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Further Studies in the Rearrangement of Bis(diphenylphosphino)amines upon Chloramination

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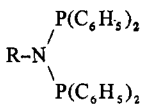
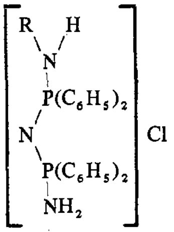
Chloramine reacts with a variety of bis(diphenylphosphino)amines in which the nitrogen atom bridging the two phosphorus atoms is also bonded to an alkyl group. It has been shown in all cases where the substituent is a hydrocarbon or hydrogen that the resulting phosphonium salt is rearranged to a structure in which the alkyl group is bonded to a nitrogen atom that is bound to only one phosphorus atom. Possible mechanisms for the chloramination reaction are discussed.

Synthesis of aminophosphonium chlorides by the chloramination of phosphines and aminophosphines has been well established.[1-3] In a recent publication[4] from this laboratory it was reported that the chloramination of bis(diphenylphosphino)amines results in phosphonium salts with a structure that is rearranged when compared with either previously reported[5,6] chloramination products of P-N-P compounds or the starting material. The parent bis(diphenylphosphino)amine has the structure



in which the bridging nitrogen atom is bonded to an R group as well as to the two phosphorus atoms. The phosphonium salts produced upon chloramination of the bis(diphenylphosphino)amines in which R is H, CH_3, and $C_6H_5CH_2$ have been shown to have the following rearranged structure



in which the R group is bonded to a nitrogen atom that has only one adjacent phosphorus atom.

The present work was undertaken to determine if, as in the three cases previously studied,[4] the chloramination of a wider variety of bis(diphenylphosphino)amines would result in rearranged phosphonium salts. In order to extend this work, it was necessary to synthesize several new bis(diphenylphosphino)amines, and they are described in the Experimental Section.

Experimental Section

Materials. Solvents were distilled and stored over calcium hydride with the exceptions of diethyl ether and the anhydrous ethanol. Diphenylchlorophosphine, obtained from Aldrich Chemical Co., was vacuum distilled (bp 113° (0.14 mm)) and stored under nitrogen.

Analyses. Elemental analyses were obtained compliments of Burroughs-Wellcome Co., Greenville, N. C., and Galbraith Laboratories, Inc., Knoxville, Tenn. The analytical data are recorded in Table I. Ir were recorded on a Perkin-Elmer Model 137 spectrometer and on a Beckman IR-12 spectrometer. Proton nmr spectra were recorded on a Perkin-Elmer R-20 spectrometer using TMS as an internal reference. The ^{31}P spectra of bis(diphenylphosphino)-*n*-butylamine and its chloramination product were obtained at 24.285 MHz using H_3PO_4 as an external reference. Other ^{31}P spectra were obtained by Charles Moreland, University of North Carolina at Raleigh, at 40.5 MHz using P_4O_6 as an internal reference on a Varian HA-100 spectrometer (the nmr data are recorded in Table III). Mass spectra were determined with a Varian-Mat CH4B spectrometer using a direct inlet system. Optical rotations were determined with the use of a Rudolph Model 80 polarimeter.

For the infrared data, Table II, and the mass spectral data, Table III, see paragraph at end of paper regarding supplementary material.

Procedure for Reactions. The aminophosphines reported in this study were synthesized by the reaction of diphenylchlorophosphine and the appropriate amine in the presence of triethylamine as an HCl acceptor. This is a general procedure reported in the literature,[4,5,7] and the following new compounds were synthesized by this method: bis(diphenylphosphino)-*n*-butylamine, bis(diphenylphosphino)-*n*-pentylamine, and bis(diphenylphosphino)-α-methylbenzylamine.

The chloramine generator used in this work is basically the same as those described previously.[8,9] The new phosphonium salts reported

Table I. Analytical Data

Compd	Mp, °C	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
$CH_3(CH_2)_3N[P(C_6H_5)_2]_2$	78–79	76.18	75.82	6.2	6.4	3.17	3.15
$CH_3(CH_2)_4N[P(C_6H_5)_2]_2$	95–97	76.46	76.52	6.86	6.88	3.08	2.93
$C_6H_5CH(CH_3)N[P(C_6H_5)_2]_2$	151–154	78.53	78.80	5.97	5.97	2.86	2.64
(+)-$C_6H_5CH(CH_3)N[P(C_6H_5)_2]_2$	116–117	78.53	78.39	5.97	6.06	2.86	2.90
$[CH_3(CH_2)_2NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$	206–208	65.70	66.03	6.11	6.25	8.51	8.48
$[CH_3(CH_2)_3NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$	173–175	66.20	66.04	6.35	6.35	8.27	8.17
$[CH_3(CH_2)_4NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$	179–181	66.66	66.62	6.54	6.53	7.97	8.05
$[C_6H_5CH(CH_3)NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$	167–168	69.10	69.07	5.80	5.81	7.56	7.44
(+)$[C_6H_5CH(CH_3)NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$	158–162	69.10	67.95	5.80	5.78	7.56	7.97

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(1) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, 81, 2982 (1959).

(2) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, 3, 617 (1964).

(3) S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *Inorg. Chem.*, 6, 515 (1967).

(4) D. F. Clemens, M. L. Caspar, D. Rosenthal, and R. Peluso, *Inorg. Chem.*, 9, 960 (1970).

(5) D. F. Clemens and H. H. Sisler, *Inorg. Chem.*, 4, 1222 (1965).

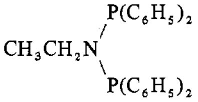
(6) R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *Inorg. Chem.*, 2, 753 (1963).

(7) G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.*, 1543 (1954).

(8) R. Mattair and H. H. Sisler, *J. Amer. Chem. Soc.*, 73, 1619 (1951).

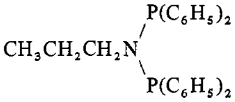
(9) H. H. Sisler, F. T. Neth, R. S. Drago, and D. Yancy, *J. Amer. Chem. Soc.*, 76, 3906 (1954).

Table IV. Mass Spectral Data



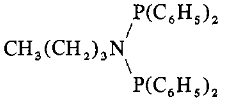
$CH_3CH_2N\begin{matrix}/P(C_6H_5)_2\\ \backslash P(C_6H_5)_2\end{matrix}$

Mass	Relative intensity	Mass	Relative intensity
413	35.6	108	30.1
384	69.4	105	5.4
304	5.4	93	12.1
302	4.9	85	12.7
263	19.8	83	4.9
262	90.8	79	13.4
229	6.7	78	44.3
228	30.5		
201	5.4		
200	6.1		
186	35.1		
184	100.0		
181	5.4		
171	4.2		
152	10.4		
142	4.3		
134	4.8		
123	30.8		
119	4.3		
118	7.8		
116	6.7		
110	77.6		
109	42.5		



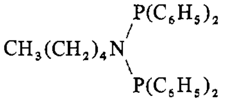
$CH_3CH_2CH_2N\begin{matrix}/P(C_6H_5)_2\\ \backslash P(C_6H_5)_2\end{matrix}$

Mass	Relative intensity	Mass	Relative intensity
427	60.0	185	49.8
412	6.1	184	19.1
384	96.7	183	100.0
346	4.4	181	7.3
345	4.4	170	5.2
318	6.1	153	11.2
308	4.4	123	11.1
307	6.7	109	23.4
305	9.1	108	29.3
263	4.1	107	17.7
262	10.5	93	5.3
242	5.9	78	12.0
241	23.4	77	19.2
229	4.4		
227	4.7		
213	4.4		
211	3.8		
210	19.6		
201	8.8		
200	16.8		
199	5.3		
186	10.3		



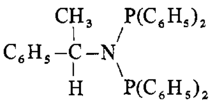
$CH_3(CH_2)_3N\begin{matrix}/P(C_6H_5)_2\\ \backslash P(C_6H_5)_2\end{matrix}$

Mass	Relative intensity	Mass	Relative intensity
441	55.2	200	3.6
384	94.0	199	2.5
362	2.4	186	5.2
334	3.9	185	52.3
330	6.1	184	16.7
307	3.3	183	98.4
306	7.5	181	7.0
305	2.7	170	4.6
304	7.6	152	8.7
290	2.2	142	3.3
262	22.4	134	3.7
261	100.0	112	9.7
256	3.6	110	16.6
255	11.9	109	26.9
228	3.1	108	11.5
216	4.5	93	5.9
215	23.9	78	7.8
214	3.1		
202	2.4		
201	3.6		



$CH_3(CH_2)_4N\begin{matrix}/P(C_6H_5)_2\\ \backslash P(C_6H_5)_2\end{matrix}$

Mass	Relative intensity	Mass	Relative intensity
455	54.0	184	13.1
440	4.9	183	88.5
384	100.0	172	3.9
345	5.1	153	7.9
326	2.6	142	3.3
308	3.8	122	8.2
307	7.7	110	14.7
306	3.3	109	24.6
305	7.5	108	9.0
270	3.3	93	4.7
269	7.9	85	3.3
262	9.4	78	3.4
215	3.6	77	7.1
214	19.8		
202	3.1		
201	4.6		
200	5.6		
199	3.1		
186	11.5		
185	51.5		



$\begin{matrix} & CH_3 & \\ C_6H_5- & C & -N\begin{matrix}/P(C_6H_5)_2\\ \backslash P(C_6H_5)_2\end{matrix} \\ & H & \end{matrix}$

Mass	Relative intensity	Mass	Relative intensity	Mass	Relative intensity	Mass	Relative intensity
489	0.9	228	1.8	171	1.4	106	9.5
421	1.0	218	1.1	153	1.2	105	2.8
398	1.0	202	2.1	152	3.7	104	2.0
384	100.0	201	4.0	141	1.4	94	1.7
304	1.0	200	6.5	133	1.0	93	19.9
303	1.8	199	6.5	123	7.0	92	2.8
302	5.9	198	1.0	121	1.8	91	2.3
301	4.3	187	3.2	110	2.7	90	1.5
263	1.2	186	16.7	109	5.9	80	3.1
262	5.3	185	4.5	108	4.0	79	2.9
261	1.2	184	28.8	107	4.4	78	7.7
		182	1.9				

Table IV. (*Continued*)

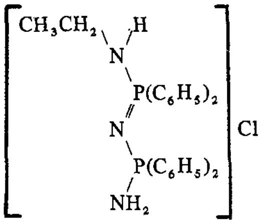
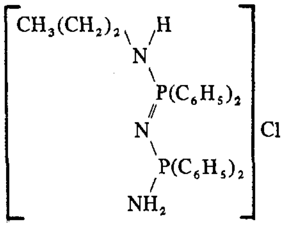
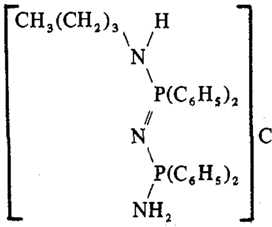
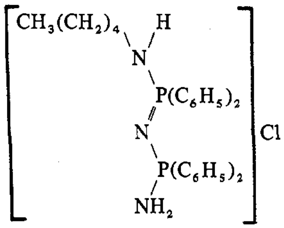
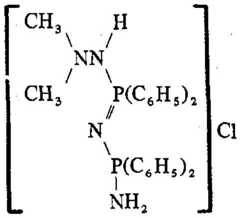
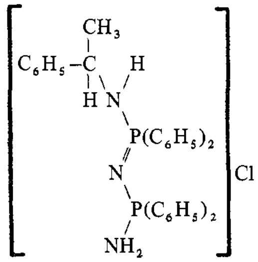
Mass	Relative intensity	Mass	Relative intensity	Mass	Relative intensity	Mass	Relative intensity
							
443	27.6	245	14.9	459	1.6	245	0.5
428	35.0	201	30.0	458	1.9	202	0.3
414	26.2	200	74.4	442	.04	201	0.7
400	100.0	199	75.0	428	6.9	200	2.2
387	15.0	198	41.7	414	4.5	199	0.4
367	16.7			400	100.0	198	0.6
338	40.0			379	0.6	192	0.2
324	41.5			364	0.2	185	0.9
323	68.3			339	0.3	184	0.3
308	18.4			337	0.5	183	1.6
306	11.7			323	4.3	162	0.5
277	14.9			308	0.3	125	0.7
262	23.4			306	0.2	123	1.5
247	11.7			277	0.2	78	0.6
246	13.4			263	0.5		
							
507	2.4	261	3.5	521	1.5	200	4.0
473	16.5	245	5.6	485	9.1	186	3.6
471	14.1	201	10.6	470	4.0	185	15.0
456	2.4	200	40.1	456	4.1	184	6.0
442	5.3	199	5.9	442	5.6	183	28.3
428	41.2	198	9.4	428	32.3	162	15.1
414	16.5	192	7.3	414	13.6	153	3.0
400	100.0	185	14.1	400	100.0	152	3.5
395	5.8	183	23.4	393	2.0	125	1.8
386	2.4	161	18.8	384	1.8	124	2.6
380	2.4	152	2.6	366	2.5	123	3.1
365	1.4	151	2.7	339	4.6	110	4.1
339	7.0	150	3.5	338	7.1	109	5.6
338	7.1	119	3.5	324	70.0	108	11.7
323	71.2	114	15.3	308	4.1	95	2.0
308	4.1	112	30.8	306	2.8	93	1.5
306	2.4	105	3.6	277	4.6	91	1.8
277	3.9	103	4.4	263	9.5	78	5.8
263	7.6	102	3.4	247	2.5	77	7.3
262	4.1	77	12.9	246	2.3	46	3.8
				245	7.8		
							
460	37.0	385	5.5	277	9.3	184	24.0
459	72.2	339	18.4	263	12.7	124	14.8
415	18.4	338	38.3	245	10.9	122	38.8
414	94.0	324	28.8	201	12.7	78	5.6
413	94.2	323	100.0	200	25.1	77	13.0
400	94.4	321	5.6	199	11.1		
399	38.2	308	3.7	198	16.7		
386	7.4	306	5.6	186	11.1		

Table IV. (*Continued*)



Mass	Relative intensity	Mass	Relative intensity	Mass	Relative intensity	Mass	Relative intensity
527	36.0	384	12.7	201	34.4	111	16.9
521	42.4	339	14.4	200	91.2	110	31.4
505	39.0	338	14.4	199	27.8	109	39.7
493	12.7	324	23.8	198	42.1	108	187.3
486	15.3	323	81.1	186	41.0	107	76.4
455	21.2	321	23.8	185	15.5	106	71.3
445	22.1	308	9.6	184	74.7	105	31.4
429	12.7	306	14.2	162	17.4	80	127.4
428	15.2	278	18.5	126	74.7	79	110.5
414	22.8	264	22.8	125	21.8	78	201.6
400	100.0[a]	245	15.5	124	140.3		
392	11.7	202	12.3	122	2.5		

[a] Peak *m/e* 400 is more intense than any other peak of *m/e* greater than 124 and is taken as the base peak.

Table V. Nmr τ Values for NCH Protons in Aminophosphines and Phosphonium Salts

Compd	τ of phosphine	τ of phosphonium salt
$[(CH_3)_2N]_3P$	7.57[a]	7.11[b]
$[(CH_3)_2N]_2PCH_3$	7.37[a]	7.16[b]
$[(CH_3)N]P(CH_3)_2$	7.53[a]	7.08[b]
$[(C_7H_5)_2N]_3P$	7.25[c]	6.68[c]
$[(C_2H_5)NH]P(C_4H_9)_2$	7.34[d]	6.85[d]
$[(CH_3)_2N]_2PC_6H_5$	7.70[b]	7.15[b]
$[(CH_3)_2N]P(C_6H_5)_2$	7.97[b]	7.05[b]
$CH_3N[P(C_6H_5)_2]_2$	7.70[d]	7.60[d]
$CH_3CH_2N[P(C_6H_5)_2]_2$	6.79[d]	7.29[d]
$CH_3(CH_2)_2N[P(C_6H_5)_2]_2$	6.77	7.51
$CH_3(CH_2)_3N[P(C_6H_5)_2]_2$	6.80	7.52
$CH_3(CH_2)_4N[P(C_6H_5)_2]_2$	6.81	7.47
$C_6H_5C(H)CH_3N[P(C_6H_5)_2]_2$	5.28	6.15

[a] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964). [b] Reference 3. [c] Reference 2. [d] Reference 11.

in this study are: $[CH_3(CH_2)_2NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, $[CH_3(CH_2)_3NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, $[CH_3(CH_2)_4NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, and $[C_6H_5CH(CH_3)NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$.

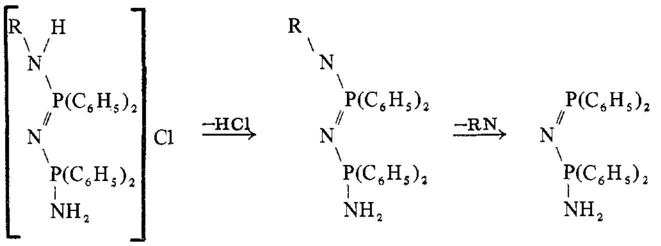
Results and Discussion

The mass spectra of the bis(diphenylphosphino)amines all showed peaks corresponding to the molecular weight of the parent ion as well as a fragment at *m/e* 384 corresponding to $N[P(C_6H_5)_2]_2$. Other peaks were observed at *m/e* 307 corresponding to $P(C_6H_5)_2NP(C_6H_5)$, *m/e* 262 corresponding to $P(C_6H_5)_3$, *m/e* 200 corresponding to $HNP(C_6H_5)_2$, *m/e* 199 corresponding to $NP(C_6H_5)_2$, *m/e* 185 corresponding to $P(C_6H_4)_2$, and *m/e* 108 corresponding to PC_6H_5.

The *m/e* 384 peak is one of the more intense peaks and represents the fragment obtained from the loss of the hydrocarbon group attached to nitrogen. There are some peaks in most compounds of this nature that can only be accounted for by considering fragments coming together with the formation of a new bond. An example of this is the peak at *m/e* 262 corresponding to triphenylphosphine, $(C_6H_5)_3P$.

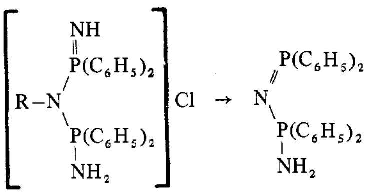
An indication of phosphonium salt formation is the ^{31}P nmr signal for the chloramination products which is observed as two peaks about 3 ppm apart at around −20 ppm from H_3PO_4 as opposed to a single peak around −60 ppm for the parent aminophosphines. Such an upfield shift is consistent with quaternization of the phosphorus atom.[3]

Although the mass spectra of the chloramination products showed no more than a very weak peak for the parent ions, all mass spectra showed significant peaks corresponding to the species M − HCl (molecular ion minus hydrogen chloride). In addition, each showed a peak of greatest intensity for the key fragment *m/e* 400 corresponding to $C_{24}H_{22}P_2N_2$ (calcd, 400.126), except the phosphonium salt of bis(diphenylphosphino)-α-methylbenzylamine for which the *m/e* 400 peak was more intense than any other of mass greater than *m/e* 124. This composition corresponds to the loss of RN from a M − HCl fragment as shown with the following rearranged model



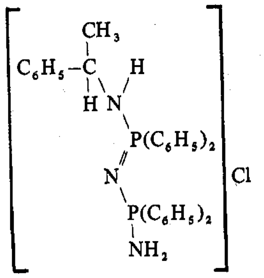
Such an origin for the *m/e* 400 peak has been justified by metastable analyses[4] which indicate that the *m/e* 400 peaks for the chloramination products of bis(diphenylphosphino)methylamine and bis(diphenylphosphino)benzylamine are the daughters of the M − HCl peaks.

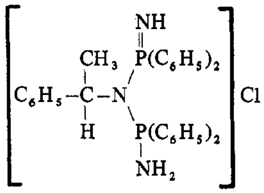
In order for the unrearranged structure to give the *m/e* 400 peak, the expected fragmentation patterns would be the separate



losses of a nitrogen and an R group from M − HCl or the separate losses of an NH and an R group from M − Cl. This fragmentation is unlikely because it would require cleavage of an N=P double bond in preference to an N–P single bond.

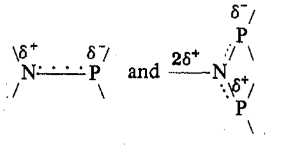
Nmr evidence for rearrangement was difficult to obtain in the cases of the bis(diphenylphosphino)alkylamines because the splitting of the methylene protons adjacent to nitrogen is very complex. However, for the chloramination product of bis(diphenylphosphino)-α-methylbenzylamine, the α proton was seen as a broad hump in the base line, resulting from coupling with the three α-methyl protons, the hydrogen attached to nitrogen, and the phosphorus atom bound to nitrogen. However, when D_2O was added to a deuteriochloroform solution of this sample, the spectrum displayed the α proton as a multiplet which resembled a rough quartet. This change in the α-proton peak must be indicative of rearrangement, for if the molecule were unrearranged as shown below, then the α proton would couple with the α-methyl protons and with the phosphorus atoms. Thus, replacement of the nitrogen protons with deuterons five atoms away would not change the α-proton peak.



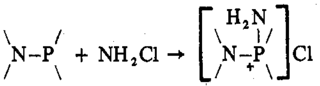


A study of the structures and the nmr absorptions of the protons on the carbon bonded to the nitrogen atoms of the starting bis(diphenylphosphino)amines and their chloramination products reported herein compared with those for a number of aminophosphines in the literature further indicates rearrangement. See Table V.

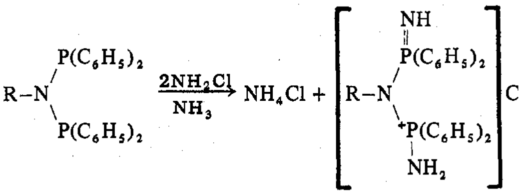
First it must be noted that, as a group, the NCH protons for the bis(diphenylphosphino)amines are found at about τ 6.8. In particular they are downfield from the starting aminophosphines containing only one P atom. This may be explained with the use of two models where some double bonding takes place between the nitrogen and the phosphorus atoms. Presumably there is pπ–dπ bonding between a filled nitrogen 2p orbital and an empty phosphorus 3d orbital.[10-12] In this case the nitrogen would donate more of its electron density to two phosphorus atoms than to one.[13] The greater the electron donation to phosphorus the greater the δ+ on nitrogen, and the greater the δ+ on the nitrogen the more electronegative the nitrogen becomes. It is well known that electron withdrawal effects play a dominant role in the chemical shifts of protons on adjacent atoms.[3,14] Thus, the downfield shift in the NCH protons of the bis(diphenylphosphino)amines compared with aminophosphines containing only one phosphorus is expected.



It may also be seen that when the aminophosphines containing only one phosphorus bound to nitrogen are chloraminated the NCH protons are generally shifted downfield. As in the preceding case, this shift is caused by a reduction in electron density around the nitrogen atom. However, in this case the phosphorus atom has acquired a positive charge through the formation of the phosphonium salt.

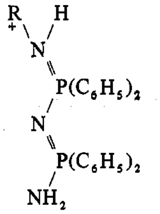


Thus, the NCH peak would be predicted to fall downfield as observed. Finally, consider the chloramination products of the bis(diphenylphosphino)amines. If these phosphonium salts possessed the structure originally proposed, then the NCH protons would be expected to be shifted downfield from those of the parent compounds. This would be analogous to the preceding case, since the nitrogen would be bonded to a positively charged phosphorus atom.

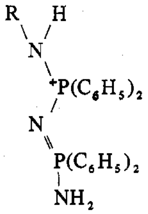


Based on this model, a downfield shift of the NCH protons would be expected. Such was not observed. In fact, there was a general upfield shift as shown in the preceding table.

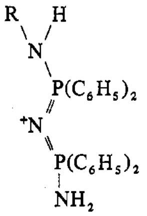
Such a shift can, however, be explained in terms of the rearranged structure. Here the NCH group is bonded to only one phosphorus atom. The following five resonance forms which are drawn without phenyl interactions indicate that the positive charge need not reside primarily in the proximity of the NCH group.



1



2



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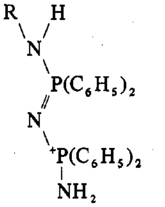

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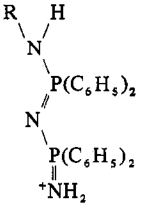

5

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(10) A. H. Cowley and R. P. Pinell, *J. Amer. Chem. Soc.*, 87, 4454 (1965).

(11) A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, 80, 1107 (1958).

(12) R. M. Kren and H. H. Sisler, *Inorg. Chem.*, 9, 836 (1970).

(13) G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 3984 (1962).

(14) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, 34, 1099 (1961).

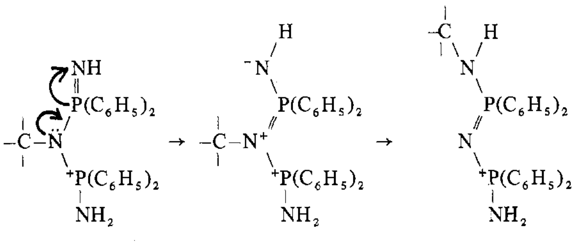
Of the five resonance structures shown, the first would be expected to shift the NCH proton downfield because the nitrogen is positively charged. The chloramination products of the aminophosphines containing only one phosphorus bonded to nitrogen generally show NCH peaks at about the same τ values as the parent bis(diphenylphosphino)amines. Thus, the second form would not be expected to show a substantial downfield shift from its parent aminophosphine. For structures **3**, **4**, and **5**, it is expected that the NCH nitrogen is less electronegative than in the parent bis(diphenylphosphino)-amine.

Two points are made with this comparison of data. First, the fact that there is not a downfield shift in the NCH absorption with the chloramination of bis(diphenylphosphino)-amines serves as evidence that the unrearranged structure of these salts is invalid. Second, the upfield NCH shifts upon formation of the phosphonium salts may be explained and perhaps expected.

In order to propose possible pathways for the rearrangement to occur, it is assumed that the originally proposed structure is formed as an intermediate and that the atoms in this structure are reordered in such a manner that the rearranged structure is obtained. Manipulation of models of the unrearranged chloramination products of these bis(diphenylphosphino)amines suggests two pathways by which the rearrangement might occur. Despite the difficulty in rotating the phosphorus about the P-N bond because of bulky phenyl groups, the imide nitrogen may be brought into close proximity to the first carbon in the R group and to the nonadjacent phosphorus atom by rotation of various bonds within the molecule.

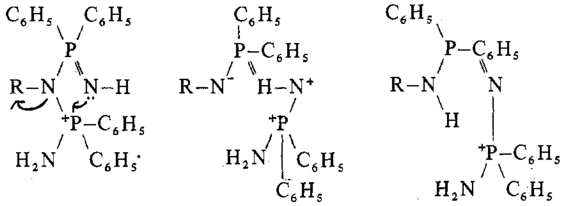
Proximity of the imide nitrogen to the carbon adjacent to the bridging nitrogen implies the possibility of a base-catalyzed Stevens-type rearrangement.[15-18]

The rearrangement observed in our laboratory could be considered a 1,3 shift, and it might occur by the following pathway provided that the excess ammonia present in the chloramination reaction is basic enough to act as catalyst.



Since the normal Stevens rearrangement involves a group migrating from a positively charged nitrogen atom to a nearby carbon atom, and the above rearrangement involves the migration from one nitrogen to another with a different electronic configuration, the above might be referred to as a quasi-Stevens rearrangement.

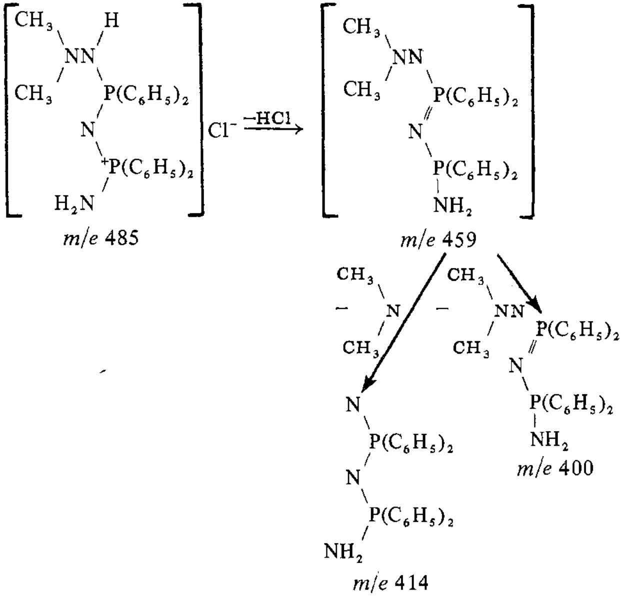
The other rearrangement pathway suggested by the models is an SN2 intramolecular reaction. It would be initiated by an attack of the imide nitrogen atom's free electron pair on the more distant phosphorus atom to produce a four-membered ring or transition state which could react further by the breakage of a P-N bond and the transfer of the imide proton to the amino nitrogen as shown below.



For bis(diphenylphosphino)-D-α-methylbenzylamine, the optical activity is $[\alpha]^{25}$D 143°, and it is $[\alpha]^{24}$D 39° for the phosphonium salt recrystallized once from chloroform-ether. If this rotation is representative of the pure product, then retention of configuration is suggested. Thus, either of the preceding proposed pathways seem reasonable since retention of configuration would be expected for both.

Since the bis(diphenylphosphino)amines have been shown to be rearranged with chloramination, a mass spectral examination of the phosphonium salt of 1,1-bis(diphenylphosphino)-2,2-dimethylhydrazine was carried out to determine whether an analogous rearrangement may occur in a P-N-P compound when the third atom bonded to nitrogen is not carbon. This compound showed no peak of significant intensity for the parent compound. There was, however, a significant M − HCl peak (*m/e* 459; relative intensity, 72.2) as well as a peak corresponding to the subsequent loss of $(CH_3)_2N$ from M − HCl (*m/e* 414; relative intensity, 94.0) and a peak at *m/e* 400 (relative intensity 94.4) corresponding to the ion $P(C_6H_5)_2NP(C_6H_5)_2NH_2$.

The following rearranged structure and decomposition pathway are proposed as being reasonable.



If the chloramination product were unrearranged as shown below, the mass spectrum would be expected to show a very strong peak at 399 resulting from the decomposition pattern shown in Scheme I. Such was not observed.

In summary, it has been shown that chloramine reacts with a variety of bis(diphenylphosphino)amines in which the nitrogen bridging the two phosphorus atoms is also bonded to an R group. It has been shown in all cases where R represents a hydrocarbon or hydrogen that the resulting phosphonium salt is rearranged in such a way that the R group is bonded to a nitrogen atom that is bound to only one phosphorus atom.

Moreover, preliminary evidence indicates that such a rearrangement also takes place when the third atom attached to the bridging nitrogen is another nitrogen atom.

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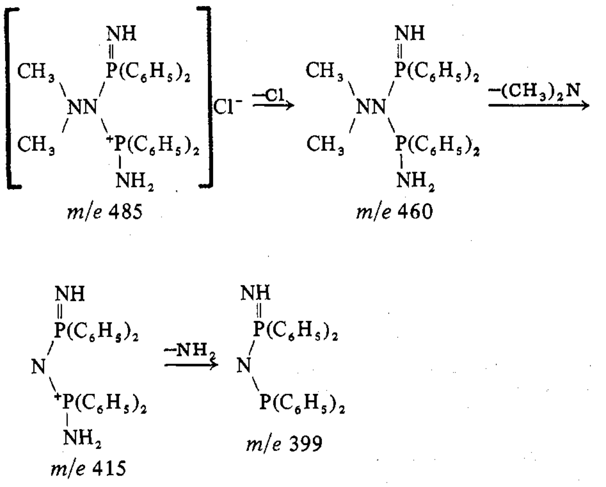
(15) T. S. Stevens, *J. Chem. Soc.*, 2107, (1930).

(16) C. R. Hauser and S. W. Kantor, *J. Amer. Chem. Soc.*, **73**, 1437 (1951).

(17) R. K. Hill and T. H. Chan, *J. Amer. Chem. Soc.*, **88**, 866 (1966).

(18) J. H. Brewster and M. W. Kline, *J. Amer. Chem. Soc.*, **74**, 5179 (1952).

Scheme I



Acknowledgment. The authors wish to express their appreciation to Professor Charles Moreland for his assistance in obtaining some of the ^{31}P nmr data included in this paper.

Supplementary Material Available. The infrared data, Table II, and the mass spectral data, Table III, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-333.

Registry No. $CH_3CH_2N[P(C_6H_5)_2]_2$, 2960-41-0; $CH_3(CH_2)_2N[P(C_6H_5)_2]_2$, 42998-67-4; $CH_3(CH_2)_3N[P(C_6H_5)_2]_2$, 42946-01-0; $CH_3(CH_2)_4N[P(C_6H_5)_2]_2$, 42998-68-5; $C_6H_5CH(CH_3)N[P(C_6H_5)_2]_2$, 42998-69-6; (+)-$C_6H_5CH(CH_3)N[P(C_6H_5)_2]_2$, 42998-70-9; $CH_3CH_2NHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-71-0; $CH_3(CH_2)_2NHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-72-1; $CH_3(CH_2)_3NHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-73-2; $CH_3(CH_2)_4NHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-74-3; $C_6H_5CH(CH_3)NHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-75-4; (+)-$C_6H_5CH(CH_3)NHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-76-5; $(CH_3)_2NNHP(C_6H_5)_2NPCl(C_6H_5)_2NH_2$, 42998-77-6; $[CH_3CH_2NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-78-7; $[CH_3(CH_2)_2NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-79-8; $[CH_3(CH_2)_3NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-80-1; $[CH_3(CH_2)_4NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-81-2; $[C_6H_5CH(CH_3)NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-82-3; (+)-$[C_6H_5CH(CH_3)NHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-83-4; $[(CH_3)_2NNHP(C_6H_5)_2NP(C_6H_5)_2NH_2]Cl$, 42998-84-5.

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Reaction of Oxygen Atoms with Diborane

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The reaction of oxygen atoms with diborane has been studied in a discharge-flow reactor using a time-of-flight mass spectrometer as a detector. When a large excess of atoms is present, the rate constant for the disappearance of diborane is $k_2 = (4.21 \pm 2.7) \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1} at room temperature, with an activation energy of 4.8 ± 0.5 kcal mol^{-1}. Under conditions of excess B_2H_6 the reaction is considerably faster and is chemiluminescent with emission due primarily to the transition $BO(A(^2\pi) \rightarrow X(^2\Sigma), v' \leqslant 5)$. The species H_2O, BH_2O_2, and possibly BH_2O are observed as products or intermediates, and the presence of OH is inferred. The B_2H_6-in-excess data are interpreted in terms of a chain reaction initiated by $O + B_2H_6 \rightarrow BH_3O + BH_3$ and propagated by $BH_3 + O \rightarrow OH + BH_2$; $OH + B_2H_6 \rightarrow H_2O + BH_3 + BH_2$. When O atoms are in excess, B_2H_6 disappearance is controlled by the first reaction above, while O atoms are catalytically removed in the sequence $O + B_2H_6 \rightarrow BH_3 + BH_3O$; $BH_3O + O \rightarrow BH_3 + O_2$; $2BH_3 \rightarrow B_2H_6$.

Introduction

There are several recent reviews of the chemistry of boron compounds,[1-3] but, perhaps surprisingly in view of the early interest in boron compounds as high-efficiency fuels, the oxidation of boron hydrides is not extensively discussed therein. Some early work by Bauer and coworkers[4,5] concerned borane-oxygen mixtures at the explosion limits; the behavior of such mixtures exhibited strong qualitative similarities to H_2-O_2 mixtures. A mechanism for B_2H_6-O_2 explosions was proposed in which the chain-branching steps

$$BH_3 + O_2 \rightarrow BH_3O + O \tag{1}$$

$$O + B_2H_6 \rightarrow BH_3O + BH_3 \tag{2}$$

$$BH_3O + B_2H_6 \rightarrow BH_3 + B_2H_6O \tag{3}$$

are identical with those in the H_2-O_2 reaction[6] if the correspondence $BH_3 \leftrightarrow H$ be made. Although the mechanism accounts for the main features of the explosion limit behavior, no direct observation of the intermediates was reported.

The oxygen-containing compounds $H_2B_2O_3$ and $H_3B_3O_3$ have been observed in the slow oxidation of B_5H_9,[7-9] but these species, although unstable, are not sufficiently reactive to account for the explosive nature of pentaborane-oxygen mixtures. A study of the photooxidation of diborane,[10] initiated by flash photolysis of B_2H_6-O_2 mixtures, resulted in the conclusion that reaction 2 above is not an important step. Other significant results of this flash photolysis experiment were the spectroscopic observation

(1) T. Wartik, Ed., *Advan. Chem. Ser.*, No. 32 (1961).

(2) R. T. Holtzmann, Ed., "Production of Boranes and Related Research," Academic Press, New York, N. Y., 1967.

(3) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967.

(4) W. Roth and W. H. Bauer, "Fifth Symposium on Combustion," Reinhold, New York, N. Y., 1955, p 710.

(5) W. H. Bauer and S. E. Wiberly, *Advan. Chem. Ser.*, No. 32, 115 (1961).

(6) B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," 2nd ed, Academic Press, New York, N. Y., 1961.

(7) E. A. Grimm and R. F. Porter, *Inorg. Chem.*, 8, 731 (1969).

(8) W. V. Brooks, C. C. Costain, and R. F. Porter, *J. Chem. Phys.*, 47, 4186 (1967).

(9) G. H. Lee, W. H. Bauer, and S. E. Wiberly, *J. Phys. Chem.*, 67, 1742 (1963).

(10) M. D. Carabine and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, 296 1 (1967).