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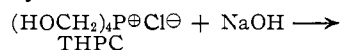
Phosphonium Compounds. III. Mechanism of Hydroxide Cleavage of Tetrakis(hydroxymethyl)phosphonium Chloride¹

BY MARTIN GRAYSON

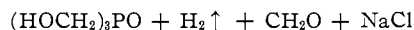
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The rate of reaction of tetrakis(hydroxymethyl)phosphonium chloride (THPC) with excess NaOH in water at 25° was followed by hydrogen evolution. The reaction is pseudo-second order in initial hydroxide and THPC concentrations with a dependence on the initial concentration differential, $[\text{OH}^-] - [\text{THPC}]$, which, in effect, represents the conjugate base of THPC. Monoalkyltrishydroxymethylphosphonium chlorides also give this reaction but at widely varying rates. Hydrogen evolution is prevented by use of stoichiometric amounts of base and the products are phosphines instead of phosphine oxides.

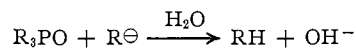
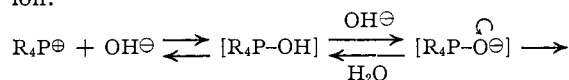
The preparation and reactions of tetrakis-(hydroxymethyl) phosphonium chloride (THPC) were reported by A. Hoffman.² He found that the salt decomposed in aqueous base to give tris-(hydroxymethyl)-phosphine oxide, hydrogen gas and formaldehyde. The cleavage of tetraalkyl phosphonium hydroxides was discovered by Cahours and A. W. Hofmann.³ It is now well



THPC



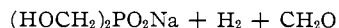
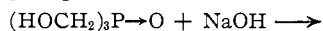
established that the Cahours-Hofmann reaction gives a hydrocarbon and a tertiary phosphine oxide by attack of hydroxide ion on a transient pentacovalent adduct of the phosphonium cation and a second hydroxide ion.⁴⁻⁶



We were attracted to the reaction of THPC with base as an unusual variation of the Cahours-Hofmann reaction in view of the formation of hydrogen gas and formaldehyde rather than methanol and the questions of stoichiometry and mechanism unanswered by the early work. We were also interested in the possibility of preparing tris-(hydroxymethyl)-phosphine from THPC which would open up some interesting synthetic possibilities.

Results and Discussion

With excess sodium hydroxide in water at room temperature, THPC rapidly evolves one equivalent of hydrogen gas and gives tris-(hydroxymethyl)-phosphine oxide and formaldehyde as the other reaction products. Air has no effect on the reaction. Additional hydrogen is not evolved at room temperature, despite extended reaction times with a large excess of base. The second mole of hydrogen reported by Hoffman² is evidently formed only at higher temperatures by conversion of the tertiary phosphine oxide to bis-(hydroxymethyl)-phosphinic acid which he isolated as the barium salt.



Cleavage of tertiary phosphine oxides by vigorous treatment with base is a well established reaction and needs no further discussion.⁷

We have found that monoalkyltris-(hydroxymethyl)-phosphonium salts also liberate hydrogen on treatment

(1) Presented in part at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961; part II, ref. 18.

(2) A. Hoffman, *J. Am. Chem. Soc.*, **43**, 1684 (1921); **52**, 2995 (1930).

(3) A. Cahours and A. W. Hofmann, *Ann.*, **104**, 1 (1857).

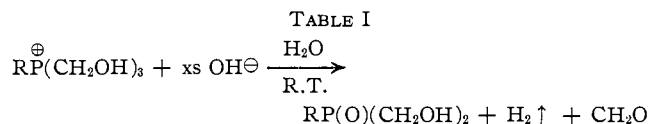
(4) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

(5) M. Zanger, C. A. VanderWerf and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3806 (1959).

(6) H. Hoffmann, *Ann.*, **634**, 1 (1960).

(7) L. Horner, H. Hoffmann and H. G. Wippel, *Ber.*, **91**, 64 (1958).

with excess base but, in general, less readily than THPC. There appears to be a considerable variation in rate with the size of the alkyl group. Cyclohexyl- and isobutyltris-(hydroxymethyl)-phosphonium chlorides react quantitatively with a 5-fold excess of sodium hydroxide in 20 and 40 minutes, respectively, at ambient temperatures. On the other hand, the *n*-butyl and methyl compounds as well as phenyltris-(hydroxymethyl)-phosphonium chloride do not give hydrogen when dissolved in water and treated with a large excess of sodium hydroxide. This is also the case with dialkyl- and diarylbis-(hydroxymethyl)-phosphonium salts which give no hydrogen even in the presence of a 20-fold excess of base. The trisubstituted THPC homologs were not examined but are presumably also unreactive (see subsequent discussion). Some pertinent properties of the monoalkyl derivatives are listed in Table I.



R:	HOCH ₂	C ₆ H ₁₁	iso-C ₄ H ₉	<i>n</i> -C ₄ H ₉	CH ₃	C ₆ H ₅
σ^{*a}	+ 0.555	- 0.150	- 0.125	- 0.130	0.00	+0.60
pK_a^b	5.5	8.2	...	8.2	8.3	...
N.m.r.(P ³¹), p.p.m. ^c	-26	-28	-30	-28	-27	...

^a R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N.Y., 1956. ^b Half-neutralization equivalent point (glass electrode). ^c Singlets rel. 85% H₃PO₄; solid compounds run as satd. solution in H₂O.

In Table I note that the inductive effect of the substituent group R, as measured by the Taft *sigma star* value, apparently bears no relationship to the reactivity order. Furthermore, the simple monoalkyl compounds all have the same acidity and almost identical shielding of the phosphorus atom. The comparable acidity of the reactive compounds is further indicated by their identical *pH* threshold for hydrogen evolution; gas formation begins just over a *pH* of 11 in each case during potentiometric titration.

Rationalization of the difference in reactivity between the cyclohexyl and isobutyl compounds, on the one hand, and the *n*-butyl and methyl compounds on the other may be arrived at rather simply. We have found that exact neutralization of any of these acidic salts followed by removal of volatiles gives the tertiary phosphine corresponding to loss of a methylol group (see below). It is also true, however, that these tertiary phosphines cannot reduce aqueous base to hydrogen. In other words, the Cahours-Hofmann reaction requires a phosphonium group. Therefore, the difference between the reactive compounds and those which do not give hydrogen may well lie in appreciable dissociation of the latter to tertiary phosphine at high *pH*. This idea was verified by an experiment with the *n*-butyl

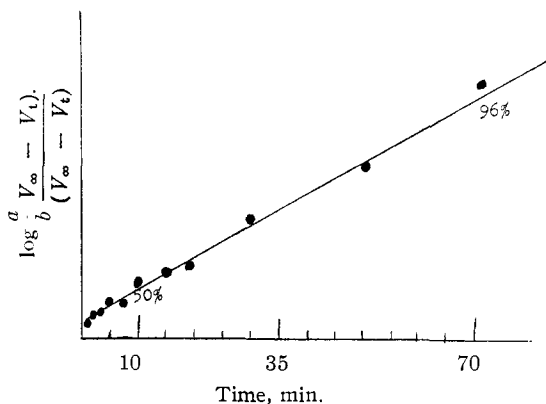
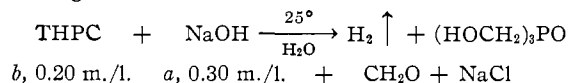
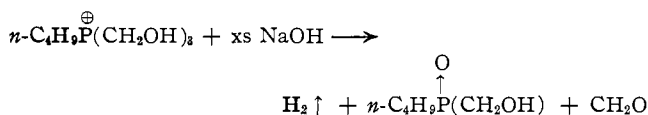


Fig. 1.—Reaction rate as a second-order function.



compound under conditions less favorable to equilibrium dissociation and more favorable to kinetic control by the hydrogen-producing reaction. Rather than dissolve the phosphonium salt in water and add moderately concentrated sodium hydroxide, the compound was added neat to a tenfold excess of 8 *M* sodium hydroxide at room temperature. Evolution of hydrogen gas began immediately and 80% of the theoretical amount was collected in a few hours.



It is likely that the formation of hydrogen was favored as much by the use of more concentrated base as by hindering predissociation by direct solution of the salt in the base. The point is that Cahours-Hofmann reactions are normally second order in hydroxide ion concentration and should be kinetically favorable at high *pH*.^{5,6} Dependence of rate on base concentration does therefore appear to be the case for the THPC systems, but we felt experimental verification of the exact order was desirable. The steric effect which is evidently operating in the case of the cyclohexyl and isobutyl compounds may be simply a retardation of the dissociation of *sp*³-hybridized phosphonium compound to the relatively more pyramidal (*p*³) tertiary phosphine. However, B-strain appears to be unimportant in the methylphosphines.⁸ It is more likely, therefore, that steric acceleration⁹ of the hydrogen-forming reaction is involved and this will be considered further in the light of the probable mechanism of the reaction. The low reactivity of phenyltris-(hydroxymethyl)-phosphonium chloride must be viewed in terms of the reduced nucleophilicity of arylphosphines¹⁰ which would favor dissociation. Since the hydroxymethyl and phenyl groups have about the same inductive effect (Table I), the great reactivity of THPC may well be the result of kinetic control resulting from a favorable entropy factor due to the large number of hydroxy-methyl groups available for reaction.

The rate of reaction of THPC with excess sodium hydroxide was followed by measurement of the change in hydrogen volume with time at constant pressure with fixed total volume of reactants. Data from a typical run are plotted in Fig. 1 as a function equivalent to $\log((a-x)/(b-x))$. The reaction appears to obey the normal second-order rate law. This is decidedly un-

expected in view of the established third-order character of cleavage reactions of benzylphosphonium hydroxides.^{5,6} It should be noted, however, that the graphical method is an insufficient criterion of reaction order in this case.

Reactions of over-all A plus B stoichiometry in which two molecules of A and one of B take part in the slow step have a second-order term in the integrated third-order rate expression and could give a plot as in Fig. 1.¹¹ Comparison of specific second- and third-order rate constants for a given run, however, does indicate that second-order kinetics are obeyed at any specific initial base concentration within the precision of our experimental method (Table II). Nevertheless, the specific second-order rate increases as we increase the ratio of hydroxide to THPC in a series of runs. This is shown in Table III in which an increase in this ratio from 1.25 to 3.75 results in a six fold rise in *k*₂. The critical variable, however, is not the NaOH:THPC ratio but the amount of hydroxide in excess of the THPC present. This would represent the surplus hydroxide after an essentially complete neutralization. The correlation is evident from the relatively constant number shown in the last column of Table III produced by dividing the specific rate constant by the difference between the base and THPC concentrations.

TABLE II
COMPARISON OF SECOND- AND THIRD-ORDER^a CONSTANTS

$$\text{NaOH} + (\text{HOCH}_2)_3\text{PCl} \xrightarrow[25^\circ]{\text{H}_2\text{O}} \text{H}_2 + (\text{HOCH}_2)_3\text{PO} + \text{CH}_2\text{O} + \text{NaCl}$$

0.30 m./l. 0.20 m./l.

<i>t</i> , min.	<i>V_t</i> , ml. H ₂	<i>k</i> ₂ , l. m. ⁻¹ min. ⁻¹	<i>k</i> ₃ , l. ² m. ⁻² min. ⁻¹
1.5	50	(0.245)	(0.84)
2.7	100	.292	1.05
4.3	150	.307	1.15
6.5	200	.306	1.21
9.5	250	.301	1.27
13.7	300	.292	1.31
20.2	350	.282	1.38
30.0	400	.278	1.52
47.8	450	.281	1.78
69.1	480	.301	2.17
∞	503
		0.293 ± 0.009	

^a Calculated by expression of ref. 11.

TABLE III
SUMMARY OF RATE DATA: THPC + NaOH (25°, H₂O)

Run	Concn., m./l.			<i>k</i> ₂ ^a , l. m. ⁻¹ min. ⁻¹	<i>k</i> ₃ / (<i>a</i> - <i>b</i>)
	NaOH (a)	THPC (b)	Other		
1	0.25	0.20	0.166	3.3
2	.25	.20	0.20 (NaCl)	.164	..
3	.30	.20292	2.9
4	.30	.20	0.20 (CH ₂ O)	.223	..
5	.375	.20441	2.5
6	.375	.10	1.0!	3.7

^a Average values (±2-3%) except for single runs 2 and 4.

We interpret this to mean that the observed pseudo-second-order kinetics are the result of reaction of a species formed by neutralization of THPC by one equivalent of hydroxide with excess hydroxide which remains at constant concentration in a given run. This is a direct consequence of the stoichiometry of the reac-

(11) C. G. Swain, *ibid.*, **70**, 1119 (1948). The expression

$$k_3 = \frac{1}{t(b-a)^2} \left[\frac{x(b-a)}{a(a-x)} + \ln \frac{b(a-x)}{a(b-x)} \right]$$

was developed for the trityl chloride-methanol reaction in which one mole of trityl methyl ether is formed from one mole of each reactant (A + B) but 2 moles of methanol (A) take part in the slow step; $[dA/dt = k_3(a-x)^2(b-x)]$.

(8) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 503 (1945).

(9) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

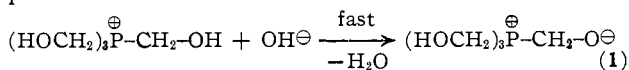
(10) W. A. Henderson and S. A. Buckler, *ibid.*, **82**, 5794 (1960).

tion which is such that hydroxide is consumed only in an amount equivalent to the THPC present.

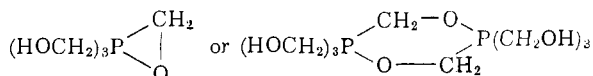
Two other significant facts are noted in Table III. As run 2 indicates, there appears to be no retardation or acceleration of rate in the presence of sodium chloride. Hoffmann⁶ had observed a retardation in the rate of cleavage of benzylphosphonium salts when alkali metal halides were added. With larger cations, such as the phosphonium salts themselves, an accelerated hydroxide cleavage was observed. This acceleration was attributed to a salt effect although the product tertiary phosphine oxides had a similar influence on the rate. In any case, whatever the basis for this observation, judging from our preliminary investigations the THPC system does not appear to be subject to these effects.

Comparison of runs 3 and 4, Table III, shows that added formaldehyde has a small effect on the rate. This reinforces our supposition that dissociation of reactive salts does not occur to an appreciable extent after neutralization. Had this in fact been the case, added formaldehyde would be expected to reverse the dissociative equilibrium and accelerate the hydrogen-forming process by providing a higher concentration of reactive intermediate. The slight retardation actually observed may be attributed to reduced base activity through interaction with the carbonyl group or its hydrate.

These results may be interpreted by either of two mechanisms which have a common first step, *i.e.*, the formation of a zwitterion by a rapid, essentially complete neutralization.

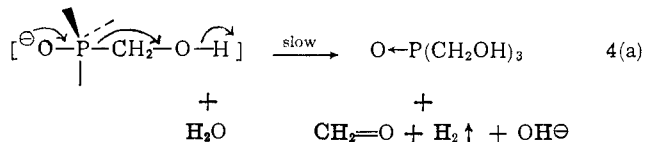
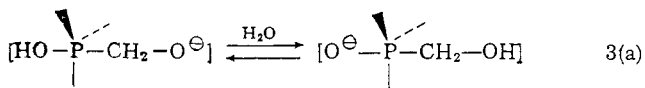
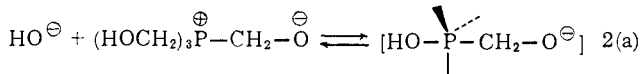


The zwitterion might also be written as a neutral phosphorane monomer or dimer species



The first mechanism (a) conforms most closely to the concept of colinear phosphoryl group formation and anion departure in the Cahours-Hofmann reaction which has been deduced from the formation of inverted oxide from optically active phosphonium salt.¹² The second or cyclic mechanism (b) merits equal consideration in view of the enhanced reactivity of cyclic phosphates in solvolysis.¹³ In both cases, the zwitterion of step 1 is the effective reactant being consumed at some fixed hydroxide concentration which is the amount in excess of the THPC concentration.

COLINEAR MECHANISM



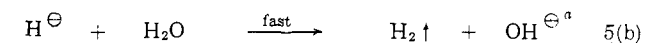
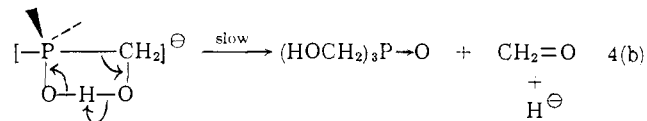
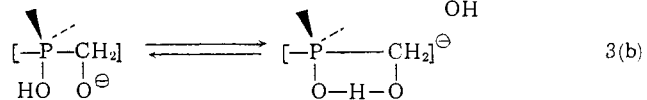
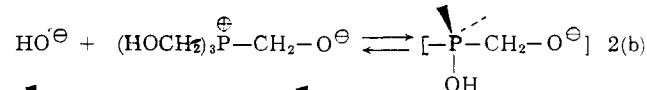
Direct formation of formaldehyde, phosphine oxide and hydride ion from the product of step 2a has not been written since this would require hydride formation from

(12) A. Bladé-Font, C. A. VanderWerf and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 2396 (1960).

(13) F. H. Westheimer, Abstracts, 140th Meeting American Chemical Society, Chicago, Ill., September, 1961, p. 94-Q.

a hydroxyl group attached directly to phosphorus in which hydrogen is normally very acidic.

CYCLIC MECHANISM



* A referee suggests that separate existence for hydride ion is unlikely and the cyclic mechanism should include hydrogen formation in the slow step as 4a. Kinetically, of course, one cannot distinguish between these alternatives.

Note that in both mechanisms, addition of hydroxide to the zwitterion gives a pentavalent phosphorane which is already an anion. This is probably the chief point of difference from the usual Cahours-Hofmann process. The entry of hydroxide in the cyclic mechanism is at an equatorial position on the resulting phosphorane bipyramid permitting formation of the cyclic transition state with the axial methylene oxide group.^{14a,b} The cyclic mechanism differs from the colinear one in that a separate fast step for hydride consumption is required and the energy of hydrogen formation is lost in the slow step. Of course, this may well be compensated by the favorable entropy anticipated for such a mechanism.

We mentioned earlier the steric acceleration of hydrogen formation with monoalkyltris(hydroxymethyl)phosphonium salts by bulky alkyl groups. This effect may be rationalized on the basis of the geometry of the phosphorane intermediates proposed here. It seems reasonable that crowding would be reduced in the order: $\text{RP}(\text{CH}_2\text{OH})_2 > \text{RP}^+(\text{CH}_2\text{OH})_3 > \text{RP}(\text{OH})(\text{CH}_2\text{OH})_3$, being least in the pyramidal phosphorane^{14b} with the bulky alkyl group (R) in the equatorial position where two of the opposed hydroxymethyl groups have been pushed back from 109° in the phosphonium compound to 120° (Fig. 2). Although the third hydroxymethyl

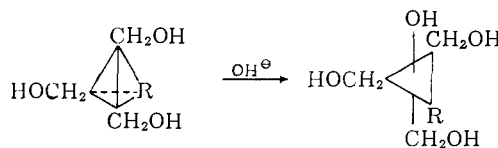


Fig. 2.

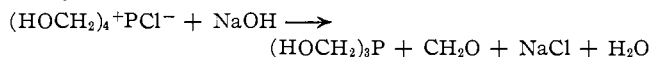
group is closer to R (90°), there is much room for compression toward the small hydroxyl group in the other axial position. Thus bulk will favor hydrogen formation by reducing dissociation to tertiary phosphine and formaldehyde and by accelerating formation of less strained phosphorane and products (a methylol group is lost in the slow step).

Formation of Tertiary Phosphines.—As stated earlier, one of our objectives in this work was the preparation of tertiary hydroxymethylphosphines from the correspond-

(14) (a) It should be obvious that this mechanism can also be invoked with hydroxyl in the axial position and the methylene oxide group equatorial; *e.g.*, simply reversing the positions of the groups shown in the product of 2(b). This is a somewhat more ambiguous situation, however, since the incipient $\text{P} \rightarrow \text{O}$ group is again colinear with an opposite, axial hydroxymethyl. Cyclic hydrogen transfer here could be followed by colinear elimination. The present state of our knowledge does not permit a choice between these details. (b) Discussion in terms of the alternative square pyramidal transition state has been omitted for simplicity.¹³

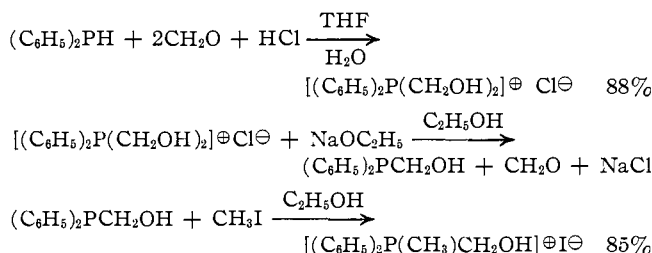
ing phosphonium salts for synthetic purposes. This was in fact accomplished and we will summarize our results here briefly. This aspect of the work was not developed extensively in view of the corroborative evidence provided by a number of publications subsequent to our initial efforts.¹⁵⁻¹⁷

It was discovered early in this work that an excess of base was required for hydrogen formation with THPC. When a water or ethanol solution of THPC was exactly neutralized with sodium hydroxide, no hydrogen gas whatever was formed. The tertiary phosphine, tris-(hydroxymethyl)-phosphine, was isolated in quantitative yield as an oil.



The phosphine was converted to a methiodide as well as other quaternary salts, a quinone adduct and so forth. Oily quaternary salts were characterized as tetraphenyl boron derivatives. Ethanolic hydroxide or ethoxide are convenient reagents since sodium chloride precipitates and the filtrate can be used directly in synthesis where formaldehyde does not interfere. It should be noted here that excess sodium ethoxide does not give an ether-forming decomposition as found earlier with benzyl phosphonium salts.¹⁸ A negligible amount of hydrogen gas was liberated after several days at room temperature (6.5% of theory), but diethyl ether was not detectable by gas chromatography.

The formation of tertiary phosphines was demonstrated also for the mono- and disubstituted alkyl and arylhydroxymethyl phosphonium salts. The alkyl compounds can be prepared sequentially from THPC with base and alkyl halide or directly from the phosphine, formaldehyde and acid, which is most convenient. The latter is essential for the aryl compounds.



This sequence was also carried out with diisobutylphosphine with equally good results. Preparation of tertiary phosphines from monohydroxymethyl trialkyl or triaryl phosphonium salts and base has been reported earlier.^{19,20}

Acknowledgments.—The author is indebted to Professors Herbert C. Brown and William E. McEwen for helpful discussions and to Mrs. Kay Loeffler for preparation of several phosphonium salts.

Experimental²¹

Kinetics.—Reactions of tetrakis-(hydroxymethyl)-phosphonium chloride or THPC (Hooker Chem. Co., recrystallized from 2-propanol; m.p. 149–150°) with sodium hydroxide (0.500 *N* stock solution) were carried out at 100.0-ml. total volume in a single neck flask of ca. 110-ml. capacity to which was fitted a pressure equalizing dropping funnel for rapid addition of the base solution and a water displacement gas buret consisting of a 1-

(15) H. Hellmann and O. Schumacher, *Angew. Chem.*, **72**, 211 (1960).

(16) S. Trippet, *J. Chem. Soc.*, 2813 (1961).

(17) K. A. Petrov and V. A. Parshina, *J. Gen. Chem. (USSR)*, **31**, 3417, 3421 (1961).

(18) M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).

(19) M. M. Rauhut, I. Hechenblekner, H. A. Currier, F. C. Schaefer and V. P. Wystrach, *ibid.*, **81**, 1103 (1959).

(20) H. Hoffmann, *Angew. Chem.*, **72**, 77 (1960).

(21) Melting points are uncorrected. Microanalyses by Galbraith Laboratories, Knoxville, Tenn., and Microanalytical Group of these laboratories.

liter cylinder calibrated in 10-ml. subdivisions. The reaction vessel was submerged in a water-bath maintained at $25 \pm 0.2^\circ$ during reaction. The reagents were equilibrated at this temperature before mixing. Stirring was accomplished with a Teflon coated bar magnet and an external magnetic stirring motor of commercial design. Vigorous stirring was always employed. Gas solubility corrections were not applied. Infinity volumes were taken after a minimum of $2.5 \times$ the time for 90% reaction. These were quite reproducible (within 1%) for runs of widely varying duration after correction for initial THPC concentration. These also corresponded closely to the calculated, theoretical gas volume plus water vapor. Identity and purity of the hydrogen were confirmed by mass spectrometric analysis of the gas from several runs. Formaldehyde in the product was confirmed by standard derivatives and odor and tris-(hydroxymethyl)-phosphine oxide was isolated and identified by infrared spectroscopy (especially peaks at 1040 and 1140 cm^{-1}). In a typical run for which data is recorded in Table II, 3.80 g. (0.020 mole) of THPC was dissolved in 40 ml. of deionized water under nitrogen in the apparatus and brought to thermal equilibrium. Then 60.0 ml. (0.030 equiv.) of stock base at bath temperature was placed in the dropping funnel, nitrogen flow stopped, and the system closed and vented to the gas buret. The base was then added in a fraction of a minute and readings taken at known intervals.

Exploratory reactions with various phosphonium salts were carried out in the same apparatus without the water-bath.

Cyclohexyltris-(hydroxymethyl)-phosphonium Chloride.—Cyclohexylphosphine (25 ml., 22.2 g., 0.19 mole, b.p. 152–153°) was dissolved in an ice-cold mixture of 150 ml. of tetrahydrofuran and 50 ml. of concd. HCl under N_2 . To this was added in 1–2 minutes at 10–12° a solution of 60 g. of 37% formalin (22.1 g. real, 0.74 mole) in 50 ml. of tetrahydrofuran. After a mild exotherm, the mixture was stirred under N_2 overnight at room temperature. After removal of volatiles on the water-pump at 40–50°, the residue crystallized from acetone–petroleum ether. After drying in vacuum, there was obtained 31.2 g., m.p. 87.5–88.5° (67.5%). Recrystallization from acetone–ethanol and drying gave white platelets of m.p. 88.5–89.5°.

Anal. Calcd. for $\text{C}_6\text{H}_{20}\text{PO}_3\text{Cl}$: C, 44.54; H, 8.31; P, 12.80; Cl, 14.61. Found: C, 44.24; H, 8.23; P, 12.51; Cl, 14.88.

Tris-(hydroxymethyl)-isobutylphosphonium Chloride.—Preparation by the procedure described above gave material of m.p. 52–53° (acetone).

Anal. Calcd. for $\text{C}_7\text{H}_{18}\text{PO}_3\text{Cl}$: C, 38.81; H, 8.37; P, 14.30; Cl, 16.37. Found: C, 39.33; H, 8.27; P, 14.24; Cl, 16.03.

Tris-(hydroxymethyl)-phenylphosphonium Chloride.—Preparation by the procedure described above gave material of m.p. 79.5–80.5° (methanol–acetone). *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{PO}_3\text{Cl}$: C, 45.68; H, 5.96; P, 13.09; Cl, 14.98. Found: C, 46.04; H, 6.02; P, 13.18; Cl, 14.80.

Bis-(hydroxymethyl)-diphenylphosphonium Chloride.—Diphenylphosphine (25 ml., 27 g., 0.145 mole) was added to a solution of 100 ml. of concd. HCl, in 200 ml. of tetrahydrofuran at 20° under N_2 . Solution was not complete until after dropwise addition (0.5 hour) of 40 g. of 37% formalin (15 g. real, 0.50 mole) in 50 ml. of tetrahydrofuran. A mild exotherm was observed. The mixture was stirred for 2 hours at room temperature and the solvent removed at 50° with water pump vacuum. The residue was evaporated on a steam-bath. The solid formed on cooling was triturated with acetone and dried to give 36 g. (88%), m.p. 161–162°. Recrystallization from 2-propanol gave m.p. 161°. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{18}\text{PO}_2\text{Cl}$: C, 59.48; H, 5.71; P, 10.96; Cl, 12.54. Found: C, 59.06; H, 5.63; P, 11.00; Cl, 12.51.

Diisobutylbis-(hydroxymethyl)-phosphonium Chloride.—Preparation by the procedure described above gave material of m.p. 134–134.5° (acetone). *Anal.* Calcd. for $\text{C}_{10}\text{H}_{24}\text{POCl}$: C, 49.44; H, 9.97; P, 12.76; Cl, 14.61. Found: C, 49.51; H, 10.15; P, 12.89; Cl, 14.84.

Tris-(hydroxymethyl)-phosphine.²²—Sodium hydroxide (1.6 g., 0.040 mole) in 25 ml. of water was added rapidly to 7.6 g. (0.040 mole) of THPC in 50 ml. of water under N_2 at room temperature in a closed system connected to a gas buret. No gas evolution was observed after stirring 20 hours. The solvent was stripped at 50–60° with water-pump vacuum and 50 ml. of ethanol was added and the sodium chloride was filtered under N_2 . Removal of ethanol in vacuum (45°) gave 4.8 g. (97%) of clear, viscous liquid. Infrared analysis indicated absence of $\text{P}=\text{O}$ and confirmed the presence of primary alcohol and $\text{P}-\text{CH}_2$ groups. A trace of carboxylate, presumably formate, was present.

Tris-(hydroxymethyl)-methylphosphonium Iodide.—Sodium hydroxide (4.0 g., 0.10 mole) dissolved in 150 ml. of ethanol was added rapidly, under N_2 , to 19.0 g. (0.10 mole) of THPC in 100 ml. of ethanol at ambient temperature in a Grignard flask. After stirring 1 hour, the solution was filtered from sodium chloride under N_2 pressure and 28 g. (0.20 mole) of methyl iodide was

(22) M. Reuter, U. S. Patent 2,912,466 (1959); German Patent 1,035,135 (1958).

added. After cooling during the initial, mild exotherm, the solution was kept overnight at room temperature. After drying *in vacuo*, the clear sirupy residue weighed 26.4 g. (99%). *Anal.* Calcd. for $C_4H_{12}PO_3 \cdot I$, 47.7. Found: I, 47.2. Solution in water and addition of an equivalent of sodium tetraphenylboron gave a white solid of m.p. 170–171° dec. after drying and recrystallization from acetone–benzene. *Anal.* Calcd. for $C_{28}H_{32}PBO_3$: C, 73.37; H, 7.04; P, 6.76. Found: C, 73.30; H, 6.99; P, 6.27.

***n*-Butyltris-(hydroxymethyl)-phosphonium Iodide.**—An ethanol solution of tris-(hydroxymethyl)-phosphine was prepared from 10.0 g. (0.25 mole) of sodium hydroxide and 47.5 g. (0.25 mole) of THPC under N_2 and treated, after filtration, with 132 g. (0.72 mole) of *n*-butyl iodide. After standing overnight and drying, first with water-pump vacuum and finally at 80–90° with an oil-pump, there was obtained 73.5 g. (95% yield) of clear liquid. *Anal.* Calcd. for $C_7H_{15}PO_3 \cdot I$: I, 41.2. Found: I, 39.1. Treatment of an aqueous solution with sodium tetraphenyl boron gave a white solid which was washed with water, dried and recrystallized from acetone–benzene; m.p. 145–146° dec. *Anal.* Calcd. for $C_{31}H_{38}PBO_3$: C, 74.40; H, 7.65; P, 6.19. Found: C, 74.18; H, 7.52; P, 6.68.

Hydroxymethylmethyldiphenylphosphonium Iodide.—Sodium (2.3 g., 0.10 g. atom) in 150 ml. of ethanol, after complete reaction was added under N_2 to 28.3 g. (0.10 mole) of bis-(hydroxymethyl)-diphenylphosphonium chloride in 250 ml. of ethanol at 40° in 20

minutes. After 30 minutes, the mixture was filtered to remove sodium chloride and heated at 40–50° in vacuum to give 20.7 g. (96%) of waxy, hygroscopic solid. The solid was dissolved in 75 ml. of ethanol and treated with 30 g. (0.20 mole) of methyl iodide in an ice-bath (exotherm). After 30 minutes, cooling was discontinued and the solution was kept 2 hours at room temperature, then dried in vacuum to give 30.5 g. (85%) of waxy solid, m.p. 223–225° (dec.) after recrystallization from methanol–benzene. *Anal.* Calcd. for $C_{14}H_{11}PO \cdot I$: C, 46.95; H, 4.50; P, 8.65; I, 35.43. Found: C, 47.58; H, 4.83; P, 9.03; I, 34.67.

Hydroxymethyldiisobutylmethylphosphonium Iodide.—Sodium (2.3 g., 0.10 g. atom) was allowed to react with 150 ml. of ethanol and the solution was added to 24.3 g. (0.10 mole) of bis-(hydroxymethyl)-diisobutylphosphonium chloride in 100 ml. of ethanol in 20 minutes under N_2 at ambient temperatures. After standing overnight, sodium chloride was filtered under N_2 pressure and the filtrate was dried to give 17.3 g. (98%) of oily residue. The residue was dissolved in 75 ml. of acetone and treated with 28 g. (0.20 mole) of methyl iodide in an ice-bath. After standing overnight and removal of volatiles, 24.6 g. (77%) of soft solid remained. A portion of this product in water was converted to the tetraphenyl borate which was washed with water and dried; m.p. 168–170°. Recrystallization from acetone–benzene gave m.p. 176–177°. *Anal.* Calcd. for $C_{34}H_{44}PBO$: C, 79.99; H, 8.69; P, 6.07. Found: C, 80.13; H, 8.97; P, 6.26.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

The Action of Elementary Fluorine upon Organic Compounds. XXVI. The Direct Fluorination of Some Perfluoroalkyl-*s*-triazines¹

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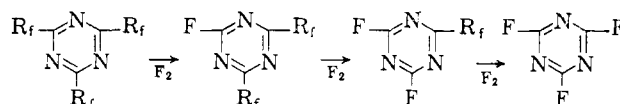
The direct vapor-phase fluorination of tris-(trifluoromethyl)- and tris-(pentafluoroethyl-*s*-triazines has been studied under a variety of operating conditions. When a packed T-reactor was employed, a novel substitution reaction occurred in which the perfluoroalkyl groups were progressively replaced by fluorine yielding some interesting unsymmetrical-*s*-triazines. The new perfluorinated secondary amines $C_2F_5NFC_2F_5$, $CF_3NFC_3F_7$ and $C_3F_7NFC_3F_7$ were also isolated. The jet fluorination of these two triazines led to the formation of several unsaturates including $CF_3CF=NC_2F_5$, $CF_3N=CFC_2F_5$, $C_2F_5CF=NC_3F_7$ and $CF_3CF=NF$ together with their saturated analogs.

Recently the direct fluorination of the simple *s*-triazine cyanuric fluoride⁵ has been found to yield several new highly fluorinated heterocyclic compounds, together with a number of unusual saturated and unsaturated cleavage products. By analogy, it seemed likely that the fluorination of the related compounds tris-(trifluoromethyl)-*s*-triazine, $(CF_3CN)_3$, (I), and tris-(pentafluoroethyl-*s*-triazine, $(C_2F_5CN)_3$, (II), would yield equally interesting results.

The resistance of perfluoroalkyl-*s*-triazines toward fluorination has been demonstrated by Young,⁶ who has reported that only a limited reaction occurred between I and an excess of silver difluoride at 150°. The stability of the triazine nucleus toward free radical attack was more strikingly demonstrated during the present research, since even under the most drastic fluorinating conditions used, considerable amounts of the reactant were recovered. Contrary to the results of the fluorination of cyanuric fluoride, which yielded both tetra- and hexafluoro adducts, II gave no stable ring adduct, although in the case of I there was spectroscopic evidence indicating that an impure product, b.p.

near 93°, may have contained the corresponding tetrafluoride-adduct.

Instead it was found that the perfluoroalkyl groups of I and II were progressively replaced by fluorine as



It is of interest that the infrared spectra of these replacement products exhibited a regular relationship between the degree of substitution and the locations of the planar ring stretching absorptions. As expected, this substitution was favored by vigorous operating conditions especially when a packed T-reactor was employed.

In the case of I, the unsymmetrical-*s*-triazines produced were 2,4-bis-(trifluoromethyl)-6-fluoro-*s*-triazine and 2,4-difluoro-6-trifluoromethyl-*s*-triazine, which were identified spectroscopically. Both of these have been prepared earlier by a different method.⁷ The fluorination of II yielded 2,4-bis-(pentafluoroethyl)-6-fluoro-*s*-triazine and the new 2,4-difluoro-6-pentafluoroethyl-*s*-triazine. The synthesis of the former compound has recently been reported by Kober,⁸ who prepared it by the reaction of 2,4-bis-(pentafluoroethyl)-6-chloro-*s*-triazine with several different fluorinating agents. The structures of both of these perfluoroethyl-*s*-triazines were established by spectroscopic and chemical evidence. The neutral hydrolysis of the former yielded the new pentafluoropropionylurea, indicating ring cleavage,

(7) E. Kober and C. Grundmann, *ibid.*, **81**, 3769 (1959).

(8) E. Kober, H. Schroeder, R. F. W. Rätz, H. Ulrich and C. Grundmann, *J. Org. Chem.*, **27**, 2577 (1962).

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(5) J. B. Hynes and L. A. Bigelow, *J. Am. Chem. Soc.*, **84**, 2751 (1962).

(6) J. A. Young, W. S. Durrell and R. D. Dresdner, *ibid.*, **82**, 4553 (1960).