Reactions of *tert*-Butyl Peresters. XI. Reactions of Alkyl *tert*-Butylperoxy Alkylphosphonates, Dialkyl *tert*-Butylperoxy Phosphates, and Other Phosphorus Esters with Benzene and Aluminum Chloride, and Reactions of Dialkyl *tert*-Butylperoxy Phosphates with Phenylmagnesium Bromide[1]

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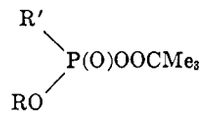
Reactions of alkyl *tert*-butylperoxy alkylphosphonates (1), dialkyl *tert*-butylperoxy phosphates (2), and other phosphorus compounds of general structure **3** [R = alkyl; R′ = alkyl, alkoxy; X = OR, OH, H, Cl, OP(O)R′(OR), $OCMe_3$] with benzene in the presence of aluminum chloride proceed rapidly at 5° to produce primarily the corresponding monoalkyl benzene derived from cleavage of the P···O···R linkage of the phosphorus compound. In the cases of 1 and 2, *tert*-butylbenzene and phenol are also found, derived from cleavage of the peroxide linkage. Reactions of dialkyl *tert*-butylperoxy phosphates (2) with phenylmagnesium bromide produce high yields of *tert*-butyl phenyl ether and moderate to high yields of the corresponding dialkylphosphoric acid **8**.

The ability of organophosphorus esters to alkylate alcohols and amines is well documented and has been recognized for many years. These reactions usually proceed at elevated temperatures and generally do not require catalysts.[2] Nucleophilic reactions involving organophosphorus compounds both *in vivo* and *in vitro* have been the subject of an enormous amount of research.[3] In contrast, electrophilic reactions involving organophosphorus esters are relatively unexplored.

We have been systematically investigating the chemistry of peroxy phosphates **1** and **2** (R, R′ = alkyl) as model systems for hypothetical intermediates *in vivo*. In view of the apparent implication of alkylation re-



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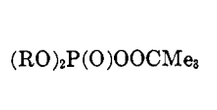

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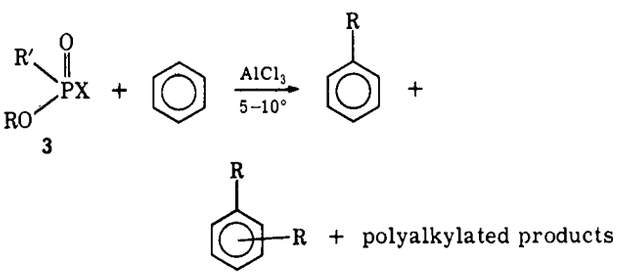
actions in carcinogenesis and cancer chemotherapy,[4] and of dealkylation reactions in the aging of phosphorylated enzymes,[5] it was of interest to examine the alkylation reactions of peresters **1** and **2** under both electrophilic and nucleophilic conditions. We have reported on our investigation of the reaction of peresters **2** with amines[6] and triphenylphosphine.[7] Now we wish to report on the reactions of **1** and **2** and other phosphorus compounds (**3**) containing P···O···R linkages with benzene in the presence of aluminum chloride and on the reactions of **2** with phenylmagnesium bromide.

Although the Friedel–Crafts type reactions of esters of carboxylic acids have been widely studied, relatively few investigations of the analogous reactions of esters of inorganic acids have been reported.[8] The reactions of organophosphorus esters have, to our knowledge, been discussed only in three short papers. Thus, the reactions of trialkyl phosphates (**3**, R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9; X, R′ = OR) with benzene in the presence of either aluminum chloride[9,10] or boron trifluoride[11] give the corresponding aralkyls. None of these studies dealt with the details and scope of these reactions.

Our studies show that the reactions of phosphorus compounds of general structure **3** (R = alkyl; R′ = alkyl, alkoxy; X = H, OH, OR, Cl, OP(O)(OR)R′, $OCMe_3$) containing P···O···R linkages readily proceed at 5–10° with benzene in the presence of aluminum chloride to give alkylated benzenes. The results



shown in Table I indicate that the variations in the structure of the phosphorus ester have no decisive effect on the nature and yield of products.[12] In all cases, the O–C bond was cleaved to give the attacking

(1) (a) This investigation was supported by grants from the Public Health Service, U. S. Department of Health, Education, and Welfare (GM 16741) and from the Graduate School of the University of Wisconsin—Milwaukee. (b) For the previous paper in this series see ref 7.

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(11) J. F. McKenna and F. J. Sowa, *J. Amer. Chem. Soc.*, **59**, 1204 (1937).

(12) It should be noted that the use of phosphorus esters as alkylating agents for aromatic compounds on laboratory scale has a potential synthetic value since they are industrially available, nontoxic liquids as opposed to most low molecular weight alkylating agents, which are gases.

TABLE I

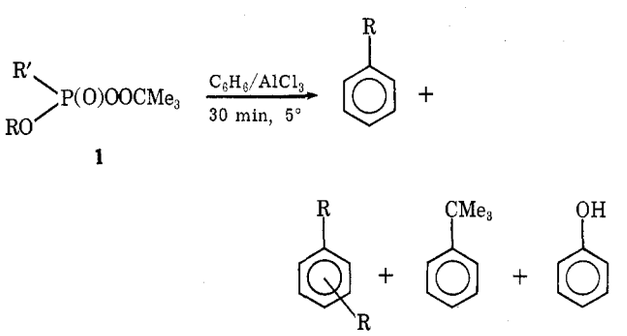
PRODUCTS OF THE REACTIONS OF ORGANOPHOSPHORUS ESTERS, RO(R')P(O)X, WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Registry no.	R	R'	X	C_6H_5R, %	$C_6H_4R_2$, %	Registry no.	R	R'	X	C_6H_5R, %	$C_6H_4R_2$, %
78-40-0	C_2H_5	C_2H_5O	C_2H_5O	17	33	34637-92-8	CH_3	C_2H_5	OH	36	4
513-02-0	*i*-C_3H_7	*i*-C_3H_7O	*i*-C_3H_7O	42	13	1832-53-7	C_2H_5	CH_3	OH	92	1
126-73-8	*n*-C_4H_9	*n*-C_4H_9O	*n*-C_4H_9O	34[a]		1832-54-8	*i*-C_3H_7	CH_3	OH	95	<1
6163-75-3	CH_3	C_2H_5	CH_3O	33	7	1832-55-9	*n*-C_4H_9	CH_3	OH	90[j]	<1
683-08-9	C_2H_5	CH_3	C_2H_5O	27	24	32288-17-8	C_2H_5	CH_3	OP(O) CH_3(OEt)	69	1
	C_2H_5	CH_3	C_2H_5O[b]	12	8						
	C_2H_5	CH_3	C_2H_5O[c]	1		34637-96-2	CH_3	C_2H_5	OP(O) (OMe)Et	64	<1
	C_2H_5	CH_3	C_2H_5O[b,d]	32	18						
1445-75-6	*i*-C_3H_7	CH_3	*i*-C_3H_7O	43	7	34637-97-3	C_2H_5	CH_3	$OCMe_3$	76[k]	1
1067-69-2	*i*-C_3H_7	C_2H_5	*i*-C_3H_7O	2	12	34637-98-4	*i*-C_3H_7	C_2H_5	$OCMe_3$	70[l]	
2404-73-1	*n*-C_4H_9	CH_3	*n*-C_4H_9O	59[e]	8	813-77-4	CH_3	CH_3O	Cl	20	9
2404-58-2	*n*-C_4H_9	C_2H_5	*n*-C_4H_9O	36[f]	4	814-49-3	C_2H_5	C_2H_5O	Cl	31	47
762-04-9	C_2H_5	C_2H_5O	H	30	12	10419-79-1	*i*-C_3H_7	*i*-C_3H_7O	Cl	43	2
1809-20-7	*i*-C_3H_7	*i*-C_3H_7O	H	16[g]	6	5284-09-3	C_2H_5	CH_3	Cl	40[m]	
	i-C_3H_7	*i*-C_3H_7O	H	30[h]	3		C_2H_5	CH_3	Cl	32[n]	28
1809-19-4	*n*-C_4H_9	*n*-C_4H_9O	H	7[i]		1445-76-7	*i*-C_3H_7	CH_3	Cl	64[c,o]	
17176-77-1	$C_6H_5CH_2$	$C_6H_5CH_2O$	H	60							

[a] *n*-Bu 8%, *sec*-Bu 26%. [b] Reaction time 2 hr at 10°. [c] Method 2. [d] Reaction time 4 hr at room temperature. [e] *n*-Bu 8%, *sec*-Bu 51%. [f] Bu 4%, *sec*-Bu 32%. [g] Reaction time 1 hr at room temperature. [h] Reaction time 24 hr at room temperature. [i] *n*-Bu 15%, *sec*-Bu 52%. [j] *n*-Bu 19%, *sec*-Bu 71%. [k] And *tert*-butyl benzene 37%. [l] And *tert*-butylbenzene 72%. [m] Reaction time 20 hr at room temperature. [n] Reaction time 1 hr at 5° and then 24 hr at room temperature. [o] Reaction time 36 hr at room temperature.

carbonium ion, R^+, while no products derived from P–C cleavage were detected. The reaction does not proceed when R is aromatic. Thus, the reactions of triphenyl phosphate (**3**, R = C_6H_5; X, R' = C_6H_5O) form no products derived from P···O···C_6H_5 cleavage.[13]

The reactions of peresters of alkylphosphonic acids (**1**, R = Me, Et, *i*-Pr, *n*-Bu; R' = Me, Et) in the presence of aluminum chloride were investigated under a variety of conditions. With high dilution, *i.e.*, large benzene to peroxy alkylphosphonate ratio, *e.g.*, 135:1, lowered temperature (5°), and short stirring time (15–30 min), the following products, resulting from cleavage of both the O–C and the O–O–C linkages, are isolated.



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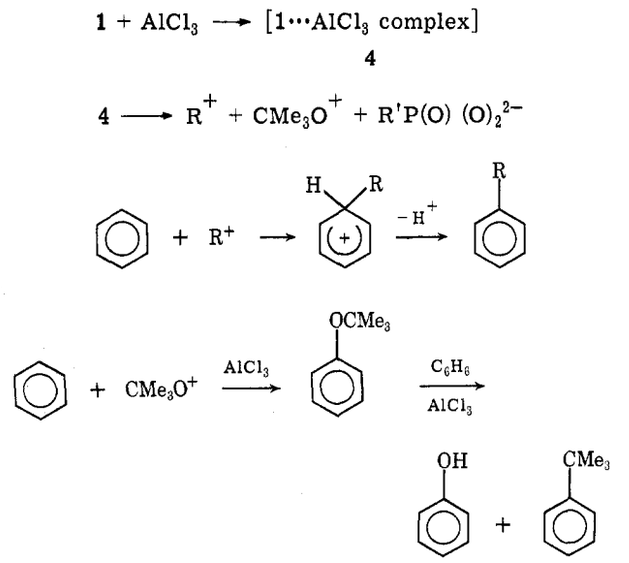
This reaction is rather sensitive to experimental conditions. With the ratio of $1:AlCl_3:C_6H_6$ = 0.01:0.034:1.35, low temperature (5°), and short duration (15 min), the amount of *tert*-butylbenzene is 8–35%, phenol is 12–66%, and alkylation is 40–85% with monosubstitution predominating. If the ratio is changed to 0.05:0.1:0.8, or the reaction time is increased to 20 hr and the temperature to 23–26°, the *tert*-butylbenzene and phenol are no longer detected, while the amount of dialkylation increases (Table II). It has been shown in our laboratory that the use of methylene chloride–nitromethane solutions of aluminum chloride and benzene results in nonisomerizing conditions for the reactions of phosphorus esters.[14] If the "milder" complex of $AlCl_3$–CH_3NO_2 is used for the reaction of **1** with benzene, the amount of *tert*-butylbenzene isolated is much greater (50%) while the amount of alkylated product derived from the RO moiety is low especially when the incipient carbonium ion is CH_3^+ or $C_2H_5^+$ (Table II).

The formation of *tert*-butylbenzene and phenol might be explained by a mechanism in analogy to the proposed mechanism for the reaction of *tert*-butyl hydroperoxide with toluene.[15] Since the O···O linkage is the weakest bond in the peroxide molecule, the initial heterolytic cleavage probably occurs at this bond, aided by the polarization enhanced by the electrophilic Lewis acid. Coordination of the aluminum chloride probably involves all oxygens of the



(13) G. Sosnovsky, E. H. Zaret, and B. Böhnel, *Synthesis*, 203 (1971).

(14) M. W. Shende, M.S. Thesis, University of Wisconsin—Milwaukee, 1971.

(15) S. Hashimoto and W. Koike, *Bull. Chem. Soc. Jap.*, **43**, 293 (1970).

TABLE II

PRODUCTS FROM THE REACTIONS OF $(RO)R'P(O)OOCMe_3$ WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Registry no.	R	R′	Experimental method[a]	Product yield, % — RC_6H_5 R =		$Me_3CC_6H_5$	HOC_6H_5	Alkyl group accounted as aralkyls, %
6795-02-4	Me	Et	A	Me	40	6	7	40
	Me	Et	C	Me	0.5	35	13	0.5
31238-29-6	Et	Me	A	Et	69	15	9	69
	Et	Me	C	Et	0.5	44	15	0.5
	Et	Me	B	Et	95	0	0	95
31238-30-9	*i*-Pr	Me	A	*i*-Pr	62	11	8	62
	i-Pr	Me	C	*i*-Pr	53	33	17	53
	i-Pr	Me	C[b]	*i*-Pr	67	40	10	67
31238-31-0	*i*-Pr	Et	A	*i*-Pr	62	12	9	62
	i-Pr	Et	C	*i*-Pr	66	25	20	66
31238-32-1	*n*-Bu	Me	A	*n*-Bu	46.5	2	2	83
				sec-Bu	35			
	n-Bu	Me	C	*n*-Bu	17	2	2	20
				sec-Bu	3			
31246-33-0	*n*-Bu	Et	A	*n*-Bu	50	3	2	85
				sec-Bu	35			
	n-Bu	Et	C	*n*-Bu	20	3	2	30
				sec-Bu	10			

[a] See Experimental Section for details. [b] Reaction time 24 hr at room temperature.

TABLE III

PRODUCTS OF THE REACTIONS OF BENZENE SOLUTIONS OF DIALKYL *tert*-BUTYLPEROXY PHOSPHATES, $(RO)_2P(O)OOCMe_3$, WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE[a]

Registry no.	$(RO)_2P(=O)$-$OOCMe_3$ R =	$AlCl_3$, mol	Reaction time after addition, hr	Reaction of R group, %		Yield, % — C_6H_5R	$C_6H_4R_2$	$C_6H_5CMe_3$	C_6H_5OH
10160-45-9	Et	0.038	0.5	33		33	<1	16	6
	Et	0.034	20	90		90	<1	0	14
18963-66-1	*n*-Pr	0.038	0.5	71.5	*n*-C_3H_7	15	16.5	20	12
					i-C_3H_7	40			
10160-46-0	*i*-Pr	0.03	20	74		24	50	0	12
	i-Pr	0.034	0.5	64		52	12	15	<1
10160-47-1	*n*-Bu	0.038	0.5	60	*n*-C_4H_9	0	<1	21	23
					sec-C_4H_9	60			

[a] Stirred at 5° for 15 min after addition; products analyzed by glc.

perester to some extent and aids in the formation of the alkyl (R^+) and alkoxy (CMe_3O^+) species which subsequently react with the aromatic nucleus.

Under similar conditions the reaction of *tert*-butyl hydroperoxide with benzene produces a mixture of *tert*-butylbenzene and phenol in 15–20% yield, whereas in the presence of aluminum chloride–nitromethane this reaction results only in a 10% yield of a 1:1 mixture of the same products even after 20 hr of reaction.

The analogous reaction of diisopropyl *tert*-butylperoxy phosphate (**2**, R = *i*-C_3H_7) with benzene and aluminum chloride at 5° produces mainly cumene, diisopropylbenzene, phenol, and, depending on the reaction conditions, *tert*-butylbenzene. The *tert*-butylbenzene is found only if the reaction is worked up soon after the addition of the perester is completed. If the reaction mixture is kept at ambient temperature for 24 hr or if the perester is added neat at 5–15°, little or no *tert*-butylbenzene is isolated. These results are consistent with the rearrangements and dealkylation reactions which have been reported for *tert*-butyl phenyl ether and *tert*-butylbenzene under similar conditions.[16] The products of the reactions of peresters **2** with benzene and aluminum chloride are shown in Table III. Similarly, solutions of aluminum chloride and benzene in nitromethane–methylene chloride react with methylene chloride solutions of peresters **2** to produce mainly the corresponding monoalkylbenzene and *tert*-butylbenzene and low yields of phenol and dialkylbenzene. The results of the glc analyses of these experiments are presented in Table IV. The dialkylbenzenes were detected in such small amounts that their yields are insignificant.

TABLE IV

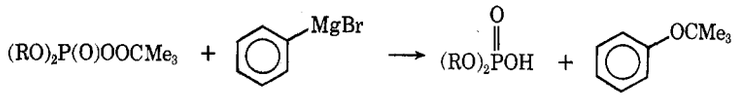
PRODUCTS FROM THE REACTIONS OF DIALKYL *tert*-BUTYLPEROXY PHOSPHATES, $(RO)_2P(O)OOCMe_3$, WITH BENZENE AND ALUMINUM CHLORIDE IN NITROMETHANE–METHYLENE CHLORIDE SOLUTION

$(RO)_2P(=O)OOCMe_3$ R =	Reaction time after addition, hr	Reaction of R group, %		Yield, % — C_6H_5R	$C_6H_5CMe_3$	C_6H_5OH
Et	4	2		2	40	<1
n-Pr	4	20	*n*-C_3H_7	13	55	5
			i-C_3H_7	7		
i-Pr	20	90		90	56	4
i-Pr	3	21		21	16	2
n-Bu	4	38	*n*-C_4H_9	38	40	2
			sec-C_4H_9	0		

(16) S. Natelson, *J. Amer. Chem. Soc.*, **56**, 1583 (1934), and references cited therein.

TABLE V

REACTION OF DIALKYL *tert*-BUTYLPEROXY PHOSPHATES WITH PHENYLMAGNESIUM BROMIDE



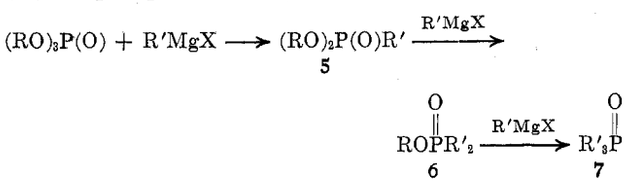
Perester **2** R =	Amount of perester **2**, mol	C_6H_5Br, mol	Method	Addition time, hr	Addition temp, °C	Additional stirring, hr	Additional stirring temp, °C	Yield of $C_6H_5OCMe_3$, %	Yield of $(RO)_2P(=O)OH$, %
i-C_3H_7	0.03	0.05	A	0.58	10–15	0.1	10	60	*a*
C_2H_5	0.03	0.05	A	1.33	5–10	4	*b*	78	*a*
n-C_4H_9	0.03	0.05	A	0.5	4–15	19	*b*	74	*a*
C_2H_5	0.03	0.063	B		5–15	1	0–5	82	30
n-C_3H_7	0.023	0.063	B		5–15	0.25	5		
						0.75	*b*	86	58
i-C_3H_7	0.03	0.063	B		5–15	0.25	5		
						0.50	*b*	88	71
n-C_4H_9	0.03	0.063	B		5–15	0.25	5		
						1.0	*b*	95	88

[a] Identified spectroscopically. [b] Room temperature.

The reactions of *tert*-butyl perbenzoate with Grignard reagents produce high yields of the *tert*-butyl ether derived from the Grignard reagent,[17] whereas the

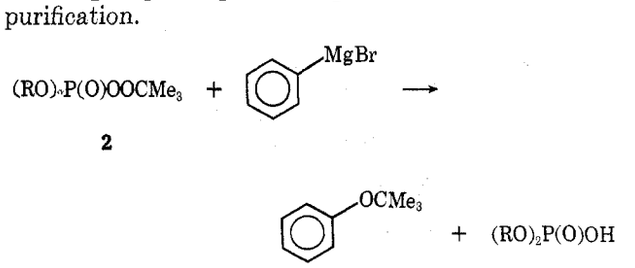
$$C_6H_5C(O)OOCMe_3 + ArMgX \longrightarrow C_6H_5C(O)OH + ArOCMe_3$$

reaction of phosphate esters with Grignard reagents has been found to involve nucleophilic displacement of alkoxy or aryloxy groups in a stepwise sequence to yield the corresponding phosphonate (**5**), phosphinate (**6**), and phosphine oxide (**7**).[18]



R, R′ = alkyl, aryl

We have now found that the reaction of phosphorus peresters **2** (R = alkyl) with the phenyl Grignard reagent follow the pathway of the carbon peresters and not that of phosphate esters to give high yields of *tert*-butyl phenyl ether and moderate to high yields of the corresponding dialkylphosphoric acid **8** (Table V). In addition, low yields of biphenyl and phenol are isolated. These products are formed as a result of using regular grade magnesium without further purification.



Experimental Section

Trialkyl phosphates were commercial samples and were distilled before use. Dialkyl hydrogen phosphites and dialkyl phosphorochloridates were prepared by the method of Fiszer and Michalski.[19] Dialkyl *tert*-butyl-[7] and dialkyl *tert*-butylperoxy phosphates[20] were prepared as described in our earlier papers. The dialkyl alkylphosphonates were prepared *via* the Arbuzov reaction.[21] The phosphonochloridates in turn were readily obtained by chlorination with PCl_5 of the Arbuzov products.[22] The alkylphosphonic acid monoesters were prepared by alkaline hydrolysis[23] of the same Arbuzov products. The dialkyl dialkylpyrophosphonates were prepared by reaction of the corresponding chlorides in the presence of base such as pyridine and water,[24] while the *tert*-butyl alkyl esters of alkylphosphonic acid were synthesized from the corresponding chlorides and potassium *tert*-butoxide.[25] Alkyl *tert*-butylperoxy alkylphosphonates were prepared by way of the parent chlorides and were then purified with lead tetraacetate to give analytically pure samples following a distillation in small lots.[26]

The benzene used as substrate and solvent was distilled from and stored over sodium. All other materials were best commercial grade available used without further purification. Glc analyses were performed on a Varian Aerograph Model 1700 dual column instrument equipped with WX detectors and a linear temperature programmer. The areas of the peaks obtained were determined either by triangulation or with a planimeter. All boiling points and melting points are uncorrected.

Analytical Procedures.—An Aerograph 1700 dual-column gas chromatograph was used. The following overall conditions were maintained: block temperature, 225°; injector temperature, 215°; bridge current, 150 mA; sample size, 2 μl with the appropriate attenuations. Column 1 was 6 ft × 0.25 in., 20% Carbowax 20M on Chromosorb W, 80–180°, 40–50 ml of He/min. Column 2 was 5 ft × 0.25 in., 3% SE-30 on Varapack, 80–200°, 40–50 ml of He/min. All identification of products was by comparison of retention times and "spiking" with authentic samples. Infrared analysis for verification of the presence of various functional groups was performed on a Perkin-Elmer Infracord spectrophotometer, Model 137.

Reactions of Alkylphosphonates (3, X = OR, OH, OP(O)(OR)R′, Cl, $OCMe_3$). General Procedure 1 (Table I).—To a suspension of 0.09 mol of aluminum chloride in 90 ml (1.01 mol) of benzene was added dropwise a solution of 0.03 mol of phosphonate in 30 ml (0.34 mol) of benzene. After the addition, the mixture was stirred for 20 hr at room temperature and was then hydrolyzed by pouring it onto 50 ml of ice-cold 10% HCl.

(17) S.-O. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, **81**, 4230 (1959); C. Frisell and S.-O. Lawesson, *Org. Syn.*, **41**, 91 (1961).

(18) K. D. Berlin and M. E. Peterson, *J. Org. Chem.*, **32**, 125 (1967), and references cited therein.

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The organic layer was separated, and the aqueous layer was extracted several times with ether. The combined organic layers were washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by distillation of the solvents at 1 atm pressure under nitrogen. The products were analyzed by gas chromatography.

General Procedure 2.—To a cooled (10°) solution of 120 ml (1.35 mol) of benzene and 80 ml (1.26 mol) of methylene chloride was added a cooled (10°) solution of 0.034 mol of aluminum chloride in 12 ml of nitromethane. To the well-stirred mixture was then added at 5° a solution of 0.01 mol of phosphonate **3** in 12 ml (0.19 mol) of methylene chloride. After stirring at ambient temperature for 20 hr, the reaction mixture was hydrolyzed by the dropwise addition of ice water at 5–10°. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were then washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by distillation of the solvents at 1-atm pressure under nitrogen. The products were identified by gas chromatography.

Reactions of Alkyl *tert*-Butylperoxy Alkylphosphonates (1). General Procedures (Table II). A. In Benzene.—To a well-stirred suspension of 0.034 mol of aluminum chloride in 90 ml (1.01 mol) of benzene was added at 5° a solution of 0.01 mol of alkyl *tert*-butylperoxy alkylphosphonate in 30 ml (0.34 mol) of benzene. The reaction mixture was then stirred at 5° for 15 min, and was then hydrolyzed by pouring it onto 25 ml of ice-cold 10% HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by distillation of the solvents at 1 atm pressure under nitrogen. The products were then identified by gas chromatography.

B. In Benzene.—To a well-stirred suspension of 0.10 mol of aluminum chloride in 70 ml (0.79 mol) of benzene was added, as rapidly as possible at 5–10°, 0.05 mol of alkyl *tert*-butylperoxy alkylphosphonate. The reaction mixture was then stirred at 5° for 1 hr and at ambient temperature for 36 hr, and was then hydrolyzed by the dropwise addition of 75 ml of water at 5–10°. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by distillation of the solvents at 1 atm pressure under nitrogen. The products were then identified by gas chromatography.

C. In Methylene Chloride.—To a cooled (10°) solution of 120 ml (1.35 mol) of benzene and 80 ml (1.26 mol) of methylene chloride was added a cooled (10°) solution of 0.034 mol of aluminum chloride in 12 ml of nitromethane. To this mixture then was added at 5° a solution of 0.01 mol of alkyl *tert*-butylperoxy alkylphosphonate in 12 ml (0.19 mol) of dichloromethane. The reaction was then stirred at ambient temperature for 4 hr, and was hydrolyzed by the dropwise addition of 50 ml of ice water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by distillation of the solvents at 1 atm pressure under nitrogen. The products were then identified by gas chromatography.

Reactions of Dialkyl Phosphate Esters (3, R′ = OR; X = OR, Cl, H). General Procedure 3 (Table I).—The ester (0.2 mol) was added at 8–10° over 1 hr to a well-stirred suspension of 93.6 g (0.7 mol) of aluminum chloride in 355 ml (4.0 mol) of benzene. The mixture was stirred for 1 hr and was then poured onto crushed ice. The organic layer was separated, washed with 5% sodium bicarbonate solution (2 × 50 ml) and then 50 ml of water, dried ($CaCl_2$), and fractionally distilled, yielding the alkyl benzenes, whose identity and purity were confirmed by glc.

Reactions of *tert*-Butyl Hydroperoxide. A. In Benzene.—A solution of 0.15 mol of *tert*-butyl hydroperoxide (dried over $MgSO_4$) in 90 ml (1.01 mol) of benzene was added at 5–8° to a suspension of 0.30 mol of aluminum chloride in 270 ml (3.04 mol) of benzene. The reaction was stirred at 5° for 2 hr, and worked up according to General Procedure 1. The organic extract was then concentrated to give 7.04 g (35%) of *tert*-butylbenzene which was identified by ir and gas chromatography. Acidification of the base extract followed by extraction with ether afforded, after washing with water and drying ($MgSO_4$), 4.70 g (33%) of phenol, as identified by ir and gas chromatography.

B. In Methylene Chloride.—To a cooled (15°) solution of 120 ml (1.35 mol) of benzene and 80 ml (1.26 mol) of methylene chloride was added a cooled (10°) solution of 0.35 mol of aluminum chloride in 15 ml of nitromethane. To this well-stirred mixture at 5° was then added a solution of 0.015 mol of *tert*-butyl hydroperoxide (dried over $MgSO_4$) in 12 ml of methylene chloride. The reaction was then stirred at ambient temperature for 20 hr, since there was no visible reaction after 4 hr, and was worked up according to General Procedure 2.

Reactions of Benzene Solutions of Dialkyl *tert*-Butylperoxy Phosphates 2 with Benzene in the Presence of Aluminum Chloride. General Procedure 4 (Table III).—A solution of dialkyl *tert*-butylperoxy phosphate (0.01 mol) in 30 ml (0.34 mol) of benzene was added at 5° over 45 min to a well-stirred suspension of 5.00 g (0.038 mol) of aluminum chloride in 90 ml (1.0 mol) of benzene. After the addition was completed, the cooling bath was removed and the mixture was stirred at ambient temperature for the specified time. The reaction mixture was hydrolyzed by pouring it into 120 ml of 10% ice cold hydrochloric acid solution. The organic layer was separated and the aqueous solution was extracted with ether. The combined organic layers were then washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by removal of the solvents by distillation at 1 atm pressure under nitrogen. The residual oils were analyzed by glc.

Reactions of Methylene Chloride Solutions of Dialkyl *tert*-Butylperoxy Phosphates 2 with Benzene and Aluminum Chloride in Nitromethane–Methylene Chloride Solution. General Procedure 5 (Table IV).—A precooled solution of 4.58 g (0.034 mol) of aluminum chloride in 12 ml (0.22 mol) of nitromethane was added to a cold (15°) solution of 120 ml (1.35 mol) of benzene and 80 ml (1.26 mol) of methylene chloride. To the resulting solution was added at 2–5° a solution of 0.01 mol of dialkyl *tert*-butylperoxy phosphate in 12 ml (0.19 mol) of methylene chloride. After the addition was completed, the ice water cooling bath was removed and the reaction mixture was stirred at ambient temperature for the specified time. Ice water was added dropwise over approximately 15 min and the organic layer was separated. The aqueous solution was extracted with ether and the combined organic layers were washed with 10% sodium bicarbonate solution and then water, dried ($MgSO_4$), and concentrated by removing the solvents by distillation at 1 atm pressure under nitrogen. The residual o ils were analyzed by glc.

Reactions of Dialkyl *tert*-Butylperoxy Phosphates 2 with Phenylmagnesium Bromide. General Procedure 6. A. Preparative Method.—Bromobenzene (7.9 g, 0.05 mol) was added dropwise into a well-stirred mixture of 1.3 g (0.053 g-atom) of magnesium and 20 ml of absolute ether at such a rate as to maintain gentle reflux. After the addition was completed, the mixture was refluxed for 1 hr and was then cooled to 5°. Dialkyl *tert*-butylperoxy phosphate (0.03 mol) was added as specified in Table V. The mixture was then stirred for the prescribed period and hydrolyzed by the addition, with cooling, of 9 ml of saturated ammonium chloride solution. The liquid phase was decanted from the inorganic salt and was concentrated by distillation of the ether. The residual oil was then distilled to yield *tert*-butyl phenyl ether, bp 68–70° (10 mm) [lit.[17] bp 57–59° (7 mm)].

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.60; H, 9.33.

B. Analytical Method. Determination of the Volatile Products by Glc and Isolation of Dialkyl Phosphates.—A solution of 9.88 g (0.063 mol) of bromobenzene in 40 ml of absolute ether was added with stirring to 1.63 g (0.066 g-atom) of magnesium at such a rate as to maintain gentle reflux. The mixture was refluxed for 1 hr after the addition was completed and was cooled to 5°. Anhydrous ether (40 ml) was added in one portion and then a solution of 0.03 mol of dialkyl *tert*-butylperoxy phosphate in 40 ml of anhydrous ether was added dropwise at 5–15°. After the addition was completed, the mixture was stirred with ice water cooling for 15 min and was then stirred at room temperature as specified in Table V. The mixture was hydrolyzed by adding 50 ml of water dropwise at 20°. The organic layer was separated. The aqueous layer was acidified with 10% hydrochloric acid solution and was extracted with ether. The combined ether solutions were washed several times with 10% sodium hydroxide solution and then distilled water, dried ($MgSO_4$), and concentrated on a rotary evaporator to yield an oil which was analyzed by glc on column 2.

The sodium hydroxide extracts were acidified with 10% hydrochloric acid solution and were then evaporated to dryness

in vacuo. The residual solids were extracted with ether several times and the combined ether extracts were dried ($MgSO_4$) and concentrated, yielding dialkyl phosphates (**8**) which were identified as their dicyclohexyl amine salts (Table VI).

TABLE VI

Registry no.	$(RO)_2$-P(O)OH R =	Dicyclohexyl Amine Salt Mp, °C (solvent)	Mmp,[a] °C
34608-90-7	Et	132–134 (ligroin)	133.5–134.5
14530-43-9	*n*-Pr	131–133 (acetone)	133–134
13941-64-5	*i*-Pr	171–173 (acetone)	172–173
34638-10-3	*n*-Bu	104–105 (acetone)	106–107

[a] Preparation of the authentic samples was reported in A. F. Gasiecki, M. S. Thesis, University of Wisconsin—Milwaukee, 1970.

Registry No.—Benzene, 71-43-2; $AlCl_3$, 7446-70-0; phenylmagnesium bromide, 100-58-3.

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Steric and Electronic Effects on the Stereochemistry of the Alkaline Hydrolysis of Acyclic Dialkoxyphosphonium Salts. Pseudorotation of Intermediates in Phosphorus Ester Reactions

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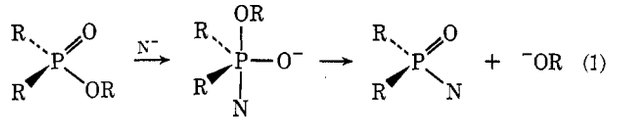
The stereochemistry of the alkaline hydrolysis of three acyclic dialkoxyphosphonium salts, (*R*)- and (*S*)-menthoxymethoxymethylphenylphosphonium hexachloroantimonate (**2**) and ethoxymethoxymethylphenylphosphonium hexachloroantimonate (**3**), was investigated and compared to the previous results obtained for the alkaline hydrolysis of (*R*)- and (*S*)-ethoxymenthoxymethylphenylphosphonium hexachloroantimonate (**1**). The extent to which the intermediate phosphorane containing one apical alkoxy group and one equatorial alkoxy group can undergo pseudorotation prior to direct loss of the apical alkoxide increases by a factor of 10 and 70 as the apical alkoxy group is varied from methoxy to ethoxy or menthoxy, respectively, but decreases by a factor of 0.6 and 0.3, respectively, as the same variation is made in the equatorial alkoxy group. Thus, depending only on the nature of the alkoxy ligands, a reaction can proceed either with predominant (>90%) direct loss of an alkoxide or predominantly by a pathway involving pseudorotation. In contrast to previous explanations, the "bulky" menthoxy group exerts no observable steric driving force to occupy the less hindered equatorial position of a phosphorane. The extension of these results to the relative stability of intermediates in nucleophilic displacement reactions of phosphorus esters is discussed.

In light of the demonstrated stability[1-3] of pentacoordinated phosphorus compounds containing alkoxy or aryloxy and carbon ligands (oxyphosphoranes[1]), analogous species containing a hydroxy ligand[4] must be considered as probable intermediates in displacement reactions at phosphorus in phosphorus esters. However, these hydroxyphosphoranes differ from the isolated aryl- or alkyloxyphosphoranes in that they have a facile route for decomposition (eq 1). Thus, at best, they would be unstable intermediates.



(1)

Several workers have obtained indirect evidence that such intermediates are formed in reactions of cyclic phosphorus esters and that they have sufficient stability to undergo pseudorotation[5] prior to or competitive with product formation. In the hydrolysis of five-membered ring phosphorus esters,[2,7] the product ratios obtained have been explained by formation of a phosphorane intermediate which may undergo pseudorotation or directly decompose to products, depending on the system. The retention of configuration[8,9] observed in the transesterification of four-membered ring esters (phosphetanes) has been credited to the formation of the cyclic phosphorane, pseudorotation, and decomposition to products. Pseudorotation has also been invoked in the hydrolysis[10] of these phosphetane esters.

In contrast to cyclic esters, there seems to be little information that reactions of acyclic esters involve intermediates of any detectable degree of stability. It has been argued[1a,2b] that acyclic oxyphosphoranes are less stable than cyclic oxyphosphoranes containing a five-membered ring; while the reverse order of stability is observed in the tetracoordinated phosphorus esters. These stability differences may imply that the

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