THE DECOMPOSITION OF SATURATED OXYGEN-, NITROGEN-, AND SULFUR-
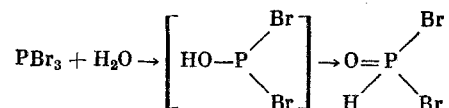# CONTAINING HETEROCYCLIC AND ACYCLIC COMPOUNDS BY PHOSPHORUS HALIDES

N. P. Volynskii

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It is most convenient to carry out the synthesis of model cyclic sulfides, substituted thiacyclohexanes and thiophanes, from the homologs of tetrahydropyran (THP) and THF. However, on decomposing these compounds to the corresponding dibromides, as well as in other cases of preparing dibromides, condensation and isomerization are almost always observed.

According to [1, 2] the decomposition of 2-alkyl-THP by boiling with HBr acid and passing HBr through simultaneously led to 1,5-dibromoalkanes with an impurity content of up to 30% of isomeric 1,4-dibromides. We showed in [3] that in contrast to unsubstituted THP [4], 3-alkyl-THP was chiefly resinified on decomposition by the action of HBr or HBr acid. Under aprotic conditions, with the slow introduction of HBr acid into a mixture of 3-aklyl-THP and PBr₃ at 145±5°C, the even cleavage of the THP ring took place. The 2-alkyl(cycloakyl)-1,5-dibromopentanes so obtained are converted into the 3-substituted thiacyclohexanes, the individuality of which has been confirmed by capillary GLC. This paper deals with a study of the limits to which this new method of cleavage of ethers is applicable.

It has been found that the 3-alkyl-substituted THP as well as the dialkyl ethers are fairly stable to PBr_3 (130-150°, 1 h). However, on adding 48% HBr slowly to a mixture of these compounds with PBr_3 under similar conditions they are converted quantitatively into the dibromides (or bromides). It was shown by separate experiments that the hydrolysis of PBr_3 (1 mole) by an equimolar amount of H_2O at 20 and 130°C leads to the exclusive formation of H_3PO_3 (1/3 mole); 2/3 mole of the PBr_3 is recovered unchanged. H_3PO_3 does not affect the cleavage reaction. For example, on heating methyl octyl ether with PBr_3 (125°C, 1.5 h) in the presence of H_3PO_3 only 4% $C_8H_{17}Br$ was formed, while 80% of the $C_8H_{17}OCH_3$ was recovered unchanged. If conc. HBr is gradually (1 h) introduced into a mixture of $C_8H_{17}OCH_3$ and PBr_3 at 125°C, then $C_8H_{17}Br$ is formed evenly (yield ~90%), the CH_3Br formed simultaneously being liberated as the HBr acid is added. Since the individual action of PBr_3 and 48% HBr differs from their combined action, it is logical to suggest that a new, extremely active component is formed, e.g., the bromoanhydride of phosphorous acid:

$$PBr_3 + H_2O \rightarrow \left[HO-P\begin{matrix} Br \\ \\ Br \end{matrix} \right] \rightarrow O=P\begin{matrix} Br \\ \\ H \quad Br \end{matrix}$$

In the absence of an ether, PBr_3, as noted above, is hydrolyzed to H_3PO_3; in the presence of ROR' the cleavage of the C—O bond takes place.* The total absence of resin formation enables one to conclude that the process takes place in aprotic medium by an S_Ni mechanism of intramolecular, nucleophilic substition†; the formation of the P—O bond takes place with the simultaneous displacement of the Br atom from its electron pair to C:

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*The formation of a P—O bond (86 kcal/mole) instead of a P—Br bond (63 kcal/mole) duplicates the consumption of energy in the simultaneous conversion of the C—O bond into C—Br (86 and 68 kcal/mole) [5].
†For the S_Ni mechanism see [6].

TABLE 1. Decomposition of 3-Butyl-4-chloro-THP (I) and 3-Butyl-THP (II)

Experimental conditions				Yield of dibromide, %	Recovery of unreacted substance, %
initial substances	reagent	temperature °C	period of adding reagent (react. time), h		
(I), ZnCl$_2$	HBr	150[a]	1,5	—	—
(I), AcOH, ZnCl$_2$	PBr$_3$ ·	120[a]	1,5	—	75
(I), H$_3$PO$_4$	PBr$_3$	150[a]	2	22	—
(I), PBr$_3$	H$_3$PO$_4$	150[b]	1,5	32	23
(I), PBr$_3$, ZnCl$_2$	H$_3$PO$_4$, then conc. HBr	150[b]	2,5	63	—
(II), conc. HBr, conc.H$_2$SO$_4$	—	120[a]	1	—	64
(II), conc. HBr, conc.H$_2$SO$_4$	—	Boiling [a]	3	—	43
(II)	HBr	140–150[a]	1,5	—	—
(II), PBr$_3$	Conc. HBr	140–150[b]	1,5–2	84[c]	—
(II), PBr$_3$	The same	140–150[b]	1	68	22

[a]Strong resin formation.
[b]Complete absence of resin formation.
[c]Bp 100°C (4 mm), n_D^{20} 1.4988, d_4^{20} 1.4208. Found: Br 55.4%. C$_9$H$_{18}$Br$_2$. Calculated: Br 55.87% (cf. [4]).

TABLE 2. Decomposition of Tetrahydrofurans[a]

Experimental condition				Yield of dibromide, %	Recovery of unreacted substance, %
initial substances	reagent	temperature °C	period of adding reagent (reaction time), h		
THF, PBr$_3$	—	95	2	10	43
3,4)Tetramethylene-THF, PBr$_3$	—	150	1,5	63	—
3,4-Tetramethylene-THF, PBr$_3$	conc. HBr	125–130	2	82 b	—
2-Ethyl-THF[c], PBr$_3$	—	100	2	43[c]	—

[a]Absence of resin formation.
[b]Bp 93°C (3 mm), n_D^{20} 1.5432, d_4^{20} 1.6351. Found: Br 58.5%. C$_{18}$H$_{14}$Br$_2$. Calculated: Br 59.19% (cf. [13]).
[c]Similar results are obtained for 2-methyl-THF in [7].
[d]cf. [14].
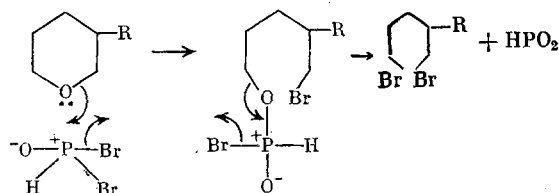
The cleavage of the more reactive ring in THF by means of PBr$_3$ was first described in [7]. Under mild conditions (90–100°C, 2 h) 1,4-dibromoethane was formed from 2-methyl-THF with a yield of >90%; the mechanism of the reaction was not considered.

We have shown that the cleavage of the ring in THF by the action of PBr$_3$ in the absence of α-alkyl substituents takes place only at elevated temperatures. For example, the cleavage of THF by the action of PBr$_3$ in the absence of moisture (2 h, 95±3°C) virtually does not take place at all; cis-3,4-tetramethylene-THF with PBr$_3$ forms cis-1,2-bis(bromomethyl)cyclohexane only under severe conditions (150°C, 1.5 h) with a yield of 65%. On the other hand, 2-ethyl-THF is readily decomposed by the action of PBr$_3$ (95°C, 1 h), giving exclusively 1,4-

TABLE 3. Decomposition of Ethers and Thioethers under Aprotic Conditions

initial substances	reagent	tempera- ture, °C	period of adding re- agent (reac- tion time), h	Yield of dibromide (bromide), %	Recovery of un- reacted sub- stances, %
cis-3-Oxabicyclo[3.3.1]nonane, PBr₃	—	150	1	—	75
cis-3-Oxabicyclo[3.3.1]nonane, PBr₃	conc.HBr	150	2	65[b]	—
Methyl octyl ether, PBr₃	—	150	1	—	88
The same	conc.HBr	125	2	88.5[c]	—
2-Butyl-4-methoxybutanol, PBr₃	—	130	1	50[d]	—
Anisole[e], PBr₃	conc.HBr	160	1.5	—	73

The first row spans the column "Experimental conditions" header.

[a]Absence of resin formation.

[b]Bp 98°C (3 mm), n_D^{20} 1.5380, d_4^{20} 1.6067. Found: Br 59.0%. $C_8H_{14}Br_2$. Calculated: Br 59.19% (cf. [15]).

[c]Bp 97°C (28 mm), n_D^{20} 1.4512, d_4^{20} 1.1001 (cf. [16]).

[d]cf. [12].

[e]Diphenyl ether and also dialkyl sulfides, 2- and 3-substituted thiophanes, and 2-, 3-, and 4-substituted thiacyclohexanes are not decomposed under these conditions.

dibromohexane without resin formation or the formation of structural isomers. We have proved this by converting the dibromide into 2-ethylthiophane, the individuality of which was confirmed by GLC.

It seems to us that the formation of dibromoalkanes in the reaction between a cyclic ether and PBr₃ takes place by the mechanism
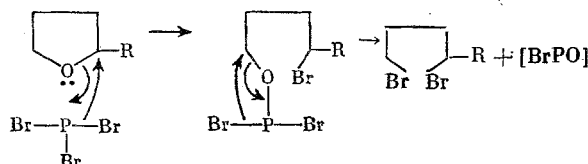
Whereas the dialkyl ethers and cyclic ethers are readily decomposed by the method we propose, diphenyl ether and anisole are unchanged under these conditions. The sulfides behave simi- larly with the only exception that even the dialkyl sulfides and thiacycloalkanes (commenc- ing with thiophane) having alkyl substituents in all the positions possible are stable to treatment with PBr₃ and conc. HBr under the most severe conditions (165°C). This is used as the basis of a method for purifying dialkyl sulfides, thiophanes, and thiacyclohexanes from impurities of three- and four-membered sulfides as well as from oxygen-containing and unsaturated compounds. The exceptional stability of sulfides to the action of [OP(H)Br₂] is explained by the comparative stability of the C —S bond.*

It is easy to see a definite analogy between AcBr and the bromoanhydride of phosphorous acid:

The presence of the electropositive group CH₃ lowers the ability of the central C atom to add on to the free electron pair of the O atom in an ether. Consequently, [OP(H)Br₂] is a stronger decomposing agent, which we have confirmed experimentally. At the same time, the presence of α-alkyl substituents in ethers promotes decomposition for the same reasons, by increasing the nuclophilicity of the O atom (cf. the data presented above for THF and its 2- alkyl-substituted derivatives).

*The energy of the C —S bond is 65 kcal/mole, P —S is 50 kcal/mole [5].

In this connection we may note the incorrectness of the statements in [8-10] on steric hindrances being created by the α-alkyl substituents in the Braun reaction since there is a clear analogy between the decomposition of oxygen- and nitrogen-containing compounds:
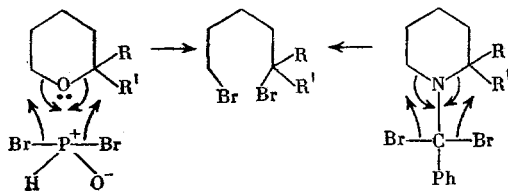
Leonard and Nommensen [8] were unable to isolate the unstable and readily hydrolyzable 2,6-dibromo-2,6-dimethylpentane [11] from the reaction products of N-benzoyl-2,2,6,6-tetramethylpiperidine and PBr$_5$; however, benzonitrile was isolated with a yield of 70%, which should undoubtedly be considered as confirmation that the Braun reaction also proceeded normally in the case of 2,2,6,6-tetraalkyl-substituted piperidines. The ready decomposition of N-acetyl-2,2-dimethyl- and 2,2,6,6-tetramethylpiperidine in acid medium by the reverse Ritter reaction, caused in fact by the presence of α-alkyl substituents, is known [10].

The simplicity of the method we propose should be emphasized. Thus, at 125-150°C the reaction takes place after 1.5-2 h with amounts from 5-500 g of the initial substances. The high yields of dibromide (or bromide) make this method irreplaceable in the synthesis of cyclic sulfides; in many cases virtually only the individual compounds are formed.

Dibromides can also be synthesized by the bromination of methoxy alcohols (alkoxy alcohols in the general case) following the scheme we developed in [12]. It is not normally required to add water in the decomposition of methoxy alcohols by PBr$_3$ since the active reagent may be formed by the alcohol hydroxyl. However, since the yield of dibromide does not exceed 50% on carrying out the process in this way the bromination of methoxy alcohols leads analogously to the decomposition of cyclic ethers.

EXPERIMENTAL

Decomposition of Ethers under Aprotic Conditions by the Action of 48% HBr on a Mixture of Ether with PBr$_3$. 70 ml (0.74 mole) PBr$_3$ was added fairly rapidly to 1 mole of cyclic ether at 120-130°C. If there was an increase in temperature, the rate of addition was reduced; in the absence of a thermal effect, PBr$_3$ was added immediately. Furthermore, depending on the structure of the cyclic ether 35 ml conc. HBr was added uniformly at 125 ±5°C or 145 ±5°C over the course of 1.5-2 h. After a few minutes the liquid became cloudy and acquired a bright-orange color.* When the evolution of HBr ceased, the mixture was cooled and a small amount of an inert solvent (benzene, hexane) added. The solution was separated from the bottom acidic layer and filtered through a Buchner funnel containing a thick filter paper† with a deposited layer of Na$_2$SO$_4$. The flask and filter were washed with the same solvent and then the product was kept under vacuum with heating (to 100°C). A colorless dibromide was obtained, suitable for subsequent reactions without further purification. Yield ~100%.

An analytically pure preparation was isolated by vacuum distillation. The unpurified product may contain traces of P$_2$O$_3$. In order to free the substance from this impurity it is useful to pass a stream of air for several minutes through the dibromide heated to 70-80°C before distillation.

Decomposition of the dialkyl ethers was achieved similarly at 125 ±5°. When a readily volatile bromide is formed, the partial entrainment of PBr$_3$ is observed; therefore, 100 ml PBr$_3$ and 80 ml conc. HBr were used per 1 mole of ROR', where R is a methyl or another low-molecular-weight radical. The experimental data are presented in Tables 1-3. For comparison, the tables include experiments whose conditions differed from the optimum.

*The color is caused by the formation of ~1 g of a solid inorganic substance consisting of 68-75% P and 32-25% O (by difference).
†For the preparation of the filters see [3].

CONCLUSIONS

1. The limits of applicability have been studied of a new method for decomposing saturated cyclic oxides and dialkyl ethers involving their conversion into dibromides and bromides respectively under aprotic conditions, with the gradual addition of conc. HBr to a mixture of the compound being decomposed with PBr_3.

2. The mechanism of the decomposition of the C—O bond in ethers on reaction with the phosphorus halides is discussed.

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