Ether Cleavage by Triphenyldibromophosphorane[1,2]

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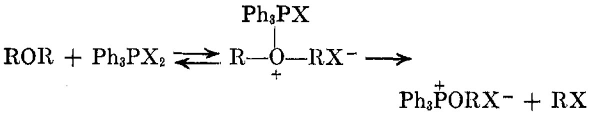
Triphenyldibromophosphorane has been found to effect the cleavage of dialkyl and phenyl ethyl ethers under essentially neutral conditions. Primary and secondary alkyl groups gave good yields of alkyl bromides with benzonitrile or chlorobenzene as the solvent. Cleavage of alkyl *tert*-butyl ethers in DMF solvent converted the *tert*-butyl group primarily to isobutene. No rearrangements were observed. The phenyl group was first obtained as part of a phosphonium bromide salt which was converted to bromobenzene at higher (>230°) temperatures. Vinyl and β-chloroalkyl ethers were much less reactive. Two epoxides, a ketal, and three thioethers were treated with inconsistent results.

The common methods for the cleavage of nonactivated ethers have employed strong acids. Milder conditions using boron trihalides (or diborane or sodium borohydride plus iodine) have been extended recently[3] and found to give cleavage at room temperature or below in most cases. However, only with BI_3 are both carbon–oxygen ether bonds cleaved and BF_3 gives alkenes with other than methyl and ethyl ethers (which form stable adducts). Less commonly, ethers have been cleaved by strong bases (*e.g.*, alkyl- and aryllithium reagents,[4] alkali metals[5]).

The finding that alkylhalotriphenoxyphosphoranes[6] and triphenyldihalophosphoranes[7,8] would effect the conversion of alcohols to alkyl halides led us to consider tertiary phosphine dihalides for the cleavage of ethers[9] as a method to avoid the presence of strong acids and bases. Ethers would be expected to react with the tertiary phosphine dihalides[10] to form an oxonium intermediate (eq 1). This conjugate–Lewis acid of the ether could then react in the usual manner



$$ROR + Ph_3PX_2 \rightleftharpoons R\text{—}\overset{\overset{\large Ph_3PX}{|}}{\underset{+}{O}}\text{—}RX^- \longrightarrow Ph_3\overset{+}{P}ORX^- + RX \quad (1)$$

to give alkyl halide and a quasiphosphonium ion[11] intermediate corresponding to that proposed for phenols and alcohols,[7,8,9b,12,13] which, for dialkyl ethers, could afford a second molecule of RX (eq 2). The present

$$Ph_3\overset{+}{P}ORX^- \longrightarrow Ph_3PO + RX \quad (2)$$

study was directed toward and limited to the finding of conditions with triphenyldibromophosphorane which would effect cleavage yet appreciably reduce the side reactions caused by strong acids and bases. No effort was made to find optimum conditions; therefore yields higher than those obtained should be possible with some ethers. Tertiary phosphine dihalides are known to react with a number of functional groups (*e.g.*, acidic hydrogen, reactive carbonyl, alkoxide, hydrazine, and peroxide) and these would interfere if present.

Acetonitrile, benzonitrile, dimethylformamide (DMF), 1-methyl-2-pyrrolidone, chlorobenzene, and the less polar *p*-xylene were all used as the solvent with varying degrees of success and particular advantages and disadvantages. Acetonitrile and also carbon tetrachloride could be used for preforming the reagent if isolation of the latter was desired, but their low boiling points precluded general use in cleavage reactions. The reagent could be formed (with cooling) in DMF but not in 1-methyl-2-pyrrolidone (decomposition occurred). For other than short ether cleavage reaction times these solvents (especially the pyrrolidone) formed gases and dark, nonvolatile by-products. *p*-Xylene as the reaction solvent led to high boiling products. Long reaction times gave some darkening with all solvents but least with benzonitrile and chlorobenzene. With DMF and acetonitrile, work-up was facilitated by adding water and extracting the alkyl halide. Yields of alkyl halide for short reaction times (often corresponding to incomplete reaction) were comparable for the various solvents except for certain bromide products (*e.g.*, *tert*-butyl bromide) which reacted with DMF.[14] Cleavage reactions were run under an

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[1] Supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. From the Ph.D. thesis of F. J. F.

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TABLE I

CLEAVAGE OF PRIMARY AND SECONDARY SYMMETRICAL ETHERS

Ether	Solvent	Temp, °C	Time, hr	RBr product[a]	Bp (mm), °C[b]	Yield of RBr, %[c]	Total RBr, %[d]
n-Pentyl	C_6H_5CN	122–130	4	*n*-Pentyl	128–129.5	77.8	98.9
n-Butyl	C_6H_5CN	122	4	*n*-Butyl	100–101	71.9	76
Allyl	C_6H_5CN	121	1	Allyl	69–70	63.4	68.6
Isopropyl	C_6H_5CN	122–127	9	Isopropyl	59–60	59.2 (62.7)[e]	66.7 (70.7)[e]
Tetrahydrofuran	C_6H_5Cl	126	0.67	1,4-Dibromobutane	94–95 (14)		75.1

[a] Shown by vpc to be identical with an authentic sample. [b] Boiling range of pure product fraction. [c] Yield of pure isolated product. [d] Total recovered yield of halide; the yield of pure product plus the percentage in other distillation fractions as determined by vpc. [e] Based on recovered ether.

TABLE II

CLEAVAGE OF ALKYL *tert*-BUTYL ETHERS

Alkyl *tert*-butyl ether	Solvent	Temp, °C	Time, hr, >90% reaction	Total time, hr	Yield of RBr, %[a]	Total RBr, %[b]	*tert*-BuBr, %	Isobutene, %
n-Butyl	DMF	60–110	1	2	69.6	89.5	1.5	(Small)[c]
sec-Butyl	DMF	70–80	2	4.5	37.5	66.9	1	51.3[d]
Isobutyl	DMF	80	3.5	3.5	18.4	53.5	4.4	11.5[d]
tert-Butyl	DMF	*ca.* 25	0.1	1	(Small)[c]	(Small)[c]		(Small)[c]
Neopentyl	DMF	77–91	4	4		33.9 (41.8)[e]	(Small)	37.4[d]

[a] Yield of pure isolated product. [b] Total recovered yield (see Table I). [c] Identified but not measured. [d] Isolated as the dibromide. [e] Based on recovered ether.

inert atmosphere and were monitored by the vpc analysis of aliquots.

Several series of ethers of different types were studied. The first, symmetrical ethers having primary or secondary alkyl groups, were cleaved in benzonitrile or chlorobenzene and the results are summarized in Table I. Allyl ether and tetrahydrofuran were cleaved most and isopropyl ether, probably due to steric factors, least readily. The lower yields for the more volatile bromide products are thought to be due, at least in part, to loss by volatilization. Bromine addition to the allyl unsaturation did not appear to have occurred.

Another series studied was of alkyl *tert*-butyl ethers (Table II). The selection of DMF as the solvent provided the desired simplification in work-up mentioned above and also conditions corresponding to those reported[9b] for the reaction with alcohols. However, it was found that little *tert*-butyl bromide was obtained. The rapid conversion of the bromide to isobutene under the reaction conditions, and more rapidly than in DMF alone, was shown to occur. Thus hydrogen bromide was being formed as the reaction progressed, and some ether cleavage *via* proton-acid catalysis was probably also occurring. That the latter was not the primary mode of reaction was indicated by the fact that, with the exception of di-*tert*-butyl ether for which the reaction rate was too rapid to follow by the procedure used, the rate of disappearance of starting ether did not accelerate as the amount of hydrogen bromide increased. In addition, starting ether was recovered in two cases after extended reaction time. Benzonitrile is therefore suggested instead of DMF to avoid the formation of stronger acids and for the isolation of *tert*-alkyl bromides. The reason for the somewhat lower yields of alkyl halide from the *sec*-butyl and neopentyl groups was not apparent in that no alkenes or isomeric alkyl bromides were observed.[15]

Ethers containing an α-vinyl or -aryl group, one having a β-chloro group, and furan were tested. The bond linking these groups to the ether oxygen was quite resistant to cleavage. The reaction of phenetole, for example, produced ethyl bromide (40%) under the conditions used for the dialkyl ethers but the solid product containing the aromatic moiety required heating above 230° to form bromobenzene (24%). The solid product was found to correspond to that formed by the reaction of phenol with the reagent and therefore was most probably the known $(PhOPPh_3)^+Br^-$ species.[7,12] Dihydropyran in DMF at room temperature or with no solvent at 220° gave essentially no volatile products or recovered ether. Di-2-chloroethyl ether in benzonitrile at 125° appeared to give halogen exchange as the main reaction with less than one-fourth of the ether cleaved after 12 hr. A reasonable path for the halogen exchange would be abstraction of the chlorine by Ph_3P^+Br assisted by back-side participation of ether oxygen electrons (analogous to the formation of sulfur and nitrogen mustard gases) followed by halogen substitution with bromide or chloride. The tendency for this reaction to occur may account, in part, for the slowness of the cleavage process. Other possible factors are steric shielding and inductive effects by the halogens.

It is reasonable to consider that the cleavage of the second carbon–oxygen bond to form the halide is the same as that found in the conversion of alcohols to halides by this type of reagent, *i.e.*, nucleophilic reaction of halide ion with an alkoxyphosphonium intermediate. The probable finding of the corresponding intermediate in the cleavage of phenetole supports this. With regard to the cleavage of the first ether carbon–oxygen bond, a likely course would be equilibrium formation of an oxonium salt and subsequent elimination of the alkyl bromide as depicted above (eq 1). A side reaction would be the formation of an alkene and hydrogen bromide from alkyl groups other than methyl. It would appear that there is little tendency for car-

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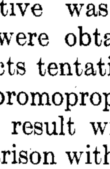
[15] Other than isobutene, no by-products were found for the reactions of the other ethers, though dimethylammonium bromide could be obtained from the water-soluble portion when DMF was the solvent.

bonium ion formation as no rearranged bromides were found. When a *tert*-butyl group was present, the small yields of *tert*-butyl bromide indicate some SN1 reaction. The isobutene could have been formed *via* β elimination on the oxonium salt or on *tert*-butyl bromide under the conditions employed.

Three epoxides and a ketal were also examined as special ether-like compounds. The reaction with 1,2-epoxypropane in DMF gave a good yield of 1,2-dibromopropane but 1,2-epoxycyclohexane gave several unidentified products including an unsaturated bromo compound in rather low yield but no dibromocyclohexane. 1-Chloro-2,3-epoxypropane gave a mixture from which none of the corresponding dibromo derivative was obtained. From 2,2-dimethoxypropane were obtained methyl bromide and two other products tentatively identified as 2-bromopropene and 2,2-dibromopropane.

The result with 1,2-epoxypropane is of interest in comparison with the inertness of di-2-chloroethyl ether since a reasonable intermediate in the formation of 1,2-dibromopropane would be **1** and/or **2** having a β-halo group and thus analogous to the intermediate (**3**) expected from the chloro ether. This suggests that the low reactivity of the chloro ether is due to nonformation of **3**. The results with epoxycyclohexane are consistent with the probable intermediate (**4**) undergoing primarily elimination (rather than substitution by bromide) to form a nonvolatile phosphonium salt plus some cyclohexenyl bromide.



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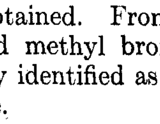

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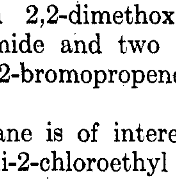

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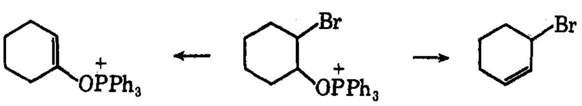

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Treatment of alkyl sulfides under conditions which were effective with ethers showed the sulfides to be very resistant to cleavage. *n*-Butyl sulfide and triphenylphosphine dibromide in DMF at 155° or in benzonitrile at 207° gave only a trace of *n*-butyl bromide. This was formed at the start of the reaction and appeared to be due to the presence of a small amount of hydrogen bromide as there was no further change on extended heating. 3-(Ethyl propanoate) sulfide in DMF at 155° was also inert. Benzyl sulfide, in contrast, reacted fairly rapidly and benzyl bromide and triphenylphosphine sulfide was identified as products.

Experimental Section

General.—Melting points were taken on a Fischer apparatus and are uncorrected. A 580 × 10 mm glass helices packed column fitted with a heated jacket and total reflux, partial take-off head was used for fractional distillations unless otherwise noted. Nmr spectra were obtained on a Varian Model A-60 analytical spectrometer with tetramethylsilane as an internal standard. Vpc analyses were made with an Aerograph Model A-90-C using a 0.25 in. × 5 ft silicone Dow 710 on Chromosorb W column. Peak identities were determined by comparisons (retention times and mixed chromatography) with authentic samples.

Triphenylphosphine was generously provided by M & T Chemicals, Inc., and was not further purified. Baker Analyzed Reagent bromine was used as obtained. DMF (Aldrich Chemical Co., Inc.) was distilled, bp 43–44° (12 mm), from sodium sulfate or dried over Linde 4Å molecular sieves. Ethers for which no preparation is given were stock samples which were dried and redistilled.

The nmr spectra of the ethers used and the alkyl halides isolated were in agreement with their molecular structures.

Neopentyl Chloride.—The method was that of Whitmore and Fleming[16] who reported no details. In that explosions or fires occurred unless specific precautions were taken, a detailed procedure is given here. 2,2-Dimethylpropane (Phillips Petroleum Co.) (88 g, 1.22 mol) was condensed into a tared, oven-dried apparatus swept with dry, O_2-free nitrogen and consisting of a 500-ml, three-necked, round-bottom flask equipped with a sealed (ground glass) stirrer, a solid CO_2 cooled condenser, a drying tube ($CaSO_4$), and a gas inlet. Cl_2 gas was then admitted very slowly over the hydrocarbon until a light yellow color was apparent in the liquid and the condensate. Cl_2 admission was then stopped and reaction was initiated by short bursts of light from a 100-W bulb directed at the gas inlet joint. When condensation was observed on the inside of this joint, a slow flow of Cl_2 was resumed. The addition rate was increased slowly until a steady production of HCl and a slow, steady drip from the condenser occurred. When a weight increase of 43 g had occurred (equivalent to 88.5 g, 1.25 mol of Cl_2), addition was stopped and the mixture, after attaining room temperature, was removed and distilled to give 54.3 g (42%) of pure [bp 83.5–84.5° (lit.[16] 84.4°)] neopentyl chloride.

Di-*tert*-butyl Ether.—The method of Erickson and Ashton[17] was used with the modification of a dry, O_2-free nitrogen atmosphere. Vpc analysis of the reaction mixture after 24 hr showed 44.9% ditertiary butyl ether, 27.8% 2-methyl-2-propanol, and 27.4% 2-chloro-2-methylpropane (exclusive of diethyl ether and isobutene) and after 48 hr 59, 39.4, and 1.7%, respectively, of these compounds. Filtration, washing with water, drying, and distillation gave 2.099 g [bp 105–106° (lit.[17] 106.5–107°)] consisting of 97.1% ditertiary butyl ether and 2.9% 2-methyl-2-propanol and a residue (1.947 g) of pure ether, total yield 35.6%.

***tert*-Butyl *n*-Butyl Ether.**—The method of S.-O. Lawesson and N. C. Yang[18] was modified in the work-up to include, for a 0.5-mol reaction, washing with four 100-ml portions of 5% $FeSO_4$ following the 2 *N* NaOH washes. The product (31.3 g, 47.5%) obtained [bp 123.5–124.5° (lit.[19] 124°)] was shown by vpc to be 95.1% *tert*-butyl *n*-butyl ether, 3.49% 2-methyl-2-propanol, 0.44% 1-chlorobutane, and 1.05% unknown compound.

***tert*-Butyl *sec*-Butyl Ether.**—The method for *tert*-butyl *n*-butyl ether was used and gave 36.3 g (56.9%) of product, bp 24–25 (10 mm) and 114.5–115.5° (760 mm) (lit.[20] 114–115°).

***tert*-Butyl Neopentyl Ether.**—The method for *tert*-butyl *n*-butyl ether was used and gave 59.3 g (82.3%) of product, bp 122–123°.

Anal. Calcd for $C_9H_{20}O$: C, 75.00; H, 13.89. Found: C, 75.11; H, 13.87.

***tert*-Butyl Isobutyl Ether.**—The method for *tert*-butyl *n*-butyl ether was used and gave 55.01 g of material [bp 112.5–114° (lit.[20] 114°)] shown by vpc to consist of 97.5% (82.5% yield) of product.

Triphenyldibromophosphorane.—The following procedure is representative of those used with the various solvents (benzonitrile, DMF, CCl_4, acetonitrile, and chlorobenzene).

The method of Schaefer and Higgins[21] was followed using a 200-ml flask, oven-dried glassware, a positive pressure O_2-free N_2 atmosphere, 20.2 g (0.077 mol) of triphenylphosphine, 12.3 g (0.077 mol) of Br_2, and 100 ml of dry benzonitrile. Colorless crystalline phosphorane precipitated when the addition of Br_2 was *ca.* one-half complete.

If solvent-free product was desired, acetonitrile or CCl_4 was used as the solvent, the flask was then cooled to −68° or until the solvent solidified and connected to an aspirator through a

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solid CO_2 cooled trap, and the pressure was reduced to *ca.* 12 mm. The solvent, especially the last portion, was removed slowly as the mixture was allowed to come slowly to room temperature (too high temperatures or vacuum cause sublimation of the phosphorane and leave a yellow-orange tinged product). The dry product was carefully protected from moisture. The addition of 1-methyl-2-pyrrolidone at this point afforded solutions in this solvent.

Procedure for Reaction of Ethers and Sulfides with Triphenyldibromophosphorane.—The phosphorane reagent was prepared immediately prior to use. For benzonitrile and chlorobenzene solvents, the ether was added in one portion to the preheated reagent mixture (unless specified otherwise) and this temperature was maintained until vpc analysis showed the presence of little or no starting ether. The cooled mixture was transferred with the aid of ethyl ether or CCl_4 to a boiling flask and distilled (vacuum if needed) through the column described in the General section. Further work-up was as given for a particular ether.

A. **Di-*n*-pentyl Ether.**—The reagent (0.052 mol), benzonitrile (50 ml), and the ether (6.6 g, 0.0416 mol) were heated at 122–130° for 4 hr and then distilled. The material having a boiling point up to 72° (12 mm) was washed with aqueous Na_2CO_3, dried ($MgSO_4$), and distilled. The fraction (2.02 g) of bp 120–128° contained 60.7% 1-bromopentane, the fraction (9.83 g, 78%) of bp 128–129.5° was pure 1-bromopentane, and the residue (12.9 g) contained 11% 1-bromopentane, total yield 12.47 g (99%).

B. **Di-*n*-butyl Ether.**—The distillate (12 mm) from 0.077 mol of the reagent in benzonitrile (100 ml) and 10 g (0.077 mol) of the ether mixed at room temperature and heated at 122° for 4 hr was collected in solid CO_2 cooled traps, washed with aqueous Na_2CO_3, dried ($MgSO_4$), and distilled. The fraction (15.17 g, 71.9%) of bp 100–101° was pure 1-bromobutane. A forerun (1.66 g, bp 35.5–100°) contained 50% 1-bromobutane, total yield 16 g (76%).

C. **Diallyl Ether.**—The distillate (12 mm) from 0.052 mol of the reagent in benzonitrile (50 ml) and 4.9 g (0.05 mol) of the ether heated at 121° for *ca.* 1 hr was collected. The fraction (7.67 g, 63.4%) of bp 69–70° was pure allyl bromide and a forerun (1.24 g, bp 35–69°) contained 50% allyl bromide, total yield 8.29 g (68.5%).

D. **Diisopropyl Ether.**—The reagent (0.53 mol), benzonitrile (50 ml), and the ether (5.1 g, 0.05 mol) were heated at 122° for 6 hr and then at 127° for 3 hr, and the mixture was distilled (12 mm) using a solid CO_2 cooled receiver and trap. The combined contents of the receiver and trap were washed with aqueous Na_2CO_3, dried ($MgSO_4$), and distilled. The fraction (7.28 g, 59.2%) of bp 59–60.1° was >99% 2-bromopropane, the forerun (0.505 g, bp 35–59°) contained 44.2% 2-bromopropane, and the residue (4.743 g) contained 14.5% 2-bromopropane and 6% diisopropyl ether, total yield 8.19 g (66.7%, 70.7% net).

E. **Tetrahydrofuran.**—The reagent (0.052 mol), 50 ml of chlorobenzene, and the ether (3.6 g, 0.05 mol) were heated at 126° for 1 hr. Diphenylmethane (75 ml) was added prior to distillation. The fraction (13.194 g) collected at 94–95° (*ca.* 14 mm) contained 61.5% 1,4-dibromobutane, yield 75.1%.

F. ***tert*-Butyl *n*-Butyl Ether.**—The ether (29.3 g, 0.225 mol) was added to the reagent (0.25 mol) in *ca.* 175 ml of DMF at room temperature. After 12 min vpc analysis showed a small amount of 2-bromo-2-methylpropane and a larger proportion of isobutene in addition to the ether. There was no further change after 42 min at room temperature or after 1 hr at *ca.* 60°. The mixture was heated to 110° over a 1-hr period during which time (at 85°) darkening and gas evolution began and increased as the temperature rose. Analysis showed 1-bromobutane, 2-bromo-2-methylpropane, isobutene, and a small amount of the ether. Distillation (12 mm) of the mixture after an additional hour at 115° and addition of the distillate (*ca.* 170 ml) to 450 ml of ice water caused separation of an oil. Extraction with three 75-ml portions of ethyl ether left a dark, tarry residue which contained no starting ether or bromoalkanes and was discarded. Distillation of the dried ($MgSO_4$) ether extract gave 21.715 g (bp 99.5–102°) of liquid containing 98.8% 1-bromobutane. The forerun (3.53 g, 85–99.5°) contained 13.5% 2-bromo-2-methylpropane and 75.4% 1-bromobutane, and the residue (6.492 g) contained 53.3% 1-bromobutane. The total yield of 1-bromobutane was 89.5%, and of 2-bromo-2-methylpropane 1.55%.

G. ***tert*-Butyl *sec*-Butyl Ether.**—A solid CO_2 cooled trap was placed in the N_2 exit line of the apparatus. The ether (30 g, 0.231 mol) was added to 0.25 mol of the reagent and 200 ml of DMF and the temperature of the mixture was raised to 70° in 20 min. Analysis showed the presence of a very small amount of 2-bromobutane, a larger amount of isobutene, and starting ether. After 2 hr (80°) gas evolution had become pronounced and this temperature was maintained for 2.5 hr. Analysis during this period showed little change in composition. The distillate (*ca.* 12 mm) from the mixture was added to ice water and extracted with ethyl ether. The dried ($MgSO_4$) extracts were distilled. Forerun fractions (3.206 g, bp 62–87°, and 1.35 g, bp 87–88°) contained 9.9 and 1.2% 2-bromo-2-methylpropane and 64.6 and 95.3% 2-bromobutane, respectively. The volatile portion (5.95 g) of the residue was pure 2-bromobutane. The total yield of 2-bromobutane was 66.9% and the yield of 2-bromo-2-methylpropane was 1.05%.

Bromine was added to the contents of the cold trap until the red-brown color persisted. The mixture was allowed to stand overnight at room temperature and yielded 25.7 g (51.3%) of 1,2-dibromo-2-methylpropane.

H. ***tert*-Butyl Isobutyl Ether.**—The ether (30 g, 0.231 mol) was added to 0.25 mol of the reagent in 220 ml of DMF and the mixture was maintained at room temperature for 2 hr. Analysis showed small amounts of 1-bromo-2-methylpropane and isobutene. The mixture was then heated such that it reached 80° after 1 hr and was held at this temperature for 3 hr. During this period there was a steady decrease in ether content and a slow increase in the alkyl bromide, except in the last minutes when the latter began to decrease. The mixture was distilled (*ca.* 12 mm) with a maximum pot temperature of 105°. A tarry residue remained. The distillate was added to 400 ml of cold water, the mixture was extracted (ethyl ether) and the dried ($MgSO_4$) extracts were distilled. The fraction (6.184 g) of bp 88.3–91.2° contained 94% (5.81 g) 1-bromo-2-methylpropane, 3.98% 2-bromo-2-methylpropane, 1.88% isobutene, and 0.179% *tert*-butyl iso-butyl ether. During the collection of this material isobutene was continuously evolved from the mixture, hence the observed boiling range.

The volatile portion (11.5 g) of the pot residue consisted of 94.2% (10.83 g) 1-bromo-2-methylpropane, 1.79% unchanged ether, 3.46% 2-bromo-2-methylpropane, and 0.47% isobutene. An additional 0.26 g of 1-bromo-2-methylpropane was found in the forerun (bp 60–88.3°) for a total of 16.9 g (53.5%). The yield of 2-bromo-2-methylpropane was 4.43% and of isobutene (including the dibromide from reaction of the contents of the cold trap with bromine) was 19%.

I. **Di-*tert*-butyl Ether.**—The ether (5.13 g, 39.6 mmol) was added to 40 mmol of the reagent and 50 ml of DMF. The mixture became warm and darkened and the undissolved reagent disappeared in *ca.* 5 min. Some gas was evolved. The flask was covered with Al foil and allowed to stand for 2 days. Analysis showed the presence of 2-bromo-2-methylpropane and isobutene (*ca.* 1:2) but no ether. Distillation (*ca.* 12 mm) was accompanied by gas evolution and gave less than 0.1 g of the alkyl bromide.

In a separate run on a test tube scale no starting ether remained after 5 min.

J. ***tert*-Butyl Neopentyl Ether.**—The ether (34.6 g, 0.24 mol) was added to 0.25 mol of the reagent and 225 ml of DMF. No reaction had occurred after 2 hr. The mixture was then heated such that it reached 77° in 45 min and 91° 4 hr later. At *ca.* 80° the mixture darkened and evolved gas and the latter continued until *ca.* 85°. After an additional day at room temperature, the mixture was distilled (12 mm). The majority of distillate was collected up to 43°, after which time the rate decreased and, finally, a viscous colorless material (bp 87–88°) crystallized and plugged the receiver. The distillate (containing some of the high boiling solid) was added to 300 ml of cold water and extracted with ethyl ether. The dried ($MgSO_4$) extract was distilled. The fraction of bp 96–101° (1.471 g) contained 65.5% neopentyl bromide, 19.6% unchanged ether, 3.16% 2-bromo-2-methylpropane, 2.81% isobutene, and 6.39% ethyl ether. The fraction of bp 101–104.5° (6.547 g) contained 75% neopentyl bromide, 0.5% isobutene, and 23.5% of unchanged ether. A third fraction of bp 104.5–105° (7.917 g) contained 65.4% neopentyl bromide and 33.9% unchanged ether. The volatile portion (3.3 g) of the residue contained 37.55% neopentyl bromide and 60.8% unchanged ether. The total recovered unchanged ether was 6.52 g and the total yield of neopentyl bromide was 11.81 g (32.8%, 40.5% net) and of isobutene (including the dibromide from the contents of the cold trap) 37.4%. The nonvolatile portion of the residue contained

2.39 g of colorless hygroscopic, crystalline solid, mp 128–134°, which was not characterized further.

An *n*-propyl alcohol solution of the material which plugged the receiver in the vacuum distillation was heated at 80° for 10 min. Analysis showed the presence of 1-bromopropane. On standing, colorless crystals of triphenylphosphine oxide [mp 153–154° (lit.[22] 156°)] separated. The crystalline material of bp 87–88° (12 mm) was probably triphenyldibromophosphorane as this is known to react with alcohols to form alkyl bromides and triphenylphosphine oxide.[7,9b]

The residue from the vacuum distillation was dissolved in water plus benzene–ether. After concentration, the black water solution yielded crystalline dimethylammonium chloride, and a total of 63.6 g (93%) of triphenylphosphine oxide was obtained from the organic solution.

K. Ethyl Phenyl Ether. In Benzonitrile.—To 0.104 mol of the reagent in 100 ml of benzonitrile at 110° was added 12.2 g (0.1 mol) of the ether and the mixture was heated to 124° over a 45-min period and maintained at that temperature for 7 hr during which time analysis showed a continual decrease in ether and an increase in bromoethane.[23] From the distillate [bp up to 79° at (12 mm)] and the contents of two solid CO_2 cooled traps was obtained a total of 4.35 g (40%) of bromoethane (bp 38.5–40°).

The distillation residue, from which small aggregates of colorless crystals had separated after 1 day, was dissolved in dichloromethane and CCl_4 was added slowly until colorless crystals began to separate. After 2 days the mixture was chilled and the collected hygroscopic tan and white solid was washed with a little cold solvent mixture. Dissolution of a sample in wet acetone formed phenol (vpc and mp 38–41°). Reaction with H_2O gave an acidic solution and an oil from which, after dissolution in ether and chromatography over alumina, was obtained triphenylphosphine oxide (mp 154–155°). The properties of the solid corresponded to those of the product obtained from the reaction of phenol with the reagent and thus the solid was probably triphenylbromophenoxyphosphine but a satisfactory elemental analysis could not be obtained.

Neat.—The reagent (0.52 mol) was prepared in 60 ml of acetonitrile and the solvent was removed. The ether (6.1 g, 0.05 mol) was added and the mixture was heated on a sand bath. Above 140° bromoethane was given off and removed by distillation. Near 180° the mixture became black. The bath temperature was kept at 230–245°. After 45 min a small sample of the mixture was dissolved in wet acetone and vpc analysis of the solution showed phenol and bromobenzene (2:1) but almost no ether. After an additional 1.5 hr at 230°, the black glass which formed on cooling was dissolved in dichloromethane. Water (200 ml) was added and the mixture distilled. The initial distillate was made slightly acidic and extracted with ethyl ether and the dried ($MgSO_4$) extracts were concentrated. A small amount of phenol was removed by washing with aqueous NaOH and then removal of the solvent gave 1.91 g (24%) of bromobenzene. A small amount (0.09 g) of phenol (mp 38–41°) was obtained from the distillation residue.

L. 1,2-Epoxypropane.—The epoxide (5.8 g, 0.1 mol) was added to 0.107 mol of the reagent and 100 ml of DMF and the mixture was cooled (water bath) until the exothermic reaction had subsided and the reagent had disappeared (*ca.* 5 min). Analysis showed the absence of epoxide and a small amount of a volatile product. The mixture was then heated at 127° for *ca.* 45 min. Vacuum distillation afforded a colorless distillate and a dark gray crystalline residue. The latter was impure triphenylphosphine oxide, mp 149–153°. The addition of one-half of the distillate (half was lost) to 150 ml of cold water formed an oil layer and extraction (ether) and concentration of the dried ($MgSO_4$) extracts gave 9.87 g of light yellow oil which was shown by vpc analysis to contain 8.17 g (corresponding to 81% yield) of 1,2-dibromopropane.

M. 2,2-Dimethoxypropane.—The solvent was removed (vacuum distillation) from 0.107 mol of the reagent prepared in 100 ml of acetonitrile and the ketal (5.2 g, 0.05 mol) was added. After 3 hr at room temperature, the now dark mixture was heated. At *ca.* 100° bromomethane and at *ca.* 230° HBr were evolved. After 45 min at 230° the mixture was cooled and the black glossy material dissolved in 80 ml of DMF and then distilled. The distillate was added to 300 ml of H_2O and the whole mixture was extracted with ethyl ether. Removal of solvent from the dried ($MgSO_4$) extracts left 9.32 g of oil. Vpc analysis showed 41.2% of material (bp *ca.* 120°) which gave an nmr spectrum consistent with the structure of 2,2-dibromopropane (37.6% yield) and 13.9% of low boiling (*ca.* 50°) material which rapidly decolorized bromine and slowly reacted with alcoholic silver nitrate. This product was thought to be 2-bromopropene (21.5% yield).

N. Dibenzyl Sulfide.—The sulfide (10.7 g, 0.05 mol) was added to 0.052 mol of the reagent in 100 ml of DMF. After standing at room temperature overnight (the reagent had dissolved), the mixture was heated rapidly to 150°, then at 120° for 1 hr, at 140° for 2 hr, and at 150° for 2.5 hr during which time vpc analysis showed three products with increasing amounts of the two highest boiling products (the lower boiling of which was benzyl bromide) and decreasing amounts of the lowest boiling product. The highest and lowest boiling products were not starting sulfide or benzyl alcohol, respectively, and were not identified. The cold distillate [bp up to 59° (12 mm)] from the red-brown mixture was added to 300 ml of water and ice. Ether extraction and removal of the solvent from the dried ($MgSO_4$) extracts left a residue which contained *ca.* 2.4 g (14%) of benzyl bromide and *ca.* 4.9 g of DMF. Addition of 40 ml of ether to a solution of the pot residue in 30 ml of acetonitrile gave two layers and enough additional acetonitrile was added to form a homogeneous solution. Concentration under a N_2 stream to one-half volume and then cooling caused separation of crystalline triphenylphosphine sulfide which was collected, rinsed with cold acetonitrile, and dried at 0.01 mm for 12 hr, 7.57 g (51.5%), mp 156.5–158° (lit.[24] 157–158°).

Registry No.—Triphenyldibromophosphorane, 1034-39-5; *n*-pentyl ether, 693-65-2; *n*-butyl ether, 142-96-1; allyl ether, 557-40-4; isopropyl ether, 108-20-3; tetrahydrofuran, 109-99-9; *n*-pentyl bromide, 110-53-2; *n*-butyl bromide, 109-65-9; allyl bromide, 106-95-6; isopropyl bromide, 75-26-3; 1,4-dibromobutane, 110-52-1; *n*-butyl *tert*-butyl ether, 1000-63-1; *sec*-butyl *tert*-butyl ether, 32970-45-9; isobutyl *tert*-butyl ether, 33021-02-2; *tert*-butyl *tert*-butyl ether, 6163-66-2; neopentyl *tert*-butyl ether, 32970-46-0; dibenzyl sulfide, 538-74-9; ethyl phenyl ether, 103-73-1.

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(22) R. Sauvage, *C. R. Acad. Sci.*, **139**, 674 (1904).

(23) Some bromoethane was lost *via* the N_2 exit line.

(24) L Maier, *Helv. Chim. Acta*, **47**, 27 (1964).