

The light source used in all experiments was a General Electric Projection DDB, 115–120 v., 750-w. bulb housed in a standard manual 35-mm. slide projector. A Corning No. 3387 filter and 4 cm. of distilled water in a Pyrex glass cell were used to absorb

radiation below 450 m μ and above 1000 m μ , respectively.

Acknowledgment. We wish to thank Dr. J. R. Leto for suggesting the low-temperature infrared experiments and for helpful discussions.

A Proton Magnetic Resonance Study of Some Dialkylaminophosphorus Derivatives

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Chemical shift and P³¹-H coupling constant data have been obtained for 24 dimethylamino- and diethylamino-substituted phosphorus compounds. The P³¹-H coupling constants of the diethylaminophosphines were also determined by H¹[H¹] double resonance. In general, increasing the covalency of the phosphorus atom by addition of oxygen or sulfur, or replacement of R₂N-groups by halogen atoms, increases the magnitude of J_{P³¹-H} and simultaneously decreases the τ value of the N-methyl or N-methylene protons. Examination of the spectra of three aminophosphine-methiodide adducts has established that it is only the phosphorus atoms that are quaternized. The preparation of three new phosphorus-nitrogen compounds is described.

Introduction

Most of the n.m.r. studies that have been carried out on phosphorus compounds have involved the determination of P³¹ chemical shifts.^{1,2} Although it is possible to determine spin-spin coupling constants from P³¹ n.m.r. spectra,^{1,2} more accurate values can sometimes be obtained from the n.m.r. spectra of other nuclei, particularly when the magnitude of the coupling is small. Recent proton magnetic resonance studies³⁻⁶ of organophosphorus compounds have yielded some useful data on chemical shifts and P³¹-H coupling constants. In some cases⁷⁻¹² the relative signs of the P³¹-H coupling constants have been reported, although these have not been related to the C¹³-H

coupling constant over one chemical bond which is commonly taken as a reference.

Most of the work cited above refers to compounds in which the phosphorus atom is attached to alkyl groups or hydrogen atoms. In this study we report on the effect of inserting a nitrogen atom between the alkyl group and the phosphorus atom. We were also interested in the extent to which nitrogen lone pairs are involved in π -bonding to phosphorus, and the effect of the charge and covalency of the phosphorus atom on the P³¹-H coupling constants and H¹ chemical shifts. The n.m.r. spectra of some of the compounds have been reported previously^{13,14} (see also Tables I and II).

Table I. N.m.r. Data for Dimethylaminophosphines

Compd. no.	Compound	$\tau_{\text{CH}_3(\text{N})}$	$\tau_{\text{CH}_3(\text{P})}$	J_{PNCH}	J_{PCH}
1 ^a	[(CH ₃) ₂ N] ₃ P	7.57	...	8.82	...
2 ^a	[(CH ₃) ₂ N] ₃ P(O)	7.42	...	9.47	...
3 ^a	[(CH ₃) ₂ N] ₃ P(S)	7.40	...	11.01	...
4	[(CH ₃) ₂ N] ₂ PCl	7.35	...	12.33	...
5	[(CH ₃) ₂ N] ₂ -P(O)Cl	7.32	...	12.87	...
6	[(CH ₃) ₂ N] ₂ -P(S)Cl	7.31	...	15.27	...
7 ^a	(CH ₃) ₂ NPCL ₂	7.18	...	13.03	...
8 ^a	(CH ₃) ₂ NP(O)Cl ₂	7.13	...	15.87	...
9 ^a	(CH ₃) ₂ NP(S)-Cl ₂	7.01	...	17.69	...
10 ^a	[(CH ₃) ₂ N] ₂ PCH ₃	7.37	8.86	8.73	7.49
11 ^a	(CH ₃) ₂ NP-(CH ₃) ₂	7.53	9.01	9.77	5.55

^a N.m.r. data reported previously. See ref. 13 for compounds 1, 2, 3, 7, 8, 9; and ref. 14 for compounds 1, 10, 11.

However, since several of these spectra were determined at 25 Mc.p.s. it was decided to rerun the compounds at 60 Mc.p.s. in the hope of measuring the coupling constants more accurately.

Experimental Section

The compounds of general formula (R₂N)₃P, (R₂-N)₂PCL, and R₂NPCL₂ were prepared by treatment of

(13) G. Martin and G. Mavel, *Compt. rend.*, 2095 (1962).

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(2) L. C. D. Groeneweghe, L. Maier, and K. Moedritzer, *J. Phys. Chem.*, 66, 901 (1962).

(3) G. O. Dudek, *J. Chem. Phys.*, 33, 624 (1960).

(4) R. C. Axtmann, W. E. Shuler, and J. H. Eberly, *ibid.*, 31, 850 (1959).

(5) H. David, G. Martin, G. Mavel, and G. Sturtz, *Bull. soc. chim. France*, 1616 (1962), and previous papers in this series.

(6) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 20, 449 (1964).

(7) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, 42, 2282 (1964).

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(10) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *ibid.*, 85, 2665 (1963).

(11) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, 39, 1518 (1963).

(12) P. T. Narasimhan and M. T. Rogers, *ibid.*, 34, 1049 (1961).

Table II. N.m.r. Data For Diethylaminophosphines

Compd. no.	Compound	$\tau_{\text{CH}_3(\text{N})}$	$\tau_{\text{CH}_2(\text{N})}$	J_{PNCH}	J_{HH}
12 ^a	$[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}$	8.99	7.07	8.33	7.07
13	$[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}(\text{O})$	8.94	6.99	9.94	7.05
14	$[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}(\text{S})$	8.91	6.90	11.40	6.98
15	$[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{P}(\text{S})\text{Cl}$	8.90	6.87	11.24	7.05
16	$[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{P}(\text{O})\text{Cl}$	8.88	6.86	13.44	6.97
17	$[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{P}(\text{S})\text{Cl}$	8.85	6.76	14.82	7.07
18	$(\text{C}_2\text{H}_5)_2\text{NPBr}_2$	8.82	6.61	13.85	7.09
19	$(\text{C}_2\text{H}_5)_2\text{NPCl}_2$	8.91	6.71	13.30	7.29
20	$(\text{C}_2\text{H}_5)_2\text{NP}(\text{O})\text{Cl}_2$	8.79	6.67	17.15	7.13
21	$(\text{C}_2\text{H}_5)_2\text{NP}(\text{S})\text{Cl}_2$	8.74	6.47	18.94	7.04

^a N.m.r. data reported previously. See ref. 23.

PCl_3 with the appropriate quantity of secondary amine in ether solution following the procedure of Burg and Slota.¹⁵ The aminophosphine sulfides, $(\text{R}_2\text{N})_x\text{P}(\text{S})\text{Cl}_{3-x}$, were prepared by sulfurization of the corresponding aminophosphines either in petroleum ether or in the absence of a solvent.¹⁶ The aminophosphine oxides, except $[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}(\text{O})$, were prepared from POCl_3 and the appropriate quantity of secondary amine by a very similar procedure to that used in the PCl_3 reactions.¹⁵ $[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}(\text{O})$ was prepared by H_2O_2 oxidation of $[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}$. The methiodide $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot \text{CH}_3\text{I}$ and the aminophosphines $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2$ and $[(\text{CH}_3)_2\text{N}]_2\text{PCH}_3$ were also prepared by previously described procedures.^{15,17} All the above compounds, except the methiodides were purified by vacuum line procedures or by conventional fractional distillation until they yielded satisfactory elemental analyses. All operations, such as sample preparation, purification, or storage, were performed *in vacuo* or under a dry nitrogen atmosphere.

The new compounds prepared in the course of this study are listed.

$(\text{C}_2\text{H}_5)_2\text{NPBr}_2$. Anhydrous $(\text{C}_2\text{H}_5)_2\text{NH}$ (50 g., 0.684 mole) was added dropwise with stirring to 108.6 g. (0.400 mole) of PBr_3 at *ca.* -20° over a period of 1 hr. Toward the end of the reaction the mixture became very viscous. After the addition of the $(\text{C}_2\text{H}_5)_2\text{NH}$ was complete, 100 ml. of anhydrous ether was added dropwise. After standing overnight the orange-yellow ammonium salt was filtered off and washed several times with anhydrous ether. The filtrate and washings were combined, the ether was removed at reduced pressure, and the resulting liquid was fractionally distilled. The fraction boiling at $68-72^\circ$ (4 mm.) was collected, yield 26.8 g. (25.5%). *Anal.* Calcd. for $(\text{C}_2\text{H}_5)_2\text{NPBr}_2$: C, 18.27; H, 3.83; Br, 60.79. Found: C, 18.10; H, 3.89; Br, 60.82.

$[(\text{CH}_3)_2\text{N}]_3\text{P} \cdot \text{CH}_3\text{I}$ and $[(\text{CH}_3)_2\text{N}]_2\text{PCH}_3 \cdot \text{CH}_3\text{I}$. Both methiodides were prepared by adding CH_3I to an ether solution of the appropriate aminophosphine. The precipitated methiodide was isolated on a frit and vacuum dried. *Anal.* Calcd. for $[(\text{CH}_3)_2\text{N}]_3\text{P} \cdot \text{CH}_3\text{I}$: C, 27.55; H, 6.94; I, 41.49. Found: C, 27.44; H, 6.75; I, 41.53. Calcd. for $[(\text{CH}_3)_2\text{N}]_2\text{PCH}_3 \cdot \text{CH}_3\text{I}$: C, 26.07; H, 6.57; I, 45.96. Found: C, 26.02; H, 6.48; I, 46.21.

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

(16) C. Steube and H. P. Lankelma, *ibid.*, **78**, 976 (1956).

(17) E. M. Evleth, L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, **27**, 2192 (1962).

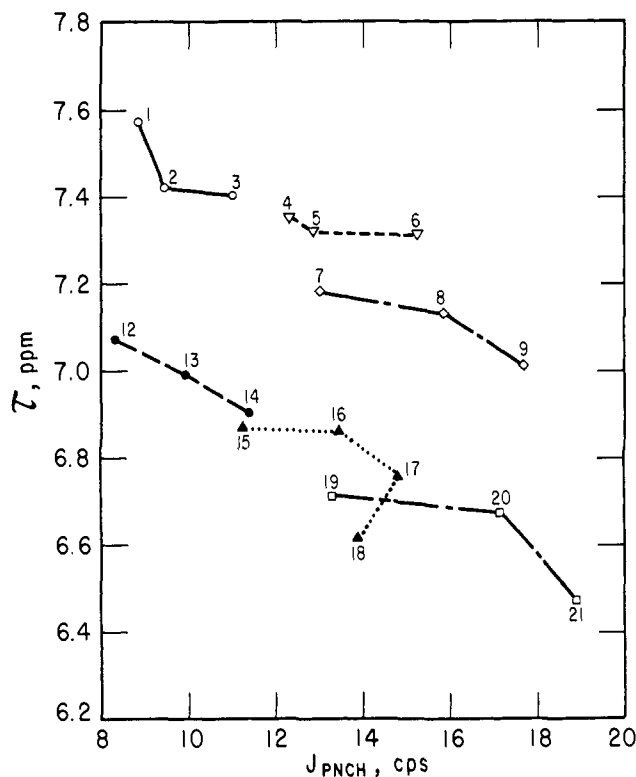


Figure 1. Relationship between the τ values of N-methyl (compounds 1-9) or N-methylene (compounds 12-21) protons and $\text{P}^{31}\text{-H}$ coupling constants of various dialkylaminophosphorus compounds.

Apparatus and Technique. Spectra were taken at 60 Mc.p.s. on a Varian Associates A-60 spectrometer. The methiodides were run as saturated solutions in CH_2Cl_2 with tetramethylsilane internal standard. All other samples were run as neat liquids. The general procedure was to distil the liquid directly into the n.m.r. tube either from a high vacuum system or by conventional fractional vacuum distillation. The n.m.r. tube was sealed off *in vacuo* and the coupling constant data were obtained by running the spectra in the absence of an internal standard. The τ values were determined after opening the n.m.r. tube in a drybox, adding TMS, resealing, and rerunning the spectrum. This procedure did not introduce any perceptible changes in the spectra.

The $\text{H}^1[\text{H}^1]$ double resonance experiments were performed on a Varian Associates A-60 spectrometer equipped with a V-6058 decoupler.

Results and Discussion

From Table I it can be seen that the general trend in the methylamino compounds is that an increase in the covalency of the phosphorus atom by addition of sulfur or oxygen, or replacement of dimethylamino groups by chlorine atoms, increases the magnitude of J_{PNCH} and simultaneously decreases the τ value of the N-methyl protons. As can be seen from Figure 1, the changes in J_{PNCH} and τ are not in general linearly related. A much nearer linear relationship exists between J_{PNCH} and the number of chlorine atoms on the phosphorus atom (Figure 2).

Comparison of $[(\text{CH}_3)_2\text{N}]_3\text{P}$, $[(\text{CH}_3)_2\text{N}]_3\text{P}(\text{O})$, and $[(\text{CH}_3)_2\text{N}]_3\text{P}(\text{S})$ with $(\text{CH}_3)_3\text{P}$, $(\text{CH}_3)_3\text{P}(\text{O})$, and $(\text{CH}_3)_3\text{P}(\text{S})$

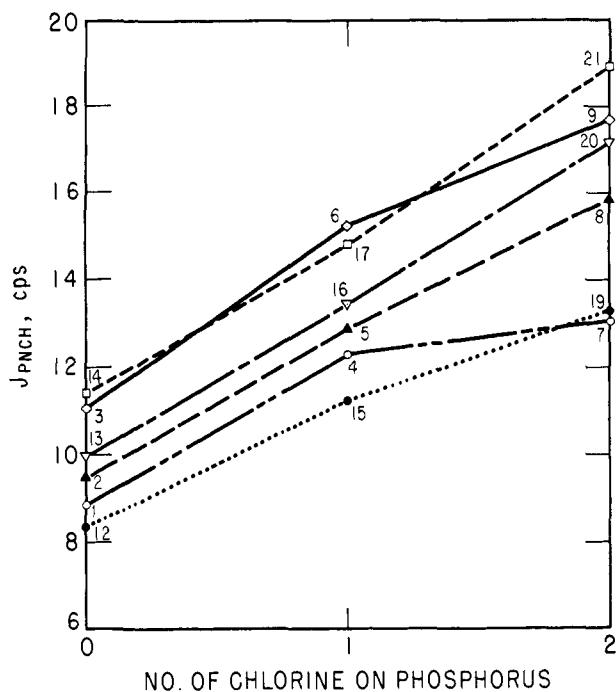
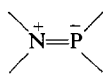


Figure 2. Relationship between P^{31} -H coupling constants and the number of chlorine atoms on the phosphorus atom for various dialkylaminophosphorus compounds.

$P(S)^6$ reveals that insertion of a nitrogen atom has relatively little effect on the magnitude of the P^{31} -H coupling constant. In fact, the P^{31} -H coupling constant is larger for $[(CH_3)_2N]_3P$ than $(CH_3)_3P$.

In the trimethylphosphine series it was found that J_{PCH} increased in the order $(CH_3)_3P < (CH_3)_3P(S) < (CH_3)_3P(O)$. This was explained⁶ on the basis of the per cent s character in the P-C bonds, the idea being that the placing of an electronegative group such as =O or =S on the phosphorus atom diverts s character into the P-C bonds. Since the electronegativity of oxygen is greater than sulfur, the P-C bonds are presumed to have more s character in $(CH_3)_3P(O)$ than $(CH_3)_3P(S)$. Such a simple relationship does not appear to hold for the dimethylaminophosphines, since in each of the three series of compounds studied (*i.e.*, compounds 1, 2, 3; 4, 5, 6; and 7, 8, 9) the P^{31} -H coupling constant increased in the order phosphine < phosphine oxide < phosphine sulfide. In this respect J_{PNCH} of the dimethylaminophosphines behaves more like J_{PCH} of the triethylphosphine series.⁶

The methyl-substituted aminophosphines 10 and 11 are interesting in that the coupling constant over three chemical bonds (J_{PNCH}) is larger than the coupling constant over two chemical bonds (J_{PCH}). One possible explanation for this is that some double bonding takes place between the nitrogen and phosphorus atoms *via* contributions of the type



which presumably involve $P_{\pi}-d_{\pi}$ bonding between a filled nitrogen 2p orbital and an empty phosphorus 3d orbital. Karplus¹⁸ has explained the π -bonded contribution to H^1-H^1 coupling constants in acyclic

(18) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

unsaturated systems as arising from $\sigma-\pi$ configuration interaction. This could also be the case in unsaturated organophosphorus systems since, *e.g.*, the P^{31} -H coupling across $P-C=C-H$ (*trans*)¹¹ is greater than that in the corresponding saturated system.^{6,12} Additional evidence for π -bonding of the above type is our observation (*vide infra*) that only the phosphorus atoms of aminophosphines are sufficiently basic to quaternize.

On the other hand, the effect could be explained without invoking π -bonding. A molecule such as $(CH_3)_2NP(CH_3)_2$ has two types of methyl groups; those attached to nitrogen and those attached to phosphorus. Since the electronegativity of nitrogen (3.0) is greater than that of phosphorus (2.1), the nitrogen atom could divert more s character into the C-H bonds of its methyl groups than could the phosphorus; *i.e.*, the hydrogen atoms on the N-methyl groups will have more s electron density than those of the P-methyl groups. This, in turn, could make J_{PNCH} larger than J_{PCH} because one of the factors governing the magnitude of a coupling constant is the s electron density at the nuclei in question.

The ten diethylamino compounds studied (Table II) had first-order spectra. In all cases the methyl hydrogens appeared as triplets which were well separated from the methylene resonance. In no case was splitting of the methyl triplet observed; hence we have no evidence for "long-range" (*i.e.*, P-N-C-C-H) coupling of the type recently described by Kaplan, Singh, and Zimmer.¹⁹

Table III. N.m.r. Data for Methiodides

Compd. no.	Compound	$\tau_{CH_3(N)}$	$\tau_{CH_3(P)}$	J_{PNCH}	J_{PCH}
22	$[(CH_3)_2N]_3P \cdot CH_3I$	7.20	7.82	10.08	14.09
23	$[(CH_3)_2N]_2PCH_3 \cdot CH_3I$	7.22	7.75	10.30	13.48
24	$(CH_3)_2NP(CH_3)_2 \cdot CH_3I$	7.21	7.76	11.26	13.42

The appearance of the methylene resonance was found to depend upon the magnitude of J_{PNCH} . Three types of methylene resonance could be distinguished: (1) when J_{PNCH} is large (~ 19 c.p.s.), no overlapping of the quartets takes place (Figure 3a); (2) when J_{PNCH} is approximately 13.5 c.p.s., two components of each quartet overlap to give six lines of intensity 1:3:4:4:3:1 (Figure 3b); (3) in all other cases, an intermediate degree of overlapping of the quartets takes place (Figure 3d).

The correctness of these assignments was shown by $H^1[H^1]$ double resonance experiments. In all ten cases (compounds 12-21) irradiation of the methyl resonance caused the methylene resonance to collapse to a doublet (Figure 3c). There was excellent agreement between the J_{PNCH} values measured from the doublet of the double resonance experiments and the values obtained from the separation of the quartets of the undecoupled spectra.

The coupling constants, J_{PNCH} , and τ values of the diethylamino compounds were found to vary in the same general way as in the dimethylamino compounds;

(19) F. Kaplan, G. Singh, and H. Zimmer, *J. Phys. Chem.*, **67**, 2509 (1963).

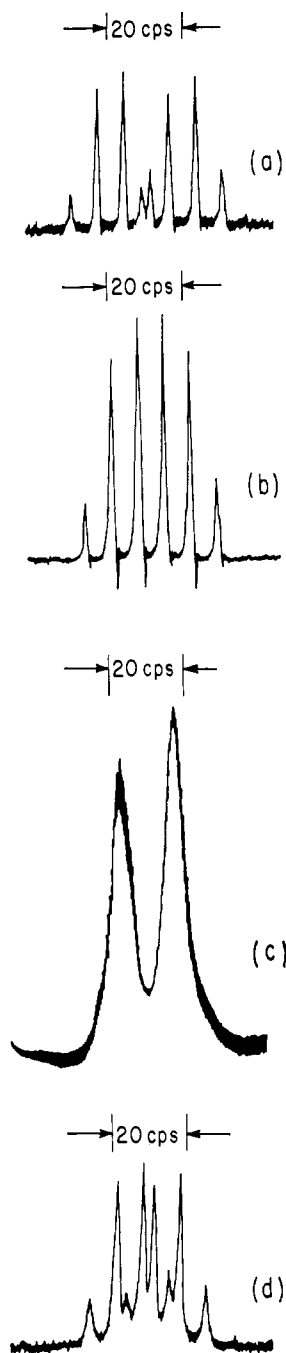


Figure 3. The methylene resonance of (a) $(C_2H_5)_2NP(S)Cl_2$, (b) $(C_2H_5)_2NPBr_2$, (c) $(C_2H_5)_2NPBr_2$ decoupled, and (d) $[(C_2H_5)_2N]_3P(O)$.

i.e., J_{PNCH} increases and the τ values of the CH_2 and CH_3 protons decrease as the covalency of the phosphorus is increased by oxidation or sulfurization, or as $(C_2H_5)_2N-$ groups are replaced by halogen atoms (see Figures 1 and 2). As with the dimethylamino compounds, J_{PNCH} increases in the order phosphine < phosphine oxide < phosphine sulfide.

It is of interest to determine the relative donor properties of the phosphorus and nitrogen atoms in compounds containing P-N linkages. In the adduct $(NH_2)_3P \cdot BH_3$,²⁰ it has been shown by X-ray crystal-

(20) G. Kodama and R. W. Parry, *J. Inorg. Nucl. Chem.*, **17**, 125, (1961).

lography²¹ that P-B bonding takes place. Likewise infrared and chemical evidence have shown that it is the phosphorus atom that coordinates in the adducts $[(CH_3)_2N]_3P \cdot BH_3$ ²² and $(CH_3)_2NP(CH_3)_2 \cdot CH_3I$.¹⁵ Also, Hart and Sisler²³ have shown that it is always the phosphorus atom of aminophosphines that is chloraminated.

The spectra of the methiodide adducts (Figure 4) unequivocally establish that it is only the phosphorus

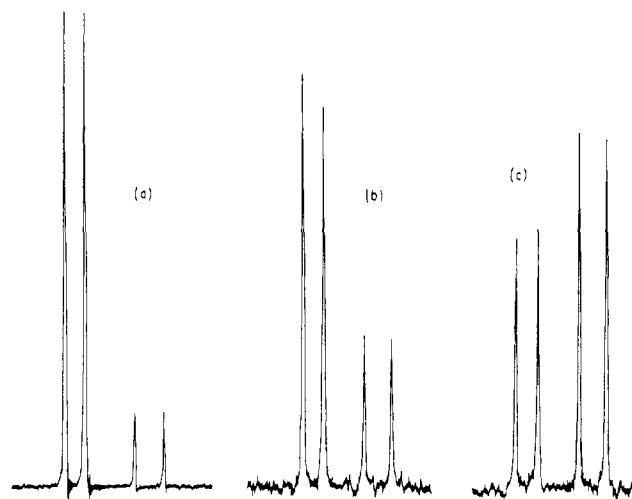


Figure 4. The H^1 n.m.r. spectra of (a) $[(CH_3)_2N]_3P \cdot CH_3I$, (b) $[(CH_3)_2N]_2PCH_3 \cdot CH_3I$, and (c) $(CH_3)_2NP(CH_3)_2 \cdot CH_3I$. The ratios of the areas under the doublets are 6:1 in (a), 2:1 in (b), and 2:3 in (c).

atom which becomes quaternized upon reaction of the aminophosphines with CH_3I . Firstly, more than two doublets would be observed if a nitrogen atom of $[(CH_3)_2N]_2PCH_3 \cdot CH_3I$ or $(CH_3)_2NP(CH_3)_2 \cdot CH_3I$ had been quaternized. Furthermore the 6:1, 2:1, and 2:3 ratios observed for the peak areas of the low- and high-field doublets of compounds **22**, **23**, and **24** can only be interpreted in terms of the CH_3 group being attached to the phosphorus atom. The assignment of the lower-field doublet to the N-methyl group is in agreement with our assignments in the parent aminophosphines (compounds **10** and **11**). As suggested by several authors,^{14,15,23,24} the basicity of the nitrogen is presumably diminished (and that of the phosphorus enhanced) by π -bonding between a filled 2p orbital on the nitrogen atom and a vacant 3d orbital on the phosphorus atom.

Finally it might be noted that when the phosphorus atom bears a positive charge, as in the methiodide adducts, J_{PCH} is larger than J_{PNCH} . As in the case of $(CH_3)_3P$,⁶ quaternization leads to a large increase in the $P^{31}-H$ coupling constant. Again the explanation could be that quaternization results in more s character in the P-C bonds because of a change in bonding from p^3 in aminophosphines to sp^3 in the phosphonium salts.

(21) C. E. Nordman, *Acta Cryst.*, **13**, 535 (1960).

(22) T. Reetz and B. Katlafsky, *J. Am. Chem. Soc.*, **82**, 5036 (1960).

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

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

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ment of most of the spectra. The authors are also very grateful to Dr. J. C. Davis, Jr., for performing the double resonance experiments.

The Stereochemistry of Complex Inorganic Compounds. XXIX.¹ The Base Hydrolysis of the Optically Active α -Dichlorotriethylenetetraminecobalt(III) Cation

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The base hydrolysis of the optically active α -dichlorotriethylenetetraminecobalt(III) ion and α -chloroaquatriethylenetetraminecobalt(III) ion, under certain conditions, leads to a product of inverted configuration, while the same reaction, when carried out in the presence of a silver(I) or mercury(II) ion, proceeds with retention of configuration. The inversion is shown to take place during the second base hydrolysis in the formation of the dihydroxotriethylenetetraminecobalt(III) cation. Several possible mechanisms for the reactions are suggested. The method for assigning the relative configurations of cobalt complexes based on chirality about the C_2 axis is also discussed.

Introduction

The base hydrolysis of optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) ion, under certain conditions, leads to a product of inverted configuration.² This reaction represents the only thoroughly studied optical inversion in transition metal chemistry. In the hope of finding another example of this, and thereby extending our knowledge of the inversion, we have undertaken a study of the base hydrolyses of other cobalt(III) tetramine complexes. This paper gives some results of work done with the optically active α -dichlorotriethylenetetraminecobalt(III) cation.

In general, little synthetic or mechanistic information on cobalt trien³ complexes is available. Perhaps the best known complex of this series is $[\text{Co}(\text{trien})\text{Cl}_2]^+$. The cation can exist in five isomeric forms, two enantiomeric pairs of *cis* isomers, designated α and β , and a *trans* form (Figure 1). The preparation⁴ and partial resolution⁵ of the α form were reported several years ago. However, only recently have the β ⁶ and *trans*⁷ isomers been isolated and characterized. All previous attempts had resulted in the formation of the more

stable α form. The rate of acid hydrolysis of the α ,⁸ β , and *trans* isomers as well as the stereochemical pathway⁴ of their reactions have been determined.⁹ No similar study has been made of the base hydrolysis of these materials. However, it has been observed that the treatment of $\text{D}^*\text{-}\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ with hydroxide ion gives a product with a negative rotation, αD .¹⁰

Results

In a previous publication,² the configuration of $\text{D}^*\text{-cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ was designated as Λ on the basis of its relationship to $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$. The latter ion was assigned this configuration by examining the chirality about its C_3 axis; *i.e.*, the chelate rings form a left-handed system.¹¹ However, if the ion is viewed along one of the C_2 axes it is seen that the chelate rings form a right-handed system. Using a previous notation this is the D^* configuration.¹² There are a number of advantages inherent in choosing the C_2 (D^*) instead of the C_3 (Λ) as the axis of chirality: (1) historically, this isomer has been designated *d* or *D* and this notation is still used in much of the present literature; (2) D^* corresponds to the positive (dextro) specific rotation, $[\alpha]_{\text{D}}$, and a positive "Cotton effect" in the optical rotatory dispersion (O.R.D.) curve for the first cobalt(III) band; (3) this scheme can be used for ions that do not possess a C_3 axis but do have a C_2 axis. The latter point is important when considering *cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+, $\alpha\text{-}[\text{Co}(\text{trien})\text{Cl}_2]^+$, and related ions.¹³*

Recent rotatory dispersion and circular dichroism studies¹⁴ indicate that the D^* isomers of α - or β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ possess the same configuration as $\text{D}^*\text{-cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$. Spectroscopic and stereochemical considerations also show that the O.R.D. curve of the α isomer has a negative "Cotton effect" at long wave length, while the β isomer does not.¹⁴ The shapes of

(1) Paper XXVIII: E. Kyuno, L. J. Boucher, J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **86**, 3656 (1964).

(2) For a discussion see ref. 1 and the references cited therein.

(3) Trien represents triethylenetetramine.

(4) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

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