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Ring Opening Reactions of Tetrahydrofurane with Phosphorus Halides

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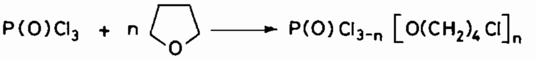
The reaction of THF with $P(O)Cl_3$ or PX_3 (X = Cl, Br) affords $P(O)Cl_{3-n}[O(CH_2)_4Cl]_n$, $n = 1$–3 or $PX_{3-n}[O(CH_2)_4X]_n$, $n = 1,2$, respectively; in the presence of mercury(II) halides the reaction of THF and PBr_3 leads to the phosphorus acid ester $P[P(O)(O(CH_2)_4Br)_2]_3$.

Ring opening of the strained three- and four-membered ring ethers with phosphorylchloride is well known [1–3] and leads to ω-chloroalkyl phosphates, which are useful as fire retardants and plasticizers. There are no reports concerning this reaction involving the essentially nonstrained tetrahydrofurane (THF). The five-membered ring is known to be stable to ring opening, except for conditions that cause ether cleavage reactions of open chain ethers.

We found reaction (1) ($n = 1$) to proceed slowly at ambient temperature. This reaction is efficiently cata-


(1)

lyzed by mercury(II) halides leading to $P(O)Cl_{3-n}[O(CH_2)_4Cl]_n$ with $n = 1$ and also to products with $n = 2$ and 3. The ring opening of THF by alkyl halides and Hg(II) salts has been reported by Watanabe *et al.* [4]. They proposed the initial formation of an O alkyltetrahydrofuranium ion followed by the SN2-like attack by the mercurate as the reaction pathway. A corresponding mechanism may possibly be effective for the title reaction. In a side reaction, polymerization of THF takes place. The polymerization of THF catalyzed by other phosphorus compounds has been reported [5–8].

TABLE I. Reaction of PX_3 with THF[a]

X	Molar ratio PX_3:THF	Time	Products (%)	
			$X_2PO(CH_2)_4X$	$XP(O(CH_2)_4X)_2$
Cl	1:3	20 d[b]	trace	–
Br	1:1	2 d	25	–
Br	1:2	2 d	35	trace
Br	1:3	2 d	40	trace
Br	1:10.5	3 d	80	20

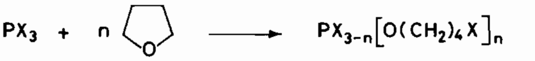
[a] Ambient temperature; percentages obtained by integration of ^{31}P NMR signals. [b] d = day.

TABLE II. Reaction of PCl_3 with THF Catalyzed by HgX_2[a]

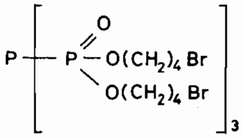
X	Molar ratio PCl_3:THF:HgX_2	Time	$Cl_2PO(CH_2)_4Cl$ (%)
Cl	1:3:0.05	20 d[c]	10[b]
Br	1:3:0.05	20 d	40
I	1:3:0.05	20 d	50
Cl	1:3:saturated	20 d	10
Br	1:3:saturated	30′	80
I	1:3:saturated	6 d	70

[a] Ambient temperature. [b] 70% after 2 d reflux. [c] d = day.

Phosphorous chloride reacts with THF in the presence of a catalyst according to eqn. (2) (X = Cl, $n = 1$) [9]. We found that this reaction also


(2)

proceeds in the absence of a catalyst but at a slower rate compared with $P(O)Cl_3$. Phosphorous bromide reacts much faster (see Table I) according to eqn. (2) (X = Br, $n = 1$ [10] and 2). Mercury(II) halides again catalyze the reaction with PCl_3 (see Table II) leading to the products $n = 1$, 2 eqn. (2). The catalytic activity increases in the order $HgCl_2 < HgBr_2 < HgI_2$. In contrast, the reaction of PBr_3 with THF catalyzed by mercury halides leads to the phosphorus acid ester **1**. Other esters (e.g. Et) of this phosphorus



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acid were first obtained by Fluck *et al.* [11] from PX_3 and $HP(O)(OR)_2$ in the presence of a base. The product **1** seems to be formed via the phosphorous acid triester ($n = 3$, eqn. (2)), which either reacts with PBr_3 according to eqn. (3) [12] or with HgX_2 to yield the asymmetric phosphito–P mercury com-

$$3P[O(CH_2)_4Br]_3 + PBr_3 \longrightarrow \mathbf{1} + 3Br(CH_2)_4Br \qquad (3)$$

$$P[O(CH_2)_4Br]_3 + HgX_2 \longrightarrow \underset{\mathbf{2}}{XHgP(O)[O(CH_2)_4Br]_2} + Br(CH_2)_4Br \qquad (4)$$

pound **2** (eqn. (4)) [13], which in turn reacts with PBr_3 according to eqn. (5):

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$$3XHgP(O)[O(CH_2)_4Br]_2 + PBr_3 \longrightarrow 1 + 3XHgBr \qquad (5)$$

Halide exchange reactions between HgX_2 and PY_3 (eqn. (6)) are observed whenever Y is heavier than X.

$$\begin{array}{lll} HgX_2 + PY_3 \longrightarrow & HgXY + & PXY_2 \\ & HgY_2 & PX_2Y \\ & & PY_3 \end{array} \qquad (6)$$

According to preliminary results, ether cleavage of open chain ethers with phosphorus halides also occurs.

Experimental

Analytical grade chemicals (Merck) were used. THF was dried and distilled before use. The reactions were monitored and the products were characterized by ^{13}C and ^{31}P NMR spectroscopy on a multinuclear Bruker WP 80 instrument operating in the FT mode. $P(O)[O(CH_2)_4Cl]Cl_2$ ($\delta(^{31}P)$: 0.0, $\delta(^{13}C)$: C-1: 71.5, C-2: 27.7, C-3: 30.8, C-4: 45.9, $^2J(P,C)$: 14 Hz). $P(O)[O(CH_2)_4Cl]_2Cl$ ($\delta(^{31}P)$: 4.0; $\delta(^{13}C)$: C-1: 70.7, C-2: 28.3, C-3: 29.6, C-4: 45.3; $^2J(P,C)$: 9 Hz). $P(O)[O(CH_2)_4Cl]_3$ ($\delta(^{31}P)$: −2.2. $P[O(CH_2)_4Cl]Cl_2$ ($\delta(^{31}P)$: 177; $\delta(^{13}C)$: C-1: 70.6, C-2: 28.1 C-3: 29.7, C-4: 44.3). $P[O(CH_2)_4Cl]_2Cl$ ($\delta(^{31}P)$: 166). $P[O(CH_2)_4Br]Br_2$ ($\delta(^{31}P)$: 200; $\delta(^{13}C)$: C-1: 73.4, C-2: 29.4, C-3: 29.9, C-4: 33.9). $P[O(CH_2)_4Br]_2Br$ ($\delta(^{31}P)$: 183). $P\{P(O)[O(CH_2)_4Br]_2\}_3$ ($\delta(^{31}P)$: 22.9(d), −87.8(q), $J(P,P)$: 164 Hz).

Acknowledgements

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References

1 *U.S.S.R. Patent 459471* (1975) to Yu. N. Afanas'ev, V. V. Kormachev, I. A. Abramov, E. L. Gefter and V. A. Kikhtin.

2 B. Muth, G. Ocskay, L. Knapp, B. Bartha, G. Biro and T. Schleicher, *Hung. Teljes* 5420 (1972).

3 Z. Kubica, E. Stich, H. Szewczyk and K. Rudnicki, *Polimery, 24,* 321 (1979).

4 N. Watanabe, S. Uemura and M. Okano, *Bull. Chem. Soc. Jpn., 48,* 3205 (1975).

5 P. Dreyfuss and M. P. Dreyfuss, *Adv. Polymer. Sci., 4,* 428 (1967).

6 F. Yamada, I. Horji, T. Yasui and I. Shinohara, *J. Macromol. Sci., A14,* 635 (1980).

7 R. de Jaeger, T. Abouchaccra, A. Ouassini and J. Heubel, *Z. Allg. Anorg. Chem., 489,* 204 (1982).

8 T. Abou Chakra, R. de Jaeger and J. Heubel, *Z. Allg. Anorg. Chem., 501,* 191 (1983).

9 N. I. Shuikin, I. F. Bel'skii and I. E. Grushko, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk,* 557 (1963); *U.S.S.R. Patent 168293* (1965) to N. I. Shuikin, I. F. Belskii and I. E. Grushko.

10 N. P. Volynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2528 (1979).

11 D. Weber and E. Fluck, *Z. Naturforsch., Teil B, 30,* 60 (1975).

12 H. S. Aaron and L. L. Szafranec, *Phosphorus, 6,* 77 (1976).

13 A. Yamasaki and E. Fluck, *Z. Anorg. Allg. Chem., 396,* 297 (1973).