Anal. Calcd. for $C_{12}H_{10}P_2O_7Ba \cdot 2H_2O$; P, 12.4. Found: P, 12.3. R_f 0.51 (propyl alcohol–concd. ammonia–water, 6:3:1).

A 1.1-g. sample *i.e.* 18% of barium phenyl hydrogen phosphate was recovered by adding 10 ml. of pyridine and 20 ml. of acetonitrile to the latter filtrate.

Anal. Calcd. for $C_6H_5PO_4Ba \cdot H_2O$; P, 9.45. Found: P, 9.31. R_f 0.51 (propyl alcohol–concd. ammonia–water, 6:3:1).

Reaction of Ketene Dimer with *p*-Chlorophenyl Dihydrogen Phosphate.—By the same procedure barium di-*p*-chlorophenyl pyrophosphate was obtained in 70% yield.

Anal. Calcd. for $C_{12}H_8Cl_2P_2O_7Ba \cdot 2H_2O$: P, 10.9. Found: P, 11.1.

Reaction of Ethyl Vinyl Ether with Diethyl Hydrogen Phosphate.—To a solution of ethyl vinyl ether (2.4 g., 0.03 mole) in 10 ml. of dry ether, a solution of diethyl hydrogen phosphate (5.1 g., 0.03 mole) in 5 ml. of dry ether was added dropwise with continuous stirring. Stirring was continued for 3 hr. at room temperature. After removal of ether and diethyl acetal which contains acetaldehyde, the residue was distilled under reduced pressure and 4.5 g. (92%) of tetraethyl pyrophosphate, b.p. 148–149°/1.5 mm., was obtained.

Reaction of Diethyl Phosphorochloridite with Diethyl Hydrogen Phosphate.—To a solution of diethyl hydrogen phosphate (3.1 g., 0.02 mole) in 15 ml. of dry benzene, a solution of diethyl phosphorochloridite (1.6 g., 0.01 mole) and diethylaniline (1.5 g., 0.01 mole) in 10 ml. of dry benzene was added dropwise over a period of 8 min. with vigorous stirring at room temperature. Stirring was continued for an additional 20 min. The mixture was cooled to 0° and the precipitate of diethylanilinium chloride was removed from the filtrate. Benzene was removed from the filtrate under reduced pressure and the residual materials fractionated. One gram (72%) of diethyl phosphite, b.p. 72–74/14 mm. and 2.8 g. (97%) of tetraethyl pyrophosphate, b.p. 124–130°/0.5 mm. were obtained.

Reaction of Diethyl Phosphorochloridite with Phenyl Dihydrogen Phosphate.—To a solution of phenyl dihydrogen phosphate (1.74 g., 0.01 mole) and pyridine (1.58 g., 0.02 mole) in 15 ml. of dry acetonitrile, a solution of diethyl phosphorochloridite (1.57 g., 0.01 mole) in 10 ml. of dry acetonitrile was added with continuous stirring at room temperature. After 15 min., a further 1.74 g. of phenyl dihydrogen phosphate was poured into the solution. It was allowed to stand overnight at room temperature and excess pyridine was added. The solution was allowed to stand for 15 min. after which a solution of 2.5 g. of barium chloride was added. A large amount of white precipitate was filtered and was washed with two 80-ml. portions of cold water and dried *in vacuo* over phosphorus pentoxide at room temperature. Barium diphenyl pyrophosphate, 4.32 g. (86%), was obtained. The R_f of this compound was 0.80 in a mixture of propyl alcohol, concd. aqueous ammonia, and water (6:3:1).

Reaction of Tetraethyl Pyrophosphite with Diethyl Hydrogen Phosphate.—A solution of diethyl hydrogene phosphate (3.1 g., 0.02 mole) in 4 ml. of dry benzene was added to a solution of tetraethyl pyrophosphite (2.6 g., 0.01 mole) in 6 ml. of dry benzene with continuous stirring. Then the solution was kept at 45° for 1.5 hr. and allowed to stand overnight at room temperature. After removal of the benzene, diethyl phosphite, 1.2 g. (87%), b.p. 65°/5 mm., and 2.8 g. (97%) of tetraethyl pyrophosphate, b.p. 128–131°/0.6 mm., were obtained.

Reaction of Tetraethyl Hypophosphate with Ethanol in the Presence of Aluminum Ethoxide.—A solution of tetraethyl hypophosphate (III) (2.8 g., 0.01 mole) in 20 ml. of dry benzene was added to the suspension of aluminum ethoxide (1.6 g., 0.01 mole) in 10 ml. of dry benzene. The suspension soon became clear. The solution was stirred for an additional 20 min. after which a mixture of 0.5 g. of absolute ethanol and 5 ml. of dry benzene was added dropwise. It was then heated at 60° for 30 min.; the solution became gruelly. The thick mixture was allowed to stand overnight and then distilled under reduced pressure; 0.7 g. (51%) of diethyl phosphite, b.p. 70–72°/10 mm. and 1.0 g. (55%) of triethyl phosphate, b.p. 93–95°/10 mm., were obtained and 2.2 g. of white solid was left in the flask.

Acknowledgment.—The authors wish to express their gratitude to Dainippon Celluloid Co., Ltd., for the gift of ketene dimer.

Reactions of Phosphines with Cyclic Carbonate Esters

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Received October 23, 1961

Reactions of ethylene and substituted ethylene carbonates with secondary and tertiary phosphines result in oxidation of the phosphine and liberation of the olefin corresponding to the carbonate used. Secondary phosphines are converted to alkylenebis- or 2-hydroxyalkylphosphine oxides, depending upon the choice of carbonate. With higher-molecular weight ethylenic carbonates, phosphine oxidation and subsequent olefin synthesis occur only if a catalyst is used, or if the phosphine is sufficiently basic, or if there is a hydroxyl substituent on the carbonate. Large-ring carbonates (*e.g.*, tetramethylene carbonate) do not oxidize tertiary phosphines. Triphenyl phosphite reacts with ethylene carbonate in the presence of copper to yield tetraphenyl ethylenediphosphonate.

Under properly controlled reaction conditions, cyclic carbonates are excellent hydroxyalkylating agents. Ethylene carbonate and propylene carbonate react with compounds containing active hydrogen to yield 2-hydroxyethyl and 2-hydroxypropyl derivatives.[1–6] In an attempt to prepare 2-hydroxyethyl phosphines we therefore chose ethylene carbonate as a hydroxyethylating agent for secondary phosphines and from these reactions obtained some unexpected results.

Ethylene carbonate reacted with representative

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(1) W. W. Carlson, U. S. Patent 2,448,767 (September 7, 1948).

(2) W. W. Carlson and L. H. Cretcher, *J. Am. Chem. Soc.*, **69**, 1952 (1947).

(3) M. S. Morgan and L. H. Cretcher, *ibid.*, **68**, 781 (1946).

(4) F. Strain, W. E. Bissenger, *et al.*, *ibid.*, **72**, 1254 (1950).

(5) F. Strain, U. S. Patent 2,441,298 (May 11, 1948).

(6) K. Yanagi and S. Akiyoshi, *J. Org. Chem.*, **24**, 1122 (1959).

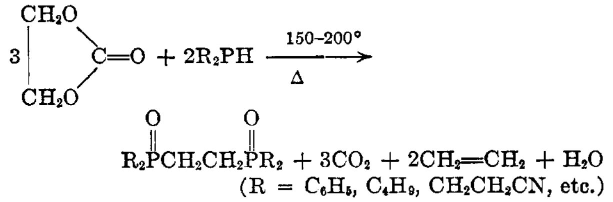
TABLE I

REACTIONS OF SECONDARY PHOSPHINES AND PHOSPHINE OXIDES WITH CYCLIC CARBONATES

Reactants		Reaction Conditions				
Phosphines	Carbonate	Temp.	Solvent	Catalyst	Product	Yield (%)
$(C_6H_5)_2PH$	Ethylene	210°	None	None	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(C_6H_5)_2$[a]	58
$(C_6H_5)_2PH$	Ethylene	82.4°	2-Propanol	HMBG[b]	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(C_6H_5)_2$	58.5
$(C_6H_5)_2PH$	Ethylene	144.4°	Xylene	None	....	[c]
$(C_6H_5)_2PH$	Propylene	185°	None	None	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2\overset{CH_3}{\overset{\|}{C}}H\,\overset{O}{\overset{\|}{P}}(C_6H_5)_2$	48[d]
$(C_6H_5)_2PH$	Vinylene	120–160°	None	HMBG	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(C_6H_5)_2$	58
$(C_6H_5)_2\overset{O}{\overset{\|}{P}}H$	Ethylene	200°	None	None	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(C_6H_5)_2$	50
$(C_6H_5)_2\overset{O}{\overset{\|}{P}}H$	Propylene	82.4°	2-Propanol	HMBG	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2\overset{CH_3}{\overset{\|}{C}}HOH$[e] $(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2\underset{CH_3}{\underset{\|}{C}}H\overset{O}{\overset{\|}{P}}(C_6H_5)_2$[g]	32 (77[f])
$(C_6H_5)_2\overset{O}{\overset{\|}{P}}H$	Propylene	118°	1-Butanol	HMBG	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2\underset{CH_3}{\underset{\|}{C}}HOH$	79[h]
$(C_4H_9)_2PH$	Ethylene	160°	None	None	$(C_4H_9)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(C_4H_9)_2$[i]	33
$(NCCH_2CH_2)_2\overset{O}{\overset{\|}{P}}H$	Ethylene	180°	None	None	$(NCH_2CH_2C)_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(CH_2CH_2CN)$[j]	52

[a] White crystalline solid, m.p. 273–275°. Lit. m.p. 256–257° [K. Issleib and D. W. Muller, *Chem. Ber.*, **92,** 3175 (1959)]. *Anal.* Calcd. for $C_{26}H_{24}P_2O_2$: C, 72.55; H, 5.62; P, 14.39. Found: C, 72.50; H, 5.83; P, 14.32. [b] Heptamethylbiguanide. [c] This reaction was allowed to run overnight. During this time the solvent evaporated and the pot temperature rose to over 200°. Infrared analysis identified the crude reaction mixture as the alkylenebis(phosphine oxide). [d] Crude yield. Product could not be made to crystallize from a variety of organic solvents. [e] Colorless liquid, b.p. 160–165°/0.25 mm. *Anal.* Calcd. for $C_{15}H_{17}O_2P$: C, 69.21; H, 6.49; P, 11.90. Found: C, 70.91; H, 6.95; P, 10.32. [f] Crude yield. Upon attempted distillation 32% of the 2-hydroxy alcohol was obtained. The remaining 45% of material was pyrolyzed to a tar which upon extraction with benzene yielded 10.5% of the alkylenebis(phosphine oxide). [g] White crystalline solid, m.p. 53–54°. *Anal.* Calcd. for $C_{27}H_{26}P_2O_2$: C, 72.97; H, 5.90; P, 13.94. Found: C, 73.17; H, 6.18; P, 13.73. [h] Crude yield. [i] White crystalline solid, m.p. 165–166°. *Anal.* Calcd. for $C_{18}H_{40}P_2O_2$: C, 61.68; H, 11.50; P, 17.67. Found: C, 60.68; H, 11.12; P, 17.52. [j] White crystalline solid, m.p. 224–225°. *Anal.* Calcd. for $C_{14}H_{12}P_2N_4O_2$: C, 51.04; H, 3.66; N, 16.89; P, 18.76. Found: C, 49.52; H, 6.37; N, 16.56; P, 17.94.

secondary alkyl- and arylphosphines to give ethylenebisphosphine oxides in yields of 40–60%, plus carbon dioxide and ethylene (Table I).

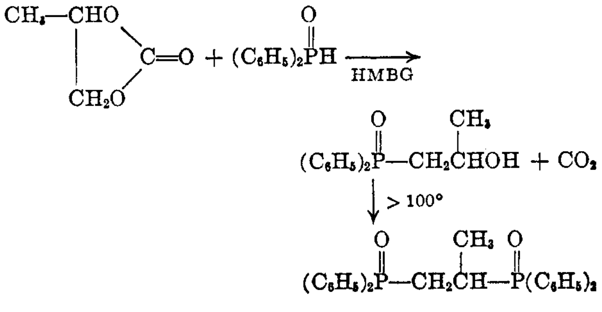


$$3\,(CH_2O)_2C{=}O + 2R_2PH \xrightarrow[\Delta]{150\text{–}200°} R_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}R_2 + 3CO_2 + 2CH_2{=}CH_2 + H_2O$$

$(R = C_6H_5, C_4H_9, CH_2CH_2CN, etc.)$

Secondary phosphine oxides also give alkylenebisphosphine oxides but no ethylene is produced (Table I).

At lower temperatures, in a solvent such as 2-propanol, the reaction does not take place unless a basic catalyst such as heptamethylbiguanide (HMBG) is used. Under similar basic conditions vinylene carbonate reacts with diphenylphosphine to yield ethylenebis(diphenylphosphine oxide), while propylene carbonate reacts with diphenylphosphine oxide to yield a 2-hydroxypropylphosphine oxide. However, this latter reaction is extremely slow and the 2-hydroxypropylphosphine oxide that is formed decomposes upon heating in the presence of diphenylphosphine oxide to give methylethylene bis-(diphenylphosphine oxide).



$$CH_3CHO(CH_2O)C{=}O + (C_6H_5)_2\overset{O}{\overset{\|}{P}}H \xrightarrow[HMBG]{} (C_6H_5)_2\overset{O}{\overset{\|}{P}}{-}CH_2\overset{CH_3}{\overset{\|}{C}}HOH + CO_2 \xrightarrow{>100°} (C_6H_5)_2\overset{O}{\overset{\|}{P}}{-}CH_2\overset{CH_3}{\overset{\|}{C}}H{-}\overset{O}{\overset{\|}{P}}(C_6H_5)_2$$

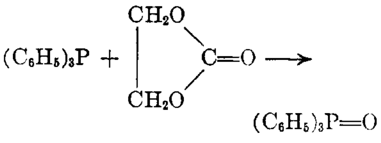
TABLE II

REACTIONS OF TERTIARY PHOSPHINES WITH CYCLIC CARBONATES

Reactants		Reaction Conditions				Product Yield, %		
Phosphine	Carbonate	Time, Hr.	Temperature	Solvent	Catalyst	Phosphine Oxide	Olefin	Phosphine, % Recovered
$(C_6H_5)_3P$	Ethylene	2	190–210	None	None	93	68	None
$(C_6H_5)_3P$	Ethylene	24	119	Acetic acid	None	None	0.8	60
$(C_6H_5)_3P$	Ethylene	15	118	1-Butanol	HMBG	None	2.2	84
$(C_6H_5)_3P$	Propylene	7	230	None	None	99	40	None
$(C_4H_9)_3P$	Ethylene	0.5	160–175	None	None	None	4.0	50[a]
$(NCCH_2CH_2)_3P$	Ethylene	24	145	None	None	None[b]	32	None[b]
$(C_6H_5)_3P$	Phenylethylene	4	250	None	None	None	None	...[c]
$(C_6H_5)_3P$	Phenylethylene	8	250–260	None	Hydroquinone	50	11.5	None
$(C_6H_5)_3P$	Phenylethylene	8	250–260	None	K_2CO_3	11.5	34.6	None
$(C_6H_5)_3P$	Phenylethylene	3	270	None	Cu/K_2CO_3	None[b]	66.5	None[b]
$(C_6H_5)_3P$	Phenylethylene	2	285	None	Cu	29.6	80	20
$(C_6H_5)_3P$	Phenylethylene	24	195	1-Octanol	Hydroquinone	53	62.5[d]	None
$(C_4H_9)_3P$	Phenylethylene	5	140–220	None	None	46[e]	62	...[e]

[a] An 80% yield of ethylene glycol was obtained from this reaction, indicating that the tributylphosphine had catalyzed the decomposition of the carbonate. [b] The reaction mixture was pyrolyzed to an intractable tar from which it was impossible to isolate any crystalline material. [c] Since there was no carbon dioxide evolution and hence no evidence of reaction, this experiment was not worked up. [d] Crude yield of mixture of styrene and 1-octanol which co-distilled. [e] Styrene was contaminated by a small quantity of tributylphosphine.

These results indicated that the reaction of cyclic carbonates with secondary phosphines involves preliminary oxidation of the phosphine. It appeared reasonable then that the oxidation step might be isolated with tertiary phosphines. It was found that when ethylene carbonate and triphenylphosphine were heated under nitrogen, over a temperature range of 130–200°, triphenylphosphine oxide and ethylene were obtained in good yield (Table II).



$$(C_6H_5)_3P + \begin{array}{l} CH_2O \\ \,|\qquad\diagdown \\ \,|\qquad\;\; C{=}O \\ \,|\qquad\diagup \\ CH_2O \end{array} \longrightarrow (C_6H_5)_3P{=}O + CH_2{=}CH_2 + CO_2$$

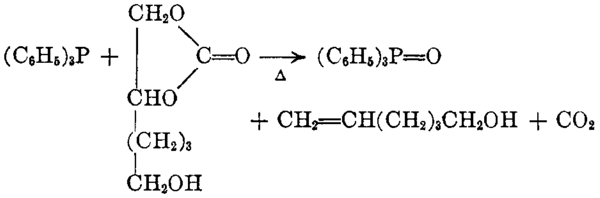
Propylene carbonate under similar conditions also oxidized the tertiary phosphine although at a slower rate. However, oxidation did not take place when the noncyclic diethyl carbonate was used.

We have also found that the reactions of triphenylphosphine and ethylene carbonate do not appear to be catalyzed by acid or base at moderate temperatures. An attempted reaction of triphenylphosphine and ethylene carbonate in refluxing glacial acetic acid resulted only in the decomposition of the carbonate and recovery of the unoxidized phosphine. Likewise, the oxidation of triphenylphosphine by ethylene carbonate did not occur in refluxing 1-butanol with heptamethylbiguanide as catalyst.

Although the oxidation of tertiary phosphines proceeds quite readily with ethylene and propylene carbonates, phenylethylene carbonate did not react with triphenylphosphine under neutral conditions at temperatures up to 250°. After examining this reaction under a variety of conditions (Table II) we found that copper powder will catalyze the reaction to yield 80.5% styrene. Using a more basic phosphine seems to favor olefin formation. When tributylphosphine was allowed to react with phenylethylene carbonate, the reaction was completed within five hours at 140 to 220° and yielded approximately 46% styrene.

Pattison[7] has reported that cyclic carbonate esters containing activating hydroxyl groups readily decompose above 150° to their cyclic ethers, whereas cyclic carbonates containing no hydroxyl groups can be distilled at high temperatures without decomposition. This decrease in carbonate stability has been ascribed to intramolecular catalysis with hydrogen bonding between the hydroxyl group and the ether oxygen of the ester.[8]

In view of this potentially greater reactivity, a hydroxyl-substituted carbonate was prepared from 1,2,6-hexanetriol and allowed to react with triphenylphosphine.



$$(C_6H_5)_3P + \begin{array}{l} CH_2O \\ \,|\qquad\diagdown \\ \,|\qquad\;\; C{=}O \\ \,|\qquad\diagup \\ CHO \\ \,| \\ (CH_2)_3 \\ \,| \\ CH_2OH \end{array} \xrightarrow[\Delta]{} (C_6H_5)_3P{=}O + CH_2{=}CH(CH_2)_3CH_2OH + CO_2$$

The theoretical carbon dioxide was evolved within one hour at 195 to 205° and a quantitative yield of the crude, unsaturated alcohol was obtained.

In considering the mechanism of the reaction of tertiary phosphines with cyclic carbonates, it should be noted that this reaction is not the first case of tertiary phosphine oxidation accompanied by olefin formation. Wittig cites two examples.[9] The first is the reaction of a phosphorane with an active carbonyl compound. In such a reaction the phosphorane unites with the carbonyl group to form a betaine, followed by closing of this betaine

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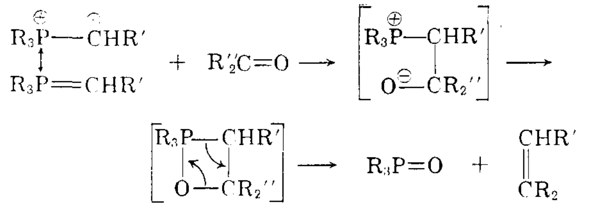
(7) D. Pattison, *J. Am. Chem. Soc.*, **79**, 3455 (1957).

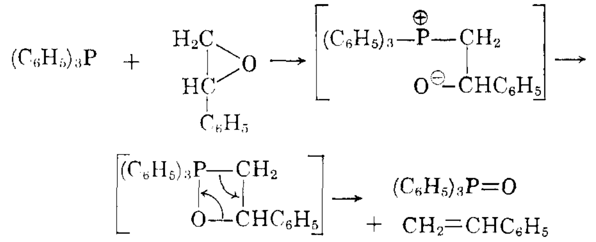
(8) H. B. Henbest and B. J. Lovell, *Chem. & Ind.*, **278** (1956); *J. Chem. Soc.*, 1965 (1957).

(9) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

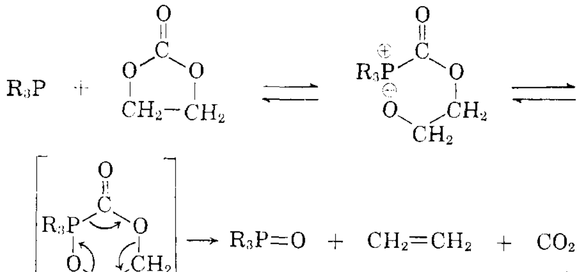


to a four-membered ring, with subsequent fission of the ring to products.

The second example is the formation of olefins from the reaction of triphenylphosphine and an epoxide at high temperatures. This reaction, too, proceeds through a betaine intermediate; however, it has been successful only with cinnamyl and styrene oxides.



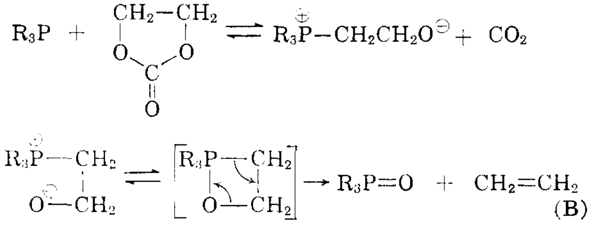
Mechanistically, the reaction of cyclic carbonates with tertiary phosphines is more involved than the analogous epoxide reaction. Phosphines can be oxidized by cyclic carbonates by either of two routes. The phosphine can attack at the carbonyl carbon of the carbonate with the formation of a six-membered cyclic intermediate that decomposes to products.



(A)

This route is similar to the reaction of amines with the carbonyl group of cyclic carbonates to yield carbamates,[4] which decompose on heating to yield 2-hydroxyethylamines and carbon dixoide.[5]

The phosphorus atom can also attack at the ether carbon of the carbonate to form a betaine and carbon dioxide, followed by closing of the betaine to a four-membered ring with subsequent fission of the ring to products.

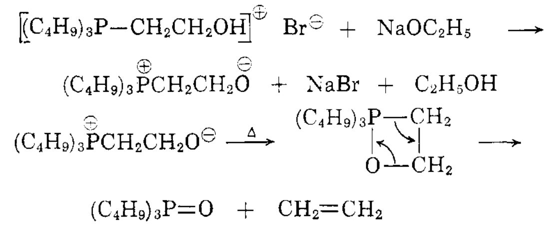


(B)

This route is similar to the mechanism proposed by Wittig[9] for the reaction of tertiary phosphines and epoxides.

A number of arguments may be adduced in favor of mechanism B aside from resemblance to the Wittig olefin and epoxide reactions. For one, the failure of acid catalysis to promote these reactions is indicative of nucleophilic attack at some site other than the carbonyl group. In addition, there is an apparent analogy to lactone chemistry favoring ether attack (B). Second-row elements show a preferential selectivity for attack at the saturated rather than the unsaturated carbon atom of lactones. Thus, when reacting with a lactone, oxygen-containing nucleophiles will usually attack at the carbonyl carbon while analogous sulfur compounds will attack at the ether carbon.[10] Similar selectivity in the nitrogen-phosphorus series seems reasonable.

More concrete evidence for mechanism B was obtained by an experiment designed to isolate the second step of the mechanism. Tributyl-2-hydroxyethylphosphonium bromide was prepared and treated with sodium ethoxide. Decomposition of the resulting betaine intermediate yielded the theoretical volume of ethylene, in less than one minute at temperature below 100°, thus indicating that the betaine



is a very reactive species. It is, therefore, most probable that the slow step in the reaction of cyclic carbonates with phosphines involves ring opening and loss of carbon dioxide to give the betaine. Possibly, the only exception to this would be the case of phenylethylene carbonate which required vigorous treatment with triphenylphosphine to form styrene. Wittig[11] has recently shown that the same betaine formed from triphenylphosphinemethylene and benzaldehyde is quite stable.

The mechanism of the reaction of ethylene carbonate with secondary phosphines is more complex. Although the exact sequence of the early stages has not been positively established, it is clear that the reaction involves both oxidation and condensation to give a stoichiometry of two moles of phosphine to three moles of carbonate. It is most likely that the phosphine is first oxidized by the carbonate *via* the same mechanism as the tertiary phosphines with the evolution of carbon dioxide and ethylene, but it is possible that a 2-hydroxyethylphosphine forms

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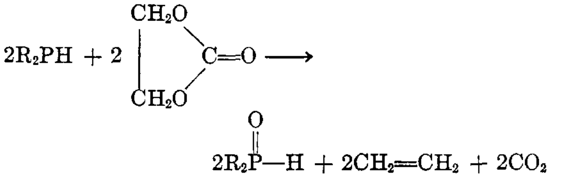
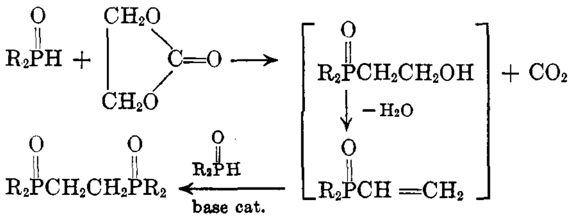
(10) P. D. Bartlett and G. Small, *J. Am. Chem. Soc.*, **72**, 4867 (1950).

(11) G. Wittig, H. D. Weigmann, and M. Schlosser, *Chem. Ber.*, **94**, 676 (1961).

before oxidation occurs. Secondary phosphine oxides react readily with ethylene carbonates to give a 2-hydroxyethyl phosphine oxide (Table I). Presumably, the 2-hydroxyethylphosphine oxide then dehydrates thermally or possibly with the assistance of a base-catalyzed elimination to give the vinylphosphine oxide. The unsaturated compound then adds a second mole of secondary phosphine oxide to give the ethylenebisphosphine oxide. Base catalysis for the latter Michael-type addition is well established for compounds with related phosphoryl structure and activated olefins.[12] When secondary phosphine oxides are allowed to react with cyclic carbonates, only the second step of the above mechanism is involved and, therefore, the reaction stoichiometry is two moles of phosphine oxide to one mole of carbonate.



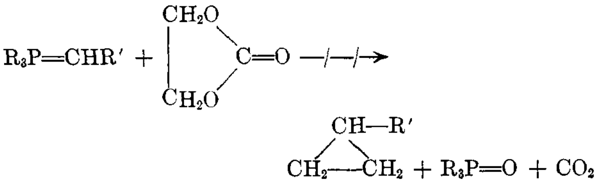
(1)



(2)

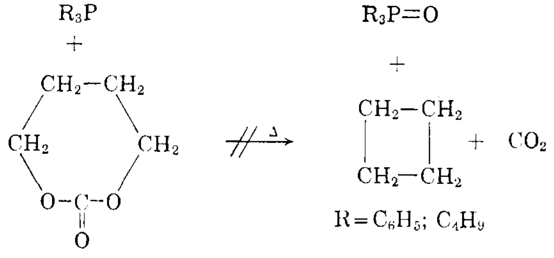
This mechanism is not unlikely, since ethylene was evolved in the reactions of secondary phosphines and cyclic carbonates and since a 2-hydroxyalkylphosphine oxide was actually isolated from the reaction of propylene carbonate and diphenylphosphine oxide. Furthermore, ethylenebis(diphenylphosphine oxide) has repeatedly been isolated in small yields in the preparation of diphenylvinylphosphine from vinyl Grignard reagent and chlorodiphenylphosphine using an alkaline work-up procedure.[13] Finally, it should be noted that the reaction of vinylene carbonate with diphenylphosphine did give ethylenebis(diphenylphosphine oxide rather than vinylenebis(diphenylphosphine oxide). However, since the other products of this reaction were not isolated, further speculation on the mechanism would not be justified.

Some further synthetic applications of the reactions of phosphines and cyclic carbonates were investigated. Several attempts were made to prepare alicyclic compounds by two alternative routes. In a recent communication,[14] Denney reported the reaction of carbethoxymethylenetriphenylphosphorane with styrene oxide to give ethyl 2-phenylcyclopropanecarboxylate. However, analogous reactions involving the thermal decomposition of phosphoranes in the presence of ethylene and phenylethylene carbonates, *e.g.*,



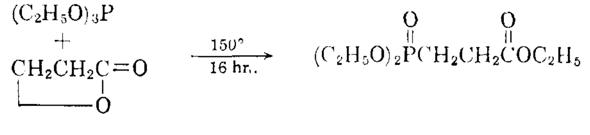
did not yield any cyclopropane derivatives. Two attempts to prepare cyclopropanes via carbethoxymethylenetriphenylphosphorane with phenylethylene carbonate and via benzoylmethylenetriphenylphosphorane with ethylene carbonate were unsuccessful and resulted in decomposition of the cyclic carbonate with partial recovery of the unreacted phosphorane. Some triphenylphosphine oxide was obtained in these reactions, probably by cleavage of the phosphorane by water introduced with the hygroscopic cyclic carbonates.

A second route to alicyclics, the direct reaction of tetramethylene carbonate with triphenyl- and tributylphosphines,



did not give cyclobutane but resulted in decomposition of the carbonate to tetrahydrofuran, with recovery of the unoxidized phosphine.

The reactions of triethyl and triphenyl phosphite with ethylene carbonate were also examined. It has been reported that triethyl phosphite reacts with β-propriolactone to give diethyl carbethoxyethyl phosphonate[15]



However, under the same conditions, triethyl phosphite did not react with ethylene carbonate.

When triphenyl phosphite was heated with ethylene carbonate, no reaction occurred; however, in the presence of a small quantity of copper powder tetraphenyl ethylenediphosphonate was formed in 40.5% yield.

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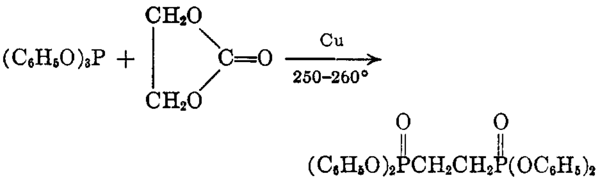
[12] A. N. Pudovik and B. A. Arbuzov, *Zhur. Obschei Khim*, **21**, 1837 (1951).

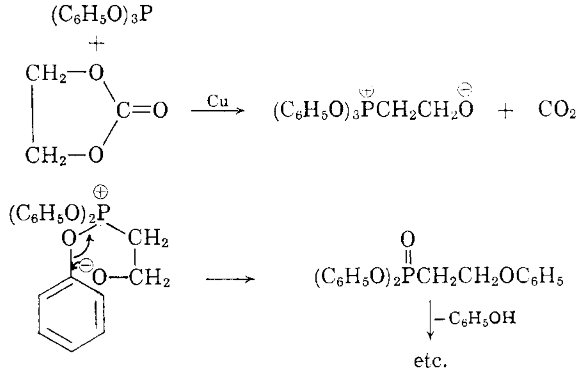
[13] R. Rabinowitz, *J. Org. Chem.*, in press.

[14] D. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

[15] H. W. Coover and J. B. Dickey, U. S. Patent 2,652,416 (September 15, 1953).



This result is not surprising since tertiary phosphites are known to undergo an Arbuzov rearrangement in the presence of alcohols resulting in the formation of phosphorus carbon bonds.[16] The first step of the reaction leading to a vinyl phosphonate may well proceed via a cyclic intermediate although other mechanisms are conceivable. The copper in this case most probably catalyzes the decomposition of the cyclic carbonate in the same way that copper catalyzed the decomposition of phenylene carbonate when it was heated with triphenylphosphine to form styrene



The process might then be completed by addition of a second phosphite molecule to the vinyl compound followed by a final rearrangement to the bisphosphonate. Detailed information concerning this reaction is not presently available and further speculation is unwarranted.

Experimental[17]

General Reaction of Secondary Phosphines and Phosphine Oxides with Cyclic Carbonates.—The individual conditions for the reactions of secondary phosphines and phosphine oxides are given in Table I. Ethylene and propylene carbonate are commercially available and vinylene carbonate was prepared by the dehydrochlorination of chloroethylene carbonate formed by the chlorination of ethylene carbonate.[18]

In general, these experiments were carried out by mixing the secondary phosphine or phosphine oxide at room temperature under nitrogen with a two-fold excess of cyclic carbonate. This mixture was heated with the reaction system open only to a gas burette. At temperatures varying from 120–150°, an *exotherm* occurred, accompanied by the vigorous evolution of gas. When this evolution subsided, the reaction mixture was cooled, washed with cold water to remove unreacted carbonate, and extracted with either benzene or chloroform. The organic extract was dried, filtered, and concentrated to yield crystalline alkylenebisphosphine oxides which, after recrystallization from benzene-hexane mixtures, were identified by infrared spectroscopy, microanalysis, and melting point data.[19] In some of the reactions of secondary phosphines and cyclic carbonates the gases evolved were analyzed by mass spectrometry and found to be mixtures of carbon dioxide and ethylene.

In those experiments that were run in solution, a 2:1 ratio of cyclic carbonate to secondary phosphine (or secondary phosphine oxide) was mixed with sufficient solvent to make the phosphine concentration 3 to 4 *M* and heated to the reflux temperature of the solvent. When heptamethylbiguanide was used as a catalyst, 0.5 ml. of it was added at reflux temperature. Refluxing was continued until the theoretical volume of gas for each reaction had been evolved. The mixture was then cooled, treated with hexane, and the viscous sirup which separated from solution was worked up as described above.

General Reaction of Tertiary Phosphines with Ethylene and Propylene Carbonates.—Conditions for the reactions of tertiary phosphines with ethylene and propylene carbonates are given in Table II. The same general procedure was used as described for the secondary phosphines and phosphine oxides and the reaction ratio was 1 mole of tertiary phosphine to 1 mole of cyclic carbonate. The tertiary phosphine oxides were identified by melting point and by infrared analysis. Ethylene and propylene were collected over water in a gas burette, and yields of olefin were determined by mass spectrometric analysis of the gases evolved during reaction.

General Reaction of Tertiary Phosphines with Phenylethylene Carbonate.—Data for these experiments are also given in Table II. The phenylethylene carbonate was prepared in 85% yield (m.p. 56–57°) from phenyl-1,2-ethanediol and diethyl carbonate as described by Johnson.[20] These reactions were carried out using the same procedure as above, with the exception that the styrene was distilled from the reaction mixture at atmospheric pressure as it formed. When all of the styrene had distilled and carbon dioxide evolution ceased, the pot residue was worked up for tertiary phosphine oxide by the usual technique. The styrene, in each case, was identified by refractive index as well as infrared and mass spectrometric analysis.

Attempted Reaction of Triphenylphosphine with Diethyl Carbonate.—Triphenyl phosphine (13.1 g., 0.05 mole) was mixed with an excess (11.8 g., 0.1 mole) of diethyl carbonate and heated at 140° for 24 hr. with the reaction system connected to a gas burette. During this time there was no apparent gas evolution. Upon cooling and treating the reaction mixture with petroleum ether, 9.5 g. or 72.5% of unchanged triphenylphosphine (m.p. 77–78°) was recovered. The ether filtrate was discarded without any attempt to isolate the remaining unchanged phosphine.

Preparation of (4-Hydroxybutyl)ethylene Carbonate.—Diethyl carbonate (296 g., 2.5 moles) was mixed with 268.5 g. (2.0 moles) of 1,2,6-hexanetriol and heated to 105°. Ethanol distilled from the reaction mixture until the temperature rose to 145°. The remaining alcohol was then removed *in vacuo*. The residue was washed twice with water, taken up in chloroform, and the chloroform extract dried over calcium sulfate overnight. The dry chloroform extract was filtered and concentrated. The remaining sirupy residue weighed 115.7 g. and represented a 36% yield of (4-hydroxybutyl)ethylene carbonate.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.48; H, 7.55; O, 40.76. Found: C, 52.21; H, 7.12; O, 40.76.

Reaction of Triphenylphosphine with (4-Hydroxybutyl)-ethylene Carbonate.—Triphenylphosphine (26.2 g., 0.1 mole) was mixed with 16.0 g. (0.1 mole) of (4-hydroxybutyl)ethylene carbonate and heated to 185°. Carbon dioxide was evolved at this temperature and heating was continued until the theoretical volume of gas had been collected (1 hr)

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[16] J. Cason and W. N. Baxter, *J. Org. Chem.*, **23**, 1302 (1958).

[17] Melting points are uncorrected.

[18] M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **75**, 1263 (1953).

[19] Analyses and literature melting points reported in Table I.

[20] W. K. Johnson, U. S. Patent 2,799,616 (July 16, 1957).

Upon cooling, the reaction mixture solidified to a yellow mass which was extracted with warm petroleum ether, followed by several extractions with warm hexane. The extracts were combined, filtered, and the insoluble solid which had been collected was dried. It weighed 14.5 g., melted at 150–151°, and represented a 70% yield of triphenylphosphine oxide. Concentration of the petroleum ether–hexane extracts yielded 10.0 g. of a viscous orange sirup which infrared analysis and mass spectrometry identified as the crude 5-hexen-1-ol in quantitative yield. When this sirup was distilled at atmospheric pressure, 3.5 g. of a yellow oil was obtained which distilled at 160–165°/atm.[21] with a great deal of charring. Infrared analysis of this material showed bands characteristic of 5-hexen-1-ol contaminated by an aldehyde carbonyl impurity. Analysis was confirmed by mass spectrometry which found a major component of mass 100 (5-hexen-1-ol) with a small impurity of mass 98 (5-hexen-1-al). Attempted redistillation of this alcohol under reduced pressure only increased the aldehyde impurity.

Base Decomposition of Tributyl-2-hydroxyethylphosphonium Bromide.—Metallic sodium (0.61 g., 0.27 g.-a.) was dissolved in 100 ml. of absolute ethanol. A 10-ml. aliquot of this ethoxide solution was mixed under nitrogen with 0.88 g. (0.0027 mole) of tributyl-2-hydroxyethylphosphonium bromide in 2 ml. of absolute ethanol. The reaction system was opened to a gas burette and the ethoxide mixture was stirred at room temperature for 17 hr. No gas was evolved during this time. The ethanol was removed *in vacuo* and heating was resumed. At 40° a vigorous evolution of gas began and continued for 1 min. over a temperature range of 40–70°. At the end of this time, the theoretical volume of gas had been collected. The gas was identified by mass spectrometry as ethylene. Infrared analysis of the reaction residue indicated that it was tributylphosphine oxide.

Attempted Reactions of Cyclic Carbonates with Phosphoranes.—Two unsuccessful attempts were made to react cyclic carbonates with phosphoranes: (1) Carbethoxymethyl triphenylphosphorane (0.078 mole) which had been prepared by Wittig's procedure[9] was heated with 12.8 g. (0.78 mole) of phenylethylene carbonate at 130° until the evolution of gas subsided. Upon cooling the reaction mixture and extracting it with benzene and diethylether 12.3 g. (57%) of triphenylphosphine oxide was obtained. Concentration of the ether filtrate yielded a sirupy residue weighing 14.7 g. which was identified by infrared analysis as a mixture of triphenylphosphine oxide and phenylethylene carbonate.

(2) Nineteen grams (0.05 mole) of benzoylmethylenetriphenylphosphorane which was prepared as described by Ramirez[22] was mixed with 4.4 g. (0.05 mole) of ethylene carbonate and heated at 175° until the evolution of gas subsided. The reaction mixture was treated as the previous experiment and yielded 10.5 g. (55%) of unchanged benzoylmethylenetriphenylphosphorane, 2.0 g. (14.5%) of triphenylphosphine oxide, and less than 1 g. of unchanged ethylene carbonate.

Analysis by mass spectrometry and gas chromatography indicated that no cyclopropanes were formed in either experiment.

Preparation of Tetramethylene Carbonate.—Diethyl carbonate (130.0 g., 1.1 moles) was mixed with 90.12 g. (1.0 mole) of 1,4-butanediol and 1.0 g. (0.008 mole) of potassium carbonate and heated. At 90° ethanol began to distill from the reaction mixture and heating was continued until the temperature rose to 130° and 96% of the theoretical yield of ethanol had been collected. Upon cooling, the reaction mixture was taken up in 200 ml. of benzene, washed with three 100-ml. portions of water, and dried overnight over calcium sulfate. After drying, the benzene and unchanged starting materials were removed by distillation and the remaining sirupy residue crystallized from acetone to yield 45 g. (58.8%) of tetramethylene carbonate (m.p. 60–61°). The carbonate was recrystallized once from acetone–diethyl ether before analysis.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94; O, 41.34. Found: C, 51.79; H, 6.79; O, 40.85.

Attempted Reactions of Tetramethylene Carbonate with Tertiary Phosphines.—Triphenylphosphine (13.1 g., 0.05 mole) was mixed with 5.8 g. (0.05 mole) of tetramethylene carbonate and heated at 190–210° over a period of 5 hr., at the end of which time gas evolution ceased. Extraction of the reaction residue with diethyl ether yielded 9.5 g. (75%) of unchanged triphenylphosphine. Mass spectrometric analysis of a sample of the gas evolved during the reaction showed that it was mostly carbon dioxide and air. No trace of cyclobutane was found in the gas sample.

This experiment was repeated adding a catalytic quantity of cupric carbonate. In this case, a clear liquid distilled from the reaction mixture and was identified by infrared spectroscopy and vapor phase chromatography as tetrahydrofuran. Upon working up the reaction mixture, the unreacted phosphine was again recovered. No cyclobutane was isolated.

In a final experiment using tributylphosphine with tetramethylene carbonate, the tributylphosphine was completely unchanged after heating for 24 hr. at 190° and the tetramethylene carbonate had decomposed to tetrahydrofuran and carbon dioxide.

Attempted Reaction of Triethyl Phosphite with Ethylene Carbonate.—Triethyl phosphite (16.6 g., 0.1 mole) and ethylene carbonate (8.8 g., 0.1 mole) were mixed under nitrogen and heated with stirring at 160°. At this temperature, the triethyl phosphite very slowly distilled from the reaction mixture and after 5 hr. the reaction was stopped. The remaining residue was distilled under reduced pressure. Infrared and mass spectrometric analysis of the major distillate (b.p. 120–125°/20 mm., n^{25}_{D} 1.4230) indicated that it was primarily ethylene carbonate with a trace amount ($>5\%$) of triethyl phosphate.

No reaction was observed when this experiment was repeated adding 1 g. (0.016 mole) of copper powder as catalyst.

Reaction of Triphenyl Phosphite with Ethylene Carbonate.—Triphenyl phosphite (16.5 g., 0.5 mole) was mixed with 4.4 g. (0.5 mole) of ethylene carbonate and heated for 6 hr. at 230°. No gas was evolved during this time. The mixture was cooled and 0.5 g. (0.008 g.-atom) of copper powder was added. Heating was resumed and gas was evolved for 5 hr. at 200–260°. At the end of this time, the reaction mixture was extracted with benzene and the benzene extract filtered to remove copper. Concentration of the benzene filtrate yielded 5.0 g. (40.5%) of a white crystalline solid (m.p. 145–146°). This solid was identified by infrared spectroscopy as tetraphenyl ethylenediphosphonate. One recrystallization from benzene gave an analytical sample (m.p. 152–153°).[23]

Anal. Calcd. for $C_{26}H_{24}P_2O_6$: C, 63.16; H, 4.89; P, 12.53. Found: C, 63.37; H, 4.49; P, 12.49.

Acknowledgment.—Microanalysis were carried out under the supervision of Dr. J. A. Kuck. Interpretation of infrared spectra was provided by Norman Colthup and mass spectrometer data by Rosemarie Herberich and J. R. Chatham.

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[21] Lit. b.p. 149°/749 mm. for 5-hexen-1-ol.

[22] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[23] Lit. m.p. 155–155.5° [M. L. Kabachnik, *Bull. acad. sci. URSS, Classe sci. chim.*, 631 (1947)].