STUDIES IN MASS SPECTROSCOPY—XXII¹

THE DECOMPOSITION OF SOME STABLE ALKYLIDENETRIPHENYLPHOSPHORANES UPON ELECTRON IMPACT. REACTIONS OCCURRING WITH AND WITHOUT DEUTERIUM/HYDROGEN SCRAMBLING IN LABELLED PHENYL RINGS

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Abstract—Interesting features of the mass spectra of some stable alkylidenetriphenylphosphoranes (where the stabilizing groups are CN, COOR, COR) are presented. Deuterium labelling in representative cases establishes that the abundant M-1 ions are formed by loss of an aromatic hydrogen (almost certainly from the *ortho* position) to give a species represented as a bridged phosphonium ion (k). This reaction occurs without randomization of the hydrogens in the phenyl rings. In contrast, analogous bridging in (e) to give (d) seems to be preceded, or accompanied by randomisation of the hydrogens in the phenyl rings.



As PART of a programme of structure elucidation of some stable phosphoranes of unusual structure,² it was desirable to use mass spectrometry as an analytical method. A study of the mass spectra of a series of stable Wittig reagents (1-11) was therefore undertaken with a view to reaching some generalizations about their behaviour upon electron impact. The study has uncovered some interesting bond-forming reactions and these, and other notable features of the spectra, are summarized in this paper.

The relative abundances of some common ions in the spectra are indicated in Table 1. The compositions of these ions have been established by high resolution measurements in a number of the compounds and plausible structures (a-i) can therefore be assigned to them.

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Compound	108	152	165	183	185	201	262	277	278	303	1-M	×
1. Ph ₃ P=C< ^{CN}	15	12	æ	100	37		e.	I		I	13	47
2. Ph ₃ P=C <h COMe</h 	÷	٢	13	24	ŝ	s	1	ę	7	100	14	15
3. Ph ₃ P=C< ^H COPh	S	ę	12	28	80	10	٢	22	s	83	26	100
4. Ph ₃ P=C <h< td=""><td>10</td><td>28</td><td>¥</td><td>73</td><td>19</td><td>16</td><td>6</td><td>84</td><td>19</td><td>31</td><td>22</td><td>10</td></h<>	10	28	¥	73	19	16	6	8 4	19	31	22	10
5. Ph ₃ P=C< ^{CN} COOMe	80	ŝ	٢	47	53	6	6	-	l	7	43	100
6. Ph ₃ P=C <cn< td=""><td>4</td><td>4</td><td>4</td><td>23</td><td>20</td><td>10</td><td>17</td><td>27</td><td>12</td><td>ł</td><td>30</td><td>100</td></cn<>	4	4	4	23	20	10	17	27	12	ł	30	100
7. Ph ₃ P=C< ^{Me} COOEt	30	10	4	11	35	25	001	99	30	1	19	16
8. Ph ₃ P=C <c0<sub>2Et</c0<sub>	10	13	8	56	6	30	7	٢	Π	86	15	37
9. Ph ₃ P=C <coome< td=""><td>4</td><td>ŝ</td><td>90</td><td>28</td><td>19</td><td>13</td><td>11</td><td>Ŷ</td><td>1</td><td>S</td><td>80</td><td>100</td></coome<>	4	ŝ	90	28	19	13	11	Ŷ	1	S	80	100
10. Ph ₃ P=C <cooet< td=""><td>19</td><td>13</td><td>18</td><td>56</td><td>31</td><td>24</td><td>31</td><td>14</td><td>7</td><td>64</td><td>25</td><td>30</td></cooet<>	19	13	18	56	31	24	31	14	7	64	25	30
11. Ph ₃ P=C< ^{Ph} COOMe	14	9	18	48	=	œ	43	S	7	-	4	100
• The Table records the ab	undances (of ions rel	ative to t	he base p	cak arbitr	arily take	n as 100	.0				

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Abundant M-1 ions are a common feature of the spectra (see Table 1 and Figs 1-4). This observation, in conjunction with the fact that even dicyanomethylenetriphenylphosphorane 1 (which contains only phenyl hydrogens) gives a prominent M-1



FIG. 1.









peak, implicates the loss of an aromatic hydrogen in this process. To examine this possibility specifically deuterated derivatives of 4 and 10 have been synthesized as follows. Reaction of the Grignard reagent (12), derived from $2,4,6-[^{2}H]_{3}$ -bromobenzene, with phosphorus trichloride gave tri $(2,4,6-[^{2}H]_{3}$ -phenyl)phosphine (13), which on reaction with the appropriate esters gave the labelled phosphoranes (4a and 10a). Tri([²H]₃-phenyl)phosphine (14), similarly derived from [²H]₅-bromobenzene, afforded the labelled phosphorane (4b).



In the spectra of **4a**, **4b** and **10a** the prominent M-1 ions of the unlabelled compounds are completely replaced by M-2 ions, thus establishing not only the elimination of an aromatic hydrogen atom in the spectra of **4** and **10**, but also specific loss from the *ortho* or *para* position. Two bond-forming reactions may be considered for this process. The first involves loss of an *ortho* hydrogen atom with C—O bond formation to give **j**. A related process, but with the P atom replaced by a CH group, is supported by labelling of the aromatic ring in compounds of the general formula PhCH—CHCOR.³ The second involves bridging between two Ph groups with loss of one *ortho* hydrogen and rearrangement of another to give **k**. The latter process must be preferred since (a) the reaction occurs without randomization of the hydrogens in the aromatic ring, while the analogue of **j** derived by loss of a hydrogen atom from PhCH—CHCOR compounds is formed with randomization of aromatic hydrogen,³ and (b) prominent M-1 peaks are generated even in the absence of a CO group [e.g. (1), triphenylphosphine oxide,⁴ and triphenylphosphine sulphide⁵].



The formulation k is also supported by the further decomposition of the M-1 ions from 5 and 9 by loss of methanol in a one step process (Fig. 3). This observation suggests that in forming the M-1 ions, an aromatic hydrogen atom has been transferred to a more labile environment. Additional support is provided by the spectrum of dicarbomethoxymethylene-tri(2,4,6-[²H]₃-phenyl)phosphorane (the d₉-derivative of 9), in which the sequence $M^+ \rightarrow M - D \rightarrow M - D - MeOD$ is observed. A 1,2-elimination of methanol in the mass spectra of esters, analogous to that postulated here, has been established by deuterum labelling.⁶



Identification of a stable phosphorane of the type under consideration is not only facilitated by the presence of an abundant molecular ion, but also by the presence of prominent peaks due to the loss of alkoxyl or carboalkoxyl groups from ester functions, or of alkyl (aryl) radicals from alkyl (aryl) keto groups. In this respect, the M—OMe (m/e 361) and M—COOMe (m/e 333) ions from dicarbomethoxymethylenetriphenylphosphorane (9, Fig. 3), or the M—Ph (m/e 303) ion from benzoylmethylenetriphenylphosphorane (3, Fig. 1) are typical. It is of interest that the M—MeOH ion (m/e 302) from carbomethoxymethylenetriphenylphosphorane (4, Fig. 2) is of approximately equal abundance to the M—MeO ion (m/e 303). The m/e 301 and m/e 302 ions apparently arise because of the presence of only one carbomethoxyl group attached to the sp²-hybridized C atom; a 1,2-elimination permits the initial loss of methanol (4 \rightarrow 1) and the resulting ion (m/e 302) can then lose a hydrogen atom in a bridging reaction (1 \rightarrow m) to give m/e 301.



There is much evidence to support the sequence $4 \rightarrow 1 \rightarrow m$. First, the transition $m/e \ 302 \rightarrow 301$ is established by the presence of an appropriate metastable peak. Second, the $[^{2}H]_{15}$ -derivative 4b specifically fragments to give peaks at $m/e \ 318$, 317 and 315, which correspond to M—MeO, M—MeOH, and M—MeOH—D fragments (i.e. the methanol elimination is a 1,2-process, followed by loss of an aromatic hydrogen in the case of 4). Third, 4a loses only a deuterium atom in the reaction corresponding to $1 \rightarrow m$, establishing that the aromatic hydrogens are not randomized in the sequence leading to $m/e \ 301$ from 4. Finally, the sequence demands that the base peak in the spectrum of 1, if available, would be an M-1 peak. In fact, since these postulates were formulated, 1 has been synthesized.⁷ The mass spectrum of 1, obtained on a sample kindly donated by the authors,⁷ contains M-1 ($m/e \ 301$) as the base peak. The metastable peak for the transition $m/e \ 302 \rightarrow 301$ has the same shape and abundance (relative to $m/e \ 301$) in the spectra of both 4 and 1; this indicates that the same reaction is involved in both cases.⁸

In the compounds studied, the presence of an abundant ion (>10%) at m/e 303 (n) is observed only when the structural units 15 or 16 (in the unionized form) are present in the phosphorane (Table 1). In the presence of the structural unit 15, n is generated by simple cleavage, while associated loss of the carboethoxyl group with hydrogen rearrangement is necessary for its genesis from 16. The spectra emphasize that whereas loss of a carboethoxyl group with hydrogen rearrangement is a facile process, this is not true for the loss of a carbomethoxyl group with hydrogen rearrangement (note the absence of an abundant ion of mass 303 in Fig. 3). Hence rearrangement of the β -hydrogen of the Et group is most reasonably implicated in this process ($16 \rightarrow 15$). When a Me group replaces the olefinic hydrogen of 15, the characteristic ion is shifted to m/e 317, while replacement of the olefinic hydrogen by a cyano group (see 5 and 6) causes a shift to m/e 328.



alkoxyl

If in the loss of an ethyl ester group with hydrogen rearrangement, the hydrogen migrates as depicted in $16 \rightarrow 15$, then the occurrence of such a process twice in the spectrum (Fig. 4) of dicarboethoxylmethylenetriphenylphosphorane (10) should give rise to ionized methylenetriphenylphosphorane (17). A metastable peak establishes that the M-COOC₂H₄ ion (*m*/*e* 348) from 10 does undergo further loss of COOC₂H₄ to *m*/*e* 276 in a one step process (Fig. 4). In analogy to previously cited cases, the only facile decomposition mode of 17 should be *via* loss of a hydrogen atom to give o (*m*/*e* 275). In fact *m*/*e* 275 is the base peak in Fig. 4. In the spectrum of the [²H]₉-derivative (10a) the M-2COOC₂H₄ species (*m*/*e* 285) specifically loses a deuterium atom to give *m*/*e* 283. Once more a bridging reaction (17 \rightarrow 0) is implicated. For additional supporting evidence, methylenetriphenylphosphorane (17) has been generated within the ion source at approximately 10⁻⁶ mm Hg pressure by pyrolysis of triphenylmethylphosphonium bromide on the direct insertion probe at 260°; a metastable peak establishes the decomposition of *m*/*e* 276 (17, 20% of base peak abundance).



In the spectrum of the $[{}^{2}H]_{9}$ -derivative (10a), the m/e 348 ion (M-COOC₂H₄) of Fig. 4 is, as expected, shifted to m/e 357 but the m/e 347 ion (M-COOEt) of Fig. 4 is predominantly (~80%) shifted to m/e 355, i.e. the latter is formed by overall loss of an ester group (with hydrogen rearrangement) and a deuterium atom. Hence the m/e 347 ion of Fig. 4 must be represented predominantly (~4 parts) as p; the remainder (~1 part) is shifted to m/e 356 in the spectrum of 10a and is therefore represented as q. The latter formulation is also consistent with the partial origin of m/e 347 by loss of carbon monoxide from the M-OEt ion (as established by an appropriate metastable peak—Fig. 4).



With the exception of that of dicyanomethylenetriphenylphosphorane (1), all the spectra contain medium or low abundance ions at m/e 201, 277 and 278. Exact mass measurements on these ions establish compositions which are consistent with the structural representations **f**, **h** and **i**, respectively. Such species can arise in three ways: (i) by electron-impact induced skeletal rearrangement of the phosphoranes (ii) by thermal rearrangement of the phosphoranes prior to electron bombardment and

(iii) by ionization of trace impurities of triphenylphosphine oxide. The mass spectrometer is a very sensitive detector of traces of triphenylphosphine oxide and the peak intensities recorded for m/e 201, 277 and 278 were reduced to the values given in Table 1 only after repeated recrystallizations of a number of the samples. Although no metastable peaks can be discerned corresponding to the formation of ionized triphenylphosphine oxide from species of greater mass to charge ratio, some electronimpact induced skeletal rearrangement in the phosphoranes cannot be rigidly excluded. In addition, it is known that stable alkylidene phosphoranes, in which the stabilizing groups contain carbonyl functions, can be decomposed thermally (e.g. $280^{\circ}/10 \text{ mm}$) to triphenylphosphine oxide and acetylenes.⁹ The minimum source temperature at which many of the spectra could be obtained, by the direct inlet procedure, was $200-280^{\circ}$.

The ions m/e 185 and m/e 183 which are common in the spectra (Table 1 and Figs 1-4) can also be related via a bridging reaction $(e \rightarrow d)$. However, here an interesting contrast is found with the bridging reactions hitherto described, namely that in the spectra of the $[{}^{2}H]_{9}$ -derivatives (4a and 10a), the process analogous to $e \rightarrow d$ occurs predominantly by loss of ${}^{1}H^{2}H$. This observation can be interpreted in terms of formation of a benzyne species (e.g. r), but there is no obvious driving force for such a reaction to occur to the large extent observed. Alternatively, if the hydrogen and deuterium atoms within a given phenyl ring of e' are randomized, then the calculated ratios of loss of ${}^{1}H_{2}$, ${}^{1}H^{2}H$ and ${}^{2}H_{2}$ are 6:24:15. The observed ratios of appropriate peaks (after correcting for natural ${}^{13}C$ abundance) and metastable peaks correspond closely to the ratios calculated for randomization of hydrogen and deuterium atoms prior to a bridging reaction, but quantitative arguments are complicated by additional small peaks in the region under consideration. A bridging reaction without hydrogen randomization is definitely excluded.



If m/e 152 is formulated as ionized o-biphenylene (b), its genesis requires skeletal rearrangement and bridging. If no randomization of hydrogen and deuterium atoms occurs, then the analogous ion from the $[^{2}H]_{9}$ -derivatives (4a and 10a) would correspond to b' (m/e 156). In fact, the peak is predominantly shifted to m/e 157 with smaller satellites at m/e 156 and m/e 158. Again it is suggested that the hydrogens of the phenyl rings are randomized in the formation of b, but quantitative arguments are reserved for a detailed study of this reaction in simpler analogues. However, it is noteworthy that the hydrogens of biphenyl are randomized prior to fragmentation¹⁰ and ionized biphenyl (m/e 154) is in fact a precursor of m/e 152 in the present instance (as evidenced by appropriate metastable peaks).



EXPERIMENTAL

Mass spectra were recorded on an AEI MS 9 double focusing instrument, employing an ionizing energy of 70 eV. Samples were introduced into the source by the direct inlet procedure. Spectra were obtained at a source pressure of approximately 5×10^{-7} mm Hg and a source temp of 200–280°.

Preparation of stable phosphoranes

Acetylmethylenetriphenylphosphorane (2) and benzoylmethylenetriphenylphosphorane (3) were prepared by the method of Ramirez and Dershowitz.¹¹ Phosphoranes containing two conjugated stabilizing groups (1, 5, 6, 8, 9, 10) were prepared by the procedure of Horner and Oedinger,¹² but using Br_2 in place of Cl_2 (except for 8 and 10). The following modifications, and details of new compounds, are noteworthy.

Carbomethoxycyanomethylenetriphenylphosphorane (5). The residue from the reaction was crystallized from EtOH. The solid which separated was a high mol wt product, formally derived from reaction of two molecules of methyl cyanoacetate with one of triphenyldibromophosphorane. This material (12% yield) was obtained as colourless plates, m.p. 215–216°, mol wt (mass spec.) 458; its structure has not been investigated further. The mother liquors were evaporated down to a smaller bulk when carbomethoxy-cyanomethylenetriphenylphosphorane crystallized from soln (60% yield), m.p. 211–212° (lit.¹² m.p. 212–213°).

Carboethoxycyanomethylenetriphenylphosphorane (6). Buff coloured needles, m.p. 208–210°. (Found: C, 74.5; H, 5.2; N, 3.7. $C_{23}H_{20}NO_2P$ requires: C, 74.0; H, 5.36; N, 3.76%).

Dicarbomethoxymethylenetriphenylphosphorane (9). The residue from the reaction, after evaporation of solvent was heated under reflux with cyclohexane. The insoluble residue was separated and crystallized from EtOH (after treatment with charcoal) to give 9 as cream coloured prisms, m.p. 180–182°. (Found: C, 69.9; H, 5.2·C₂₃H₂₁O₄P requires: C, 70.4; H, 5.35 %).

The remaining phosphoranes were prepared by literature methods without significant modifications: $4,^{13},^{13}$ and 11 from methyl bromophenylacetate.

 $[^{2}H]_{9}$ -Triphenylphosphine (13). Prepared by the method of Dodonov and Medoks¹⁴ from 2,4,6- $[^{2}H]_{3}$ bromobenzene, which in turn was available from 2,4,6- $[^{2}H]_{3}$ -aniline¹⁵ via a Sandmeyer reaction.¹⁶

 $[^{2}H]_{15}$ -Triphenylphosphine (14). $[^{2}H]_{6}$ -Benzene was brominated¹⁷ and the derived $[^{2}H]_{5}$ -bromobenzene converted to $[^{2}H]_{15}$ -triphenylphosphine by the method of Dodonov and Medoks.¹⁴

The usual reactions leading to the phosphoranes 4 and 10 furnished 4a, 4b and 10a when carried out with the deuterated phosphoranes 13 and 14. The isotopic purities of the $[^{2}H]_{9}$ -derivatives 4a and 10a were d_{6} , 2%; d_{7} , 10%; d_{8} , 35%; d_{9} , 53%, as calculated from the spectrum of the precursor $[^{2}H]_{9}$ -triphenylphosphorane (13) obtained at a nominal 9 eV (at which voltage triphenylphosphine itself shows no M-1 peak).¹⁸ The isotopic purity of 4b, similarly calculated, was d_{13} , 1%; d_{14} , 13%; d_{15} , 86%. Isotopic impurities were subtracted from the spectra in the usual way.

REFERENCES

- ¹ Part XXI, R. G. Cooks, J. Ronayne and D. H. Williams, J. Chem. Soc. C, in press.
- ² See, for example, M. A. Shaw, J. C. Tebby, J. Ronzyne and D. H. Williams, J. Chem. Soc. C, 944 (1967).
- ³ J. Ronayne, J. Bowie and D. H. Williams, J. Am. Chem. Soc. 88, 4980 (1966).
- ⁴ J. M. Miller, J. Chem. Soc. (A), 828 (1967).
- ⁵ Unpublished results from the authors' laboratory.

- ⁶ G. Wolff, R. E. Wolff and J. A. McCloskey, Tetrahedron Letters 4335 (1966).
- ⁷ C. N. Matthews and G. H. Birum, Tetrahedron Letters 5707 (1966).
- ⁸ T. W. Shannon and F. W. McLafferty, J. Am. Chem. Soc. 88, 5021 (1966).
- ⁹ S. T. D. Gough and S. Trippett, J. Chem. Soc. 2333 (1962).
- ¹⁰ J. G. Burr, J. M. Scarborough and R. H. Shudde, J. Phys. Chem. 64, 1359 (1960).
- ¹¹ F. Ramirez and S. Dershowitz, J. Org. Chem. 22, 41 (1957).
- ¹² L. Horner and H. Oedinger, Chem. Ber. 91, 437 (1958).
- ¹³ O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, Helv. Chim. Acta 40, 1242 (1957).
- ¹⁴ J. Dodonov and H. Medoks, Chem. Ber. 61, 907 (1928).
- ¹⁵ A. P. Best and C. L. Wilson, J. Chem. Soc. 239 (1946).
- ¹⁶ T. Sandmeyer, Chem. Ber. 17, 2605 (1884).
- ¹⁷ F. G. Mann and B. C. Saunders, Practical Organic Chemistry p. 173 (4th edition). Longmans (1961).
- ¹⁸ K. Biemann, Mass Spectrometry pp. 204–231. McGraw-Hill, New York (1962).