

bromoacetate (24 ml, 36.4 g, 0.218 mol) was added dropwise to this stirred solution. The mixture was then heated at reflux for 17 hr. When the deep red solution cooled, most of the solvent was removed at reduced pressure and replaced with 130 ml of H₂O, and the mixture was refluxed again for 45 min. The ethyl (2-oxocyclopentyl)acetate (15) was extracted from the cooled mixture with ether and isolated by fractional distillation: 13.3 g (36%); bp 133–135° (23 mm); ir (neat) 1730 cm⁻¹.

A 250-ml three-neck flask equipped with N₂ inlet and reflux condenser and containing 0.72 g (0.03 mol) of NaH and 25 ml of dimethyl sulfoxide (DMSO) was heated at 70–75° under N₂ for 45 min. To the cooled solution was added a solution of 10.7 g (0.03 mol) of CH₃P(C₆H₅)₃Br in 33 ml of DMSO. After an additional 10-min stirring, 5.0 g (0.03 mol) of 15 in 3 ml of DMSO was added, and stirring continued at room temperature for 1.5 hr. After 40 ml of H₂O was added, the mixture was extracted with 350 ml of petroleum ether in three portions and with 50 ml of ether. The combined extracts were dried and evaporated carefully to 25 ml. Distillation in a short-path apparatus yielded approximately 1 ml of a fraction boiling 110–140° (22 mm). This was dissolved in petroleum ether and rapidly chromatographed on a silica gel column. A total of 250 mg (5%) of ethyl (2-methylenecyclopent-1-yl)acetate (8) was recovered. No further attempts to optimize the yield were made. Purification for analysis was accomplished by preparative gc at 230°. *Anal.* Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.18; H, 9.37. Spectral data: nmr δ 4.85 (m, 2 H), 4.15 (q, 2 H), 1.27 (t, 3 H), 1.1–3.1 (9 H); ir (CHCl₃) 1730, 1655, 887 cm⁻¹. This was converted into 7, identical with that derived from 1, by treatment with NaOCH₃ in CH₃OH and isolation by gc.

Deuteration of 13. A sample of 2.50 g of 13 was refluxed for 2 hr in 10 ml of 8% NaOD in D₂O. The solution was cooled and acidified with 2.5 ml of concentrated H₃PO₄. The deuterated acid was isolated by filtration and dried, recovery 1.70 g. This was converted into the acid chloride as above, and nmr analysis indicated that 74% of the α-hydrogens were replaced by D. Conversion into 1 and then 9 was accomplished, and that benzyl ester isolated by gc. The vinyl protons (δ 4.85) exhibited 28% of the intensity expected by comparison with the intensity of the methylene protons of the benzyl group (δ 5.17). The nmr spectrum was otherwise identical with that of undeuterated material.

Registry No.—1, 5261-30-3; 3, 2910-67-0; 4, 52358-08-4; 7, 52358-09-5; 8, 52358-10-8; 13, 21622-08-2; 14, 2910-65-8; 15, 20826-94-2; cyclopentanone pyrrolidine enamine, 52358-11-9; ethyl bromoacetate, 105-36-2; ethyl cyclopentylideneacetate, 1903-22-6.

References and Notes

- (1) (a) This work has been supported by Lawrence University, The Research Corp., and the National Science Foundation (Grant. No. GR-7663); (b) Department of Chemistry, University of Wisconsin—Milwaukee.
- (2) (a) G. Stork and J. Ficini, *J. Amer. Chem. Soc.*, **83**, 4678 (1961); (b) C. J. V. Scanio and D. L. Lickel, *Tetrahedron Lett.*, 1363 (1972), and references therein.
- (3) M. Julia and F. Le Goffic, *C. R. Acad. Sci.*, **255**, 714 (1962).
- (4) (a) A. L. Wilds, J. Van Der Berghe, C. H. Winestock, R. L. Von Trebra, and N. F. Woolsey, *J. Amer. Chem. Soc.*, **84**, 1503 (1962); (b) A. L. Wilds, N. F. Woolsey, J. Van Der Berghe, and C. H. Winestock, *Tetrahedron Lett.*, 4841 (1965); (c) A. L. Wilds, R. L. Von Trebra, and N. F. Woolsey, *J. Org. Chem.*, **34**, 2401 (1969).
- (5) W. von E. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964); S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964).
- (6) G. Eglinton, J. C. Nevenzel, M. S. Newman, and A. I. Scott, *J. Amer. Chem. Soc.*, **78**, 2331 (1956); see also ref 4a.
- (7) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).
- (8) P. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961).
- (9) We thank a referee for urging the inclusion of this alternative.
- (10) T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, **89**, 3850 (1967); D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971); S. Wolff and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 226 (1972); H. E. Zimmerman and R. D. Little, *ibid.*, 698 (1972).
- (11) These spectra were kindly obtained by Dr. M. L. Druelinger of the Chemistry Department, Indiana State University.
- (12) W. S. Wadsworth, Jr., and William D. Emmons, "Organic Syntheses," Collect. Vol. V, Wiley, New York, N.Y., 1973, p 547.
- (13) G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, **127**, 620 (1925).
- (14) New England Ultraviolet Co., Middletown, Conn.
- (15) Benzyl alcohol was washed successively with saturated NaHSO₃, 45% KOH, and saturated NaCl, dried, and distilled at reduced pressure.
- (16) G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
- (17) Since the initial submission of this paper, a report has appeared presenting evidence for the detection of an intermediate analogous to 2 arising in a copper-catalyzed decomposition of another β,γ-unsaturated diazo ketone; H. E. Zimmerman and R. D. Little, *J. Amer. Chem. Soc.*, **96**, 4623 (1974).

Chlorocyclophosphazene-Epoxy Reactions. Catalysis by Lithium Halides

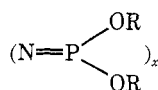
David F. Lawson

Central Research Laboratories, The Firestone Tire and Rubber Company, Akron, Ohio 44317

Received January 15, 1974

The reactions of chlorocyclophosphazenes with epoxides catalyzed by soluble salts were investigated. Lithium halide catalysts were found to be most effective for the preparation of fully substituted β-chloroethyl phosphazene esters from (N₂P₂Cl₂)_x and ethylene oxide. Tetraalkylammonium halides, lithium perchlorate, or cesium fluoride-hexamethylphosphoramide gave significantly lower oxirane incorporations. All reactions were extremely slow. The relative effectiveness of lithium halide catalysts is believed to be due to their ability to cleave an oxirane ring; promotion of reaction through a salt effect is also possible. Rearrangement of β-chloroethoxyphosphazene to N-(β-chloroethyl)oxophosphazenes appears to be a facile process.

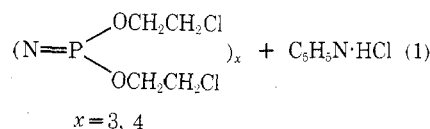
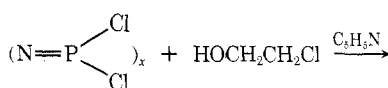
Although the alkoxyphosphazene esters 1 are fairly well known as a general class of compounds,¹ studies of phosphazene esters which contain haloalkyl substituents other than fluoroalkyl have been limited in number and scope. The first reported haloalkyl ester was prepared by the bromination of an allyloxycyclotriphosphazene ester.² More recently, β-chloroethoxy- and 2,3-dichloropropoxy



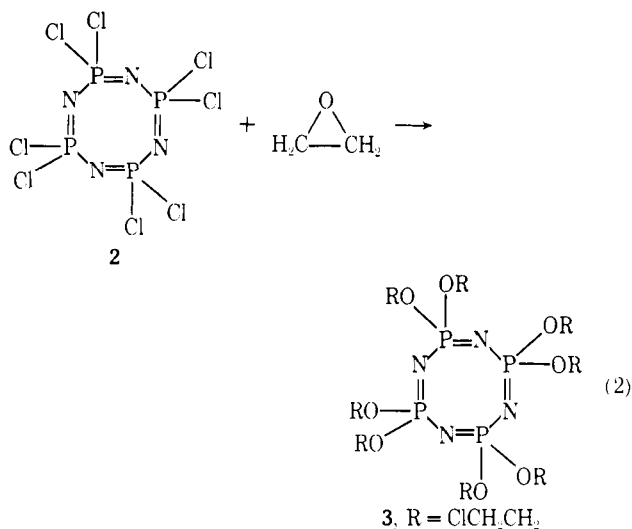
1, R = alkyl, aryl; x = 3, 4, ... n

phosphazene esters which contain haloalkyl substituents other than fluoroalkyl have been limited in number and scope. The first reported haloalkyl ester was prepared by the bromination of an allyloxycyclotriphosphazene ester.² More recently, β-chloroethoxy- and 2,3-dichloropropoxy

esters were prepared by reactions of the chlorophosphazene oligomers with the corresponding alcohols in pyridine,³ e.g., reaction 1.



An appealingly direct route to chloroalkoxy phosphazene esters, e.g., 3, is through the reaction of chlorophosphazenes with epoxides, (reaction 2). The analogous prep-



ation of β -haloalkyl phosphate esters from oxiranes and phosphoryl halides is a facile process. The synthesis of bis(2,3-dichloropropoxy)phosphazene octamer has been reported, using $(\text{NPCl}_2)_3$ and epichlorohydrin with TiCl_4 catalyst.⁴ However, the same reaction repeated with chlorophosphazene cyclic tetramer, $(\text{NPCl}_2)_4$, 2, gave only poly(epichlorohydrin). We thus investigated other potential catalysts for the chlorophosphazene-epoxide reaction. The work reported here is a study of the effect of soluble salt catalysts in several chlorophosphazene-epoxide reactions, as well as a brief examination of the products and their thermal behavior.

Results and Discussion

The uncatalyzed reactions of $(\text{NPCl}_2)_3$ or $(\text{NPCl}_2)_4$ with ethylene oxide are extremely slow. The maximum incorporation obtained in a reaction of this type after five days was 29% (THF solvent, closed vessel, 50°, tetramer 2) and no fully substituted esters were isolated. Little nmr evidence for POCH could be found. Uncatalyzed reactions at elevated temperatures and pressures in a Carius tube afforded no improvement, although some decomposition of the partially formed products was noted at temperatures of 100 to 180°.

Whereas conductance measurements showed that phosphonitrilic chlorides autoionize at temperatures in excess of 200 to 230°,⁵ radiotracer experiments indicated that chloride ion exchanged readily in the presence of tetraalkylammonium chloride in acetonitrile at room temperature.⁶ Since it seemed reasonable that salts of this type might also promote chlorophosphazene-epoxide reactions by inducing ionization of the P-Cl bond, reactions of $(\text{NPCl}_2)_4$ with ethylene oxide in the presence of (a) tetraalkylammonium halides, (b) lithium halides, (c) lithium perchlorate, or (d) cesium fluoride were examined. Results of these experiments are summarized in Table I.

Tetraalkylammonium Halides. An improvement in net epoxide incorporation over uncatalyzed conditions was found with several tetraalkylammonium salts (experiments 2 and 3). The products resulting from these reactions were unstable, viscous oils which rapidly decolorized and fumed, liberating HCl on standing.⁷ No incorporation of ethylene oxide greater than 45–50% was achieved using either tetraethylammonium bromide or tetra-*n*-butylammonium chloride. The product mixtures had ir and ¹H nmr spectra which were similar to those of authentic octakis(2-chloroethoxy)cyclotetraphosphazene⁸ (3), although ir absorptions at 1081 and 1031 cm^{-1} were weak, and nmr bands were both broadened and shifted 0.2 ppm downfield from those of 3.

Table I
Effect of Catalyst on the Reaction of
 $(\text{NPCl}_2)_4$ with Ethylene Oxide^a

Expt	Catalyst	Catalyst concn, mol/l.	Reaction time, hr	% oxirane incorpd ^b
1	None		120	29
2	$(\text{C}_2\text{H}_5)_4\text{N}^+\text{Br}^-$	0.05	84	37
3	$(\text{C}_4\text{H}_9)_4\text{N}^+\text{Cl}^-$	0.05	96	45
4	LiCl	0.058	96	100 ^c
5	LiBr	0.058	96	90
6	LiBr	0.058	108	100
7	LiBr	0.058	24	50
8	LiBr	0.001	96	47
9	LiClO_4	0.058	72	40–50 ^d
10	$\text{CsF}\cdot\text{HMPA}^e$	0.025	120	30–35

^a Reaction procedure described in Experimental Section: THF solvent, sealed vessel, 50°, 1.74 equiv of $(\text{NPCl}_2)_4$, 3.4 equiv of ethylene oxide, 100-ml liquid volume. ^b Calculated from weight increase in product when concentrated under vacuum. ^c Dark red, discolored product. ^d Yield estimated by nmr; significant amounts of polyether also present. ^e Hexamethylphosphoramide added (1:1) in attempt to dissolve CsF.

Lithium Halides. When lithium chloride catalyst was employed (Table I, experiment 4), the yield of 3 was essentially quantitative after 96 hr. Both ir and ¹H nmr spectra of the product were identical with those of 3 prepared by reaction 1, although the product was deep red in color.

The use of lithium bromide catalyst (Table I, experiments 5 and 6) gave a quantitative yield of 3 after 108 hr. The product had ir spectra identical with those of the product of reaction 1. Only a 50% incorporation of epoxide was observed after 24 hr, the crude product mixture closely resembling those obtained using tetraalkylammonium halides (Table I, experiment 7). Extent of epoxide incorporation was also dependent on catalyst concentration (experiment 8).

Lithium Perchlorate. Maximum epoxide incorporations of 40–50% were obtained after 72 hr with lithium perchlorate catalyst (Table I, experiment 9). The partially formed products were unstable. Substantial quantities of polyethers from both ethylene oxide and solvent (THF) were also obtained.

Cesium Fluoride. It was necessary to add hexamethylphosphoramide (HMPA) in a 1:1 ratio with cesium fluoride, since the salt alone was insoluble in THF. Inclusion of HMPA did not dissolve the salt completely, as evidenced by a cloudy reaction mixture. Reaction products again resembled those from other incomplete reactions.

Reactions with Epichlorohydrin. Epichlorohydrin was found to be much less reactive than ethylene oxide toward $(\text{NPCl}_2)_4$; however, incorporations of up to 70% of theoretical were obtained when the reactions were catalyzed by lithium bromide. The results of several reactions of $(\text{NPCl}_2)_4$ with epichlorohydrin are listed in Table II. Lithium perchlorate, in contrast to lithium bromide, showed no evidence for catalysis of the chlorophosphazene-epoxide reaction, and tetra-*n*-butylammonium bromide showed very little effect. However, polymerization of epichlorohydrin was observed with lithium perchlorate.

Mechanism. Since all of the salts investigated showed some catalytic effect in the $(\text{NPCl}_2)_4$ -ethylene oxide reaction, a general mechanism involving salt effects is likely. However, the greater effectiveness of lithium bromide evidenced in both ethylene oxide and epichlorohydrin reactions suggests that lithium halides perform an added catalytic function, perhaps through a cleavage of the epoxide ring to give a lithium halohydrin salt, similar to those pos-

Table II
Effect of Catalyst on the Reaction of
(NPCl₂)₄ with Epichlorohydrin^a

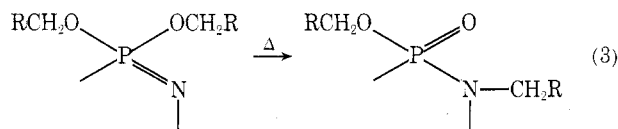
Expt	Catalyst	Catalyst concn (mol/l.)	Reaction time, hr	% oxirane incorpd ^b
1	LiBr	0.058	36	50 ^c
2	LiBr	0.058	108	70 ^d
3	LiClO ₄	0.058	108	0 ^e
4	(C ₄ H ₉) ₄ N ⁺ Cl ⁻	0.05	96	7

^a Reaction conditions described in Experimental Section: THF solvent, sealed vessel, 50°, 1.74 equiv of (NPCl₂)₄, 1.74 equiv of epichlorohydrin, 100-ml of liquid. ^b Calculated from weight increase, product concentrated under vacuum. ^c ¹H nmr showed a >6:1 ratio of 1,3-dichloro-2-propoxy- to 2,3-dichloro-1-propoxy substituents. ^d ¹H nmr showed a 4:1 ratio of 1,3-dichloro-2-propoxy- to 2,3-dichloro-1-propoxy substituents. ^e Weight increase was observed owing to formation of poly(epichlorohydrin); no evidence for POCH by ¹H nmr.

tulated for the rearrangement of epoxides.⁹ Such a mechanism might also explain the relative ineffectiveness of the poorer nucleophile, lithium perchlorate.

Products and Thermal Behavior. Product 3, prepared from ethylene oxide and 2, was typically a straw-colored oil. Small quantities of solids could be obtained from the oil after repeated extractions with petroleum ether and cooling to -50°. In some cases, solid 3 formed in the purified oil on standing and was recovered by filtration, being pressed dry on filter paper. This yielded 60–70% by weight of a colorless, waxy solid, mp 49–50°, whose spectra and analyses are described below. Isolation of solid 3 from the oils was not consistently achieved.

Although the chloroethoxyphosphazenes are stable for extended periods at ambient conditions, when heated to 100–120° as under vacuum distillation,³ the oils are known to fume (HCl detected), discolor, and resinify. Since Shaw and coworkers have shown that alkoxyphosphazene esters readily undergo thermal alkoxyphosphazene-oxophosphazene rearrangement¹⁰ (eq 3), facile phosphazene forma-



tion may contribute to thermal instability of 3, with the added complication of HCl elimination.

Careful examination of the ir spectrum of unheated 3 revealed a small shoulder at 1250 cm⁻¹, corresponding to P=O stretch (Table III), but no evidence for phosphazene NCH was found by nmr. Treatment with refluxing 1,2-dichloroethane¹¹ caused the disappearance of the strong 1325-cm⁻¹ band (P=N stretch) and enhancement of the 1250-cm⁻¹ shoulder; a broad band was also found at 1285 cm⁻¹. A noticeable change in the position and width of the POCH nmr absorption was observed. The ir spectrum of residue from attempted vacuum distillation was very similar to that of halide-rearranged 3, the main difference being relative intensities of strong bands and location of weak bands. Both the product oils and the isolated solids exhibited the same thermal behavior.

It appears that some rearrangement to phosphazene accompanies the formation of β-chloroethoxy ester at temperatures ≤50°, which may account for their oily nature. Phosphazene predominates after treatment with dichloroethane and also appears to form in thermal decomposition at higher temperatures. Other processes, including evolution of HCl and cross-linking, also accompany rearrangement during thermal decomposition.

Table III
Ir and Nmr Data for
Octakis(2-chloroethoxy)cyclotetraphosphazene, 3

Identity	ν ^a (neat), cm ⁻¹	δ (CHCl ₃ -d)
3	1325, 1295 (sh, 1250), 1081, 1031, 712	3.74 (t, <i>J</i> = 5.5 Hz, <i>w</i> ^b = 14 Hz); 4.25 (m, <i>w</i> = 16 Hz)
3, refluxed for 16 hr in (CH ₂ Cl) ₂	1285 (str sh, 1250), 1081, 1031	3.74 (t, <i>J</i> = 5.6 Hz, <i>w</i> = 15 Hz); 4.38 (m, <i>w</i> = 35 Hz)
3, after attempted vacuum distillation, 130–150°, 0.5 Torr	1290 (str sh, 1250), 1085, 1030	Insoluble

^a Wavenumbers of strong bands only are listed. ^b *w*, peak width at half height.

It has been observed that the tendency of alkoxyphosphazenes to undergo rearrangement to phosphazanes is related to the presence of electron-withdrawing substituents on the alkyl group. This has been interpreted as reduction of basicity of the ring nitrogen through electron withdrawal.¹⁰ On this basis the predicted stability of β-chloroethoxyphosphazenes would be intermediate between that of ethoxy and trifluoroethoxy analogs. The very facile rearrangement observed is probably a result of intra- and intermolecular catalysis by the β-chloroethoxy groups which are susceptible to nucleophilic reactions, as well as by HCl formed in thermal dehydrochlorination.

Experimental Section¹²

Hexachlorocyclotriphosphazene (phosphonitrilic chloride trimer), mp 115°, was separated from a mixture of cyclic oligomers by fractional vacuum distillation. Octachlorocyclotetraphosphazene 2 (phosphonitrilic chloride cyclic tetramer), mp 124°, was purified by repeated fractional sublimation under vacuum of the resulting distillation residue. Reactions were carried out by the following method. A dry 300-ml glass vessel was charged with 10.0 g of purified phosphonitrilic chloride, 100 ml of freshly distilled anhydrous tetrahydrofuran, and 0.25–0.50 g of catalyst. The bottle was closed and cooled, and 15–20 ml of liquid epoxide was added quickly. The bottle was sealed and placed in a rotating bath at 50°. After reaction the bottle was cooled and opened, and the solvent was removed under vacuum. If the product was stable, catalyst was then removed by dissolving the product in chloroform, washing with water, drying (MgSO₄), and concentrating under vacuum.

Incorporation of epoxide was determined from weight gain and estimated purity from ¹H nmr. Partially esterified products were analyzed by nmr and weight gain immediately after initial concentration. In several cases, yields determined from weight gain were checked in the following manner. Concentrated product was treated with an excess of sodium 2,2,2-trifluoroethoxide in THF at 65° and worked up as a fully substituted ester; comparison by ¹H nmr of the absorptions at δ ~4.6 and 4.2–4.3 showed agreement to within 5% of the incorporations calculated by weight gain.

Fully substituted octakis(2-chloroethoxy)cyclotetraphosphazene (3) as either the solid or oils from LiBr-catalyzed reactions gave carbon, hydrogen, and chlorine analyses consistent with the expected formula (Calcd for C₁₆H₃₂N₄O₈P₄Cl₈: C, 23.55; H, 3.95; Cl, 34.76. Found (solid): C, 23.66; H, 4.00; Cl, 34.80. Found (oil): C, 23.62; H, 3.97; Cl, 34.90).¹³ No molecular ion was observable in the mass spectrum of 3, but *m/e* 740 (M⁺ - 72, loss of 2HCl) with six chlorines was detected. The ir spectrum was identical with that for 3 prepared from 2-chloroethanol by reaction 1 (see below).

Elemental and mass spectral analyses do not distinguish between isomeric phosphazene and phosphazane structures, and the only evidence for phosphazane in the oils was found in the shoulder at 1250 cm⁻¹ in the ir spectrum of 3. Purification by distillation or gas chromatography was unsuccessful owing to the high molecular weight and thermal instability of the esters. Chromatography of the oily product 3 on silica gel or alumina columns using various ratios of chloroform-hexane or chloroform-benzene gave a single eluent band identical with that of unchromatographed 3. In

view of facile O → N rearrangement, the oils may contain small amounts of *N*-alkylphosphazanes.

The TiCl₄-catalyzed reaction of octachlorocyclotetraphosphazene and epichlorohydrin was attempted by adding TiCl₄ slowly to a mixture of the other reactants at 85°, followed by heating and work-up similar to that described above.

Octakis(2-chloroethoxy)cyclotetraphosphazene, 3, by reaction 1.³ A 2-l., 3-neck round-bottom flask containing 700 ml of anhydrous pyridine and 87 g (1.5 equiv) of 2 was cooled to 15°, and 121 g (1.5 equiv) of 2-chloroethanol was added dropwise over 1 hr. After the mixture was stirred at room temperature for 20 hr, solvent was removed under vacuum below 50°. The residue was then poured into 600 g of ice-water, and the oil layer taken up with chloroform. The chloroform extract was washed with 5% HCl, 5% Na₂CO₃, and water, dried (MgSO₄), and concentrated on a rotary evaporator. The residual oil was concentrated further at room temperature and 0.1 Torr for 16 hr. The product was a viscous yellow oil, weight 145.2 g, 95% of theoretical yield, characterized by its spectrum (see following paragraph on supplementary material).

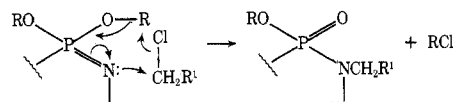
Acknowledgments. The author is grateful to personnel of the Analytical Services Division, Firestone Central Research Laboratories, for technical assistance, and to The Firestone Tire and Rubber Company for permission to publish this work.

Supplementary Material Available. Nmr spectrum of compound 3 and ir spectra of 3 prepared by reactions 1 and 2 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-3357.

Registry No.—2, 2950-45-0; 3, 52539-64-7; (C₂H₅)₄N⁺Br⁻, 71-91-0; (C₄H₉)₄N⁺Cl⁻, 1112-87-0; LiCl, 7447-41-8; LiBr, 7550-35-8; LiClO₄, 7791-03-9; CsF, 13400-13-0; ethylene oxide, 75-21-8; epichlorohydrin, 106-89-8; hexachlorocyclotriphosphazene, 940-71-6.

References and Notes

- (1) (a) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N.Y., 1967. (b) H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N.Y., 1972.
- (2) C. Hamalainen and J. D. Guthrie, *Textile Res. J.*, **26**, 141 (1956); C. Hamalainen, W. A. Reeves, and J. D. Guthrie, *ibid.*, **26**, 145 (1956).
- (3) L. A. Godfrey and J. W. Schappel, *Ind. Eng. Chem. Prod. Res. Devel.*, **9**, 426 (1970); (b) L. A. Godfrey and N. J. Pennington, German Offen. 2,016,153 (1970).
- (4) P. M. Zavlin, M. A. Sokolovskii, and I. V. Yurenko, U.S.S.R. Patent 176,402 (1965).
- (5) H. R. Allcock and R. I. Best, *Can. J. Chem.*, **42**, 447 (1964).
- (6) D. B. Sowerby, *J. Chem. Soc., London*, 1396 (1965).
- (7) Considering degree of substitution and stereochemistry, 32 partially substituted products are possible from 2. No attempt was made to identify the components of incomplete reaction mixtures.
- (8) Prepared by the method of ref 3b.
- (9) B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **93**, 1963 (1971); also F. Johnson, "Friedel-Crafts and Related Reactions," Vol. IV, G. A. Olah, Ed., 1965, pp 32-41.
- (10) B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J. Chem. Soc., London*, 4459 (1964).
- (11) Alkyl halides were shown to catalyze O → N migration,¹⁰ via



- (12) Melting points were determined in capillary tubes and are uncorrected. Chlorine analysis was by Schöniger flask combustion and Volhard titration. Carbon, hydrogen analyses performed by Galbraith Laboratories, Inc.
- (13) C, H, and N microanalyses using an F&M Model 185 analyzer gave varying high results for 3. *Anal.* (typical). Calcd: C, 23.5; H, 3.9; N, 6.9. Found: C, 25.5; H, 4.1; N, 7.4. Such results are presumably due to premature loss of HCl during analysis.

Reactions of Cyclopropanols with Halogenating Agents and Other Electrophiles

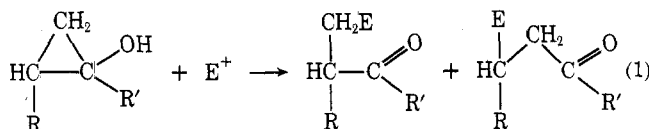
Charles H. DePuy* and Robert J. Van Lanen

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received March 27, 1974

A study has been made of the reactions of *cis*- and *trans*-2-phenyl-1-methylcyclopropanol and their methyl ethers, *cis*- and *trans*-2-methyl-1-phenylcyclopropanol, and *cis*- and *trans*-1,2-diphenylcyclopropanol with various electrophiles, including mercuric acetate, acid, and various sources of positive halogen. The direction of ring opening is found not to depend upon the stereochemistry of the starting material. The free-radical opening of optically active *trans*-2-phenyl-1-methylcyclopropanol by FeCl₃ is shown to give racemic chloro ketone. The results are compared with those from related systems.

For some time we have been interested in the mechanism and stereochemistry by which cyclopropanols and their derivatives react with electrophiles.¹ In previous studies we have reported that *trans*-2-phenyl-1-methylcyclopropanol undergoes electrophilic ring opening with retention of configuration when treated with D⁺² and that the various *cis*-*trans* isomers of 2,3-dimethyl-1-phenylcyclopropanol ring open with inversion of configuration upon reaction with mercuric acetate³ or various brominating agents.⁴ In the course of these and other studies¹ we have also had occasion to measure the effect of a ring substituent on the direction of ring opening upon attack by an electrophilic reagent (eq 1). In the work reported in this paper we have attempted to make a more systematic study of cyclopropanol ring openings as a function of the nature and stereochemis-



try of the substituents R and R', particularly as they apply to halogenation, but also for protonation and mercuration.

Results

***cis*-2-Phenyl-1-methylcyclopropanol (Ib).** The first system chosen for study in this investigation was *cis*-2-phenylcyclopropanol (Ib) since we had previously determined the product composition on ring opening of the *trans* isomer.² We were interested in determining if simple *cis*-*trans* isomerization would have any effect on the direc-