clearly not the case. Figure 2 shows also that the two *meta*-substituted benzamidinium salts are somewhat less reactive than predicted from the ρ value determined for the *para*-substituted compounds. This may be due to an appreciable steric effect of the *meta* substituents on this reaction.

Rates of hydroxide ion catalyzed hydrolysis of N,N′-dimethyl-N,N′-diphenylacetamidinium and -benzamidinium perchlorates were found not to be significantly influenced by the ionic strength of the reaction solutions in the range $\mu = 0.0075$ to $\mu = 0.055$. The two preequilibria of eq 3 should be influenced approximately equally but in opposite directions by changes in ionic strength of the medium, since the first involves ionic association and the second involves dissociation. In the rate-limiting step with hydroxide ion as a catalyst, there is a partial neutralization of charge, a process which should occur somewhat less readily at high than at low ionic strengths. The low Brønsted β value for the reaction indicates that proton transfer from the hydroxyl group of the tetrahedral intermediate to the catalyst is far from complete in the transition state, so that the charge distribution in the transition state is not greatly different from the charge distribution immediately preceding its formation. A large salt effect is therefore not anticipated, and is not observed.

The rate equation for hydroxide ion catalyzed hydrolysis of tetrasubstituted amidinium salts required by eq 3 is $k_{\text{exp}} = K_1K_2k_3[\text{OH}^-]$. The solvent deuterium isotope effect on the reaction is therefore a composite of the isotope effects on the two equilibria and the rate-limiting step of the reaction. That is,

$$k_{\text{exp H}}/k_{\text{exp D}} = (K_{1\text{H}}/K_{1\text{D}})(K_{2\text{H}}/K_{2\text{D}})(k_{3\text{H}}/k_{3\text{D}}) \text{ (if } [\text{OH}^-] = [\text{OD}^-])$$

The solvent isotope effects on the preequilibria and the rate-limiting step may be estimated by the method of Bunton and Shiner.[18,19] Application of this method yields $K_{1\text{H}}/K_{1\text{D}} = 0.65$, $K_{2\text{H}}/K_{2\text{D}} = 2.5$, and $k_{3\text{H}}/k_{3\text{D}} = 0.5$. The product of these three values is 0.8. This value, although only a rough approximation, is in reasonable agreement with experimental observation. $k_{\text{exp H}}/k_{\text{exp D}}$ was found to be 0.79 for N,N′-dimethyl-N,N′-diphenylacetamidinium perchlorate, and 0.56 for the analogous benzamidinium salt (see Table VII).

[18] C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 42 (1961).

[19] C. A. Bunton and V. J. Shiner, *ibid.*, **83**, 3207 (1961).

Carbonium Ion Formation in Solvolysis of Phosphate Triesters

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The mechanisms of solvolysis of some triesters of phosphoric acid which might form carbonium ions have been investigated. Such a pathway is shown to be predominant in the solvolysis of tri-*t*-butyl and triisopropyl phosphates, but to be negligible in the case of triallyl phosphate. The solvolytic behavior of some five-membered cyclic tertiary alkyl esters is briefly discussed.

It has been known qualitatively for many years that triesters of phosphoric acid are hydrolyzed in basic solution rather readily to the corresponding diesters, but that subsequent stages of hydrolysis are relatively slow.[2] The behavior of trimethyl phosphate and of triphenyl phosphate, recently examined in detail by Barnard, Bunton, Llewellyn, Vernon, and Welch,[3] may probably be taken as characteristic of the reactions of the triesters of primary alcohols, phenols, and thiols with hydroxide ion.

The hydrolysis of trimethyl phosphate in aqueous base is first order in hydroxide ion and first order in the ester. Isotopic tracer experiments show that the phosphorus–oxygen bond is broken exclusively;[3,4] furthermore, within the limit of experimental error of the isotopic analysis, no isotopic exchange occurs prior to hydrolysis between the phosphoryl oxygen and the oxygen atoms of the solvent.[3] A small depression of rate is observed on changing the solvent from water to 75% dioxane–25% water. The few available data suggested that changes of neutral salt concentration do not noticeably affect the rate of saponification of the triesters. The hydrolysis of triphenyl phosphate in 75% dioxane–25% water was found also to be first order in both hydroxide ion and the ester.

The kinetic order of these hydrolyses, together with the position of bond fission, establishes that hydroxide ion attacks the phosphorus atom in the rate-controlling step of the sequence.

Corresponding data are very scanty for tertiary alcohol esters of phosphoric acid. The synthesis and qualitative observations concerning the hydrolysis of tri-*t*-butyl phosphate have been briefly reported.[5] The hydrolysis of mono-*t*-butyl phosphate has been studied in detail by Lapidot, Samuel, and Weiss-Broday;[6] the undissociated acid undergoes facile carbon–oxygen cleavage, with formation of the *t*-butyl carbonium ion. Evidence has been presented that the phosphate ester of the tertiary alcohol function of mevalonic acid pyrophosphate undergoes concerted decarboxylation and phosphate elimination to form isopentenyl pyrophosphate.[7]

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[2] G. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950.

[3] P. W. C. Barnard, C. A. Bunton, D. R. Llewellyn, C. A. Vernon, and J. A. Welch, *J. Chem. Soc.*, 2670 (1961).

[4] E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **41**, 611 (1945).

[5] J. R. Cox, Jr., and F. H. Westheimer, *J. Amer. Chem. Soc.*, **80**, 5441 (1958).

[6] (a) A. Lapidot, D. Samuel, and M. Weiss-Broday, *J. Chem. Soc.*, 637 (1964); (b) L. Kugal and N. Halmann, *J. Org. Chem.*, **32**, 642 (1967).

[7] (a) G. Popjak and J. W. Cornforth, *Advan. Enzymol.*, **22**, 295 (1960); (b) C. A. Bunton and E. Humerer, *J. Org. Chem.*, **34**, 572 (1969).

In this paper we report the results of a study of the kinetics and mechanism of hydrolysis of tri-*t*-butyl phosphate, triisopropyl phosphate, and triallyl phosphate, and the synthesis and some studies of the hydrolysis of methyl pinacol phosphate and *t*-butyl pinacol phosphate.

Experimental Section

Materials.—Anhydrous pinacol (Fluka Chemical Co., purum) was dried by azeotropic distillation with benzene. After the benzene was removed, calcium hydride was added to the molten pinacol, and the pinacol was distilled *in vacuo* through a 2-ft Vigreux column.

Methanol and ethanol were dried by distillation from their magnesium salts[8] and stored in a tightly stoppered bottle.

Diethyl ether was dried over and distilled from lithium aluminum hydride immediately before use. Pentane, when used as a solvent in the chloridite preparation, was dried and stored over sodium metal wire.

Pyridine was boiled under reflux with calcium hydride, distilled, and stored over potassium hydroxide.

Triethylamine was dried by boiling under reflux with and distillation from BaO and then subjected to careful distillation through a 3-ft vacuum-jacketed column filled with glass helices. Cyclohexylamine was boiled under reflux with BaO and distilled.

Phosphorus trichloride was freshly distilled before its use in a reaction.

Dinitrogen tetroxide was synthesized by reaction of nitric oxide and oxygen. An evacuated gas manifold and an attached 12-l. flask were filled with nitric oxide to slightly less than 1-atm pressure. Oxygen was introduced into the system through another port in the manifold system. Oxygen was added until the pressure no longer decreased following its addition. One neck of a collection flask was attached to a part of the manifold system and another neck of the flask connected to a vacuum pump. The body of the flask was immersed in liquid nitrogen. The vacuum pump was started and the dinitrogen tetroxide collected and stored in the collection flask.

Other reagents were used without special purification. τ values in water are referred to DDS.

Tri-*t*-butyl Phosphite.—1.5 l. of petroleum ether (bp 30–60°) were placed in a 5-l., three-necked flask which was equipped with a dropping funnel, a mechanical stirrer, and a thermometer dipping below the surface of the petroleum ether. Triethylamine (315 g, 3.12 mol) and *t*-butyl alcohol (225 g, 3.04 mol) were then added to the flask. Stirring was begun and the flask and contents were cooled to below 0° (−10 to 0°) in an ice-salt mixture. Phosphorus trichloride (123 g, 0.895 mol) dissolved in 1 l. of petroleum ether was added dropwise to the cold mixture over a period of about 6 hr. During the addition of phosphorus trichloride, the temperature was maintained between −10° and 0°. After addition of phosphorus trichloride was complete, 1.5 l. of water was added to dissolve the precipitated amine hydrochloride. The aqueous layer was separated from the organic layer in a 6-l. separatory funnel. The organic phase, containing tri-*t*-butyl phosphite, was washed twice with approximately 500 ml of saturated aqueous sodium bicarbonate, then with about 500 ml of water. The organic layer was dried with anhydrous calcium chloride, and the petroleum ether solution was evaporated on a rotary evaporator under aspirator vacuum. After evaporation of the petroleum ether, about 220 g of crude tri-*t*-butyl phosphite was obtained.

The crude tri-*t*-butyl phosphite was distilled at 3-mm pressure, yielding approximately 160 g (71% of theory) of a liquid which boiled at 67–69°. Upon storage in a refrigerator, the liquid solidified (mp approximately 10°). An infrared spectrum of the material indicated *no* P–H stretch in the 4.5-μ region, and the nmr spectrum showed a single, sharp peak at τ 8.66 (neat liquid). The material was also converted in good yield to tri-*t*-butyl phosphate upon oxidation. Thus, the material was identified as pure tri-*t*-butyl phosphite. It is apparent that the difficulty encountered by previous workers (ref 17 and references therein) in distilling the product was occasioned by traces of acid, not by thermal instability of the compound.

Tri-*t*-butyl Phosphate.—Tri-*t*-butyl phosphite (50 g, 0.20 mol) dissolved in 100 ml of petroleum ether (bp 30–60°) in a 300-ml erlenmeyer flask was cooled in an ice bath. Dinitrogen tetroxide was passed into the cold mixture,[5] which was stirred on a magnetic stirrer. Addition of dinitrogen tetroxide was continued until the solution developed a green color (probably N_2O_3) or until unreacted NO_2 escaped from the reaction mixtures. The solution was washed with 100 ml of saturated sodium bicarbonate solution, then with water, and was dried over anhydrous calcium chloride. The dried solution was cooled in a Dry Ice–acetone bath, whereupon the tri-*t*-butyl phosphate (35 g, 66%, mp 67–70°) crystallized and was separated on a Büchner funnel. A second crop could be obtained by concentrating the mother liquor under vacuum and cooling. Recrystallization was effected by dissolving in petroleum ether at room temperature and cooling in Dry Ice–acetone. The mp after two such recrystallizations was 73–73.5° (lit.[5] mp 71–75°). The nmr spectrum showed a single absorption at 8.57 τ which under high resolution revealed coupling to phosphorus, $J \sim 0.5$ cps.

Cyclohexylammonium Di-*t*-butyl Phosphate.—Cyclohexylamine (0.8156 g, 8.24 mmol) was placed in a 50-ml volumetric flask and diluted to 50 ml with 50% v/v water–ethanol solution. The contents were transferred to a polyethylene bottle and thermostated at 60°. Tri-*t*-butyl phosphate (2.0069 g, 7.53 mmol) was then added to the solution. After 2 days, when the reaction was complete, the contents of the bottle were emptied into a 100-ml round-bottomed flask and the solvent distilled under aspirator vacuum. The solid remaining in the flask was dried under vacuum. The cyclohexylammonium di-*t*-butyl phosphate (2.287 g, 98% of theory) recrystallized from boiling 1,2-dimethoxyethane (about 0.5 g salt / 25 ml of DME), as needles, mp after three recrystallizations 189.8–190.8° (dec), nmr sharp singlet at τ 8.38 under medium resolution and broad cyclohexylammonium absorption at $\tau \sim 8$–9.

Anal. Calcd for $C_{14}H_{32}PO_4N$: C, 54.35; H, 10.43; N, 4.53; P, 10.01. Found: C, 53.96; H, 10.34; N, 4.48; P, 10.00.

Solvolysis of Tri-*t*-butyl Phosphate in $[^{18}O]H_2O$–Ethanol.—Cyclohexylamine (0.8156 g) was weighed into a 50-ml volumetric flask. Tri-*t*-butyl phosphate (2.0069 g) was added and the flask was filled to the mark with a solvent prepared by mixing 25 ml of D_2O enriched in ^{18}O to 1.51 at. % (YEDA Research and Development Co., Ltd., Rehovoth, Israel) and 25 ml of absolute ethanol.

The contents of the volumetric flask were transferred to a polyethylene bottle and the bottle placed in a 60° temperature bath. The reaction was allowed to proceed for a week. After this time, the contents of the bottle were emptied into a round-bottomed flask and the solvent was removed under vacuum. The distillate was collected in a Dry Ice–acetone bath. When the distillation was completed, the solid remaining in the distilling flask was dried under vacuum for approximately 12 hr. The weight of solid was 2.2870 g. After two recrystallizations from 1,2-dimethoxyethane, the mp of the cyclohexylammonium di-*t*-butyl phosphate was 186.4–187.4° (dec).

The oxygen of this salt was converted to carbon dioxide by pyrolysis with mercuric cyanide and mercuric chloride.[9] The carbon dioxide was purified by the method of Haake and Westheimer,[10] and analyzed on a Consolidated–Nier 21-103C mass spectrometer.[11] Its isotopic content was identical with that of a sample of natural abundance.

Triisopropyl Phosphate.—Triisopropyl phosphite (Matheson Coleman and Bell) was oxidized with dinitrogen tetroxide while being cooled in an ice bath. The product, which distilled at 71–72° (1 mm), was a colorless liquid.

Pinacol Phosphorochloridite.—The method of Arbuzov and Azanovskaya[12] was followed with slight modification. Pentane as solvent in this reaction gave essentially the same results as diethyl ether and was more easily dried. Typically, pinacol (59.0 g, 0.50 mol) and pyridine (79.1 g, 1.00 mol) were dissolved in 400 ml of dry ether (or pentane) in a dry 1-l. three-necked flask equipped with a mechanical stirrer, a dropping funnel, and

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[8] K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1960, p 242.

[9] M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, **4**, 233 (1959).

[10] P. C. Haake and F. H. Westheimer, *J. Amer. Chem. Soc.*, **83**, 1102 (1961).

[11] We are grateful to Professor F. H. Westheimer for making this instrument available to us and to Dr. G. O. Dudek for aid in the determination.

[12] A. E. Arbuzov and M. M. Azanovskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 473 (1949).

a thermometer dipping below the surface of the solution. The flask was placed in an ice–salt bath, stirring was begun, and the contents were cooled below 0°. Phosphorus trichloride (69 g, 0.5 mol) was added dropwise to the cold mixture at a rate such that the temperature could be maintained below 0°. Addition required about 6 hr. After addition was completed, the mixture was boiled under reflux for 30 min. When the reaction mixture had cooled to room temperature, pyridine hydrochloride was removed by vacuum filtration. Usually, after filtering the pyridine hydrochloride, the filtrate was cloudy or contained a precipitate, which was probably due to formation of the hydrolysis product of the chloridite. Further filtrations only needlessly exposed the active chloridite to more atmospheric moisture. The solvent was removed by distillation or by use of a rotary evaporator. A yellow, fuming liquid (70–75 g) was obtained, which upon cooling in the refrigerator precipitated more pinacol phosphonate. Filtering the phosphonate and distilling the filtrate *in vacuo* [bp 53° (3 mm)] yielded a colorless, fuming liquid. Yields of pure chloridite were low, usually in the range of 25% of theory (20–25 g). A large amount of an orange, nonvolatile, tarry residue remained in the distilling flask.

Pinacol phosphonate, a by-product of this reaction, could be purified by sublimation at steam bath temperatures at 0.1–0.2 mm (mp 103–105°).

Methyl Pinacol Phosphite.—Pinacol phosphorochloridite (20.0 g, 0.11 mol) was dissolved in 30 ml of petroleum ether (bp 30–60°) in a 100-ml erlenmeyer flask stopper with a serum cap. A solution of dry methanol (3.60 g, 0.112 mol) and triethylamine (12.00 g, 0.119 mol) was injected into the solution through the serum cap with a hypodermic syringe. During the addition, the solution was cooled in an ice bath and stirring was maintained with a mechanical stirrer. After addition was completed, the triethylamine hydrochloride was filtered, the solvent removed on a rotary evaporator, and the concentrate distilled *in vacuo*, bp 24–28° (1 mm). In this manner, 9–10 g of methyl pinacol phosphite was obtained (about 50% of theory): nmr τ 6.61 (d, J = 24 cps), 8.82, 8.70.

Alternatively, for larger preparation, the reaction was performed in a three-necked, round-bottomed flask, adding the triethylamine–methanol mixture to the chloridite through a dropping funnel, while stirring with a mechanical stirrer and cooling in ice. Yields with this procedure were similar.

Methyl pinacol phosphite was extremely reactive toward water, producing pinacol phosphonate. Added to a small test tube containing water, it dissolved instantly with the liberation of heat. Care was required in the above reactions and in further handling of both the chloridite and phosphite to avoid exposure to moisture.

Methyl Pinacol Phosphate.—(a) Methyl pinacol phosphite (10.0 g, 0.056 mol) was dissolved in 50 ml of petroleum ether in a 100-ml flask. Dinitrogen tetroxide vapors were passed into the mixture, while the flask and contents were cooled in an ice bath. The mixture was stirred with a magnetic stirrer. Methyl pinacol phosphate soon precipitated from the mixture. The end of the reaction was indicated by the escaping of red vapors of NO_2 from the flask or by formation of a green color in the solution. The ether was removed, leaving a slightly yellow solid. Generally, 9.5–10.5 g of solid were obtained (90–95% of theory).

Purification of methyl pinacol phosphate could be effected by recrystallizations from benzene or petroleum ether (bp 90–120°) but a severe loss of material accompanied these methods. Purification by sublimation at steam-bath temperatures at 0.1–0.2 mm proved to be the best method. After one sublimation, the mp was 99.8–100.9°; nmr τ 6.20 (d, J = 24 cps), 8.56, 8.61.

Anal. Calcd for $C_7H_{15}PO_4$: C, 43.30; H, 7.79; P, 15.95. Found: C, 43.32; H, 8.05; P, 15.98.

(b) Pinacol phosphonate (5.89 g, 35.9 mmol) was dissolved in 25 ml of chloroform in a 50-ml flask. N-chlorosuccinimide (4.80 g, 36.0 mmol) was added in small portions while the flask was cooled in ice. After all the N-chlorosuccinimide had been added, the solution was boiled under reflux on the steam bath for 30 min. The solution was cooled and a mixture of methanol (1.2 g, 37.5 mmol) and triethylamine (4.0 g, 39.6 mmol) was added in small portions. Upon completion of the addition of methanol and triethylamine, the amine hydrochloride and succinimide were removed by filtration. The filtrate was concentrated on a rotary evaporator and a brown, oily mass resulted. The material was washed with water. The organic layer, dark brown in color, contained mostly chloroform. Evaporation of the chloroform in a watch glass by a stream of air left a dark brown solid. This solid was washed with petroleum ether, which removed much of the brown color but dissolved very little of the solid. The solid melted at 95–100° and gave nmr and ir spectra identical with those of methyl pinacol phosphate. After one sublimation, 2.04 g of purified methyl pinacol phosphate were obtained, mp 99.2–101°.

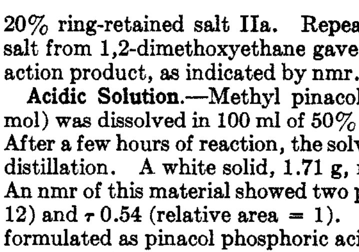
***t*-Butyl Pinacol Phosphite.**[13]—Pinacol phosphorochloridite was treated with an equivalent each of *t*-butyl alcohol and triethylamine in petroleum ether, as in the preparation of methyl pinacol phosphite. After the amine hydrochloride was filtered and the filtrate concentrated on a rotary evaporator, the concentrate was distilled *in vacuo:* nmr τ 8.68, 8.87, relative intensity 5:2.

***t*-Butyl Pinacol Phosphate.**[13]—Oxidation of *t*-butyl pinacol phosphite with dinitrogen tetroxide in petroleum ether yielded a white solid. Its mp after two sublimations at approximately 60–70° was 70.4–71.8° (0.1 mm).

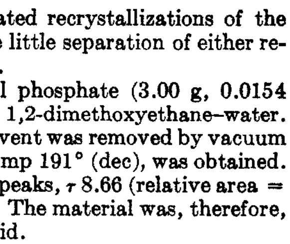
Anal. Calcd for N $C_{10}H_{21}PO_4$: C, 50.80; H, 8.9; P, 13.15. Found: C, 50.60; H, 8.90; P, 13.25.

Hydrolysis of Methyl Pinacol Phosphate. Basic Solution.—An attempt to follow the kinetics of the basic hydrolysis of methyl pinacol phosphate revealed the extremely labile nature of this compound in basic solution. A solution approximately 0.08 *N* in NaOH in 50% 1,2-dimethoxyethane–water was made 0.5 in ionic strength with $NaClO_4$ and equilibrated at 30°. A 4.00 ml aliquot of the NaOH solution required 5.63 ml of 0.0495 *N* HCl for neutralization to pH 7. To 50 ml of the sodium hydroxide solution there was added methyl pinacol phosphate, 0.5831 g (3 mmol), and a 4.00 ml aliquot was withdrawn and titrated with 0.0495 *N* HCl as rapidly as possible. The sample required 0.80 ml of the hydrochloric acid solution; thus, since 0.240 mmol of the ester had consumed 0.239 mmol of the base, the hydrolysis of the phosphate was essentially complete at the end of about 60 sec, the time required to mix the solution, withdraw the aliquot, and titrate the sample.

To investigate the products of basic hydrolysis of methyl pinacol phosphate, 3.00 g (0.0154 mol) of the ester was dissolved in 100 ml of 50% 1,2-dimethoxyethane–water solution to which 2.00 ml (0.0165 mol) of cyclohexylamine had been added. After a few hours reaction time, the solvent and remaining cyclohexylamine were removed by vacuum distillation, leaving a brown solid, 3.81 g. After one recrystallization from 1,2-dimethoxyethane, the nmr spectrum of the reaction product in D_2O was obtained. Two peaks at τ 8.78 and 8.58 were attributed to the two different types of methyl groups in the ring-opened salt I. A doublet, centered at τ 6.43 (J = 11 cps), indicated a methyl group attached to a phosphate residue. A smaller peak at τ 8.65 was attributed to ring-retained salt II. Integration of the spectrum was obscured in the methyl region by the broad peak at τ 7.8–9.0 due to the cyclohexylammonium cation protons. However, there was approximately 80% ring-opened salt I and 20% ring-retained salt IIa. Repeated recrystallizations of the salt from 1,2-dimethoxyethane gave little separation of either reaction product, as indicated by nmr.



I



IIa

Acidic Solution.—Methyl pinacol phosphate (3.00 g, 0.0154 mol) was dissolved in 100 ml of 50% 1,2-dimethoxyethane–water. After a few hours of reaction, the solvent was removed by vacuum distillation. A white solid, 1.71 g, mp 191° (dec), was obtained. An nmr of this material showed two peaks, τ 8.66 (relative area = 12) and τ 0.54 (relative area = 1). The material was, therefore, formulated as pinacol phosphoric acid.

Anal. Calcd for $C_6H_{13}PO_4$: C, 40.00; H, 7.27; P, 17.19. Found: C, 39.44; H, 7.26; P, 17.34.

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[13] We thank Mr. Kary Mullis for preparation of a sample of this compound.

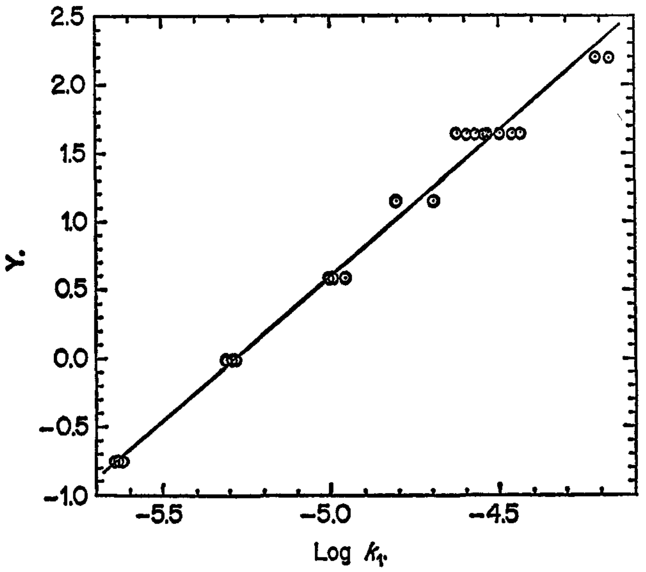

Figure 1.—Grunwald–Winstein correlation of the solvolysis rates of tri-*t*-butyl phosphate in 50% EtOH at 60°.

This is the only product of hydrolysis observed in initially neutral 1,2-dimethoxyethane–water solution.

Treating the acid with an equivalent of cyclohexylamine in 1,2-dimethoxyethane produced the cyclohexylammonium salt, which precipitated quantitatively. The single, sharp nmr peak of the salt in D_2O, other than those of cyclohexylammonium ion, was positioned at τ 8.63.

Hydrolysis of *t*-Butyl Pinacol Phosphate. Basic Solution.—Cyclohexylamine (17 ml, 0.014 mol) was dissolved in a solution of 50 ml of 1,2-dimethoxyethane and 50 ml of water. *t*-Butyl pinacol phosphate (3.00 g, 12.7 mmol) was added and allowed to react overnight. The solvent was removed by vacuum distillation, leaving 3.27 g of a white solid. An nmr spectrum in D_2O revealed a single methyl peak at τ 8.65, indicating that the only product of hydrolysis is the ring-retained salt.

Neutral Solution.—*t*-Butyl pinacol phosphate (3.00 g, 0.0127 mol) was dissolved in a solution of 50 ml of 1,2-dimethoxyethane and 50 ml of water. The reaction was allowed to proceed overnight. The solvent was removed by vacuum distillation. The solid obtained, 1.49 g, was identical in mp (191°), ir, and nmr with pinacol phosphoric acid obtained from neutral hydrolysis of methyl pinacol phosphate.

Conversion of the Hydrolysis Product into Methyl Pinacol Phosphate.—Pinacol phosphoric acid (1.605 g, 0.0892 mol) was placed in a 125-ml erlenmeyer flask and covered with 50 ml of diethyl ether. The solution was stirred on a magnetic stirrer. Small portions of diazomethane in ether solution were added to the acid until the pale yellow color of diazomethane persisted. During addition of diazomethane, vigorous gas evolution occurred and the solution remained colorless until excess diazomethane was added. The ether was removed on a rotary evaporator, whereupon a slightly discolored solid remained. Sublimation of the solid at steam-bath temperatures at 1-mm pressure gave 1.26 g (6.49 mmol, 73% of theory) of methyl pinacol phosphate, mp 99.8–101.0°. No depression of melting point occurred when it was mixed with a sample of the ester prepared by oxidation of methyl pinacol phosphite.

Solutions for basic solvolysis were prepared in each case by the following method. (Mixed solvent compositions refer to v/v per cent at room temperature.)

A quantity of a standard solution of sodium hydroxide was pipetted into a volumetric flask and a proportional quantity of the second solvent (ethanol or 1,2-dimethoxyethane) was then added with a pipet in order to achieve the desired solvent ratio. The calculated amount of sodium perchlorate was added in order to adjust the ionic strength to the desired value. The flask was then filled with solvent of the correct ratio. Except for the kinetic runs in 50% 1,2-dimethoxyethane–water, which were carried out in the volumetric flask, a quantity of the solution was pipetted into a bottle made of Teflon or of polyethylene. The containers were then equilibrated with a constant temperature bath. After temperature equilibration had been achieved, a quantity of the ester was added. The quantity of ester used was determined by the amount of base present; in most cases the concentration of ester was less than the concentration of base. A 4.00-ml aliquot was removed immediately after mixing, diluted with water, and titrated to neutrality with standard hydrochloric acid.

Data were analyzed by a least-squares treatment with the aid of the Burroughs B 5500 computer after the kinetic order had been established by preliminary fitting to standard rate expressions.

Results

The rate of consumption of base by tri-*t*-butyl phosphate (Table I) and by tri-*i*-propyl phosphate (Table II) was independent of the concentration of base as the base was varied from about 0.03 *N* to about 0.15 *N* but was clearly of the first order in ester concentration.

The variation of rate of solvolysis of tri-*t*-butyl phosphate as a function of ionizing power of the solvent in water–ethanol mixtures correlated with the Grunwald–Winstein *Y* values for these solvents[14] (Figure 1). The ^{18}O tracer experiments showed that in the solvolysis of tri-*t*-butyl bond is broken exclusively.

These results demonstrate that the solvolysis of tri-*t*-butyl phosphate under these reaction conditions has as the rate-limiting step the unimolecular ionization of the ester to the *t*-butyl carbonium ion and the di-*t*-butyl phosphate anion. The kinetic order suggests strongly that the hydrolysis of tri-*i*-propyl phosphate in water is also an ionization process, and such a process would accord with the behavior of isopropyl dihydrrogen phosphate (**6b**).

Triallyl phosphate, in contrast to the other two esters, solvolyzed at a rate proportional to the concentrations of both the ester and the base (Table III); the reaction is therefore, bimolecular, but since the point of bond cleavage has not been defined, it is not known whether attack of hydroxide ion is at phosphorus or at carbon.

Methyl pinacol phosphate solvolyzed in 50% water–dimethoxyethane in the presence of base to afford a mixture of about 80% methyl 3-hydroxy-2,3-dimethylbutyl-2 phosphate and about 20% pinacol cyclic phosphate, the ring-opened and ring-retained products, respectively. Based on the assumption that these reactions are bimolecular, it can be estimated that the rate constants for the two reactions of the esters with hydroxide ion at 30° are at least 2 (mol/l.)$^{-1}$ sec^{-1}. These rates are, then, comparable to those observed by Covitz and Westheimer in the base-catalyzed hydrolysis of methyl ethylene phosphate.[15]

t-Butyl pinacol phosphate solvolyzed rapidly in 50% water–dimethoxyethane in initially neutral solution or in the presence of cyclohexylamine. A gas was evolved (presumably isobutylene), and from the solution pinacol cyclic phosphate was isolated quantitatively as its cyclohexylammonium salt.

Discussion

The establishment of the S_N1 mechanism for solvolysis of tri-*t*-butyl phosphate in aqueous solvent mixtures

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(14) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 43; K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, New York, N. Y., 1964, p 417; J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, New York, N. Y., 1963, p 297.

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TABLE I

FIRST-ORDER RATE CONSTANTS FOR SOLVOLYSIS OF TRI-*t*-BUTYL PHOSPHATE IN VARIOUS SOLVENTS AT 60°

Solvent	Ester concn	Base concn	Half-life, hr	$k \times 10^5$ sec^{-1}	Ionic strength	Y^c
50% DME H_2O	0.0764	0.1585	8.07	2.38	0.498	...
50% DME H_2O	0.0765	0.1551	9.06	2.13	0.195	...
40% EtOH H_2O	0.0358	0.1159	2.84	6.76	0.496	2.196
40% EtOH H_2O	0.0385	0.1140	3.14	6.13	0.0494	2.196
50% EtOH H_2O	0.0392	0.0926	6.73	2.86	0.492	1.655
50% EtOH H_2O	0.1732	0.1900	6.95	2.77	0.490	1.655
50% EtOH H_2O	0.0323	0.0337	6.01	3.20	0.494	1.655
50% EtOH H_2O	0.0312	0.0322	5.73	3.36	0.032[a]	1.655
50% EtOH H_2O	0.1388	0.1438	8.12	2.37	0.484[b]	1.655
70% EtOH H_2O	0.0478	0.0895	17.35	1.11	0.499	0.595
70% EtOH H_2O	0.0388	0.0860	18.85	1.02	0.496	0.595
80% EtOH H_2O	0.0388	0.0757	37.60	0.51	0.496	0.000
80% EtOH H_2O	0.0480	0.0756	36.95	0.52	0.496	0.000
90% EtOH H_2O	0.0526	0.0755	82.81	0.23	0.494	−0.747
90% EtOH H_2O	0.0442	0.0762	80.65	0.24	0.495	−0.747

[a] No ionic salt was added in this run; the base used was cyclohexylamine rather than sodium hydroxide. [b] Solution was made 0.14 *N* in cyclohexylammonium di-*t*-butyl phosphate. [c] Grunwald–Winstein *Y* value for these solvents taken from A. H. Feinberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).

TABLE II

FIRST-ORDER RATE CONSTANTS FOR SOLVOLYSIS OF TRIISOPROPYL PHOSPHATE IN WATER AT 90°

Ester concn	Base concn	Half-life, hr	$k \times 10^6$ sec^{-1}	Ionic strength
0.0678	0.0752	44.42	4.35	0.495
0.1462	0.1497	70.11	2.75	0.490
0.0177	0.0191	39.90	4.83	0.499
0.0632	0.1506	41.81	4.61	0.491

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE SOLVOLYSIS OF TRIALLYL PHOSPHATE IN 50% ETHANOL–WATER AT 60°

Ester concn	Base concn	$k \times 10^4$ (mol/l.)$^{-1}$ sec^{-1}	Ionic strength
0.0307	0.0374	3.24	0.497
0.0320	0.0766	2.61	0.497
0.1496	0.1502	3.49	0.490
0.1532	0.1897	3.32	0.490

suggests that under similar reaction conditions triesters of phosphoric acid containing one or more *t*-alkyl groups of un-ionized *t*-alkyl di- or monoesters of phosphoric acid may be expected to undergo rapid, heterolytic carbon–oxygen fission. This behavior is analogous to that of *t*-alkyl halides, although halide ions are much better leaving groups than is di-*t*-butyl phosphate anion.

Neither the di-*t*-butyl phosphate anion nor the monoanion of *t*-butyl phosphate[16] undergoes rapid carbon–oxygen fission, although the un-ionized acids of both these esters solvolyze rapidly.[6,16]

The rapid, clean removal of a single *t*-butyl group under neutral conditions makes attractive the possibility of employing it as a protective group during phosphorylation of alcohols sensitive to the conditions used to remove other protective groups. Unfortunately, our attempts to isolate di-*t*-butyl phosphorochloridate prepared by the method of Mark and Van Wazer[17] were frustrated by its rapid decomposition. By contrast, pinacolyl phosphorochloridate and pinacolyl phosphoric acid demonstrated a stability surprising in light of the above observations, the latter being isolable from aqueous solution. Although pinacolyl phosphorochloridate phosphorylates alcohols satisfactorily, solvolysis of methyl pinacol phosphate afforded a mixture of ring-opened and ring-retained phosphate diesters which appeared to have arisen by nucleophilic attack on phosphorus. The synthetic utility of the pinacolyl group as a protective group thus seems highly limited.

The complex solvolytic behavior of *t*-butyl pinacol phosphate will be the subject of another communication.

(16) M. G. Newton and J. R. Cox, Jr., unpublished results.

(17) V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964).

Registry No.—Tri-*t*-butyl phosphate, 20224-50-4; cyclohexylammonium di-*t*-butyl phosphate, 20224-52-6; triisopropyl phosphate, 513-02-0; pinacol phosphonate, 16352-18-4; methyl pinacol phosphite, 14812-60-3; methylpinacol phosphate, 7443-26-7; *t*-butyl pinacol phosphate, 20224-35-5-; pinacol phosphoric acid, 13882-05-8; triallyl phosphate, 1623-19-4; tri-*t*-butyl phosphite, 15205-62-6.

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Pentacyclodecane Chemistry. V. The Synthesis and Acetolysis of *syn*- and *anti*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Toluenesulfonate. Evidence Concerning the Intermediacy of Bridged Carbonium Ions[1]

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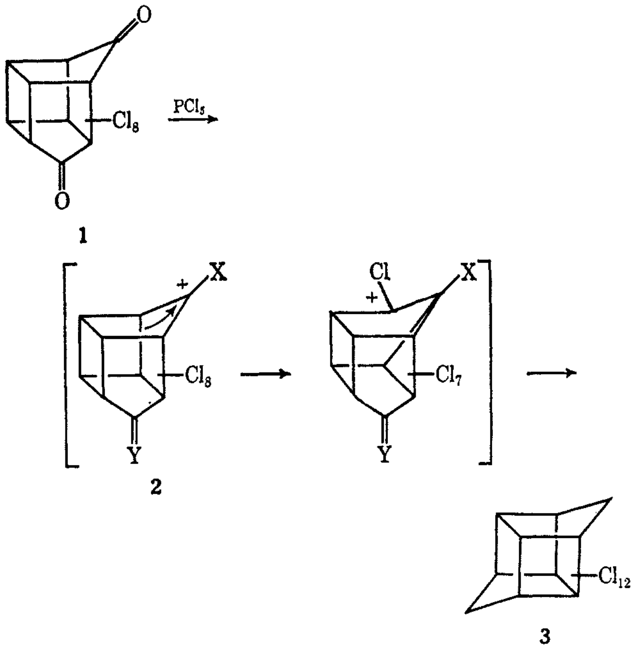
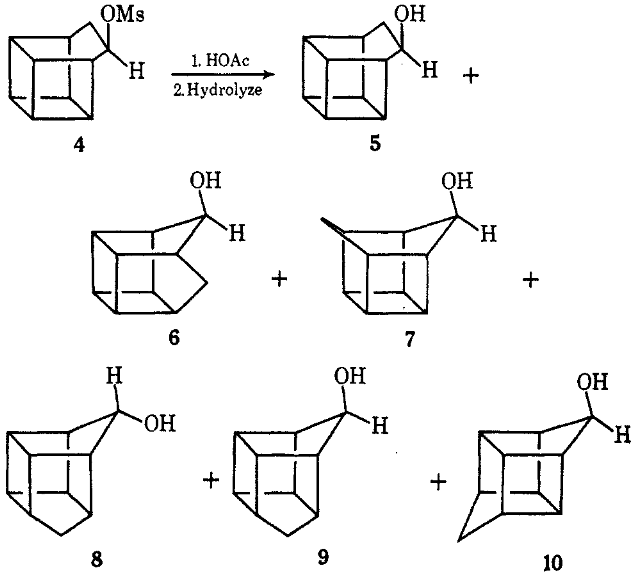
The *syn* and *anti* isomers of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol were synthesized by irradiation of *syn*- and *anti,endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol, respectively, in acetone solution. Solvolysis of the *syn*-pentacyclodecyl tosylate in unbuffered acetic acid gave almost exclusively the unrearranged *syn* acetate. Acetolysis of the *anti* tosylate gave mainly the rearranged pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]dec-6-yl acetate accompanied by 15% of unrearranged *anti* acetate. Internal return with rearrangement occurred with the *anti* tosylate. The rates of acetolysis of the *syn* and *anti* tosylates were measured; rate accelerations of 1.3×10^4 and 5×10^3, respectively, over those predicted for unassisted solvolysis were calculated from Schleyer's equation. Reduction of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one with sodium borohydride, lithium aluminum hydride, and lithium tri-*t*-butoxyaluminum hydride gave 76–80:24–20 ratios of *syn* and *anti* alcohols, respectively. The rate of borohydride reduction was determined, and an attempted correlation with the solvolysis rates was made. Equilibration of the *syn* and *anti* alcohols with aluminum isopropoxide–acetone gave a 50:50 mixture. The solvolysis reactions are best interpreted in terms of bridged carbonium ion intermediates, although other explanations cannot be ruled out entirely.

The unsymmetrical perchloro diketone **1** has been reported to rearrange to the symmetrical chlorocarbon **3** on reaction with phosphorus pentachloride.[2] The most reasonable pathway for this 1,3- to 1,4-bishomocubyl[3] rearrangement involves a carbonium ion mechanism[4] in which a 1,2-alkyl migration occurs in one of the cations **2**. A related reaction involving the acetolysis of the 1,1-bishomocubyl mesylate **4** was also recently reported.[5] Interestingly, this reaction generates all of the five possible bishomocubyl carbon skeletons **5–10**,[3,6]



X = OPCL$_4$ or Cl, Y = O or Cl$_2$



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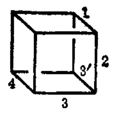
(1) Part IV: W. L. Dilling and C. E. Reineke, *Tetrahedron Lett.*, 2547 (1967). A preliminary account of this work is presented in this paper.

(2) (a) P. E. Eaton, Ph.D. Thesis, Harvard University, 1960; (b) G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964).

(3) The numbering for the bishomocubane system of nomenclature refers to the shortest path along the edges of a cube between the positions of the two methylene bridges. Thus the five possible bishomocubanes are as follows: pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane, 1,1-bishomocubane; pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,7}]decane, 1,2-bishomocubane; pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 1,3-bishomocubane; pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, 1,3′-bishomocubane; pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane, 1,4-bishomocubane.



(4) M. S. Newman and L. L. Wood, Jr., *J. Amer. Chem. Soc.*, **81**, 4300 (1959).

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(6) The stereoisomers **8** and **9** were only isolated as a mixture and were not identified individually.[5]