Gravimetric analysis as its ferric salt[21] showed it to be of at least 99.9% purity.

p-Toluenesulfinyl *p*-Tolyl Sulfone (I).—The procedure was a modification of that of Bredereck, *et al.*[12] The entire preparation and purification of the sulfinyl sulfone was carried out in a glove-box in an anhydrous nitrogen atmosphere. Anhydrous sodium *p*-toluenesulfinate (1.0 g.), prepared by heating the dihydrate at 185° and 0.1 mm. for 5 hr., was dispersed in 20 ml. of anhydrous ether. To this suspension *p*-toluenesulfinyl chloride[22] was added dropwise with vigorous shaking until the yellow color of the sulfinyl chloride persisted. After a short time the ether was decanted, and the residual solid was washed several times with anhydrous ether. The solid was then treated with dry benzene to dissolve the sulfinyl sulfone. The benzene solution was filtered, and the solvent was removed under reduced pressure at room temperature. The crystalline product was washed several times with ether, and dried under vacuum at room temperature; m.p. 76° (lit.[13] 75°; Bredereck,[12] on the other hand, reports a m.p. of 87° but says his product is identical by infrared with the compound of m.p. 75° prepared by Knoevenagel and Pollack.[13]

The sulfinyl sulfone reacted quantitatively in acetone or acetic acid with two equivalents of iodide. For determination of its purity, compound I ($\sim$ 0.1 g.) was treated with a solution of excess sodium iodide in reagent grade acetone. The flask was warmed gently until all the sulfinyl sulfone dissolved. The liberated iodine was then determined by diluting the solution with an equal volume of water and titrating with 0.1 *N* thiosulfate. The reaction of iodide with I is apparently faster than the hydrolysis of I to sulfinic acid, since when the above procedure was applied using acetic acid–0.56 *M* H_2O as the solvent rather than acetone, 92% of the expected amount of iodine was liberated. Control experiments showed that under these conditions none of the other substances involved in the disproportionation—thiolsulfonate, sulfinic and sulfonic acids—liberate iodine from sodium iodide.

Solvents and Standard Solutions.—Reagent grade acetic acid was refluxed with acetic anhydride for 24 hr. followed by distillation through a 4-ft. glass helices-packed column using a reflux ratio of 100:1. A large middle fraction was collected and redistilled under the same conditions; freezing point of the purified acid was 16.67°. Water content, as determined by titration with Karl Fischer reagent,[23] was less than 0.01%. Reagent grade concentrated sulfuric acid was dissolved in the purified acetic acid, sufficient acetic anhydride added to take up most of the water, and the solution made up to a volume such that the final sulfuric acid concentration was 5 *M*. This stock solution was used as the source of sulfuric acid for the kinetic runs. Its residual water content, determined by titration with Karl Fischer reagent,[23] was taken into account in the preparation of solutions for kinetic runs.

Stoichiometry of the Disproportionation Reaction.—The yield of thiolsulfonate was compared with that expected from the stoichiometry of reaction 1 as follows: An aliquot was removed from the solution and titrated for remaining sulfinic acid by the nitrite titration described in Procedure for Kinetic Runs. Another aliquot was then removed, thrown into ten times its volume of water, and the resulting mixture extracted several times with ether. The combined ether extracts were washed with aqueous bicarbonate until neutral, dried, and the ether removed under reduced pressure. The last traces of solvent and any tolyl disulfide (from hydrolysis of the thiolsulfonate) were removed by prolonged high vacuum drying at room temperature. The residue was quite pure *p*-tolyl *p*-toluenethiolsulfonate, m.p. 76° (lit.[24] 76°) and infrared spectrum identical with a known sample. The yield of thiolsulfonate was determined simply by weighing this residue.

Procedure for Kinetic Runs.—Solutions for kinetic runs were prepared as follows. An exact amount of *p*-toluenesulfinic acid was weighed into a 100-ml. volumetric flask, the required amount of water was added from a microburet, and about 30 ml. of acetic acid was added. The required amount of sulfuric acid (as a 5 *M* solution in acetic acid) was then added, and the solution was made up to volume with acetic acid. The solution was then placed in the reaction vessel—a 125-ml. flask equipped with a nitrogen inlet, a spiral condenser connected by capillary tubing to a mineral oil trap which prevented back diffusion of air into the system, and a series of tubes and stopcocks which made it possible to use nitrogen pressure to remove a sample from the flask without opening it to the atmosphere. Before starting a run air was removed from the system by slowly bubbling prepurified nitrogen through the solution. Once the solution was deaerated, the nitrogen flow was stopped, except when removing samples from the reaction vessel, and the flask was immersed in a constant temperature bath kept at 70 ± 0.02°. Samples (5 ml.) were withdrawn from time to time, and the reaction was quenched by the addition of an equal volume of cold water. The solution was then titrated with 0.2 *N* sodium nitrite solution using a 5-ml. microburet with the tip held below the surface of the liquid. The solution was stirred throughout with a Teflon-covered magnetic stirring bar. After each addition of nitrite solution (0.01 to 0.05 ml.) a small drop of the solution was touched to a strip of potassium iodide–starch paper. The end-point is reached when a faint pink color is developed. The indicator blank using this procedure was less than 0.01 ml. Trials with known samples of sulfinic acid showed the method gave accurate results and that the other substances present did not interfere. The method is adapted from that mentioned by Marvel and Johnson.[9] The reaction of nitrite with sulfinic acids in acid solution leads to the formation of the insoluble hydroxylamine, $(ArSO_2)_2NOH$.

(21) J. Mitchell, I. M. Kolthoff, E. S. Proskauer and A. Weissberger, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 378.

(22) *Org. Syntheses*, **34**, 93 (1954).

(23) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 105 ff.

(24) R. Otto, J. Lowenthal and A. v. Gruber, *Ann.*, **149**, 101 (1869).

[CONTRIBUTION FROM ROHM AND HAAS CO., PHILADELPHIA 37, PENNA.]

Bicyclic Phosphites[1]

BY WILLIAM S. WADSWORTH, JR., AND WILLIAM D. EMMONS

RECEIVED MAY 10, 1961

The bicyclic phosphites 1-alkyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octanes (I) represent a new class of organophosphorus compounds. They may be prepared easily in high yields and have a number of unique properties as a result of their bridged structure. Notable in this respect is the fact that they undergo a stereospecific Arbuzov reaction.

No thorough study of the preparation of phosphites containing a bridged structure, I, has been reported. Recently Verkade and Reynolds[2] prepared a bicyclic phosphite (I, R = CH_3) in 40% yield by treating trimethylolethane with phosphorus trichloride under conditions of high dilution and by using pyridine as an acid-binding agent. Barnes and Hoffman[3] have prepared the same phosphite in 50–55% yield by heating the triol and phosphorus trichloride in the absence of a sol-

(1) Presented at the 137th Meeting of A.C.S., New York, N. Y., September, 1960.

(2) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

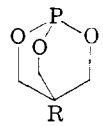
(3) R. A. Barnes, private communication.

TABLE I

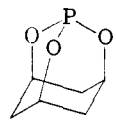
BICYCLIC PHOSPHITES, I

Compound, R =	M.p. °C.	B.p. °C.	B.p. Mm.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
CH_3	94		(Sublimes)	90						
CH_3CH_2	56	86–	0.1	98	44.78	44.36	6.78	6.90	19.15	19.21
$HOCH_2$	61	110	0.1	79	36.60	36.68	5.49	5.32	18.91	18.87
CH_3COOCH_2	77	..	..	86	40.78	40.63	5.35	5.55	15.05	15.01
$CH_2{=}C(CH_3)COOCH_2$	108	..	..	84	46.21	46.10	5.55	5.95	13.25	13.40
$CH_3(CH_2)_3CH(CH_2CH_3)COOCH_2$	..	128	0.25	86	53.75	53.85	7.98	8.16	10.67	10.78

vent and subliming out the product. Earlier Stetter and Steinacker[4] reported the successful synthesis of II in 20% yield by treating *cis*-1,3,5-cyclohexantriol with phosphorus trichloride. Conditions of high dilution and an acid acceptor, pyridine, were required. The oxidation of these



I



II

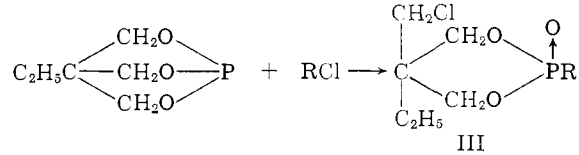
materials to phosphates and their reaction with sulfur to give thiophosphates were reported. In one case[2] reference was made to the ability of I to form stable complexes with various metal ions and addition compounds with Group III Lewis acids.

The results of our examination of the preparation of bicyclic phosphites indicated that the greatest obstacle to obtaining high yields of I was the formation of undistillable by-products. This hurdle has been overcome by using either of two procedures. The first consists of simple transesterification of a trialkyl phosphite with a trimethylolalkane. The reactants were heated together in such a manner that alcohol was removed at a minimum rate, usually over a period of several hours. The slow removal of alcohol at the lowest possible temperature is essential if by-product formation is to be kept at a minimum. Thus, trialkyl phosphites having small alkyl groups, *i.e.*, methyl or ethyl, are preferred. The structures of the bicyclic phosphites were confirmed by elemental analysis and from the observation that from a single trimethylolalkane identical products are obtained irrespective of the trialkyl phosphite used.

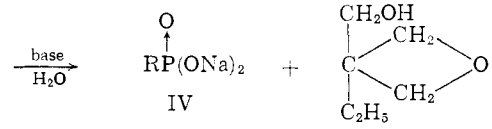
The second successful procedure was based on the addition of phosphorus trichloride to a trimethylolalkane at 0°. The reaction mixture was warmed slowly to 50–60° under a stream of nitrogen. The bicyclic phosphites (Table I) were purified by appropriate procedures. Since neither synthesis required solvent or acid-binding reagent, the bicyclic phosphites are among the cheapest and easiest of organophosphorus compounds to prepare.

Bicyclic phosphites are stable to air oxidation but hydrolyze readily when exposed to moisture. With one exception, however, they can be stored for long periods of time at refrigerator temperatures. The hydroxymethyl bicyclic phosphite derived from pentaerythritol (I, R = CH_2OH) starts to polymerize after standing at 0° for only a few hours.

The Arbuzov Reaction.—Like the simple esters of phosphorous acid the bicyclic phosphites undergo the Arbuzov reaction when treated with alkyl halides. The 2-alkyl-2-halomethyl-1,3-propanediol cyclic phosphonates (III, Table II), are prepared by heating the reactants at elevated temperatures, in some cases to 200°. In these reactions



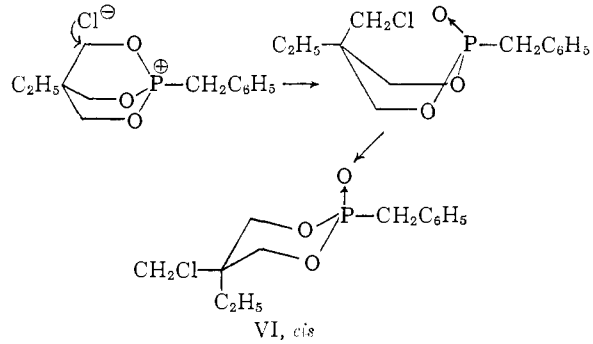
III



IV V

the bridged structure is lost and a halophosphonate is formed. The generation of a halide sterically hindered to nucleophilic attack prevents formation of polymer which might result from an Arbuzov reaction between the newly formed halocyclic phosphonate and unreacted phosphite. Saponification of the cyclic phosphonates with excess base gave disodium phosphonates IV and 3-alkyl-3-hydroxymethylpropyloxetane, V.

Vapor phase chromatography of III (R = $C_6H_5CH_2$) over Silicone packing at 290° gave but one peak, indicating that the bicyclic phosphites undergo the Arbuzov reaction to give a single isomer. A bicyclic phosphite is constrained to open to give a *cis* conformation,[5] VI, when treated with an alkyl halide, *i.e.*, benzyl chloride. This is a unique consequence of the bridged structure of the phos-



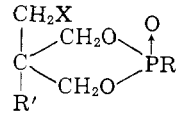
VI, *cis*

(4) H. Stetter and K. H. Steinacker, *Chem. Ber.*, **85**, 451 (1952); **87**, 205 (1954).

(5) By analogy to the substituted cyclohexanes, that conformation having the non-chlorinated alkyl groups in an axial-equatorial relationship has been assigned the *cis* conformation.

TABLE II

CYCLIC PHOSPHONATES FROM BICYCLIC PHOSPHITES



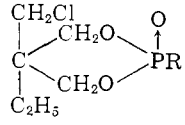
R′	R	X	Reaction temp., °C.	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
CH_3CH_2	$C_6H_5CH_2$-	Cl	170	118	91	54.12	53.86	6.78	6.28	12.27	12.57	10.72	10.85
CH_3CH_2	$C_2H_5OCOCH_2$-	Br	180	50	50	36.58	36.52	5.47	5.59	24.31	24.30	9.42	9.43
CH_3CH_2	CH_3COCH_2-	Cl	150	98	10	42.45	42.48	6.35	6.47	13.95	13.78	12.15	12.15
CH_3	CH_3-	I	80	120	85	27.61	27.39	4.60	4.90	...	...	10.20	10.39
$HOCH_2$	CH_3-	I	80	134	67	23.50	23.66	3.92	4.23	...	...	10.12	10.51
$ClCH_2$	$C_6H_5CH_2$-	Cl	210	123	50	46.51	46.74	4.55	4.62	23.00	27.96	10.02	9.75
CH_3CH_2	CH_2OCH_2-	Cl	130	85	30	39.60	39.32	6.60	6.68	14.60	14.88	12.77	12.77
CH_3	n-C_4H_9-	I	100	55	22	32.64	32.92	5.44	5.64	...	...	9.36	9.91
CH_3CH_2	Fluorenyl	Br	200	235	56	56.01	55.80	4.91	5.08	19.67	19.40	7.62	7.43
CH_3CH_2	2,4-$Cl_2C_6H_4CH_2$-	Cl	190	125	41	43.72	43.49	4.52	4.54	29.87	29.65	8.68	8.48

phite and the mechanism of the Arbuzov reaction.[6-9] The mechanism postulates the formation of a quasiphosphonium salt by a nucleophilic displacement of halogen with phosphite followed by an SN2 attack of halide ion on a bridged methylene group. A boat conformation is undoubtedly an intermediate but is presumably, by analogy to the cyclohexanes, converted to the thermodynamically stable chair form. Examination of molecular models confirms the inherent instability of the boat form due to steric repulsions.

To establish further the structure of the cyclic phosphonates their synthesis by an independent pathway was undertaken.

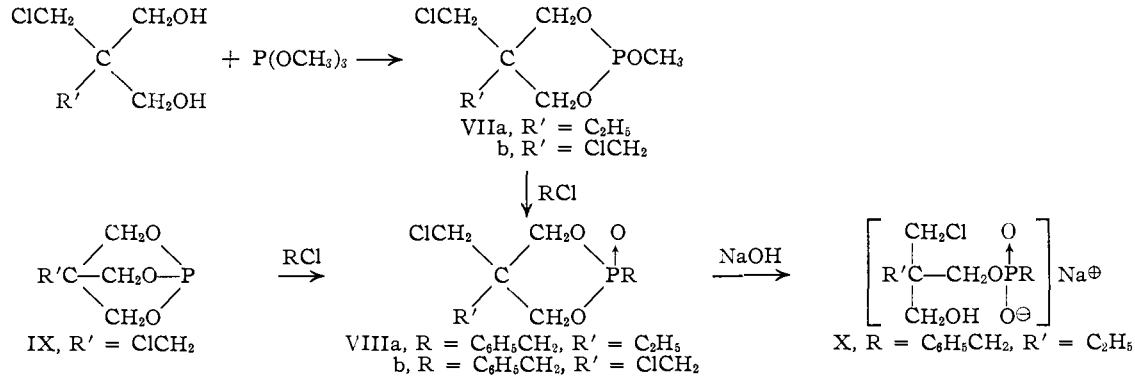
TABLE III

COMPARISON OF ANALOGOUS CYCLIC PHOSPHONATES



Compound, R =	From bicyclic phosphites, m.p., °C.	From cyclic phosphites, m.p. or b.p. (mm.), °C.
$C_6H_5CH_2$	117–118 (fr. CCl_4)	92 (fr. isooctane)
CH_3OCH_2	84–85 (fr. H_2O)	150–154 (0.3)[a]
$CH_2{=}C(CH_3)CH_2$	96–97 (fr. $C_2H_5OCOCH_3$)	130–131 (0.25)[a]

[a] Liquid at room temperature.



The first step, a simple transesterification,[10] gave a cyclic phosphite, VIIa, which due to its instability was best used immediately after its preparation. The second step was an Arbuzov reaction in which the ring is retained when a methoxyl group is attached to the phosphorus atom.[11] Treatment of VIIIa with excess base gave the same products as those obtained previously by a similar treatment of III (R = $C_6H_5CH_2$).

Vapor phase chromatography of VIIIa gave two peaks. The second peak, which was the smaller of the two, coincided with that of the pure *cis* isomer VI. The mixture was successfully separated into its two components by column chromatography using silica gel as an absorbent. The less tenaciously held material, when subjected to vapor phase chromatography, gave a lone peak coinciding with the first peak of the mixture. Thus VIIIa was obtained as a sharply melting eutectic in which the latter isomer (*trans* according to our nomenclature) predominated over the *cis* in an approximately 2:1 ratio. This ratio was determined by vapor phase chromatography and confirmed by comparison of the infrared spectrum of the mixture with that of a 2:1 mixture prepared from pure isomers.

(6) A. Michaelis and R. Kaline, *Chem. Ber.*, **31**, 1048 (1898).

(7) A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906).

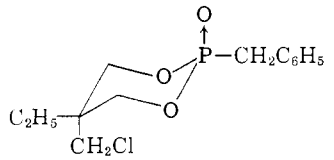
(8) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(9) W. Gerard and W. J. Green, *J. Chem. Soc.*, 2550 (1951).

(10) H. J. Lucas, F. W. Mitchell, Jr., and C. Scully, *J. Am. Chem. Soc.*, **72**, 5491 (1950).

(11) Groups larger than methoxyl, *i.e.*, propoxyl, butoxyl, etc., gave phosphonates in which ring opening predominated; A. E. Arbuzov and N. H. Rayumova, *Izvest. Akad. Nauk*, 1061 (1958).

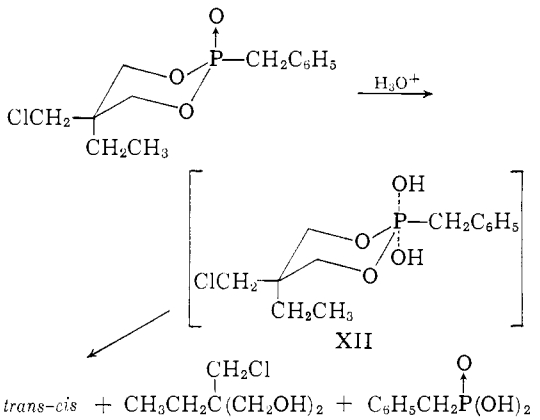
The infrared absorption due to P→O bond vibrations,[12] 1260 cm.$^{-1}$, is identical for both isomers indicating an identical environment about the phosphorus atoms. Thus, it may be concluded that the isomers differ only by the configuration of groups about the 4-position and that the *trans* isomer has the conformation XI.



XI, *trans*

The configurational difference at the four position was substantiated by the preparation of a cyclic phosphonate having identical groups in the 4-position. Regardless of the route, only one cyclic phosphonate, VIIIb, was obtained which absorbed strongly at 1260 cm.$^{-1}$. Furthermore, III (R = $C_6H_5CH_2$) and the mixture VIIIa gave a common salt, X, when treated with an equivalent of base.

The *cis* isomer VI can be equilibrated by refluxing with dilute hydrochloric acid. If heating is prolonged, *i.e.*, over 24 hours, a 2:1 *trans–cis* mixture, *via* infrared, is obtained on distillation. By-products arising from ring cleavage also are produced. The equilibration most probably goes

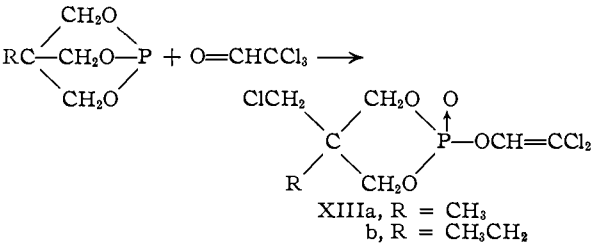


2:1 *trans–cis* + $CH_3CH_2C(CH_2OH)_2$ + $C_6H_5CH_2P(OH)_2$

through an intermediate, XII, in which the phosphorus atom makes use of its 3d-orbitals in becoming pentacovalent. That the equilibration is due to the recombination of products resulting from ring cleavage is unlikely under the conditions employed. By gently warming an aqueous dispersion the equilibration of *cis*-2-ethyl-2-chloromethyl-1,3-propanediol methoxymethylphosphonate was accomplished without the formation of by-products.

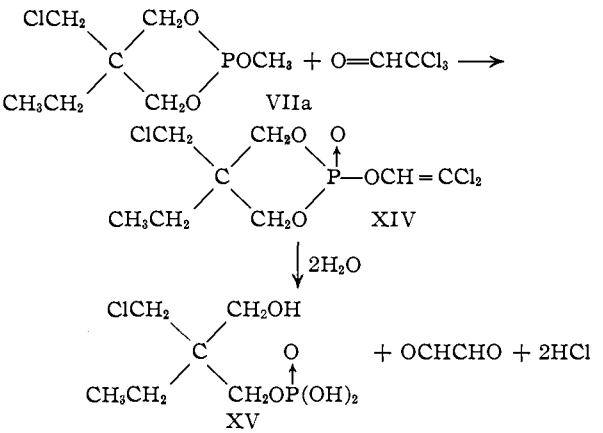
It is perhaps fortuitous that both the mixture VIIIa and product arising from equilibration of the *cis* isomer contain the isomers in an approximately identical ratio. The preparation of the mixture VIIIa in the presence of pure *cis* isomer gave a mixture enriched in *cis* isomer and thus it may be concluded that the isomer ratio in VIIIa is not equilibrium controlled.

The Perkow Rearrangement.—That the treatment of trialkyl phosphites with α-halo ketones or aldehydes produces vinyl phosphates *via* an intramolecular rearrangement is well-known.[13–19] Bicyclic phosphites behave similarly to yield cyclic vinyl phosphates XIII.



XIIIa, R = CH_3
b, R = CH_3CH_2

To determine whether the Perkow rearrangement was stereospecific, the synthesis of XIIIb by an independent pathway was undertaken. The phosphates XIIIb and XIV were similar in their physical properties (nearly identical boiling points and indices of refraction) although like the cyclic phosphonates their infrared spectra showed striking dissimilarities. The equilibration of XIIIb to XIV failed due to the facile hydrolysis of the vinyl phosphate. The attempted resolution of XIV *via* gas chromatography resulted in decomposition.



The Reaction of Halogens.—Chlorine, when added to a methylene chloride–bicyclic phosphite solution, gave the cyclic phosphorochloridate XVII. Although the reaction is similar to the trialkyl phosphite–halogen reaction in that a phosphorochloridate is formed, it is dissimilar in that a stable crystalline intermediate, assumed to be XVI, is produced at low temperatures. The intermediate, obtainable as a voluminous white precipitate by treating the bicyclic phosphite solution with chlorine gas at −10°, is of uncertain structure and may or may not be ionic. At any rate, it rearranges exothermically at elevated temperatures to XVII. A brief look at the reactions of the intermediate gave little insight as to its actual structure. Treatment with water gave a fair yield of the bi-

(12) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 312.

(13) W. Perkow, *Chem. Ber.*, **87**, 755 (1954).

(14) W. Lorenz, A. Hengheim and G. Schrader, *J. Am. Chem. Soc.*, **77**, 2554 (1955).

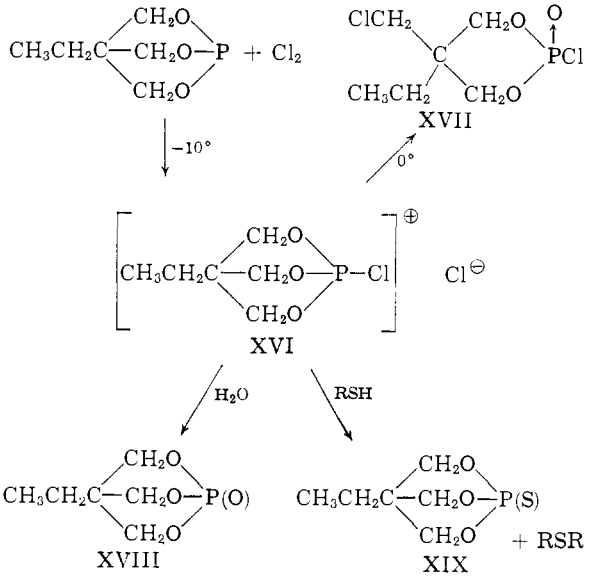
(15) W. D. Barthel, B. H. Alexander, P. A. Giang and S. A. Hall, *ibid.*, **77**, 2424 (1955).

(16) W. Perkow, *et al.*, *Chem. Ber.*, **88**, 662 (1955).

(17) J. F Allen and O. H. Johnson, *J. Am. Chem. Soc.*, **77**, 2871 (1955).

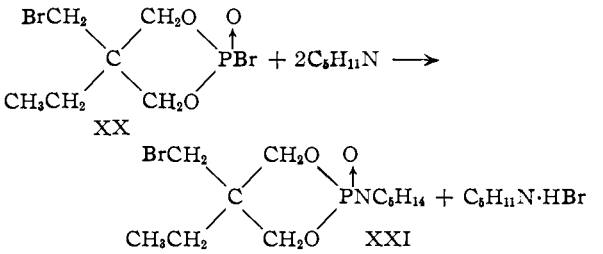
(18) H. I. Jacobson, M. J. Griffin, A. Preis and E. V. Jensen, *ibid.*, **76**, 2608 (1957).

(19) I. S. Bengelsdorf, *J. Org. Chem.*, **21**, 475 (1956).



cyclic phosphate XVIII, while mercaptans produced good yields of sulfides and bicyclic thiophosphates XIX.

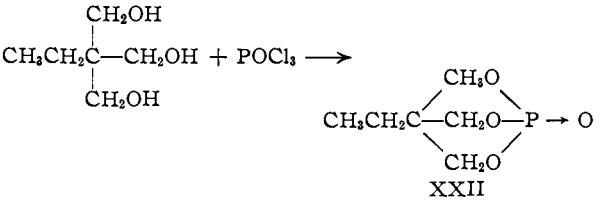
Bromine is not unlike chlorine in its reactions with bicyclic phosphites with the exception that the temperature required for stabilization of the intermediate is not as low. The cyclic phosphorobrominate XX, which is produced by allowing the intermediate to warm to room temperature, cannot be distilled due to decomposition. Evidence of its existence was obtained, however, by preparing a cyclic phosphoramidate, XXI, from a methylene chloride solution.



The synthesis of cyclic phosphorohalidates from bicyclic phosphites was not stereospecific. Cyclic phosphorohalidates prepared by treating a monocyclic phosphite with halogen were identical in every respect with the analogous materials obtained from bicyclic phosphites.

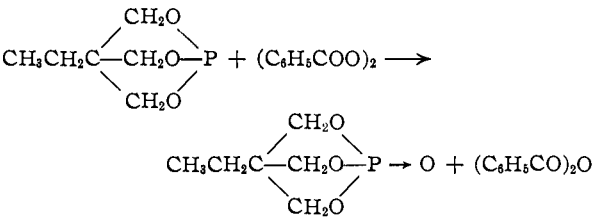
The resistance of the bridged carbon atoms in bicyclic phosphites to nucleophilic attack, as compared to the alkyl groups in trialkyl phosphites, is exemplified by the isolation of the stable crystalline intermediate XVI. As a consequence of this situation, bicyclic phosphites are less inclined to undergo rearrangements of the Arbuzov or Perkow type. They require, for example, more rigorous reaction conditions. That the inertness of the bicyclic phosphites is a consequence of their bridged structure and not due to their lack of nucleophilicity was borne out by competitive bromination at −50°. Over half the theoretical amount of bicyclic phosphite–bromine adduct required for total conversion of the bicyclic phosphite was obtained when less than one equivalent of bromine was added to one equivalent each of triethyl phosphite and a bicyclic phosphite.

The Preparation of Bicyclic Phosphates and Thiophosphates.—Bicyclic phosphates, besides being obtained by simple oxidation of the corresponding phosphite, may be prepared directly by treating a trimethylol alkane with phosphorus oxychloride.

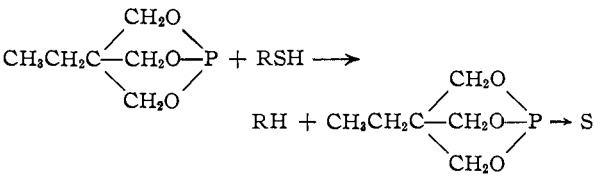


Under conditions of high dilution, Barnes and Hoffmann[3] have reported yields of bicyclic phosphates of under 20% from these reagents. In our hands yields of over 50% have been obtained under conditions identical with those required for the preparation of bicyclic phosphites from PCl_3, namely low temperatures and a stream of nitrogen to remove HCl as it is formed.

Oxidation of bicyclic phosphites with peroxides follows the path outlined for the oxidation of simple trialkyl phosphites.[20] Benzoic anhydride, for example, is obtained by treating a bicyclic phosphite with benzoyl peroxide.



Bicyclic thiophosphates which can be prepared by the classical method of heating phosphites with sulfur also can be formed by heating bicyclic phosphites with mercaptans in the presence of free radical catalysts.[21,22]



Acknowledgments.—We wish to express our appreciation to Dr. Sheldon Lewis for helpful suggestions during the course of this work. Dr. Harry Cenci, Mr. Robert Dieckmann and Mr. William Randolph aided in preparing some of the intermediates. The analyses were carried out under the direction of Mr. Clyde Nash.

Experimental

Ethyl Bicyclic Phosphite, I.—To trimethylolpropane (268 g., 2.0 moles) and distilled triethyl phosphite (332 g., 2.0 moles) was added approximately 5 drops of triethylamine catalyst. The mixture was heated with stirring to 100° at

(20) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959).

(21) F. W. Hoffman, R. J. Ess, T. C. Simmons and R. S. Hanzel, *J. Am. Chem. Soc.*, **78**, 6414 (1956).

(22) C. Walling and R. Rabinowitz, *ibid.*, **79**, 5326 (1957).

which point alcohol begins to distil off. The temperature of the mixture was raised to 130° over a period of 8 hours during which time 97% of the theoretical quantity of alcohol was collected.

At the end of the heating period the resulting clear solution was distilled giving a 90% yield of product boiling at 75–80° (0.5 mm.). The product solidified on cooling, m.p. 55–56°.

Anal. Calcd. for $C_6H_{11}O_3P$: C, 44.78; H, 6.78; P, 19.15. Found: C, 44.36; H, 6.90; P, 19.21.

Ethyl Bicyclic Phosphite from Phosphorus Trichloride.—Phosphorus trichloride (68.6 g., 0.5 mole) was cooled to 0° and trimethylolpropane (67.1 g., 0.5 mole) was added all at once. Nitrogen gas was passed into the flask in order to sweep out hydrogen chloride as it was formed. The mixture was stirred and the apparatus swept with nitrogen for a total of 8 hours during which time the temperature was gradually raised to 70°.

At the end of the reaction period the clear homogeneous mixture was distilled giving a 73% yield of product, b.p. 65–70° (0.25 mm.), m.p. 55–56.°

Hydroxymethyl Bicyclic Phosphite.—To pentaerythritol (340.3 g., 2.5 moles) and distilled triethyl phosphite (415.3 g., 2.5 moles) was added approximately 5 drops of triethylamine catalyst. The mixture was heated with stirring to 120°. After collecting the first few drops of alcohol, the temperature was reduced to 100°, and the mixture stirred at this lower temperature for approximately 24 hours. During the heating period 85% of the theoretical amount of alcohol was collected. At the end of the 24-hour period the temperature was gradually raised over a 2-hour period to 130° during which time the solution became homogeneous and clear. Approximately 92% of the theoretical amount of alcohol was collected during the total heating period.

The clear solution was flash distilled at 200° (0.25 to 1.5 mm.) giving an 89% yield of crude semi-crystalline product. An 80% yield of pure product was obtained after redistillation of crude material at 120° (0.5 mm.). The phosphite crystallized on cooling, m.p. 61°.

Anal. Calcd. for $C_5H_9O_4P$: C, 36.60; H, 5.49; P, 18.91. Found: C, 36.68; H, 5.32; P, 18.87.

Methacryloxymethyl Bicyclic Phosphite.—To hydroxymethyl bicyclic phosphite (262.4 g., 1.5 moles) dissolved in 1 liter of pure methylene chloride was added at 0° 155 g. (1.5 moles) of methacryl chloride. To the rapidly stirred solution was added 152 g. (1.5 moles) of triethylamine at −20°. When addition was complete, the mixture was allowed to come to room temperature slowly with rapid stirring. The mixture was suction filtered and evaporated at reduced pressure. The residue was recrystallized from isoöctane, giving an 80% yield of white crystalline product, m.p. 180°.

Anal. Calcd. for $C_9H_{13}O_5P$: C, 46.21; H, 5.55; P, 13.25. Found: C, 46.10; H, 5.95; P, 13.40.

***cis*-2-Chloromethyl-2-ethyl-1,3-propanediol Benzylphosphonate, III (R = $C_6H_5CH_2$).**—Ethyl bicyclic phosphite and benzyl chloride were added together in a 1:1 mole ratio. The solution was heated at 170° for 12 hours with stirring. The solution was cooled and taken up in an excess of ether. The slurry was stirred, suction filtered and the precipitate recrystallized twice from CCl_4; m.p. 117–118°, yield 91%.

Anal. Calcd. for $C_{13}H_{18}O_5ClP$: C, 54.12; H, 6.28; P, 10.72; Cl, 12.27. Found: C, 53.86; H, 6.28; P, 10.85; Cl, 12.51.

The preparation of other cyclic phosphonates, Table II, are typified by this procedure.

Treatment of *cis*-2-Chloromethyl-2-ethyl-1,3-propanediol Benzylphosphonate with Excess Bases.—2-Chloromethyl-2-ethyl-2-ethyl-1,3-propanediol benzylphosphonate (14.4 g., 0.05 mole) was added to 50 cc. of 3.0 *N* NaOH. The solution was refluxed overnight during which time it became homogeneous. Water was removed at reduced pressure and the semi-viscous residue distilled. 3-Ethyl-3-hydroxymethylpropyloxetane was collected; 4.6 g., b.p. 87–92° (0.1 mm.). The infrared spectrum of the product was identical with that of an authentic sample.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.02; H, 10.34. Found: C, 62.10; H, 10.22.

The residue from the low pressure distillation was taken up in a small volume of water and the solution treated dropwise with concd. HCl until precipitation ceased. The precipitate was removed by suction filtration and recrystallized twice from dilute HCl to give 5.2 g. of benzylphosphonic acid, IV, R = $C_6H_5CH_2$, m.p. 193–195° dec.

Anal. Calcd. for $C_7H_9O_3P$: C, 48.72; H, 5.23; P, 18.05. Found: C, 49.51; H, 5.25; P, 18.00.

2-Chloromethyl-2-ethyl-1,3-propanediol Methyl Phosphite (VIIa).—Chloromethyl-bis-hydroxymethylpropane (15.2 g., 0.1 mole), trimethyl phosphite (12.4 g., 0.1 mole) and 3 drops of triethylamine were added together. The solution was heated with stirring and methanol was collected as formed. The temperature of the mixture never rose above 110° during the 6 hours required for the removal of the theoretical amount of alcohol. A straw-colored liquid was obtained which when distilled gave a colorless, clear distillate, b.p. 65° (0.25 mm.), yield 42%.

Anal. Calcd. for $C_7H_{14}O_3ClP$: C, 39.51; H, 6.64; Cl, 16.60. Found: C, 39.42; H, 6.78; Cl, 16.70.

2-Chloromethyl-2-ethyl-1,3-propanediol Benzylphosphonate (VIIIa).—2-Chloromethyl-2-ethyl-1,3-propanediol methyl phosphite (VIIa) and benzyl chloride were added together in a 1:1 mole ratio. The mixture was heated at 190° for 2 hours with stirring. On cooling, the mixture partially crystallized. The product was washed well with ether and isolated by suction filtration. The crystalline precipitate was recrystallized twice from isoöctane; m.p. 92°, yield 46%.

Anal. Calcd. for $C_{13}H_{18}O_5ClP$: C, 54.12; H, 6.28; P, 10.73; Cl, 12.27. Found: C, 54.14; H, 6.53; P, 10.75; Cl, 12.28.

Formation of the Sodium Salt of 2-Iodomethyl-2-ethyl-1,3-propanediol Methylphosphonate.—2-Iodomethyl-2-ethyl-1,3-propanediol methylphosphonate (6.80 g., 0.02 mole) was treated with 8 g. of 10% sodium hydroxide (0.02 mole). The addition was exothermic and the normally water-insoluble phosphonate dissolved. The solution was dried at reduced pressure giving a clear colorless, gummy material. Treatment of the product with ethyl acetate gave a crystalline product. The salt was recrystallized twice from 1-butanol; m.p. 170–172°. A sample of the salt was dissolved in glacial acetic acid and titrated with 0.1 *N* perchloric acid. A neutral equivalent of 341 was obtained (theor., 344).

Anal. Calcd. for $C_7H_{13}O_5PINa$: C, 24.42; P, 9.01; I, 36.96; H, 4.31. Found: C, 24.87; P, 9.12; I, 36.49; H, 4.45.

2,2-Dichloromethyl-1,3-propanediol Methyl Phosphite (VIIb).—Dichloropentaerythritol (86 g., 0.5 mole), trimethyl phosphite (62 g., 0.5 mole) and three drops of triethylamine were added together. The mixture was heated with stirring and the theoretical amount of methanol was removed over a period of 6 hours. The reaction was run at a minimum temperature never exceeding 130°. The nonviscous liquid product was distilled giving a clear colorless distillate, b.p. 88° (0.25 mm.), 30% yield.

Anal. Calcd. for $C_6H_{11}O_3Cl_2P$: C, 30.91; H, 4.74; Cl, 30.50; P, 13.30. Found: C, 31.11; H, 4.83; Cl, 30.70; P, 13.10.

2,2-Dichloromethyl-1,3-propanediol Benzylphosphonate (VIIIb) from 2,2-Dichloromethyl-1,3-propanediol Methyl Phosphite (VIIb).—2,2-Dichloromethyl-1,3-propanediol methyl phosphite and benzyl chloride were added together in a 1:1 mole ratio. The mixture was heated overnight with stirring at 146°. On cooling, the mixture crystallized. The product was recrystallized twice from CCl_4; m.p. 124–125°, yield 72%.

Anal. Calcd. for $C_{12}H_{15}O_5Cl_2P$: C, 46.51; H, 4.85; P, 10.02; Cl, 23.00. Found: C, 45.91; H, 4.82; P, 9.63; Cl, 24.20.

2,2-Dichloromethyl-1,3-Propanediol Benzylphosphonate (VIIIb).—Chloromethyl bicyclic phosphite, IX, and benzyl chloride were added together in a 1:1 mole ratio. The mixture was heated at 210° for 2 hours with stirring. On cooling, a viscous semi-crystalline mass resulted. The product was recrystallized twice from CCl_4; m.p. 123–125°, 50% yield. The infrared spectrum of the product proved to be identical with VIIIb prepared from VIIb.

Anal. Calcd. for $C_{12}H_{15}O_5Cl_2P$: C, 46.51; H, 4.85; P, 10.02; Cl, 23.00. Found: C, 46.74; H, 4.62; P, 9.75; Cl, 22.96.

Separation of Isomers by Column Chromatography.—A 3-foot 1-inch column packed with silica gel was prepared and

a 80:20 benzene–ether solution used to elute a 2-g. sample of VIIIa. The *trans* isomer XI, m.p. 95–96° (fr. isoöctane), was removed first by passing solvent through the column. Pure *cis* isomer VI was obtained by eluting with ether after complete removal of the *trans* isomer. The authenticity of the *cis* isomer, m.p. 117–118°, was checked by comparing its infrared spectrum to that of pure *cis* isomer prepared from ethyl bicyclic phosphite and benzyl chloride. The pure isomers when subjected to vapor phase chromatography at 290°[22] gave peaks corresponding to those obtained from VIIIa. As expected, the peak obtained from the *trans* isomer corresponded to the first peak of the mixture, while the peak due to the *cis* isomer corresponded to the second peak of the mixture.

Equilibration of *cis*-2-Chloromethyl-2-ethyl-1,3-propanediol Benzylphosphonate (IIIa).—*cis*-2-Chloromethyl-2-ethyl-1,3-propanediol benzylphosphonate, (10.0 g., 0.035 mole) was refluxed for 24 hours with 40 cc. of concd. HCl. Water was removed from the homogeneous solution leaving a viscous residue. The residue was distilled at reduced pressure giving two distinct fractions. The first fraction, b.p. 90° (0.3 mm.), crystallized on standing. Its infrared spectrum proved to be identical with that of 1-chloromethyl-1,1-dihydroxymethylpropane, 27% yield. The second fraction, b.p. 182–184° (0.25 mm.), also crystallized, m.p. 92–94°. Its infrared spectrum proved to be identical with VIIIa, 41% yield.

The pot residue was taken up in a small amount of water. Acidification with dilute HCl brought down benzylphosphonic acid which was isolated by suction filtration, m.p. 192–194° dec., 17% yield.

Equilibration of *cis*-2-Chloromethyl-2-ethyl-1,3-propanediol Methoxymethylphosphonate.—*cis*-2-Chloromethyl-2-ethyl-1,3-propanediol methoxymethylphosphonate (5.0 g., 0.02 mole) was added to 10 cc. of water and the mixture refluxed for 24 hours. The resulting homogeneous mixture was freed of water giving a viscous residue. The residue was distilled under reduced pressure giving a liquid distillate soluble in ether, b.p. 150–154° (0.3 mm.), 87% yield. The infrared spectrum of the distillate was identical with the spectrum of a cyclic phosphonate prepared from VIIa and chloromethyl ether.

2-Chloromethyl-2-ethyl-1,3-propanediol β-Dichlorovinyl Phosphate (XIIIb).—Ethyl bicyclic phosphite (32.4 g., 0.2 mole) and chloral (29.48 g., 0.2 mole) were added together. The solution was heated slowly with stirring to 135° over a period of 3 hours. The viscous mixture which resulted was distilled at reduced pressure giving 44.0 g., 71.2% yield, of liquid distillate, b.p. 147–149° (0.5 mm.), $n^{27}D$ 1.4964.

Anal. Calcd. for $C_8H_{12}O_4Cl_3P$: C, 31.21; H, 3.89; Cl, 34.17; P, 10.07. Found: C, 30.83; H, 4.21; Cl, 34.20; P, 10.20.

2-Chloromethyl-2-ethyl-1,3-propanediol β-Dichlorovinyl Phosphate (XIV).—Chloral (10.5 g., 0.07 mole) was added dropwise with cooling to 2-chloromethyl-2-ethyl-1,3-propanediol methyl phosphite (VIIa, 15.2 g., 0.07 mole). The reaction was very exothermic requiring external cooling to maintain the temperature below 60°. The solution was distilled at reduced pressure, b.p. 147–149° (0.05 mm.), 50% yield, $n^{27}D$ 1.4960.

Anal. Calcd. for $C_8H_{12}O_4Cl_3P$: C, 31.21; H, 3.89; Cl, 34.17; P, 10.07. Found: C, 31.34; H, 4.10; Cl, 34.21; P, 10.19.

The Hydrolysis of 2-Chloromethyl-2-ethyl-1,3-propanediol β-Dichlorovinyl Phosphate (XIIIb and XIV).—A sample of the phosphate was refluxed with a slight excess of water until solution was complete. A portion of the colorless solution was treated with alcoholic 2,4-dinitrophenylhydrazine. The precipitate which resulted was obtained by suction filtration and dried. It gave a melting point of 324° which is identical with that of the 2,4-dinitrophenylhydrazone of glyoxal; mixed melting point undepressed.

The remainder of the solution was freed of water and the viscous clear resin which resulted allowed to stand for 2 days during which time it became crystalline. The crystalline product was recrystallized twice from $CHCl_3$; m.p. 77–78°, 79% yield.

(22) An F & M 500 vapor phase chromatograph containing a 61-cm. column of silicone rubber on Chromosorb W was used. Helium gas at a flow rate of 100 cc./min. was the carrier. In order to obtain sharp peaks a linear programmed temperature was essential.

Anal. Calcd. for $C_6H_{14}O_5ClP$: C, 31.05; H, 6.04; Cl, 15.10; P, 13.48; neut. equiv., 232. Found: C, 30.80; H, 6.11; Cl, 15.10; P, 12.36; neut. equiv., 236.

2-Chloromethyl-2-ethyl-1,3-propanediol Phosphorochloridate (XVII).—Ethyl bicyclic phosphite (32.4 g., 0.2 mole) was dissolved in 50 cc. of anhydrous ether. The solution was cooled to −20° by means of a Dry Ice–acetone-bath. Chlorine gas was bubbled into the solution giving rise to a voluminous precipitate. The gas was added until the solution took on the characteristic green color of chlorine gas. After the gas was shut off, the solution was allowed to come slowly to room temperature. At around 0° an exotherm took place which was controlled by means of an ice–water-bath; when it had ceased, the solution was completely clear and homogeneous. Ether was evaporated from the solution and the liquid residue distilled at reduced pressure, b.p. 135° (0.3 mm.), 87% yield, $n^{18}D$ 1.4876.

Anal. Calcd. for $C_6H_{11}O_3Cl_2P$: C, 30.95; H, 4.75; Cl, 30.40; P, 13.30. Found: C, 30.99; H, 4.80; Cl, 30.62; P, 13.10.

***n*-Octyl Sulfide from Ethyl Bicyclic Phosphite–Bromine Adduct.**—Ethyl bicyclic phosphite (32.4 g., 0.2 mole) was dissolved in 200 cc. of anhydrous ether. The solution was cooled to −10° and bromine (32.0 g., 0.2 mole) was added dropwise with stirring. To the cold solution maintained at −10° and containing a voluminous precipitate was added dropwise with stirring 52 g. (0.4 mole) of *n*-octyl mercaptan. After the addition of the mercaptan, the solution was allowed to come slowly to room temperature. The ether solution was filtered giving 27.5 g. of ethyl bicyclic thiophosphate XIX, m.p. 177–178°, 70% yield, mixed melting point undepressed.

The ether filtrate was freed of solvent and the liquid residue distilled under reduced pressure giving a 81% yield of *n*-octyl sulfide, b.p. 140° (0.2 mm.). The infrared spectrum of the product was identical to that of an authentic sample.

Anal. Calcd. for $C_{16}H_{34}S$: C, 74.42; H, 13.18; S, 12.40. Found: C, 74.61; H, 12.97; S, 12.45.

2-Bromomethyl-2-ethyl-1,3-propanediol-N-cyclopentylene Phosphoramide (XXI).—Ethyl bicyclic phosphite (16.2 g., 0.1 mole) dissolved in 200 cc. of anhydrous ether was treated dropwise with bromine 16.0 g. (0.1 mole) at −20°. The solution was allowed to come slowly to room temperature during which time the originally formed voluminous precipitate disappeared. To the ether solution was added dropwise piperidine (17 g., 0.2 mole) dissolved in 50 cc. of ether. The addition was exothermic and the temperature was controlled by means of an ice-bath. At the conclusion of the addition the solution was freed of solvent, leaving a solid residue. The solid was taken up in water and the product removed by filtration. The crystalline, colorless product was recrystallized twice from isoöctane; m.p. 157–158°, 74% yield.

Anal. Calcd. for $C_{11}H_{21}O_3BrNP$: C, 40.50; H, 6.47; N, 4.31; Br, 24.51; P, 9.51. Found: C, 40.61; H, 6.61; N, 4.50; Br, 24.20; P, 9.00.

2-Chloromethyl-2-ethyl-1,3-propanediol Phosphorochloridate from a Monocyclic Phosphite.—2-Chloromethyl-2-ethyl-1,3-propanediol methyl phosphite (VIIa, 10.6 g., 0.05 mole) was dissolved in 100 cc. of anhydrous ether. Chlorine gas was bubbled slowly through the solution with stirring, keeping the temperature at 20° by means of an ice–water-bath. When the solution took on the characteristic color of chlorine gas, the gas was shut off. Solvent was expelled from the reaction mixture and the liquid residue distilled under reduced pressure, b.p. 135° (0.3 mm.), 66% yield, $n^{18}D$ 1.4876. The infrared spectrum of the product was identical with the spectrum of XVII.

Competitive Experiment. Treatment of Ethyl Bicyclic Phosphite and Triethyl Phosphite with Bromine.—Ethyl bicyclic phosphite (16.2 g., 0.1 mole) and triethyl phosphite (16.6 g., 0.1 mole) were added to 100 cc. of methylene chloride. The solution was cooled to −20° and bromine (12.8 g., 0.08 mole) was added dropwise with rapid stirring. On addition of bromine to the cold solution, a white voluminous precipitate formed. The cold solution was suction filtered under nitrogen and the precipitate (20 g., 77.7% yield) added to methylene chloride which had previously been chilled to −20°. The slurry was allowed to come slowly to room temperature during which time the precipitate dissolved.

The solution was filtered and treated dropwise with piperidine (17.0 g., 0.2 mole), while maintaining the solution at room temperature. The mixture was dried at the water-pump, the residue taken up in water and the aqueous mixture suction filtered. The precipitate was recrystallized twice from isoöctane. The white crystalline product which resulted (10 g., 40% yield, m.p. 157–158°) proved by comparison of infrared spectra to be the expected monocyclic phosphoramide XXI.

Ethyl Bicyclic Phosphate (XXII).—A nearly saturated solution of ethyl bicyclic phosphite in isopropyl alcohol was prepared. The alcoholic solution was chilled and a 35% solution of alcoholic hydrogen peroxide (made from 90% H_2O_2 in isopropyl alcohol) was added dropwise with stirring until heat evolution ceased. The oxidation was extremely exothermic, requiring constant cooling during the addition of the peroxide. On cooling and standing a nearly quantitative yield of ethyl bicyclic phosphate precipitated, m.p. 202°.

Anal. Calcd. for $C_6H_{11}O_4P$: C, 40.52; H, 6.19; P, 17.48. Found: C, 40.51; H, 6.31; P, 17.42.

Methacryloxymethyl Bicyclic Phosphate.—Methacryloxymethyl bicyclic phosphite (11.6 g., 0.05 mole) was added to 25 ml. of isopropyl alcohol at room temperature. The phosphite did not dissolve completely in the alcohol. Hydrogen peroxide, 34%, was added dropwise to the alcoholic solution with stirring and cooling. An excess of peroxide was avoided by testing the alcoholic solution during the addition with KI in acetic acid. The solution was cooled in a Dry Ice–acetone-bath, filtered, and the product recrystallized from ethyl acetate. The product (10.5 g., 84% yield) polymerized on heating. Rapid melting showed the product to melt below 200°.

Anal. Calcd. for $C_9H_{13}O_6P$: C, 43.51; H, 5.24; P, 12.58. Found: C, 43.66; H, 5.49; P, 12.64.

Ethyl Bicyclic Phosphate (XXII) from Phosphorus Oxychloride.—To trimethylolpropane (134.2 g., 1.0 mole) was added dropwise phosphorus oxychloride (153.4 g., 1.0 mole), keeping the temperature below 30°. Stirring was initiated as soon as the reaction mixture became fluid. The mixture was stirred at room temperature and nitrogen gas passed over the solution in order to sweep out hydrogen chloride as it was formed. At the end of 16 hours, the temperature was gradually raised to 70° with the stirring and passage of nitrogen continuing.

The tan semi-crystalline mixture which resulted was taken up in hot water and the solution heated over a steam-bath for 1 hour. The solution was cooled and filtered, giving a 51% yield of light tan crystalline precipitate. The product was recrystallized from hot water, m.p. 202°. A mixed melting point with an authentic sample was undepressed.

Reaction of Ethyl Bicyclic Phosphite with Benzoyl Peroxide.—Ethyl bicyclic phosphite (16.2 g., 0.1 mole) and benzoyl peroxide (24.2 g., 0.1 mole) were dissolved in 100 ml. of anhydrous ether. After the solution had refluxed gently for 4 days, it was cooled and filtered giving 12.0 g. of white crystalline product. The precipitate was recrystallized twice from ethanol, m.p. 203–205° (67% yield). The infrared spectrum of this material was identical with the spectrum of ethyl bicyclic phosphate.

The filtrate was freed of solvent and the liquid residue distilled under reduced pressure giving 11.0 g. of benzoic anhydride, b.p. 144–145° (0.2 mm.), 50% yield, infrared spectrum identical with that of an authentic sample.

Reaction of Ethyl Bicyclic Phosphite with *n*-Octyl Mercaptan.—Ethyl bicyclic phosphite (32.4 g., 0.2 mole), was added to 29.2 g. (0.2 mole) of *n*-octyl mercaptan, azoisobutyronitrile (0.65 g., 2 mole %), was added and the solution heated gently with stirring to 100° where it was maintained for 1 hour. On cooling to room temperature the solution deposited white crystals of ethyl bicyclic thiophosphate, m.p. 176–178° (from alcohol), 20% yield.

Anal. Calcd. for $C_6H_{11}O_3SP$: C, 37.18; H, 5.67; S, 16.51; P, 15.98. Found: C, 37.20; H, 5.64; S, 16.32; P, 16.24.

The filtrate was distilled giving 11.0 g. (48% yield) of *n*-octane, b.p. 123–125°, $n^{25}D$ 1.3972.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, U. S. ARMY CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES, ARMY CHEMICAL CENTER, MD.]

The Stereochemistry of Asymmetric Phosphorus Compounds. IV. The Synthesis and Stereochemistry of Displacement Reactions of Optically Active Isopropyl Methylphosphonochloridate

BY HERBERT S. AARON, ROY T. UYEDA, HAROLD F. FRACK AND JACOB I. MILLER

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The reaction of phosgene with (±)- or (−)-O-ethyl ethylphosphonothioic acid gives (±)-ethyl ethylphosphonochloridate. When the sodium salt of the (−)-acid is used, the (+)-chloridate is obtained. The (+)- and (−)-isopropyl methylphosphonochloridates have been similarly prepared. The stereochemical course of this reaction, which could not be varied whether run in hexane–phosgene, acetone–phosgene or dioxane–phosgene media, has been shown to proceed with inversion of configuration. Optically active dialkyl dialkylthionopyrophosphonates are formed as by-products. Displacement reactions of the (+)- and (−)-isopropyl methylphosphonochloridates which were carried out using hydrogen sulfide, *n*-propyl mercaptide and ethoxide ions in ethanolic solutions have been shown to occur with inversion of configuration.

The literature contains a number of reports[1] on the resolution of various types of compounds containing an asymmetric phosphorus atom, and, recently, reports[2] of investigations of the stereochemistry of the reactions of these materials have begun to appear.

Of the resolved compounds recently reported, the O-alkyl alkylphosphonothionic acids have been of interest to us for use as convenient starting materials for stereospecific synthetic routes to other resolved organophosphorus compounds.[3] Ac-

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