221. ^{1}H nmr (neat, external TMS): δ 6.93 (s, area 5, C_6H_5), δ 3.79 (d, area 2, J_{PH} = 18 Hz, $C_6H_5CH_2$); ^{19}F nmr (neat, external $CFCl_3$): δ 24.1 (d, J_{PF} = 1215 Hz, of triplets, J_{HF} = 1 Hz); ^{31}P nmr (neat): δ −93.6 (t, J_{FP} = 1215 Hz, of triplets, J_{HP} = 18 Hz).

$C_6H_{10}(SPSF_2)_2$.—A mixture of cyclohexene, 6.0 g (0.073 mol), and $(F_2PS_2)_2$, 17.2 g (0.065 mol), was heated for 4.5 hr at 83°. The mixture was distilled under nitrogen at 6 mm using a 12-in. spinning-band column. A fraction, bp 69–114° (6 mm), weighing 8.1 g was redistilled and the product was collected at 104° (0.55 mm). A small amount of higher boiling impurity present in the distillate was removed by evaporation of the product under higher vacuum (~0.1 μ) in a molecular still heated to 120°. *Anal.* Calcd for $C_6H_{10}F_4P_2S_4$: C, 20.7; H, 2.9; F, 21.8; P, 17.8; S, 36.8. Found: C, 20.9; H, 3.0; F, 22.0; P, 18.2; S, 37.3. Ir (liquid film, 1010–680 cm^{-1}): 1002, 983, 900 (s), 870 (s), 745 (sh), 735 (s), 720 (s), 704 cm^{-1} (s); ^{1}H nmr: δ 3.82 (complex d, area 2, J_{PH} = *ca.* 18 Hz), δ 3.4–1.8 (multiplet, area 8); ^{19}F nmr (CH_2Cl_2): δ 23.2 (d, J_{PF} = 1208 Hz); ^{31}P nmr (neat): δ −92.1 (t, J_{FP} = 1211 Hz, of doublets, J_{HP} = 18 Hz).

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A Study of the Relative Reactivity of Phosphines and Amines toward Chloramines and Methyl Iodide

BY R. M. KREN AND HARRY H. SISLER

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The relative extent of formation of substituted ammonium and phosphonium salts during the competitive reactions of some *t*-alkylamines and -phosphines with NH_2Cl, CH_3I, and $N(CH_3)_2Cl$ in solution was determined using nuclear magnetic resonance spectroscopy. The relative reactivities of pairs of nucleophiles are explained on the basis of p_π–d_π bonding and steric factors.

Introduction

The syntheses of aminophosphonium chlorides by the chloramination of phosphines,[1,2] (dimethylamino)-phosphonium chlorides by the reaction of phosphines with dimethylchloramine,[3] and 1,1,1-trisubstituted hydrazinium chlorides by the chloramination of trialkylamines[4] are well established. In view of these similar reactions of group V electron-donor compounds with chloramines, it is of interest to find out which of the amines and phosphines react preferentially with chloramines and to try to correlate these reactivities with factors known to affect nucleophilic character[5–7] and bond strength in P–N compounds.[8,9] A comparison of the relative reactivities of amines and phosphines toward the electrophile methyl iodide is also of interest because of differences in electronic structure between methyl iodide and the chloramines.

Experimental Section

Reactants and Their Manipulation.—Trimethylphosphine and triethylphosphine were obtained from K & K Laboratories and checked for purity by nmr spectroscopy.[10] Tributylphosphine was obtained from Carlisle Chemical Works and distilled (bp 125–126° (20 mm); lit.[11] bp 149.5° (50 mm)) prior to use. The infrared spectra of the samples of the above phosphines used showed no P–O stretch[12] in the region 1300–1140 cm^{-1}. Dimethylaminodimethylphosphine was prepared as reported previously.[9] Dibutylaminodibutylphosphine was prepared by the reaction of dibutylchlorophosphine with dibutylamine, bp 114–116° (0.5 mm). *Anal.* Calcd for $(C_4H_9)_2NP(C_4H_9)_2$: C, 70.28; H, 13.27; P, 11.33; N, 5.12. Found: C, 70.16; H, 13.45; P, 11.59; N, 5.32. Chloramine was prepared by the method of Sisler and Mattair,[13] and dimethylchloramine was made by the method of Berg.[14] All solvents were dried over calcium hydride or Linde Molecular Sieve 4A and checked for purity by nmr spectroscopy prior to use.

All transfers and weighing operations involving nonvolatile and air- and moisture-sensitive materials were performed in an inert-atmosphere box (Vacuum Atmospheres Corp. Dri-Train HE-93B) filled with dry nitrogen.

Reaction Procedure and Product Characterization.—Two competing nucleophilic compounds were weighed into a reaction vessel in the drybox. The closed vessel was clamped onto the vacuum line and thoroughly stirred. It was subsequently frozen with liquid nitrogen and degassed. The electrophile (chloramine, dimethylchloramine, or methyl iodide in known amount) for which the nucleophiles were competing was placed in a vessel clamped to the vacuum line and transferred to the reaction vessel by standard vacuum techniques. The mole ratios employed were nucleophile(1):nucleophile(2):electrophile = 1.0:1.0:0.9; typically, 10.0 mmol of each of the two nucleophiles were employed in competition for 9.0 mmol of one of the electrophiles. Ten milliliters of solvent (chloroform, diethyl ether, acetone, or acetonitrile) was used for each 5 ml of nucleophile taken. The reaction flask was allowed to warm to room temperature while stirring was maintained using a stir bar and a magnetic stirrer. The

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TABLE I

COMPETITION OF NUCLEOPHILES FOR NH_2Cl, $N(CH_3)_2Cl$, AND CH_3I

Competing nucleophiles	Solvent	Products (mol %)
	NH_2Cl Electrophile	
$P(CH_3)_3$, $N(CH_3)_3$	Diethyl ether	$[P(CH_3)_3NH_2]Cl$ (100)
	Acetonitrile	$[P(CH_3)_3NH_2]Cl$ (100)
$P(C_2H_5)_3$, $N(C_2H_5)_3$	Diethyl ether	$[P(C_2H_5)_3NH_2]Cl$ (100)
	Acetonitrile-d_3	$[P(C_2H_5)_3NH_2]Cl_2$ (100)
$P(n\text{-}C_4H_9)_3$, $N(n\text{-}C_4H_9)_3$	Diethyl ether	$[P(n\text{-}C_4H_9)_3NH_2]Cl$ (100)
	Acetonitrile	$[P(n\text{-}C_4H_9)_2NH_2]Cl$ (100)
$(CH_3)_2NP(CH_3)_2$, $N(CH_3)_3$	Diethyl ether	$[(CH_3)_2NP(NH_2)(CH_3)_2]Cl$ (100)
$P(CH_3)_3$, $(CH_3)_2NP(CH_3)_2$	Diethyl ether	$[P(CH_3)_3NH_2]Cl$ (58), $[(CH_3)_2NP(NH_2)(CH_3)_2]Cl$ (42)
	Chloroform	$[P(CH_3)_3NH_2]Cl$ (60), $[(CH_3)_2NP(NH_2)(CH_3)_2]Cl$ (40)
$P(CH_3)_3$, $P(C_2H_5)_3$	Diethyl ether	$[P(CH_3)_3NH_2]Cl$ (100)
	Chloroform	$[P(CH_3)_3NH_2]Cl$ (100)
$P(CH_3)_3$, $P(n\text{-}C_4H_9)_3$	Diethyl ether (0.2 *M* soln)[a]	$[P(n\text{-}C_4H_9)_3NH_2]Cl$ (100)
	Diethyl ether (0.1 *M* soln)[a]	$[P(n\text{-}C_4H_9)_3NH_2]Cl$ (90), $[P(CH_3)_3NH_2]Cl$ (10)
	Chloroform	$[P(n\text{-}C_4H_9)_3NH_2]Cl$ (90), $[P(CH_3)_3NH_2]Cl$ (10)
$N(CH_3)_3$, $N(C_2H_5)_3$	Diethyl ether	$[N(CH_3)_3NH_2]Cl$ (100)
	Acetonitrile	$[N(CH_3)_3NH_2]Cl$ (100)
	$N(CH_3)_2Cl$ Electrophile	
$P(n\text{-}C_4H_9)_3$, $(n\text{-}C_4H_9)_2NP(n\text{-}C_4H_9)_2$	Diethyl ether	$[P(n\text{-}C_4H_9)_3N(CH_3)_2]Cl$ (100)
$P(CH_3)$, $P(n\text{-}C_4H_9)_3$	Diethyl ether	$[P(n\text{-}C_4H_9)_3N(CH_3)_2]Cl$ (90), $[P(CH_3)_3N(CH_3)_2]Cl$ (10)
	CH_3I Electrophile	
$P(CH_3)_3$, $N(CH_3)_3$	Diethyl ether	$[P(CH_3)_4]I$ (90), $[N(CH_3)_4]I$ (10)
	Acetone	$[P(CH_3)_4]I$ (82), $[N(CH_3)_4]I$ (18)
$P(C_2H_5)_3$, $N(C_2H_5)_3$	Diethyl ether	$[P(C_2H_5)_3CH_3]I$ (100)
	Acetone-d_6	$[P(C_2H_5)_3CH_3]I$ (100)
$P(n\text{-}C_4H_9)_3$, $N(n\text{-}C_4H_9)_3$	Diethyl ether	$[P(n\text{-}C_4H_9)_3CH_3]I$ (100)
	Acetone	$[P(n\text{-}C_4H_9)_3CH_3]I$ (100)
$P(CH_3)_3$, $(CH_3)_2NP(CH_3)_2$	Diethyl ether	$[P(CH_3)_4]I$ (84), $[(CH_3)_2NP(CH_3)_3]I$ (16)
	Acetone	$[P(CH_3)_4]I$ (80), $[(CH_3)_2NP(CH_3)_3]I$ (20)
$P(n\text{-}C_4H_9)_3$, $(n\text{-}C_4H_9)_2NP(n\text{-}C_4H_9)_2$	Diethyl ether	$[P(n\text{-}C_4H_9)_3CH_3]I$ (80), $[(n\text{-}C_4H_9)_2NP(n\text{-}C_4H_9)_2CH_3]I$ (20)
	Acetone	$[P(n\text{-}C_4H_9)_3CH_3]I$ (80), $[(n\text{-}C_4H_9)_2NP(n\text{-}C_4H_9)_2CH_3]I$ (20)
$P(CH_3)_3$, $P(C_2H_5)_3$	Diethyl ether	$[P(CH_3)_4]I$ (85), $[P(C_2H_5)_3CH_3]I$ (15)
	Acetone-d_6	$[P(CH_3)_4]I$ (80), $[P(C_2H_5)_3CH_3]I$ (20)
$P(CH_3)_3$, $P(n\text{-}C_4H_9)_3$	Diethyl ether (0.2 *M* soln)[a]	$[P(n\text{-}C_4H_9)_3CH_3]I$ (80), $[P(CH_3)_4]I$ (20)
	Diethyl ether (0.1 *M* soln)[a]	$[P(n\text{-}C_4H_9)_3CH_3]I$ (68), $[P(CH_3)_4]I$ (32)
	Acetone-d_6	$[P(n\text{-}C_4H_9)_3CH_3]I$ (80), $[P(CH_3)_4]I$ (20)
$N(CH_3)_3$, $N(C_2H_5)_3$	Diethyl ether	$[N(CH_3)_4]I$ (100)
	Acetonitrile	$[N(CH_3)_4]I$ (100)

[a] Concentration of *each* phosphine.

above procedure was altered in the competitions involving trimethylamine. In these cases, a known volume of liquid trimethylamine was transferred to the reaction vessel by the standard vacuum techniques and then stirred into the reaction mixture before the electrophile was added; external cooling by an ice–salt bath was employed in competitions involving trimethylamine.

After 0.5 hr, the reaction flask was removed from the vacuum line and placed in the inert-atmosphere box. In the case of dissolved products, the solution was pipetted into an nmr tube, equipped with a pressure cap, for detection of products. In the case of solid products, they were filtered off and dissolved in appropriate solvents in nmr tubes.

All spectra were run using a Varian A-60A spectrometer operating at a probe temperature of 40°. Tetramethylsilane was used as an internal standard, except in dimethyl sulfoxide-d_6, where the internal standard was sodium 3-(trimethylsilyl)propanesulfonate.

The nuclear magnetic resonance spectra obtained as above were compared with those of the known possible products, either reported previously,[3,8,15] or prepared by standard methods during the course of experimentation and characterized at that time. The chemical shifts, coupling constants, and multiplicities of the peaks confirmed the presence of the possible products when compared with nmr spectra of known compounds. When more than one product was present, the ratio of peak areas was employed to determine the relative concentrations of products.

Results and Discussion

The data presented in Table I support the following generalizations: (a) In competition reactions with chloramine, dimethylchloramine, and methyl iodide, the reactions with phosphines predominate over reactions with the amines. (b) Reactions of aminophosphines predominate over reactions with amines. (c) Reactions with phosphines predominate over reactions with aminophosphines. (d) Reactions of phosphines having less bulky alkyl groups predominate over reactions of phosphines having more bulky alkyl groups except for the competition between $P(n\text{-}C_4H_9)_3$ and $P(CH_3)_3$ discussed below. A similar generalization applies to competitions between two amines.

Among the amine–phosphine systems studied, it was only in the case of the competition of trimethylphosphine and trimethylamine for methyl iodide that the amine was able to compete at all, and even here it accounted for only 10% of the total reaction. This is in

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accord with the relative order of basicity of these two substances toward triethylborane found in an earlier study.[16] In other work,[17,18] however, trimethylphosphine has been found to be less basic toward trimethylborane than is trimethylamine, perhaps reflecting the fact that methyl groups on trimethylborane hinder bonding with the relatively small nitrogen in trimethylamine less than do the ethyl groups on triethylborane.

The findings of our present study are likewise in accord with the earlier report[19] that triethylphosphine and triphenylphosphine displace trimethylamine from certain $(CH_3)_3NR^+X^-$ species where R is a bulky group, indicating that in these instances phosphorus forms more stable "onium" salts than does nitrogen.

In view of the measurable reactivity toward methyl iodide of trimethylamine in competition with trimethylphosphine, it is somewhat puzzling that no trace of 1,1,1-trimethylhydrazinium chloride is found when these two nucleophiles compete for the electrophile chloramine; this is especially surprising when we note that chloramine has been found[20] to react more rapidly with amines than do alkyl halides. One might postulate that, in the present case, the hydrazinium chloride is formed more rapidly than the aminophosphonium salt but is then decomposed by the free phosphine to yield the aminophosphonium salt and free amine. We have stirred 1,1,1-trimethylhydrazinium chloride with trimethylphosphine for 1 week and have detected some aminotrimethylphosphonium chloride. However, less than 20% reaction had occurred in this time: evidently, such a replacement is very slow. Also, we have observed that equimolar mixtures of trialkylamines and chloramine retain oxidizing capacity (indicating the presence of free chloramine) or at least 0.5 hr at room temperature, whereas, mixtures of phosphines and chloramine lose all oxidizing properties within 30 sec under these conditions, thus indicating much more rapid formation of aminotrialkylphosphonium chlorides than of the 1,1,1-trialkylhydrazinium chlorides.

The extremely high preference of chloramine for phosphines instead of amines may be explained as follows. An enhanced stability of P–N bonds in general, resulting from a strengthening of the P–N bond by p_π–d_π interaction has been postulated.[8,9,15] It seems reasonable, also, to postulate that the high reactivity of phosphines toward chloramine may arise from p_π–d_π bonding between the phosphorus and nitrogen atoms in the activated complex formed in the course of the reaction. The reaction would be SN2 in nature,[4] and the p_π–d_π bonding would simply lower the activation energy for the reaction.[7] There is scant reason to believe that the chlorine atom is partially positively charged in chloramine[21] and is therefore the member attacked; in fact, the NH_2 moiety in chloramine has been shown[22] to be positive. Such p_π–d_π bonding in the activated complex would not be possible in the competition for methyl iodide unless hyperconjugation is assumed.

The predominance of the reaction of phosphines over aminophosphines may be rationalized in terms of two factors. First, we must consider the availability of the electron pair on phosphorus in each case, since it is known that the nucleophilic center in the aminophosphines is the phosphorus atom.[9,23] The greater electronegativity of nitrogen than that of phosphorus should lead to electron withdrawal from the phosphorus atom; from this factor alone, we would conclude that aminophosphines should be less nucleophilic than phosphines with approximately the same steric requirements. In agreement with this argument, tris(trifluoromethyl)phosphine has been shown[24] to be negligibly reactive toward methyl iodide. A second factor to consider, however, is the possibility of p_π–d_π bond interaction wherein the lone pair on the nitrogen atom is donated to an empty d orbital on the phosphorus atom. Such an interaction would tend to increase the electron density on the phosphorus, although not in the hybrid orbital of importance in forming phosphonium compounds. This partial filling of the d orbitals could inhibit π-bond formation by chloramine in the transition state described above, thereby raising the activation energy and inhibiting the reaction.[25] The results of the competition between tri-*n*-butylphosphine and di-*n*-butylaminodi-*n*-butylphosphine for dimethylchloramine may also depend on the extent of this p_π–d_π bonding in the activated complex.[26]

The competition reactions between two different phosphines or two different amines indicate that steric effects may be significant in these cases. The reactions of shorter chain phosphines and amines predominate over those of the longer chain compounds in all cases studied except the competitions between tributylphosphine and trimethylphosphine for chloramine and for methyl iodide. In these, the reactions of the tributylphosphine compounds clearly predominate. We believe that the initial reaction occurs at the less sterically hindered trimethylphosphine in both cases and that subsequently the tributylphosphine reacts with the aminotrimethylphosphonium ion or the tetramethylphosphonium ion to form the aminotributylphosphonium ion or the methyltributylphosphonium ion, respectively, the driving force for this reaction

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[26] No competition reactions between amines and phosphines for dimethylchloramine were attempted after it was noted that adducts between triethylamine and dimethylchloramine do not form. The chief product in this reaction is triethylammonium chloride.

being the volatility of trimethylphosphine. Similar displacement reactions are known for tetraalkylammonium ions[19] and 1,1,1-trialkylhydrazinium ions (*vide supra*). In order to test this hypothesis, samples of pure aminotrimethylphosphonium chloride were placed in a solvent and equilibrated with pure tributylphosphine. In solutions of the concentrations employed in the competition reactions, trimethylphosphine was identified in the vapor phase over the reaction mixture, and aminotributylphosphonium chloride was formed. In more dilute solutions, however, less trimethylphosphine was formed, indicating consequently that less tributylphosphine had reacted, reflecting the fact that at higher dilution trimethylphosphine is less volatile and tributylphosphine has therefore less tendency to displace it from the corresponding aminophosphonium salt. When the trimethylphosphine–tributylphosphine competition for chloramine was run in more dilute solution, it was found that some aminotrimethylphosphonium chloride could be isolated (see Table I).

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Vapor-Phase Studies of Hydrogen Bonding in the Trimethylamine–Methanol System[1a]

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Hydrogen bond formation in the vapor phase of the methanol–trimethylamine system has been investigated by infrared spectroscopy as well as vapor pressure measurements. From intensity measurements in the infrared region made as a function of temperature and pressure, a value for the heat of formation of $CH_3OH{-}N(CH_3)_3$ of -7.1 ± 0.2 kcal/mol is obtained. The corresponding value from the pressure study is -7.5 ± 0.3 kcal/mol. These results are compared with ΔH values on other hydrogen-bonded complexes studied in the vapor phase by these same techniques as well as by nmr.

Spectroscopic examination of simple hydrogen-bonded systems in the vapor phase has attracted increasing attention. Thus, the presence of hydrogen bonding in alcohol–amine,[2] hydrogen halide–ether,[3,4] and nitric acid–ether[2c,5,6] complexes has been detected in the vapor phase by infrared measurements.

Recently, Clague, Govil, and Bernstein studied gas-phase chemical shifts in the methanol–trimethylamine[7] and hydrogen chloride–dimethyl ether[8] systems. From the temperature and pressure variation of the proton nmr signals, the enthalpy for the dissociation of the complexes was obtained. In the case of the hydrogen chloride–dimethyl ether complex, a value of ΔH of 7.1 ± 0.8 kcal/mol was reported.[8] Interpretation of pressure measurements on this system by Gladishev and Syrkin[9] has yielded a value of 7.6 kcal/mol while infrared studies by Bilozerska and Shchepkin[10] gave a value of 5.6 kcal/mol.

The reason for the discrepancy in these results is not clear. The pressure measurements were performed some time ago. In the nmr study the necessity of estimating a chemical shift for the fully complexed hydrogen chloride molecule introduces appreciable error, while in the infrared study the quantitative assessment of intensity changes is difficult in such systems if overlapping bands are present.

The potential usefulness of vapor-phase studies of hydrogen-bonding phenomena in an environment relatively free of many of the difficulties accompanying solution work provides the impetus for the present investigation. In this paper, we report vapor-phase studies using both the infrared and the vapor-pressure methods. The results allow comparison with values on other hydrogen-bonded complexes studied in the vapor phase by these same techniques as well as by the nmr method.

Experimental Section

Methanol (Fisher) was passed through Linde molecular sieves and distilled before use. Trimethylamine (Matheson LB) was fractionated in the vacuum system by trap to trap distillation.

For the vapor-pressure measurements a Pyrex vacuum system was used. Individual samples of the components, trimethyl-

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