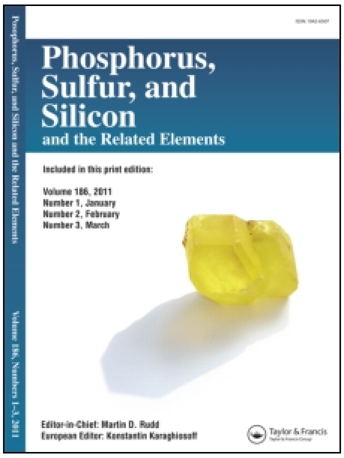

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STUDY ON THE REACTION OF HALOFORM WITH HEXAALKYL PHOSPHOROUS TRIAMIDES

Wen-Chao Zhao[a]; Zeng-Jia Yang[a]; Yu-Fen Zhao[a]
[a] Department of Chemistry, Tsinghua University, Beijing, China

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STUDY ON THE REACTION OF HALOFORM WITH HEXAALKYL PHOSPHOROUS TRIAMIDES

WEN-CHAO ZHAO, ZENG-JIA YANG and YU-FEN ZHAO*

Department of Chemistry, Tsinghua University, Beijing, China

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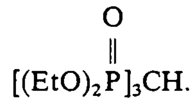
This paper reports the reactions of hexaalkyl phosphorous triamides (HEPTA) with chloroform, bromoform or iodoform. By the FAB-MS, ^{31}P-NMR, and ^{13}C-NMR study the structures of the products have been determined and a possible reaction mechanism has been proposed. Furthermore, the order of reactivity has been established to be: $CHI_3 > CHBr_3 > CHCl_3$.

Key words: Hexaalkyl phosphorous triamide; haloform.

INTRODUCTION

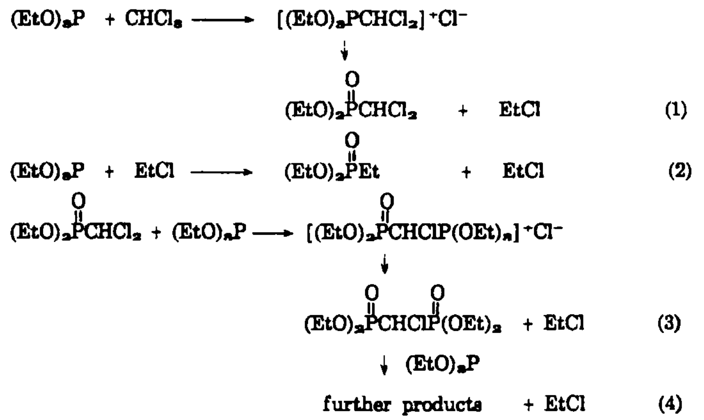
Chloroform is stable under ordinary conditions, and has been used as a solvent in general. The most common reaction for chloroform is by treatment with strong bases to form dichlorocarbene.[1] Burn, Cadogan and Bunyan[2] had reported the products and mechanism for the reaction of chloroform with triethyl phosphite.

The further product must be



$$[(EtO)_2\overset{\overset{\displaystyle O}{\|}}{P}]_3CH.$$

Of course, if the reaction (**2**) proceeded quickly, the reaction (**3**) and (**4**) might be slowed down or inhibited. In the series of the reactions **1–4**, chloroform acts only as an initiator, and is not completely consumed while triethyl phosphite is reacted further by the main reaction, i.e., the Arbuzov reaction (**2**). However, the reaction

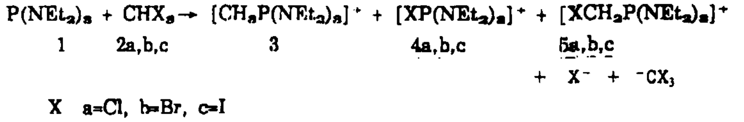


SCHEME I

of chloroform with hexaethyl phosphorous triamide (HEPTA) is different, since there no Arbuzov reaction can occur. The phosphorous atom in HEPTA is a stronger nucleophile due to the inductively releasing effect of the lone pair electrons on the nitrogen atom. But its basicity is not strong enough to convert the chloroform into dichloro-carbene. Furthermore, there was no alkene compound HClC═CClH found as reported by Freeman,[3] only the stable phosphonium salt $[(Et_2N)_3PY]^+Z^-$ was detected and proved as the product.

RESULTS AND DISCUSSION

When the liquid drops of hexaethyl phosphorous triamide got in touch with the vapour of chloroform under the chloroform refluxing condition, vigorous reaction occurred at once, and a black brown, thick product was obtained. Bromoform is more reactive; even at −10°C it was able to react with hexaethyl phosphorous triamide. The iodoform was even much more reactive. The reaction equation is as follows:



$$\underset{1}{P(NEt_2)_3} + \underset{2a,b,c}{CHX_3} \rightarrow \underset{3}{[CH_3P(NEt_2)_3]^+} + \underset{4a,b,c}{[XP(NEt_2)_3]^+} + \underset{5a,b,c}{[XCH_2P(NEt_2)_3]^+} + X^- + {}^-CX_3$$

X a=Cl, b=Br, c=I

SCHEME II The reaction of HEPTA with chloroform.

The crude products obtained were analyzed by ^{31}P-NMR, FAB-MS and ^{13}C-NMR. From the ^{31}P-NMR, it was found that the starting material was completely consumed, and there were three new peaks at 57.3 ppm, 52.0 ppm and 51.0 ppm. The compound corresponding to 57.3 ppm was proved to be the methyl tris(diethylamino)-phosphonium salt 3 by comparison with an authentic sample 6 prepared from methyl iodide and HEPTA (Table II). Also by addition of 6 to the initial reaction medium the ^{31}P-NMR signal exactly coincided with 3 (Figure 1). This means that the unknown structure 3 is 6. The FAB-MS at M/Z 262 is in agreement with structure 3. Also, the ^{13}C-NMR data was consistent for structure 3. By the same method the product 4a was characterized by comparing it with an authentic sample 7 made from carbon tetrachloride and HEPTA (Table II). Finally, the third ^{31}P-NMR peak at 51.0 ppm, was assigned to the structure 5a, M/Z 296 in the FAB-MS. The existence of the Cl atom in 4a, 5a and the Br atom in 4b, 5b, respectively, was also proved by their isotope effect (M + 2)/M values 0.33, 0.98 for each of them (Table I).

The identification of 5a was done by the deuteriochloroform replacement reaction. When deuteriochloroform was reacted with HEPTA, the FAB-MS spectra looked as shown in Figure 2. Now the peak at M/Z 298 (15%) is for the structure 5a(D) $[(Et_2N)_3PCD_2Cl]^+$ and the peak at (M + 2)/Z 300 (5 %) is due to the same chloroisotope effect.

The existence of chloroanion and carbontrichloroanion are detected by anion FAB-MS for M/Z = 35 and M/Z = 117.

Regarding the mechanism for the formation of 3, 4a, 5a in the system, a reduction reaction of the haloform must be considered.

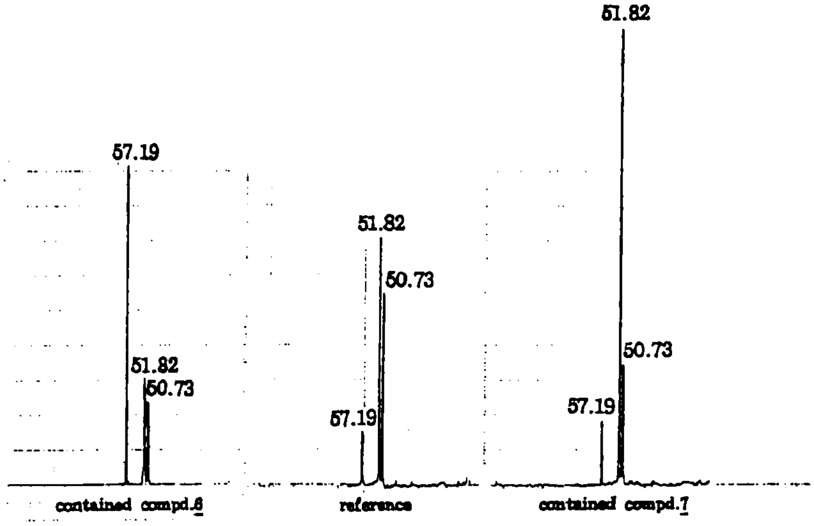


FIGURE 1

TABLE I

Reaction of P(NEt$_2$)$_3$ with CHX$_3$

Compd.		FAB-MS M/Z	(M+2)/Z	δ ^{31}P ppm	δ ^{13}C (ppm) CH$_2$	CH$_3$	structure
3		262 (60%)		57.2	38.9 (J=4, 4Hz)	12.9	[(Et$_2$N)$_3$PCH$_3$]$^+$
4	a	282 (10%)	284 (3.3%)	52.0	39.5 (J=2.9Hz)	11.7	[(Et$_2$N)$_3$PCl]$^+$
	b	326 (64%)	328 (62%)	43.3	(39.9	11.9)*	[(Et$_2$N)$_3$PBr]$^+$
	c	374 (7.0%)		26.5			[(Et$_2$N)$_3$PI]$^+$
6	a	296 (18%)	298 (6.0%)	51.0	(38.9	12.9)*	[(Et$_2$N)$_3$PCH$_2$Cl]$^+$
	b	340 (4.%)	342 (3.9%)	33.8	(38.9	11.8)*	[(Et$_2$N)$_3$PCH$_2$Br]$^+$
	c	388 (2.%)		13.3			[(Et$_2$N)$_3$PCH$_2$I]$^+$

*There is no authentic sample for reference.

TABLE II

Authentic sample's data†

structure	δ ^{31}P (ppm)	δ ^{13}C (ppm) N-CH$_2$	C-CH$_3$	P-CH$_3$
[(Et$_2$N)$_3$PCH$_3$]$^+$I$^-$	57.0	38.9 (J=4.4Hz)	12.9	11.7 (J=112.8Hz)
[(Et$_2$N)$_3$PCl]$^+$[CCl$_3$]$^-$	52.0	39.5 (J=2.9Hz)	11.7	

†Refers to experimental 5 and 6.

FIGURE 2 The identification of 5a by deuterium isotope effect.

FIGURE 3 The anion FAB-MS spectra of the products for reaction of $CHCl_3$ with HEPTA.

Downie[6] had discussed that through the following reaction—the hydrogen was substituted by halogen to reduce the trichloromethyl group into an aldehyde or dichloromethylene.

A possible mechanism is proposed in Scheme IV.

The P atom in HEPTA acted as a strong nucleophile to attack either the halo atom to give 4 or the carbon atom to give the intermediate $[(Et_2N)_3PCHX_2]^+$.

If these reactions did not proceed completely, the intermediate products will appear in the reaction mixture as we have indicated in Scheme II.

CONCLUSION

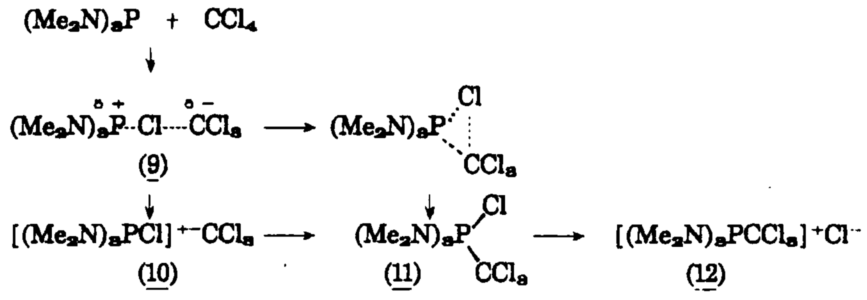
First, the reaction of hexamethyl phosphorous triamide (HMPTA) 8 with carbon tetrachloride[7] is initiated by the polarizing of the permanently dipolar phosphorus

$$R_3P + R'CX_3 + R''OH \longrightarrow R_3PO + R'CHX_2 + R''X$$

SCHEME III Downie's reaction.

$$CHX_3 + P(NEt_2)_3 \longrightarrow \underline{4} + {}^-CHX_2 \qquad (a)$$
$${}^-CHX_2 + CHX_3 \longrightarrow CH_2X_2 + {}^-CX_3 \qquad (b)$$
$$CH_2X_2 + P(NEt_2)_3 \longrightarrow \underline{5} + X^- \qquad (c)$$
$$5 + P(NEt_2)_3 \longrightarrow (Et_2N)_3P^+\text{-}{}^-CH_2 + \underline{4} \qquad (d)$$
$$(Et_2N)_3P^+\text{-}{}^-CH_2 + CHX_3 \longrightarrow \underline{3} + {}^-CX_3 \qquad (e)$$
$$CHX_3 + P(NEt_2)_3 \longrightarrow [(Et_2N)_3PCHX_2]^+ + X^- \qquad (f)$$
$$[(Et_2N)_3PCHX_2]^+ + P(NEt_2)_3 \longrightarrow (Et_2N)_3P^+\text{-}{}^-CHX + \underline{4} \qquad (g)$$
$$(Et_2N)_3P^+\text{-}CHX + CHX_3 \longrightarrow \underline{5} + {}^-CX_3 \qquad (h)$$
$$\underline{5} + P(NEt_2)_3 \longrightarrow (Et_2N)_3P^+\text{-}{}^-CH_2 + \underline{4} \qquad (d)$$
$$(Et_2N)_3P^+\text{-}{}^-CH_2 + CHX_3 \longrightarrow \underline{3} + {}^-CX_3 \qquad (e)$$

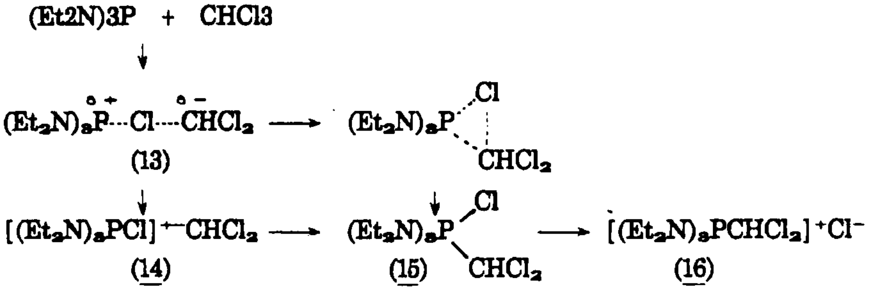
SCHEME IV A possible mechanism for the reaction of 2a, 2b, 2c with HEPTA.



SCHEME V

atom in HEPTA on carbon tetrachloride. In accord with Scheme V it leads to heterolytic bond cleavage by a direct interaction between P and Cl. The amount of charge transfer in the dipolar associate (9) then depends on the substituents carried by the P. And the primary complex already exists largely as an ion pair (10).

But, the fact that CHX_3 attacked by $P(NEt_2)_3$ may proceed at carbon or halogen as reflected in the mechanism, indicates two ways: (a)–(b)–(c)–(d)–(e) and (f)–(g)–(h)–(d)–(e) (Scheme IV). The initial steps are as shown in Scheme VI:



SCHEME VI

Second, the salt compounds composed of phosphonium ion and its counter ion sometimes show up as the molecular ion peak M^+ on FAB-MS, but its abundance was very small. For example, 379 = 282 + 117, corresponds to the structure of $[(Et_2N)_3PCl]^+ [CCl_3]^-$, but its abundance was less than 5%; 399 = 282 + 117, corresponding to the structure of $[(Et_2N)_3PCH_3]^+ [CCl_3]^-$, but its abundance was less than 2%.

Third, a reason that bromoform is more reactive than chloroform must be due to the weaker C—Br bond energy (68 kcal/mol) than C—Cl bond energy (81 kcal/mol), so the order of reaction activation energy is: $\Delta G_{Cl} > \Delta G_{Br} > \Delta G_I$, and the reactivity order of haloform is: $CHI_3 > CHBr_3 > CHCl_3$.

EXPERIMENTAL

Instrument: ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded on a JEOL FX-100 spectrometer, Bruker AM-300 spectroment. The ^{13}C-NMR spectra used chloroform-d as the internal reference at 76.9 ppm. Positive-ion FAB-MS data were obtained on a KYKY Zhp-5 double-focusing mass spectrometer from Scientific Instrument Factory, Beijing, China, equipped with a standard KYKY fast-atom gun.

Reaction:

1. $P(NEt_2)_3$ was prepared by the Stuebe's method,[4] but changing the ether into the petroleum ether as solvent in this reaction.

2. Reaction of $P(NEt_2)_3$ with $CHCl_3$: To 5 mL of refluxing chloroform was slowly dropped $P(NEt_2)_3$ (2.47 g). When the liquid drops met the vapour of chloroform, the reaction occurred at once. The solvent was removed by a rotavapor and the residue washed with 5 mL of petroleum ether. A black brown, thick liquid (3.62 g, 99%) was obtained which was soluble in chloroform and ethanol.

3. Disapproval of a free radical mechanism: when cyclohexene was added to the above reaction system, there was no corresponding carbene addition compound as checked by MS. When toluene was added to the above reaction system, the expected product ditolyl was not detected either.

4. Identification of 3a by Isotope experiment: When $P(NEt_2)_3$ was reacted with $CDCl_3$, the same phenomenon happened as in experiment 2. The FAB-MS spectra data are given as M/Z 298 (15%); 300 (5%).

5. Preparation of $[(Et_2N)_3PCl]^+$ $[CCl_3]^-$ (7): $P(NEt_2)_3$ (2.47 g) was dropped into 0°C cooled CCl_4 (0°C, 1.54 g); a vigorous reaction occurred at once. After washing with petroleum ether, a deep brown liquid product (3.93 g, 98%) was obtained with δ ^{31}P = 52.0 ppm. Anal. $C_{13}H_{30}Cl_4N_3P$ (401.18), Found (calc'd): C, 39.45% (38.92%); H, 8.04% (7.53%); N, 10.65% (10.46%). ^1H-NMR (ppm): CH_3, 1.25(t); CH_2, 3.33(6).

6. Preparation of $[(Et_2N)_3PCH_3]^+$ I^- (6): $P(NEt_2)_3$ (2.47 g) was dropped slowly into CH_3I (2 g) cooled with an ice-salt bath.[6] A white solid compd. 6 (3.81 g, 98%) was formed which was washed with petroleum ether and dried in the vacuum, M. P. 54–56°C; δ ^{31}P = 57.00 ppm. Anal. $C_{13}H_{33}IN_3P$ (389.28), Found (calc'd): C, 39.78% (40.10%); H, 8.55% (8.54%); N, 10.62% (10.79%).

7. Reaction of $P(NEt_2)_3$ with $CHBr_3$: To $CHBr_3$ (2.53 g, 0.01 mol), cooled to −10°C, was slowly added with stirring $P(NEt_2)_3$ (2.47 g, 0.01 mol). The reaction was vigorous. The product was washed with petroleum ether and dried in the vacuum. A deep brown, thick liquid (4.92 g, 98.4%) was obtained (Table I).

8. Reaction of $P(NEt_2)_3$ with CHI_3: CHI_3 (3.94 g, 0.01 mol) was dissolved in 50 ml ether, and cooled to 0°C. While the solution was stirred, $P(NEt_2)_3$ (2.47 g) was dropped in. The reaction was vigorous. A yellow solid precipitated which was filtered and washed with ether to obtain a light yellow solid (6.30 g, 98%). M.P. 96–100°C ^{31}P-NMR (ppm): 56.82 (51%), 26.54 (13%), 13.27 (36%).

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