4-Iodo-2-nitrofluorobenzene.—Attempted preparation by the diazonium method of van Hove[28] or by iodination of *o*-fluoronitrobenzene[30] at room temperature was unsuccessful. However, the latter reaction at *ca.* 100° produced the desired compound, mp 34.5–35° (lit.[28] mp 35.5°). The procedure was otherwise much as described above.

4-Fluoro-3-nitro-N,N-dimethylaniline was obtained in 27% yield by nitration of *p*-fluoro-N,N-dimethylaniline[31] by nitric acid in concentrated sulfuric acid at *ca.* −5°. The product was obtained as brilliant orange crystals, mp 46°, by crystallization from petroleum ether (bp 60–90°).

Anal. Calcd. for $C_8H_9FN_2O_2$: C, 52.17; H, 4.92. Found:[32] C, 51.99; H, 5.03.

N-(4-Substituted 2-nitrophenyl)piperidines (II).—*o*-Nitrophenylpiperidine,[33] mp 80–81°, 3-nitro-4-piperidinoacetophenone,[34] mp 92–93°, and 4-bromo-2-nitrophenylpiperidine were made by standard methods. The bromo derivative was obtained in two modifications, the one of mp 45–45.5° previously reported,[35] the other of mp 61–62°. The former was converted into the latter by crystallization from petroleum ether (bp 30–60°) with introduction of a seed crystal.

Anal. Calcd for $C_{11}H_{13}BrN_2O_2$: C, 46.33; H, 4.60. Found:[32] C, 46.23; H, 4.71.

The following are new compounds, made by condensing the relevant 4-substituted 2-nitrochlorobenzenes with piperidine: **N-(4-trifluoromethyl-2-nitrophenyl)piperidine,** mp 54.5–55.2° (from aqueous ethanol) (*Anal.* Calcd for $C_{12}H_{13}F_3N_2O_2$: C, 52.55; H, 4.78. Found:[32] C, 52.53; H, 4.97); **N-(4-methylsulfonyl-2-nitrophenyl)piperidine,** mp 124–125.5° (from carbon tetrachloride) (*Anal.* Calcd for $C_{12}H_{16}N_2O_4S$: C, 50.69; H, 5.67. Found:[32] C, 50.47; H, 5.68); and **N-(4-iodo-2-nitrophenyl)piperidine,** mp 41–42° (from ethanol) (*Anal.* Calcd for $C_{11}H_{13}IN_2O_2$: C, 39.76; H, 3.91. Found:[32] C, 39.64; H, 3.90).

Kinetic Measurements.—For the most part, reactions were followed by photometric measurements at *ca.* 420 mμ on acid-quenched aliquots, according to a technique previously described.[16] The runs with *o*-fluoronitrobenzene at 46.6 and at 25.0° (except at 0.098 *M* piperidine), and the runs with 2,4-dinitrofluorobenzene at piperidine concentrations less than 0.01 *M* were followed by photometric measurements on the reaction solutions. The runs with 2,4-dinitrofluorobenzene at piperidine concentrations greater than 0.01 *M* were performed in a Durrum–Gibson stopped-flow spectrophotometric kinetics apparatus, the essential features of which are due to Gibson,[36] with observation at 375 mμ.

Registry No.—Piperidine, 110-89-4; methanol, 67-56-1; I (R = H), 1493-27-2; I (R = Br), 364-73-8; I (R = CF_3), 367-86-2; I (R = CH_3CO), 400-93-1; I (R = CH_3SO_2), 453-72-5; I (R = NO_2), 70-34-8; 4-fluoro-3-nitro-N,N-dimethylaniline, 18542-98-8; II (R = Br), 5465-66-7; II (R = CF_3), 1692-79-1; II (R = CH_3SO_2), 18543-01-6; II (R = I), 18543-02-7.

Acknowledgments.—Nearly all the preparative work described herein was done by Messrs. Ray M. Conner, James M. Jung, and Stanley M. Williamson. Some of the kinetic determinations with *o*-fluoronitrobenzene were performed by Mrs. Carol King. We are grateful for this assistance.

(30) I. R. L. Barker and W. A. Waters, *J. Chem. Soc.*, 150 (1952).
(31) D. P. Evans and R. Williams, *ibid.*, 1199 (1939).
(32) Analysis were by Micro-Tech Laboratories, Skokie, Ill.
(33) E. Lellman and W. Geller, *Ber.*, **21**, 2281 (1888).
(34) W. Borsche, L. Stackmann, and J. Makaroff-Semljanski, *ibid.*, **49**, 2222 (1916).
(35) R. J. W. LeFevre and E. E. Turner, *J. Chem. Soc.*, 1113 (1927).
(36) Q. H. Gibson and L. Milnes, *Biochem. J.*, **91**, 161 (1964).

Phosphinic Acids and Derivatives. III. The Mass Spectra of Diarylphosphinates[1]

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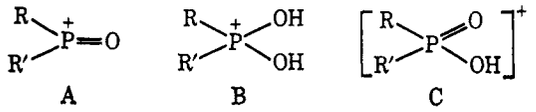
Rather than simply fragmenting as do dialkylphosphinates, diarylphosphinates cyclize to give biphenyl-2,2′-phosphorus ions, especially the biphenylphosphinylium ion, as intense peaks in their mass spectra. The fragmentation of benzophenone-2,2′-phosphinic acid does not proceed through the same pathway. This phosphorus heterocycle and diphenylmethane-2,2′-phosphinic acid apparently tend to form phosphorus heteroaromatic ions. The spectra of phenyl-*o*-tolylphosphinic acid and di-*o*-tolylphosphinic acid show that the cyclic fragmentation in these cases also involves formation of biphenylphosphorus ions rather than an alternative pathway previously found in *o*-tolyl sulfones.

We recently reported the mass spectra of some dialkylphosphinic acids and their alkyl esters.[1b,3] The most important fragments are phosphacylium ions (A), protonated phosphinate ions (B), and phosphinate ions (C).[4] We predicted that ions of type A would probably be a general phenomenon in the mass spectra



of organophosphorus compounds. Accordingly it was of some interest to examine the mass spectra of diarylphosphinic acids and esters which were available as a result of other studies carried out in this laboratory.[5] We have also included other arylphosphorus compounds which aid in the assignment of fragmentation pathways.[6]

(1) Supported in part by grants from the National Science Foundation. (a) Part I: P. Haake and G. H. Hurst, *J. Amer. Chem. Soc.*, **88**, 2455 (1966). (b) Part II: P. Haake and P. S. Ossip, *Tetrahedron*, **24**, 565 (1968).

(2) Alfred P. Sloan Research Fellow, 1964–67. Inquiries should be addressed to P. H. at Wesleyan University.

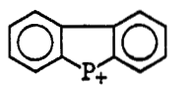
(3) P. S. Ossip, Ph.D. Thesis, UCLA, 1968.

(4) We use the following conventions. In the tables, intensities are below the *m/e* values. In the text, intensities are given in parentheses following the *m/e* value. Radical ions are given as $[X]^+$ in contrast to spin-paired ions which have a charge on a given atom. Pathways for which metastables have been observed are marked with an asterisk.

(5) (a) C. E. Diebert, Ph.D. Thesis, UCLA, 1966; (b) R. D. Cook, Ph.D. Thesis, UCLA, 1967.

(6) Deuteration studies have been used in a study of triphenylphosphine oxide: D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, **90**, 966 (1968).

The formation of bridged biphenylphosphenium ions (D),[7] previously noted by Miller and by Hughes and Woods,[8] and established by Williams, *et al.*,[6] is not prominent in the spectra reported here, but the P=O analog of D (a phosphinylium ion) and M − 1 ions with this cyclic structure (protonated phosphinic acid species) are important fragments in most cases. Therefore ions of structures A and B are again found in this study of diarylphosphinates.



D

TABLE I

NORMALIZED INTENSITIES OF PEAKS IN THE MASS SPECTRA OF THE PHOSPHINIC ACIDS **1–5**[a]

1 *m/e*	47	50	51	76	77	78	94	125	141	152
I,[b] %	11	7	25	4	43	16	14	5	7	7
1 *m/e*	199	200	217	218	219					
I, %	45	7	100	34	6					

Metastables 216.0 (218 → 217), 183.5 (218 → 200), 182.5 (217 → 199), 116.1 (199 → 152), 91.81 (217 → 141), 91.2 (218 → 141), 42.1 (141 → 77), 33.8 (77 → 51)

2 *m/e*	47	50	51	52	76	77	78	79	94	95
I, %	12	7	24	4	6	52	22	14	5	18
2 *m/e*	126	142	152	153	154	199	200	201	217	218
I, %	7	10	13	8	5	51	13	4	28	100
2 *m/e*	219	220								
I, %	45	6								

Metastables 216.0 (218 → 217), 183.5 (218 → 200), 182.5 (217 → 199), 181.6 (218 → 199), 116.1 (199 → 152), 33.8 (77 → 51)

3 *m/e*	39	41	47	50	51	63	65	77	78	89
I, %	15	6	10	4	21	12	25	24	12	13
3 *m/e*	90	91	107	109	115	137	139	141	152	153
I, %	9	24	5	4	7	7	4	5	12	5
3 *m/e*	165	166	167	195	196	197	199	212	213	214
I, %	50	24	14	4	18	8	12	9	65	15
3 *m/e*	215	217	231	232	233					
I, %	12	5	100	42	16					

Metastables 230.0 (232 → 231), 197.5 (232 → 214), 196.5 (231 → 213), 182.5 (217 → 199), 129.5 (213 → 166), 128.0 (213 → 165), 46.5 (91 → 65)

4 *m/e*	39	41	47	51	63	65	77	89	90	91
I, %	12	5	5	6	9	25	5	11	8	36
4 *m/e*	92	165	166	178	179	180	213	214	227	228
I, %	6	20	13	5	7	5	51	8	14	2
4 *m/e*	231	232	245	246						
I, %	100	16	13	20						

Metastables 217.0 (246 → 231), 210.2 (245 → 228), 196.4 (231 → 213), 46.6 (91 → 65)

5 *m/e*	39	47	50	51	63	64	65	74	75	76
I, %	4	5	15	12	6	4	11	4	10	32
5 *m/e*	77	92	93	115	123	124	139	140	141	150
I, %	15	7	7	4	22	5	18	14	9	6
5 *m/e*	151	152	153	168	169	170	186	198	199	214
I, %	9	16	4	10	4	16	17	6	4	8
5 *m/e*	215	216	217	227	231	232	244	261	262	263
I, %	7	44	7	4	9	10	4	56	37	5
5 *m/e*	278	291	292	307	308	309				
I, %	7	100	18	54	47	7				

Metastables 306.0 (308 → 307), 276.0 (307 → 291), 275.0 (308 → 291), 235.0 (292 → 262), 234.2 (291 → 261), 221–223 (308 → 262 and 307 → 261), 205.5 (262 → 232), 204.5 (261 → 231), 177.0–179.0 (262 → 216 and 261 → 215)

[a] All fragments with intensity >3% of base peak and with *m/e* >39 are included. In a few cases, peaks with intensity <3% are included because of their relevance. [b] Intensity.

(7) Ion D has been called a phosphafluorenyl ion.[6,8] Either method of nomenclature is correct, but the method used in the text has the advantage of clearly indicating the functionality of a given compound or ion. For example, ion F, of central importance in this study, could be named 9-oxo-9-phosphafluorenyl ion or biphenyl-2,2,-phosphinylium ion. The latter name has the advantage that it indicates that the ion is a phosphinylium ion and is therefore similar to other $R_2{}^+P{=}O$ ions. The phosphenium ion designation indicates that the phosphorus atom is electron deficient and analogous to a carbene in its electronic structure.

Results

Tables I and II summarize the data collected from studies of the mass spectra of phosphinic acids **1–5** and

TABLE II

NORMALIZED INTENSITIES OF PEAKS IN THE MASS SPECTRA OF THE PHOSPHINATE ESTERS **6–12**, DIPHENYLPHOSPHINE OXIDE (**13**), AND DIPHENYLBENZYLPHOSPHINE OXIDE (**14**)[a]

6 *m/e*	39	47	50	51	52	65	75	76	77	78
I, %	4	14	13	51	4	4	4	5	99	14
6 *m/e*	91	92	109	115	124	125	139	141	152	153
I, %	13	16	14	5	5	8	12	5	8	5
6 *m/e*	154	155	199	200	201	202	231	232	233	
I, %	5	26	35	6	12	22	100	36	5	

Metastables 230.0 (232 → 231), 171.4 (231 → 199), 119.0 (202 → 155), 85.5 (139 → 109), 33.8 (77 → 51)

7 *m/e*	47	50	51	52	76	77	78	94	104	105
I, %	17	6	33	4	4	88	22	9	55	14
7 *m/e*	124	125	141	142	152	153	154	155	199	201
I, %	7	17	33	7	11	7	8	18	29	28
7 *m/e*	202	203	217	218	219	231	245	246		
I, %	35	4	100	38	8	6	11	9		

Metastables 193.0 (246 → 218), 192.0 (245 → 217), 182.5 (217 → 199), 119.0 (202 → 155), 33.8 (77 → 51)

8 *m/e*	39	47	50	51	63	65	66	77	78	91
I, %	10	4	4	13	4	11	11	37	4	15
8 *m/e*	92	94	95	105	108	141	142	152	153	154
I, %	10	70	6	14	4	16	9	4	4	4
8 *m/e*	156	169	170	171	183	198	201	202	225	254
I, %	5	7	25	4	6	10	100	13	7	4
8 *m/e*	293	294	295							
I, %	77	41	8							

Metastables 292.0 (294 → 293), 46.5 (91 → 65), 33.8 (77 → 51)

9 *m/e*	47	51	65	77	78	91	92	125	155	167
I, %	3	6	6	11	6	29	5	6	11	10
9 *m/e*	199	201	202	203	217	308	309			
I, %	4	15	100	13	6	37	8			

Metastables 306.0 (308 → 307), 182.5 (217 → 199), 132.5 (308 → 202), 119.0 (202 → 155), 46.5 (91 → 65), 33.8 (77 → 51)

10 *m/e*	39	47	51	65	77	91	94	109	137	152
I, %	7	7	10	11	11	10	4	7	9	4
10 *m/e*	165	166	167	197	202	212	213	215	216	290
I, %	17	13	5	14	5	4	8	44	6	12
10 *m/e*	307	308	309							
I, %	40	100	20							

(8) (a) J. M. Miller, *J. Chem. Soc., A*, 828 (1967); (b) A. N. Hughes and M. Woods, *Tetrahedron*, **23**, 2973 (1967).

TABLE II (*Continued*)

Metastables 306.0 (308 → 307), 273.0 (308 → 290), 180.5 (215 → 197), 164.0 (166 → 165), 33.8 (77 → 51)

11 *m/e*	77	119	120	121	134	135	158	158.5	166	167
I, %	4	11	28	11	19	5	20	6	4	6
11 *m/e*	168	182	183	240	241	271	285	286	287	288
I, %	5	9	4	12	4	4	17	5	6	4
11 *m/e*	301	303	304	317	318	319				
I, %	4	6	4	27	100	20				

Metastables 316.0 (318 → 317), 256.2 (317 → 285), 200.5 (287 → 240)

12 *m/e*	39	43	47	50	51	58	63	64	65	69
I, %	9	18	17	43	15	5	12	12	8	8
12 *m/e*	74	75	76	77	78	79	89	90	91	92
I, %	11	27	100	21	6	9	5	5	13	19
12 *m/e*	93	95	96	107	109	115	119	120	123	124
I, %	7	9	7	9	4	6	6	10	10	4
12 *m/e*	126	128	133	136	137	138	139	140	141	150
I, %	6	4	6	24	6	4	22	11	4	10
12 *m/e*	151	152	153	154	155	157	165	167	168	170
I, %	15	29	10	59	6	7	4	6	12	21
12 *m/e*	171	181	184	185	186	187	197	198	199	200
I, %	5	4	30	4	17	8	7	12	12	68
12 *m/e*	201	213	214	215	216	227	228	229	230	231
I, %	8	7	10	7	11	5	4	6	27	12
12 *m/e*	232	244	245	246	257	259	262	275	276	277
I, %	4	6	15	9	4	6	12	32	18	8
12 *m/e*	291	292	293	294	305	306	321	322		
I, %	6	30	5	7	43	8	27	20		

Metastables none observed

13 *m/e*	47	50	51	52	77	78	96	107	108	109
I, %	19	5	20	4	41	36	5	5	4	6
13 *m/e*	124	125	152	153	154	155	183	184	201	202
I, %	33	11	5	5	5	9	18	4	100	45
13 *m/e*	203									
I, %	7									

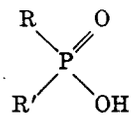
Metastables 200.0 (202 → 201), 167.5 (202 → 184), 166.5 (201 → 183), 119.0 (202 → 155), 33.8 (77 → 51), 17.7 (125 → 47)

14 *m/e*	47	50	51	65	77	78	91	124	140	152
I, %	10	4	20	10	36	6	12	5	4	6
14 *m/e*	153	154	183	199	201	202	291	292		
I, %	4	4	6	10	100	18	20	10		

Metastables 290.0 (292 → 291)

[a] All fragments with intensity >3% of base peak and with *m/e* >39 are included. In a few cases, peaks with intensity ≤3% are included because of their relevance.

phosphinate esters **6–12**, respectively. Table II also contains data for phosphine oxides **13** and **14**. Data



1, R = R′ = phenyl
2, R = R′ = phenyl (containing ~80% OD)
3, R = phenyl; R′ = *o*-tolyl
4, R = R′ = *o*-tolyl
5, R = R′ = *m*-nitrophenyl

for the cyclic phosphinic acids and esters **15–18** are in Table III. In one case,[9] spectra recorded at various

(9) The compound used was N-*p*-nitrophenyl-*p*-nitrophenylphosphinamide.

TABLE III

NORMALIZED INTENSITIES OF PEAKS IN THE MASS SPECTRA OF PHOSPHAANTHRACENES **15–18**[a]

15 *m/e*	39	47	51	63	77	82	82.5	89	106	115
I, %	5	3	5	7	5	4	7	5	15	6
15 *m/e*	139	152	163	164	165	166	183	184	212	213
I, %	7	5	10	8	62	11	18	5	100	15
15 *m/e*	229	230	231							
I, %	4	87	13							

Metastables 195.5 (230 → 212), 128.5 (212 → 165), 80.0 (165 → 115), 33.8 (77 → 51)

16 *m/e*	39	63	82.5	89	115	139	152	163	164	165
I, %	4	5	7	4	5	6	5	9	8	69
16 *m/e*	166	167	181	183	212	213	214	229	230	244
I, %	20	5	4	13	100	21	5	48	7	89
16 *m/e*	245									
I, %	14									

Metastables 184.2 (244 → 212), 128.5 (212 → 165), 119.0 (229 → 165)

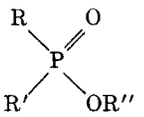
17 *m/e*	39	47	50	51	63	64	74	76	77	92
I, %	6	11	23	12	10	4	11	44	11	10
17 *m/e*	104	115	126	139	150	151	152	153	167	168
I, %	13	6	8	8	10	20	51	8	4	9
17 *m/e*	169	170	180	181	199	215	216	244	245	
I, %	9	5	100	18	17	9	64	81	12	

Metastables 191.0 (244 → 216), 183.3 (216 → 199), 132.8 (244 → 180), 128.5 (180 → 152), 116.1 (199 → 152), 55.6 (104 → 76), 55.25 (76 → 63), 33.8 (77 → 51), 32.9 (76 → 50)

18 *m/e*	47	50	74	75	76	77	123	139	150	151
I, %	5	7	4	5	10	5	4	4	5	10
18 *m/e*	152	153	164	165	168	180	181	182	199	200
I, %	27	7	4	7	4	23	44	7	27	12
18 *m/e*	201	227	228	229	230	231	257	258	259	
I, %	4	8	100	8	30	4	5	26	4	

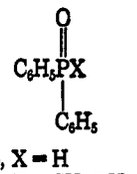
Metastables 256.0 (258 → 257), 205.0 (258 → 230), 201.5 (258 → 228), 195.5 (230 → 212), 143.8 (228 → 181), 129.4 (181 → 153), 128.2 [180 → 152), 116.2 (199 → 152), 52.3 (76 → 63), 44.5 (126 → 75), 33.8 (77 → 51), 32.9 (76 → 50)

[a] All fragments with intensity >3% of base peak and with *m/e* >39 are included. In a few cases, peaks with intensity ≤3% are included because of their relevance.



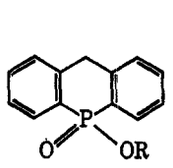
6, R = R′ = phenyl; R″ = CH_3
7, R = R′ = phenyl; R″ = C_2H_5
8, R = R′ = R″ = phenyl
9, R = R′ = phenyl; R″ = benzyl
10, R = phenyl; R′ = *o*-tolyl; R″ = phenyl
11, R = R′ = *p*-$Me_2NC_6H_4$; R″ = CH_3
12, R = R′ = *m*-nitrophenyl; R″ = CH_3

times enabled an estimate of reproducibility of the MS-9 mass spectrometer which was used in this study.

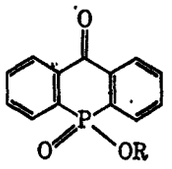


13, X = H
14, X = $CH_2C_6H_5$

It was found that the average error in the relative intensities of the ten most abundant ions was ±6% for four ions of >20% relative intensity and ±3% for six ions of 10–20% relative intensity.



15, R = H
16, R = CH_3

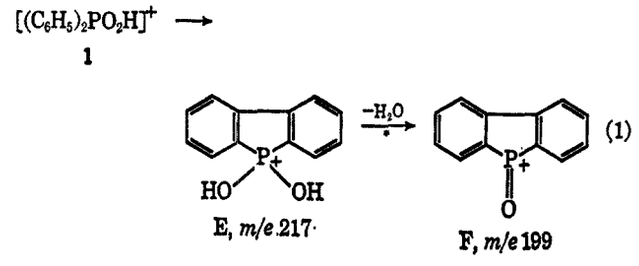


17, R = H
18, R = CH_3

Discussion

Although the fragmentation pathways are interrelated and a given ion can often fragment in more than one way to give more than one ion, we will organize this discussion, for clarity, according to types of fragmentation.[10]

Fragmentation through Cyclized Ions.—With a few exceptions, a marked feature of the mass spectra of the noncyclic acids and esters (Tables I and II) is the loss of a hydrogen atom to give an intense M − 1 fragment. Metastable peaks were observed for M → M − 1. An important fragmentation pathway then involves loss of H_2O or CH_3OH from M − 1 followed by loss of PO. For example,[4] for **1**, M = 218 (34) → (−H) 217 (100) → (−H_2O) 199 (45) accounts for the three major peaks in the spectrum.[10] Metastables are observed for these steps and also for 199 → (−PO) 152 (biphenylene radical ion) although the intensity of 152 is quite low. We attributed this to cyclization[5a] to give the protonated biphenyl-2,2′-phosphinic acid ion (E) and the biphenyl-2,2′-phosphinylium ion (F) (eq 1). Mass spectra of $(C_6H_5)_3PO$ deuterated in the phenyl rings support[5] this proposal.[5a,8] Our study of



E, *m/e* 217 F, *m/e* 199 (1)

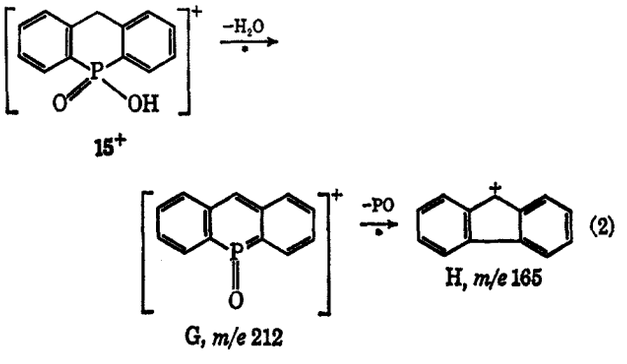
$(C_6H_5)_2PO_2D$ (**2**) is complementary—it is an H, not a D, that is lost from **2** to give M − 1, and M − 1 loses HOD to give 199.

The methyl ester of diphenylphosphinic acid, **6**, shows predominantly cyclic fragmentation involving loss of CH_3OH. The ethyl and benzyl esters, **7** and **9**, show predominantly noncyclic fragmentation and will be discussed below.

Although phenyl ester **8** gives an intense M − 1 peak, 199 is weak and 201 is the base peak. The 201 fragment could be either cyclic or noncyclic, and this problem will be discussed below along with other questions about the structures of ions.

These spectra of acids and esters offer some interesting contrasts to the mass spectrum of $(C_6H_5)_3PO$,[6] which shows 183 (15), 199 (15), 201 (20). The 183 peak is the base peak in the spectrum of $(C_6H_5)_3P$,[6] and has been attributed to D. We observe small 183 peaks in our spectra. Even with phosphine oxides **13** and **14**, 183 is fairly weak and 201 is the base peak in the spectra of both compounds.[11] There is, therefore, a very different pattern of intensities of 183, 199, and 201 than observed for $(C_6H_5)_3PO$. This raises the question of the importance of noncyclic and cyclic fragmentation pathways. The fragment of *m/e* 201 must certainly be quite stable, for in the spectrum of **14** its intensity is ~8 times that of $C_7H_7^+$ (normally a very intense peak in spectra of benzyl compounds).[12]

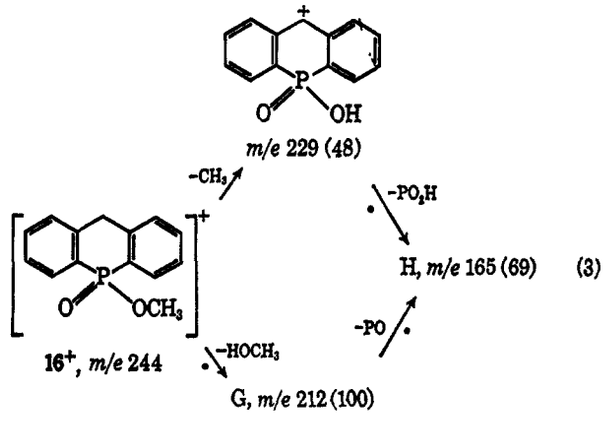
Fragmentation of Cyclic Acids and Esters.—The spectra of **15–18** have features which are relevant to understanding the cyclic fragmentation and interesting in their own right. In contrast to **1**, **15** gives a small M − 1 peak. The base peak is 212 and there is a metastable for M → 212 corresponding to loss of H_2O (eq 2). There is also a metastable for loss of PO from 212 to give 165 (62). The intensity of G suggests that



15^+ G, *m/e* 212 H, *m/e* 165 (2)

this heteroaromatic system may have considerable stability.

Methyl ester **16** undergoes the unusual loss of CH_3, not observed for other methyl phosphinates.[13] The importance of 229 (48) and the metastables for both 229 → 165 and 212 → 165 suggest the fragmentation pathway in eq 3. In this spectrum 212 is again the base peak and 165 (69) has approximately the same relative intensity as in the spectrum of **15**.



m/e 229 (48) 16^+, *m/e* 244 G, *m/e* 212 (100) H, *m/e* 165 (69) (3)

The spectra of **17** and **18** are not so similar as the spectra of **15** and **16**. It appears that M^+ for **17** loses

(10) We will ignore the intensity of hydrocarbon fragments (*e.g.*, at *m/e* 77 and 51) which are not important in understanding fragmentation involving phosphorus.

(11) A metastable for 201 → 183 is observed in the spectrum of **13**.

(12) H. Budzikiewicz, C. Djerassi, and D. H Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.

(13) Other results in this paper and ref 1b and 3.

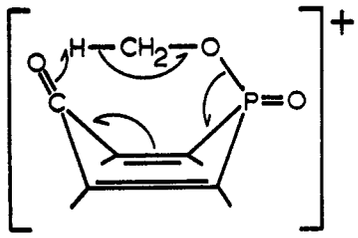
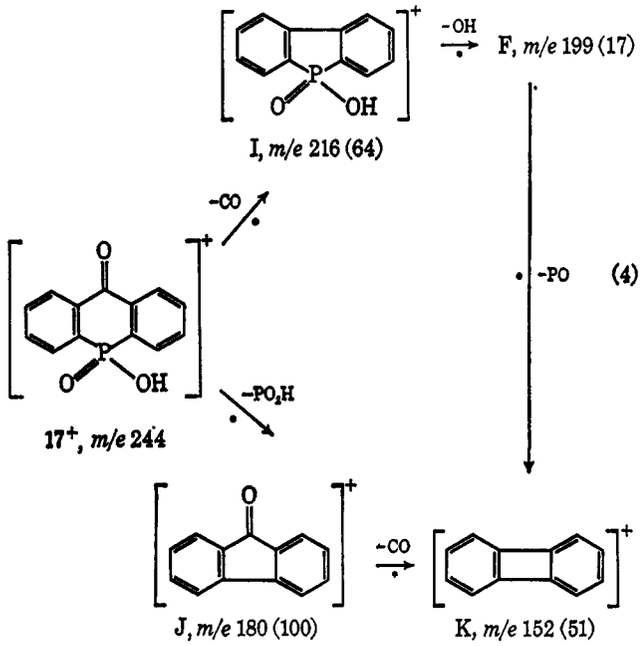
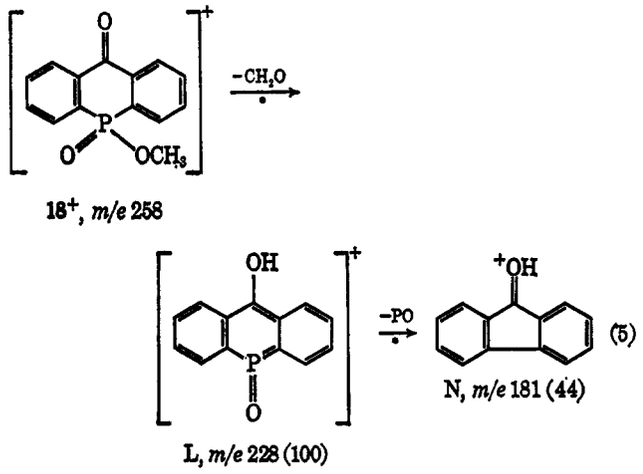


Figure 1.—Possible fragmentation mechanism of 18^+.

both CO to give I and PO_2H to give J, the latter being slightly preferred (eq 4). However, although M^+



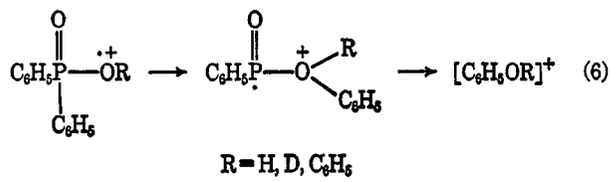
for **18** also gives an (M − CO) peak at 230 (30), the base peak is at 228 (M − CH_2O) and 181 (much weaker than 180 in the spectrum of **17**) is twice as large as 180. This suggests the interesting fragmentation in eq 5. Fragment L probably has a structure resembling fragments from 15^+ and 16^+. The 258 → 228 frag-



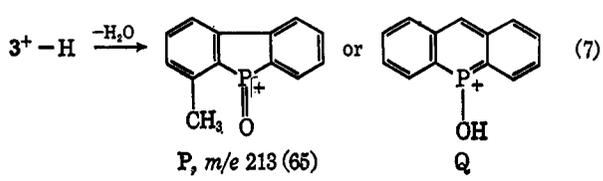
mentation may involve direct transfer of a hydrogen since **18** will have a butterfly conformation which could bring the methyl group close to the carbonyl oxygen (Figure 1). The spectrum of **18** also contains a fairly intense 199 (27) peak (F), but no metastable for its formation. There is a metastable for 258 → 230 and 199 is presumably formed from 230.

The importance of ions of types D, E, and F in other spectra is therefore only partially observed for **15–18** even though loss of CO would be a ready pathway to these biphenylphosphorus ions.

Rearrangement.—Some of the spectra show evidence for rearrangement processes analogous to those observed in the mass spectra of diaryl sulfones.[14] For example, *m/e* 94, $[C_6H_5OH]^+$, is present to the extent of 14% in diphenylphosphinic acid (**1**), *m/e* 95, $[C_6H_5OD]^+$, is 18% in the D acid (**2**), and *m/e* 170, $[PhOPh]^+$, is 25% in the spectrum of phenyl diphenylphosphinate (**8**). These fragments would result from 1,2 migration of one of the phenyl groups to oxygen (eq 6).



A notable feature of the spectra of aryl sulfones with *o*-methyl groups was loss of H_2O followed by SO with the formation of fluorene fragments, and it was concluded that both hydrogen atoms eliminated in the water molecule come from the *o*-methyl group.[14] In the spectrum of phenyl-o-tolylphosphinic acid (**3**), 213 could be either a biarylphosphinylium ion (P) or a cyclized heteroaromatic species (Q) (eq 7). The latter could form the observed 165 and 166 species through a pathway analogous to that observed with sulfones. The loss of a methyl in the spectrum of



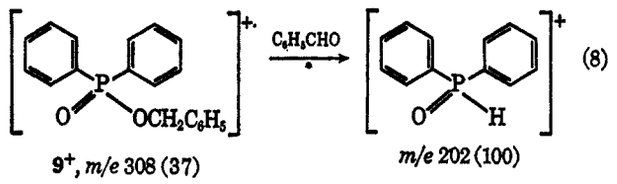
di-*o*-tolylphosphinic acid requires that in either cyclization loss of a methyl be preferred over cyclization involving loss of a hydrogen. The ambiguity between these two cyclic fragmentation pathways for the *o*-tolyl compounds will be discussed below.

Noncyclic Fragmentation.—Compounds **6–14** show some fragmentations quite similar to that observed for alkylphosphinates.[1b,3] Elimination of ethylene to give $[(C_6H_5)_2PO_2H]^+$, *m/e* 218, is so important for **7** that there are small M and M − 1 peaks. After loss of ethylene, subsequent fragmentation is similar to but not identical with **1**. Elimination of benzaldehyde from M of benzyl ester **9** yields 202 as the base peak and 201, 199, and M − 1 are all of rather low intensity (eq 8).[15]

Fragmentation of Substituted Diarylphosphinates.—The spectrum of methyl ester **11** has the unique feature that the base peak is the parent peak. There are, however, metastables and significant peaks for M →

(14) J. H. Bowie, D. H. Williams, S-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966).

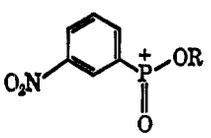
(15) Elimination reactions were frequently observed with dialkylphosphinates.[1b,3]



9^+, *m/e* 308 (37) *m/e* 202 (100) (8)

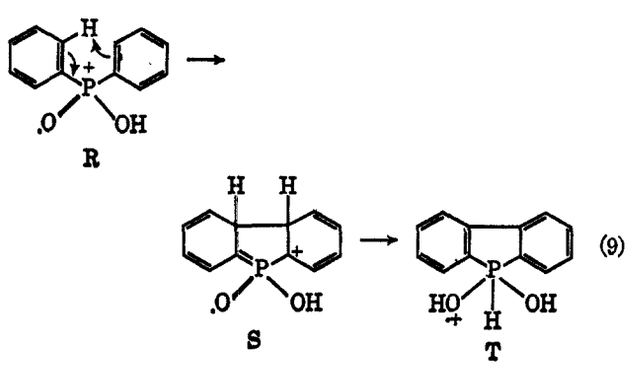
M − 1 → 285 (*p*-$(CH_3)_2N$- substituted F); so cyclization is apparently still occurring.

The nitro compounds appear to undergo cyclic and noncyclic fragmentation plus loss of O, NO, and NO_2 due to the presence of the nitro groups.[12] Prominent M − 1 peaks, 307 (54) for **5** and 321 (27) for **12**, are evidence for the cyclic pathway. Of more interest is the importance of noncyclic fragmentation in these two cases very similar to that observed for dialkylphosphinates.[1b,3] Acid **5** has 186 (17) and ester **12** has 200 (68), both of which are probably due to ion O. This noncyclic pathway is not prominent in the other compounds studied here.



O, R = H, *m/e* 186
R = CH_3, *m/e* 200

Structure of Ions.—The above data are additional evidence that biphenylphosphorus ions are common fragments in mass spectrometry of arylphosphorus compounds and may be particularly stable. In contrast to previous studies, F appears to be favored over D, presumably because D would have to be formed by loss of HO + OR and M − 1 more readily loses HOR. Why are ions like D, E, and F so important in these spectra? Although aryl-stabilized carbonium ions are known to be stable, a ready pathway for formation must also be available. We see, for example, that the cyclic benzophenone-2,2′-phosphinic acid (**17**) which needs to only lose CO and OH to form F has a much smaller ratio of 199/M than **1** for which hydrogen migrations are necessary to form F.[16] There may be a driving force for cyclization of M, shown in eq 9 for M from **1**.



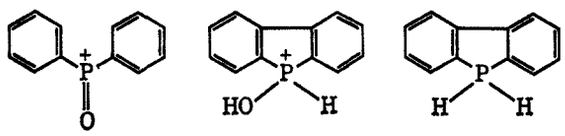
R S T (9)

Ion radicals R, S, and T are all possible representations of 1^+. The proximity of the aromatic rings may spontaneously lead to S and then T in the gas phase.

(16) Of course, there are several reasons why 199/M could be low for **17**, including a preferred alternate pathway for fragmention. Nevertheless, this ratio offers a convenient quantitative estimate of the tendency for M^+ to go to 199 which is probably as far as many M^+ fragment when they take this pathway.

An interesting question is whether M is already cyclized before giving M − 1 or whether loss of H occurs as M cyclizes to M − 1. Metastables for loss of H_2O from 1^+ and 2^+ certainly suggest that T may be the most likely structure of the parent peak. On the other hand, the predominant loss of H not D in M → M − 1 for **2** would require no scrambling of the OH and PH hydrogens in T. It seems likely that scrambling would occur if T were formed.

Ions of mass 201 are the base peaks in the spectra of $(C_6H_5)_2P(O)OC_6H_5$ (**8**) and phosphine oxides **13** and **14**. In all these spectra 199 (F) is weak. The 201 ion could be either U or V and may be both. In the spectrum of **13**, there is a metastable for 201 → 183,



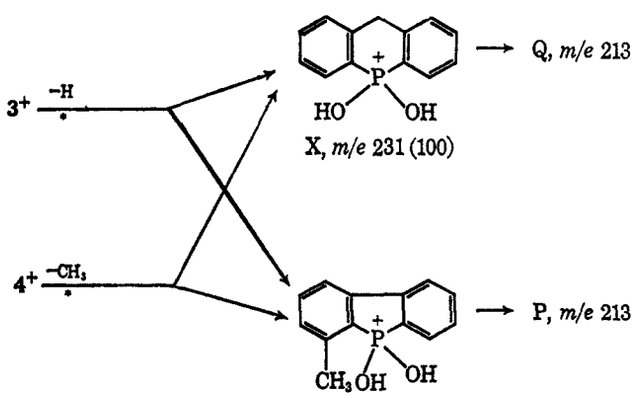
U V W

suggesting that V is the best representation of 201. Also in the spectrum of phenyl ester **8**, the M − 1 peak is very intense. This indicates that cyclization to biphenylphosphorus ions is an important pathway despite the potential easy loss of $C_6H_5O\cdot$.

The spectrum of **9** has 202 as base peak although **13** (M = 202) has 201 as a base peak. This contrast suggests that efficient 202 → 201 conversion requires an energetic 202; the 9^+ → 202 process (loss of benzaldehyde) probably involves loss of enough energy so that 202 is much less energetic than the 202 from electron impact on **13**.

In the previous studies[6,8] of arylphosphines, the straightforwardly represented $(C_6H_5)_2P^+$ and $(C_6F_5)_2P^+$ may actually be W and perfluoro W, respectively.

We have commented on the ambiguity in cyclic fragmentation pathways possible for the *o*-tolyl acids and ester, **3**, **4**, and **10**. The most important observation which bears on this problem is the loss of H from mono-*o*-tolyl acid 3^+, but the loss of CH_3 from 4^+, the di-*o*-tolyl acid, to give 213 as the second most intense peak and 231 as the most intense peak in both cases. If cyclization occurs to give X and Q, why should CH_3 be lost from 4^+? While this question is not easily answered, it is easy to explain loss of CH_3 in



4^+ → Y. Nonbonded repulsions should force **4** into the conformation shown in Figure 2 with methyl

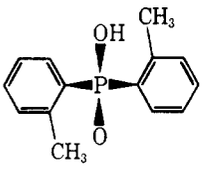


Figure 2.—Perspective view down the C_2 axis (assuming rapid proton transfer) of **4**.

groups on opposite sides of the tetrahedral phosphorus atom. Cyclization to Y would then clearly proceed through loss of a methyl. Therefore, the *o*-tolyl compounds we have studied appear to cyclize to biphenylphosphorus ions[17] in contrast to the conclusion for *o*-tolyl sulfones.[14]

Experimental Section

The compounds used in this study were mostly prepared by previously published procedures[18] during an investigation of the hydrolytic behavior of derivatives of diarylphosphinic acids. Their infrared, nmr, and mass spectra, melting points, and, where appropriate, elemental analyses, were in accord with their postulated structures.[5]

Diphenylphosphine oxide was prepared by an adaptation of Miller's[19] method. Diphenylchlorophosphine (11 g, 0.05 mol) was stirred under nitrogen in dry benzene (150 ml) at 25°, while a solution of water (0.9 ml, 0.05 mol) and triethylamine (5.05 g, 0.05 mol) in acetone (4 ml) was added dropwise over a 1-hr period. After stirring for a further 15 min, the solution was filtered, then extracted with 50 ml of 5% HCl, two 50-ml portions of 5% $NaHCO_3$, two 50-ml portions of H_2O, and finally dried over $MgSO_4$. Removal of benzene gave an oil which solidified after 3 hr at 0°. Two recrystallizations from dry ether at −40° gave white hygroscopic crystals (4.89 g, 48.4%), mp 49–51° (sealed tube) (lit.[20] mp 53–56°).

Diphenylphosphinic acid-O-d_1 was prepared with approximately 80% deuterium by dissolving the protonated acid in DMSO containing a large excess of D_2O and standing 24 hr at 25°. The solvent was removed and the partially deuterated acid dried over P_2O_5 at 100° *in vacuo*. Deuterium content was estimated from the ratio of the *m/e* 141 and 142 peaks ($PhPO_2H^+$ and $PhPO_2D^+$, respectively) present in the mass spectrum.

Mass spectra were determined with an A.E.I. MS9 mass spectrometer, using direct insertion technique, at a source temperature of 160° and electron beam energy 70 eV.

Registry No.—**1**, 1707-03-5; **2**, 18621-09-5; **3**, 18593-18-5; **4**, 18593-19-6; **5**, 18593-20-9; **6**, 1706-90-7; **7**, 1733-55-7; **8**, 1706-96-3; **9**, 5573-42-2; **10**, 18593-22-1; **11**, 18593-23-2; **12**, 18621-10-8; **13**, 4559-70-0; **14**, 2959-74-2; **15**, 18593-24-3; **16**, 18593-25-4; **17**, 18593-26-5; **18**, 18593-27-6.

Acknowledgment.—We thank Robert Marmor, Robert D. Cook, and Jean P. McNeal for assistance in preparation of some of the compounds, and Dr. David Lightner for help with the mass spectrometer.

(17) A spectrum was obtained for phenyl-*o*-tolylphosphinic acid with 85% OD. Although there is no evidence that clearly indicates which cyclic fragmentation is occurring, the data are consistent with $3^+ \rightarrow Y \rightarrow P$.

(18) K. Sasse in Houben-Weyl's "Methoden der organischen Chemie, Organische Phosphorverbindungen," Vol. 1 and 2, G. Thieme Verlag, Stuttgart, 1963.

(19) R. C. Miller, *J. Org. Chem.*, **24**, 2013 (1959).

(20) B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

Photochemical Cycloaddition. Some Applications of the Use of Enolized β-Diketones[1,2]

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Photochemical cycloaddition of the enol acetates of cyclic β-diketones to alkenes gives adducts which are β-acetoxy ketones. These accordingly undergo reverse aldol reactions under mild alkaline conditions to give cyclic 1,5-diketones. This sequence has been used for the synthesis of a number of systems containing seven- and eight-membered rings. Cyclopentane-1,3-dione enol acetate gives adducts with dichloroethylene. One of these, by the action of mild alkali, has been converted in one step and in 45% yield into γ-tropolone. Addition of the same enol acetate to chloromaleic ester gave an adduct which could be brominated, hydrolyzed, and oxidized to the α-diketone. This, on mild acid hydrolysis followed by mild alkaline hydrolysis, gave stipitatonic acid in 4% over-all yield. Cycloaddition of the enol acetate of 2-methyl-1,3-cyclopentanedione to cyclohex-2-enone ketal **42** gave a single adduct which could be reduced to the alcohol and thence to mesylate **45**. Mild treatment with base gave **46**, converted by reaction with methylmagnesium iodide, the Simmons–Smith reagent, methylation and hydrogenolysis to the ketone (**52**). Reduction gave a number of alcohols from the dehydration of which racemic β-himachalene (**36**) was obtained in a ten-step over-all synthesis. Also, the synthetic hydrocarbons could be converted into himachalene dihydrochloride (**60**) the racemate of the dihydrochloride obtained from natural himachalenes.

Some time ago we showed[4] that the process of photocycloaddition could be used for the synthesis of a δ-diketone. A typical example was the addition of acetylacetone to cyclohexene to give diketone **1**.[5,6]

A natural extension of this process appeared to be the use of cyclic β-diketones. Under these circum-

(1) Photochemical Synthesis. Part 25. Part 24: H. Izawa, P. de Mayo, and T. Tabata, *Can. J. Chem.*, **47**, 51 (1969).

(2) Part of the material presented here has been reported in preliminary form: (a) H. Hikino and P. de Mayo, *J. Amer. Chem. Soc.*, **86**, 3582 (1964); (b) G. Lange and P. de Mayo, *Chem. Commun.*, **3**, 704 (1967); (c) B. D. Challand, G. Kornis, G. Lange, and P. de Mayo, *ibid.*, 704 (1967).

(3) (a) On leave from Tohoku University, Sendai, Japan; (b) Department of Chemistry, University of Guelph, Ontario, Canada.

(4) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).

(5) At that time no consideration was given to the detailed nature of the photochemical process. Very recently[6] in this and other applications of this type of synthesis, it has been shown that a triplet of the acetylacetone is most probably involved.

(6) H. Nozaki, M. Kurita, T. Mori, and R. Noyori, *Tetrahedron*, **24**, 1821 (1968).