. As might be expected, the species corresponding to different excited states of the molecular ions can undergo different reactions. An alternative explanation is that the reactions occurring with and without scrambling take place from a common molecular ion, but that the formation of the M − 1 ion occurs more rapidly than a reversible, randomizing isomerization reaction in the common molecular ion.

These observations may be compared with the report that the isomeric *m*- and *p*-methoxyphenetoles eliminate ethylene at the same rate[18] (presumably *via* a common intermediate) but these substances eliminate ethyl radicals at different rates. The intervention of prismanes or benzvalenes prior only to the ethylene elimination could account for these observations.

## Experimental Section

Mass spectra were determined on an AE1 MS9 double-focussing mass spectrometer by the direct inlet procedure at 70 eV. The experimental procedures used to synthesize triphenylphosphine-$d_9$ **1b** and triphenylphosphine-$d_{15}$ **1d** have been described previously.[5] The triphenylphosphine-$d_{10}$ **1c** was synthesized by reaction of phenyldichlorophosphine with 2 mol of phenylmagnesium-$d_5$ bromide.[4] The conversion of the labeled triphenylphosphines **1b**, **1c**, **1d** to the corresponding labeled triphenylphosphine oxides, triphenylphosphonium bromides, and triphenylphosphine sulfides were achieved as follows.

**Deuterium-Labeled Triphenylphosphine Oxides.** The labeled triphenylphosphine (25 mg) was dissolved in ethanol (1 ml) and 30% (100 vol) hydrogen peroxide (3 ml) added, followed by the addition of 10% aqueous sodium hydroxide solution (0.1 ml). The mixture was heated on a water bath (~70°) for 2 hr. After cooling the solution, the crystalline phosphine oxides were isolated by filtration, dried, and recrystallized from ethyl acetate–petroleum ether (bp 30–60°). Product identity and purity was established by thin layer chromatography and melting point.

**Deuterium-Labeled Methyltriphenylphosphonium Bromides.** The labeled triphenylphosphines were quaternized with methyl bromide.[19]

**Triphenylphosphine-$d_9$ sulfide** was prepared by treating the labeled triphenylphosphine-$d_9$ **2b** with sulfur in benzene at room temperature.[6]

---

[15] C. N. Matthews and G. H. Birum, *Tetrahedron Letters*, 5707 (1966); the authors wish to thank Drs. Matthews and Birum for a sample of **6**.

[16] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

[17] K. R. Jennings, *Z. Naturforsch.*, **22a**, 454 (1967).

[18] See, for example, F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *J. Amer. Chem. Soc.*, **88**, 5022 (1966).

[19] N. A. Milas and C. P. Priesing, *ibid.*, **79**, 6295 (1957).