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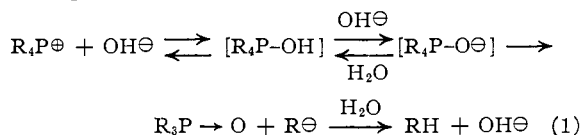
Phosponium Compounds. II. Decomposition of Phosponium Alkoxides to Hydrocarbon, Ether and Phosphine Oxide

BY MARTIN GRAYSON AND PATRICIA TARPEY KEOUGH

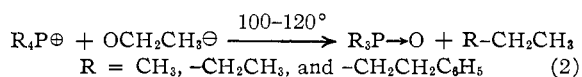
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Phosponium salts containing a benzyl group react with alcoholic sodium alkoxide to give hydrocarbon, ether and tertiary phosphine oxide: $(R_3P^{\oplus}CH_2Ar)X^{\ominus} + NaOR' + R'OH \rightarrow R_3P \rightarrow O + CH_3Ar + R'OR' + NaX$. The same products are observed with the corresponding phosphinemethylene and excess alcohol: $R_3P \leftarrow CHAr + 2R'OH \rightarrow R_3P \rightarrow O + CH_3Ar + R'OR'$. These results are unexpected in view of earlier reports in the literature for the formation of mixed hydrocarbons from tetraalkylphosponium alkoxides: $R_4P^{\oplus}OR'^{\ominus} \rightarrow R_3PO + R-R'$. The use of deuterated alcohols indicates that hydrocarbon is formed by abstraction of a proton from the alcoholic hydroxyl group. In aqueous alcohol solvents, *p,p'*-dinitrobenzyl is produced in addition to *p*-nitrotoluene from *p*-nitrobenzyltriphenylphosponium bromide and sodium hydroxide. Tetraalkylphosponium alkoxides show only dissociation reactions in alcohol at temperatures up to 200°. Ether formation is not observed when benzene is the leaving group; reaction takes place only when moisture is present and the hydroxide decomposition path is followed to give only benzene and a tertiary phosphine oxide: $R_4P^{\oplus} - C_6H_5 + OH^{\ominus} \rightarrow R_3P \rightarrow O + C_6H_6$. Tetramethylenebis-(triphenylphosponium bromide) gives tetramethylenebis-(diphenylphosphine oxide).

It has long been known that phosponium salts are decomposed by aqueous base to give tertiary phosphine oxides and hydrocarbons.¹ A detailed mechanism was proposed for the reaction involving a transient intermediate in which phosphorus has an expanded valence shell.



Recently, McEwen and co-workers have shown this reaction mechanism to be substantially correct by a kinetic study with an optically active phosponium salt.² In an important paper, Hey and Ingold report the formation of mixed hydrocarbons in the decomposition of phosponium alkoxides.³



The mechanism of this reaction is obscure, and the authors merely propose the decomposition of a pentavalent intermediate to products. Our interest in the reactions of phosponium salts containing a 2-cyanoethyl group with sodium alkoxide led us to consider the detailed chemistry of the decomposition of phosponium alkoxides in which an elimination reaction cannot occur.⁴

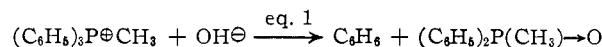
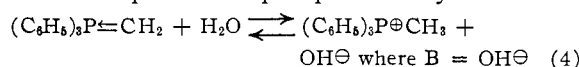
Results and Discussion

It is clear that any explanation of the base decomposition of phosponium salts not capable of elimination reactions must take into account their acid-base relationship to phosphinemethylenes.

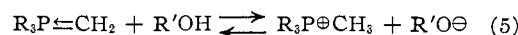


In view of this we were interested in first examining phosponium salts from which relatively stable, isolable phosphinemethylenes were produced by reaction with base. The alcoholic decomposition of

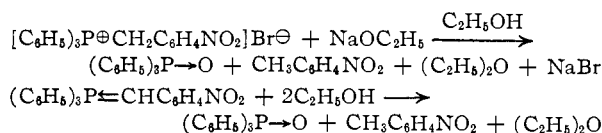
phosphinemethylenes should be related to the decomposition of phosponium alkoxides, since phosphinemethylenes and water apparently give products similar to those from phosponium hydroxide decomposition. In fact eq. 3 was implied by Coffmann and Marvel in their explanation of the aqueous decomposition of phosphinemethylenes.⁵



The preparation of phosphinemethylenes by anhydrous organometallic reagents is a well known instance of eq. 3, and alcoholic sodium alkoxides have also been used.⁶ The decomposition of phosphinemethylenes by alcohols, however, has received little attention. Mondon reports tertiary phosphine oxide by-products in ethanol but did not examine the reaction further.⁷ An equilibrium analogous to eq. 3 appears likely.



We have in fact observed that *p*-nitrobenzyltriphenylphosponium bromide with sodium ethoxide in ethanol gives the same products as pure triphenyl-*p*-nitrobenzylidenephosphorane in ethanol.



The distinguishing feature of these reactions compared to the aqueous decomposition process is the formation of an ether. The phosphinemethylene was prepared by neutralization of the phosponium salt with sodamide in liquid ammonia followed by crystallization from benzene or ethylene dichloride-petroleum ether. This compound was first prepared by Krohnke with aqueous base, but we found this method gave unsatisfactory yields.⁸ Both diethyl ether and nitrotoluene were determined quantitatively by gas-liquid chromatography and mass

(1) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).
 (2) W. E. McEwen, M. Zanger, K. F. Kumli and C. A. VanderWerf, 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959; M. Zanger, C. A. VanderWerf and W. E. McEwen, *THIS JOURNAL*, **81**, 3806 (1959).
 (3) L. Hey and C. K. Ingold, *J. Chem. Soc.*, 531 (1933).
 (4) M. Grayson, P. T. Keough and G. A. Johnson, *THIS JOURNAL*, **81**, 4803 (1959).

(5) D. D. Coffmann and C. S. Marvel, *ibid.*, **51**, 3496 (1929).
 (6) U. Schollkopf, *Angew. Chem.*, **71**, 261 (1959).
 (7) A. Mondon, *Ann. Chim.*, **603**, 115 (1957).
 (8) F. Krohnke, *Chem. Ber.*, **83**, 291 (1950).

TABLE I
PREPARATIVE CONDITIONS AND PROPERTIES OF PHOSPHONIUM HALIDES
 $R_3P + R'X \longrightarrow [R_3PR']^{\oplus}X^{\ominus}$

Phosphonium salt	Solvent	Reflux time, hr.	Yield, %	M. p., °C.	—Halogen, % ^a — Calcd.	% ^a — Found
$[(C_6H_5)_3PCH_2C_6H_5NO_2]^{\oplus}Br^{\ominus}$	C_6H_6	1.0	90.5	168–169	18.76	18.98
$[(CNCH_2CH_2)_3PCH_2C_6H_4NO_2]^{\oplus}Br^{\ominus}$	CH_3CN	.. ^b	89.5	195–196	19.25	19.41
$[(C_6H_5)_3PCH_2C_6H_4NO_2]^{\oplus}Br^{\ominus c}$	$CH_3C_6H_5$.. ^b	88.0	285–286	16.71	15.71
$[(C_6H_5)_3PCH_2C_6H_5]^{\oplus}Br^{\ominus}$	C_6H_5OH	.. ^b	76.5	274–275	18.44	18.13
$[(C_6H_5)_3PCH_2C_6H_5]^{\oplus}Cl^{\ominus}$	C_6H_5OH	1.0	68.0	>300	9.12	8.84
$[(C_6H_5)_3PC_4H_9]^{\oplus}Br^{\ominus}$	C_6H_5OH	24	90.8	249–251	20.00	19.03
$[(C_6H_5)_4P]^{\oplus}Br^{\ominus}$	CH_3COCH_3	48	89.5	99–101	23.02	22.92
$[(C_6H_5)_3PCH_2CH_2CH_2CH_2P(C_6H_5)_3]^{\oplus\oplus}2Br^{\ominus}$	C_6H_5OH	24	73.0	295–296	20.23	19.40
$[(C_6H_5)_3PCH=CHCH_2]^{\oplus}Br^{\ominus}$	C_6H_6	2.0	100	209–214	20.85	19.66
$[C_2H_5)_4P]^{\oplus}I^{\ominus}$	C_2H_5OH	5.0	77.5	270–278 ^d

^a Based on Volhard titration of crude phosphonium salt. ^b The phosphine and halide reacted at room temperature over a period of 24 hours. ^c Prepared according to procedure of Krohnke. ^d Reported⁸ m.p. 270–278°.

TABLE II
ALCOHOL DECOMPOSITION OF TRIPHENYL-*p*-NITROBENZYLIDENEPHOSPHORANE
 $(C_6H_5)_3P=CHC_6H_4NO_2 + ROH \longrightarrow (C_6H_5)_3P=O + CH_3C_6H_4NO_2 + ROR$

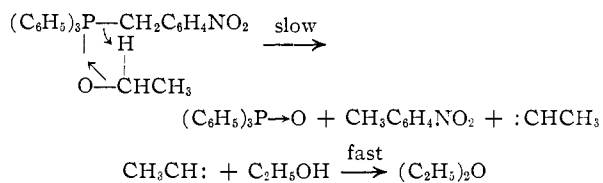
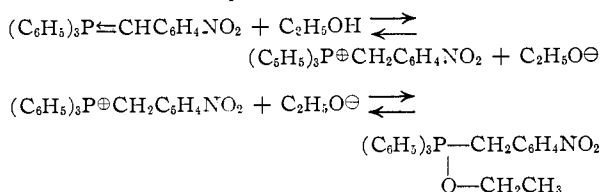
ROH	Mole $(C_6H_5)_3P=CHC_6H_4NO_2$	Products ^a				
		Yield $(C_6H_5)_3P=O$	Nitrotoluene	Yield	ROR	Yield
C_2H_5OH	0.010 ^b	0.010 ^c	CH_3-	0.010 ^{c,d}	$C_2H_5OC_2H_5$	0.010 ^{c,d}
C_2H_5OH	.0022 ^e	.0020 ^e	CH_3-	.0019 ^{c,d}	$C_2H_5OC_2H_5$.0011 ^e
C_4H_9OH	.010 ^b	.010 ^c	CH_3-	.010 ^{c,d}	$C_4H_9OC_4H_9$.010 ^{c,d}
C_4H_9OH	.0011 ^e	.0010 ^e	CH_3-	.0010 ^{c,d}	$C_4H_9OC_4H_9$.0003 ^e
C_2H_5OD	.0011 ^e	.00098 ^e	CD_3-	.00084 ^{c,d}	$C_2H_5OC_2H_5$.0003 ^e
			CD_2H-	.00013		
CD_3OH	.0014 ^e	.0012 ^e	CH_3-	.0012 ^{c,d}	CD_3OCD_3	... ^f

^a All yields are given in moles. ^b Phosphinemethylene was complexed with small amount of benzene. ^c Detected by mass spectrometry. ^d Detected by gas-liquid chromatography. ^e Recrystallized from ethylene dichloride. ^f Too volatile to be detected.

spectrometry and were found in mole ratios of unity. Similar products are formed from tributyl- and tris-(2-cyanoethyl)-*p*-nitrobenzylphosphonium bromides and sodium ethoxide or butoxide. The unsubstituted benzyl compound also decomposed to toluene, an ether and tertiary phosphine oxide. In none of these reactions were gases such as methane, ethane, ethylene, etc., detected.

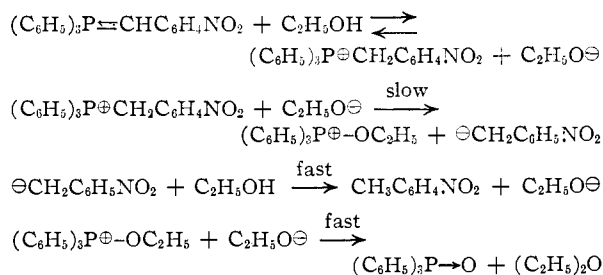
In view of the clean reaction of the pure phosphine-methylene with alcohol, deuterium tracer experiments were carried out with this material and ethanol-*d* and methyl-*d*₃ alcohol to determine the source of the proton donated to the benzyl group. The results of these experiments are listed in Table II. Although suspicions of a radical process had been raised at first by some results in aqueous ethanol discussed later, an ionic mechanism was anticipated since gaseous products typical of ethoxyl radical were absent. Two reasonable ionic mechanisms can be written, both of which give ether as one product but which supply protons from different sources.

A. Intramolecular protonation (carbene formation)



Ether formation by reaction of carbenes and alcohols has been described.⁹

B. Hydroxylic protonation (*p*-nitrobenzylidene ion formation)

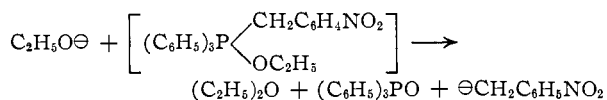


The slow step of mechanism B may also be written as an ionization of the pentavalent phosphorus intermediate. This, of course, would be indistinguishable from the direct displacement of *p*-nitrobenzylidene ion by ethoxide.

The reaction may also be rationalized in terms of still another mechanism involving a pentavalent

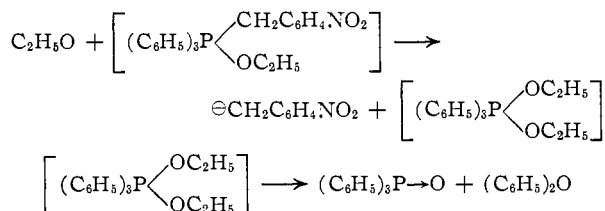
(9) J. Hine and K. Tanabe, *THIS JOURNAL*, **79**, 2654 (1957).

intermediate. This would require attack of ethoxide upon the intermediate to give diethyl ether, phosphine oxide and benzylidene ion simultaneously.

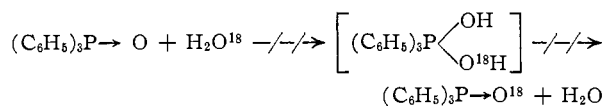


The rate of this reaction would depend on the square of the ethoxide concentration and therefore could be distinguished kinetically from B. This mechanism bears a strong resemblance to the hydroxide decomposition process.² We discount it on that basis since the chemistry of the ethoxide and hydroxide reactions is quite different. Benzene is not cleaved from aryl-alkylphosphonium salts by ethoxide whereas hydroxide readily gives such a reaction. We conclude from this that a full P → O bond is not formed in the slow step of the ethoxide process. The driving force of the phosphonium hydroxide decomposition is therefore absent in the ethoxide case. The displacement of phenide ion or carbanions is unlikely without this driving force.

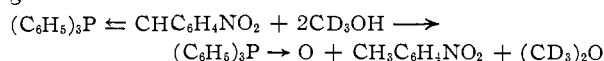
An additional mechanism in which an anion is displaced from the pentavalent intermediate to give a new intermediate which collapses to products also appears unlikely in view of the non-exchange of H₂O¹⁸ with (C₆H₅)₃P → O.¹⁰



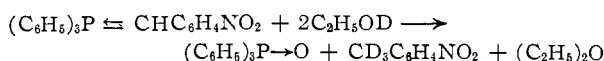
but



As indicated in Table II, we found that CD₃OH gave undeuterated nitrotoluene



whereas C₂H₅OD gave largely trideuterionitrotoluene

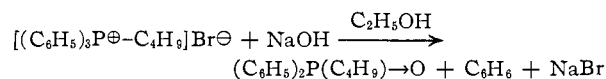


with some dideuterionitrotoluene, CHD₂C₆H₄NO₂, in a ratio of about 6 to 1. Deuterated products were analyzed by mass spectrometry. Nitrotoluene alone or in the presence of small amounts of decomposing phosphinemethylene does not exchange with C₂H₅OD under the conditions of our experiments. The corresponding phosphonium salt (C₆H₅)₃P⁺CH₂C₆H₄NO₂, however, exchanged readily in a D₂O-dimethylformamide solvent to give the deuterated salt, (C₆H₅)₃P⁺CD₂C₆H₄NO₂. These results clearly favor mechanism B with a rapid pre-equilibrium such as in eq. 5 resulting in deuteration of the phosphinemethylene by solvent to the major reacting species, (C₆H₅)₃P⁺CD₂C₆H₄NO₂.

(10) M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958).

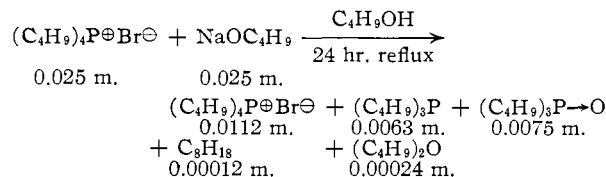
This mechanism is in keeping with the rest of our results; namely, the decreased reactivity of the unsubstituted benzyl compound compared to the *p*-nitro homolog and the inertness of the purely alkyl or aryl-alkylphosphonium salts in the absence of water.

No diethyl ether was detected when butyltriphenylphosphonium bromide was refluxed 24 hours with sodium ethoxide in ethanol, although benzene and butyldiphenylphosphine oxide were produced in 30% yield. The observed products are ascribed to traces of water introduced from the water-displacement gas collector attached to the reaction vessel.



Large amounts of recovered phosphonium salt underscore the sluggishness of the system. Further introduction of small amounts of water in a similar experiment increased the yield of butyldiphenylphosphine oxide to 82%. A reaction carried out for 120 hours in the same apparatus and examined at intervals by gas-liquid chromatography showed that most of the benzene was produced in the first half-hour and was followed by a slow, small increase in concentration with the simultaneous appearance of a benzene-water peak. Again no diethyl ether could be detected. Increased temperature also had little effect on the system. After 24 hours reflux in butanol with sodium butoxide, 38% of the butyltriphenylphosphonium bromide was recovered unchanged and 26% benzene was formed but only 2-3% of dibutyl ether was found. The small amount of dibutyl ether found is probably formed by thermal dehydration of the solvent in the presence of the organic and inorganic salts of the reaction. The benzene cleavage process was also applied to tetramethylenbis-(triphenylphosphonium bromide) to give tetramethylenbis-(diphenylphosphine oxide). The latter compound has been reported.⁷

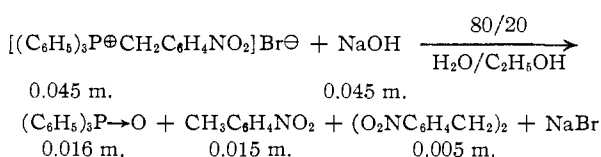
Tetraalkylphosphonium salts appear to be completely inert in solution with respect to the alkoxide decomposition process. The decomposition process reported by Hey and Ingold⁸ for tetramethyl- and tetraethylphosphonium ethoxides involves distillation to dryness and apparently proceeds, if at all, by some non-ionic process, perhaps one that is analogous to the four-center mechanism proposed for the Wittig reaction.⁶ We observed that the major reaction in refluxing butanol with tetrabutylphosphonium bromide and sodium butoxide was dissociation of the phosphonium salt.



The same reaction was carried out in an autoclave at 200° for 24 hours. Both vapor and liquid phases were examined by mass spectrometry. Only traces of butane, butene, octane and dibutyl

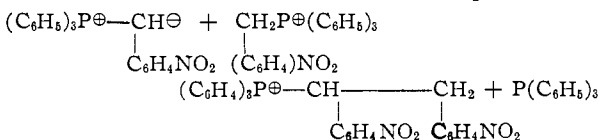
ether were found. The major product was tributylphosphine which was oxidized in the recovery process to the oxide. Tetraethylphosphonium ethoxide in refluxing ethanol was not observed to produce butane or other gaseous products. This again is in keeping with a simple ionic process such as B, above, for the decomposition reactions with formation of the tertiary phosphine oxide in a non-rate-controlling fast step.

As mentioned earlier, our first efforts at preparation of triphenyl-*p*-nitrobenzylidenephosphorane involved aqueous base neutralization as reported by Krohnke.⁸ This procedure was found to be unsatisfactory since considerable phosphinemethylene decomposition occurs. The possibility of a free radical decomposition process was suspected when *p,p'*-dinitrobenzyl was isolated as a reaction product. Krohnke actually used 20% aqueous ethanol as the solvent.



As a method of preparing the phosphinemethylene, this procedure gives a negligibly low yield of the red product contaminated with a coating of yellow nitrotoluene, and it was quickly abandoned in favor of the anhydrous ammonia technique described earlier. Krohnke reports nitrotoluene as a product of the aqueous base decomposition and in the experimental part of his paper mentions a substance of m.p. 169° extracted from the solution by ether but not investigated further. *p,p'*-Dinitrobenzyl melts at 178°.

It was quickly obvious that this was not a radical process but one in which the product distribution is solvent-dependent. The *p,p'*-dinitrobenzyl was not detected in decompositions in 80:20 alcohol-water solvent or in anhydrous ethanol. Presumably it is formed by an alkylation process such as depicted by Kantor and Hauser to explain bibenzyl-derived products from the reaction of benzylammonium salts and bases.¹¹ It is also possible, of



course, that the *p*-nitrobenzylidene ion is directly involved in the alkylation. This process may well be favored by formation of ion-pairs or organic clusters in the "organic part" of a mixed aqueous solvent with this effect increasing as the water content of the solvent rises or the solute becomes more "organic."¹² It is of interest in this connection that the well known Stevens rearrangement which has been established as an intramolecular process¹³ gives *p,p'*-dinitrobenzyl and *p*-nitrotoluene as minor products when the *p*-nitrobenzyl group mi-

grates.¹⁴ This may be interpreted also as an alkylation of starting material by a relatively stable dipolar ion intermediate or, alternatively, by direct alkylation of free *p*-nitrobenzylidene ion.

Experimental¹⁵

General Preparation of Phosphonium Halides.—In general, the phosphonium halides used in this investigation were prepared by adding an excess of alkyl halide to a refluxing stirred solution of tertiary phosphine. The conditions for these reactions and the properties of the resulting phosphonium halides are given in Table I. In one case, the preparation of tetramethylenebis-(triphenylphosphonium bromide), an excess of phosphine over the alkyl halide was used (2.5:1). Tetrabutylphosphonium bromide was the only salt prepared under a nitrogen atmosphere.

Most of the phosphonium salts described were insoluble in organic solvents and easily isolated by filtration at the completion of the reaction period. Those phosphonium salts which were soluble in the reaction solvent were isolated by stripping the excess solvent and precipitation with either hexane or diethyl ether. Crystalline tetrabutylphosphonium bromide was obtained by removing all the solvent and pumping the resulting sirupy residue for 24 hr. at elevated temperatures (75–100°).

Reaction of *p*-Nitrobenzyltriphenylphosphonium Bromide with Sodium Butoxide.—*p*-Nitrobenzyltriphenylphosphonium bromide (22.9 g., 0.05 mole) was mixed with 80.5 g. of butanol, chilled in an ice-bath and treated under nitrogen with stirring, with a chilled solution of sodium (1.2 g., 0.05 g.-atom) in 118.5 g. of butanol. A bright red color was observed immediately. The mixture was warmed to room temperature and refluxed for 4 hours, during which the red color was discharged. No gas collected in a gas buret connected to the system except for the small volume of nitrogen displaced upon heating the reaction mixture. The reaction mixture was cooled and a 15-ml. sample taken for analysis by gas-liquid chromatography. Dibutyl ether (0.027 mole) in butanol was detected by gas-liquid chromatography using a 2-meter diisodecyl phthalate column at 125°. The remainder of the reaction mixture was filtered to remove sodium bromide, then concentrated and distilled under reduced pressure. Distillation yielded 6.4 g. (0.047 mole) of *p*-nitrotoluene¹⁶ (b.p. 195° (19.0 mm.), m.p. 52°). The pot residue after distillation was dissolved in benzene, treated with charcoal and filtered. Treatment of the benzene filtrate with petroleum ether yielded 6.6 g. (0.031 mole) of triphenylphosphine oxide (m.p. 154–155°).¹⁶

Reaction of Tris-(2-cyanoethyl)-*p*-nitrobenzylphosphonium Bromide with Sodium Ethoxide.—Using the procedure described for the previous reaction, tris-(2-cyanoethyl)-*p*-nitrobenzylphosphonium bromide (20.2 g., 0.05 mole) in 100 ml. of absolute ethanol was treated with 1.2 g. (0.05 g.-atom) of sodium in 50 ml. of absolute ethanol at 0–5°. The reaction mixture turned a pinkish-red color immediately. It was refluxed for 10 hours during which time this color faded, then filtered while hot to remove sodium bromide. Upon cooling, 11.8 g. (0.056 mole) of tris-(2-cyanoethyl)-phosphine oxide¹⁶ slightly contaminated with *p*-nitrotoluene was obtained (m.p. 172–173° pure). Concentration of the filtrate from the phosphine oxide gave 2.8 g. of a mixture of *p*-nitrotoluene and tris-(2-cyanoethyl)-phosphine oxide plus a sirupy residue. This residue was pumped to dryness and yielded 4.4 g. (0.03 mole) of a yellow crystalline solid melting at 52° and identified as *p*-nitrotoluene.¹⁶ This reaction mixture was not analyzed for diethyl ether.

Reaction of Tributyl-*p*-nitrobenzylphosphonium Bromide with Sodium Ethoxide.—Tributyl-*p*-nitrobenzylphosphonium bromide (21.2 g., 0.05 mole) in 75 ml. of absolute ethanol was allowed to react with 1.2 g. (0.05 g.-atom) of sodium in 50 ml. of ethanol utilizing the previously described technique and apparatus. A deep purple red color appeared at the onset of the reaction which faded as refluxing was continued for 5 hours. After cooling, the mixture was treated with 100 ml. of water and extracted with three 50-ml. portions of benzene. The combined benzene extracts

(11) S. W. Kantor and C. R. Hauser, *THIS JOURNAL*, **73**, 4122 (1951).

(12) R. F. Hudson, private communication.

(13) R. A. W. Johnstone and T. S. Stevens, *J. Chem. Soc.*, 4487 (1955).

(14) T. S. Stevens, W. W. Snedden, E. T. Stillier and T. Thomson, *ibid.*, 2119 (1930).

(15) Melting points are uncorrected.

(16) Identity was confirmed by comparison of the infrared spectrum of this material with the spectrum of the pure compound.

were dried over calcium sulfate overnight, then filtered and the benzene removed. The benzene residue was distilled under reduced pressure and yielded 6.6 g. (0.048 mole) of *p*-nitrotoluene (b.p. 62–65° (0.25 mm.)) and 7.2 g. (0.033 mole) of tributylphosphine oxide (b.p. 145–146° (0.50 mm.)). The identity of both of these compounds was confirmed by infrared spectroscopy and mass spectrometry. No attempt was made to isolate diethyl ether in this reaction.

Preparation of Triphenyl-*p*-nitrobenzylidene phosphorane.
a. Formation in Aqueous Base.—Triphenyl-*p*-nitrobenzylidene phosphorane was prepared by a modification of K:ohnke's procedure.⁸ *p*-Nitrobenzyltriphenylphosphonium bromide (21.7 g., 0.045 mole) was mixed under nitrogen with 20 ml. of absolute ethanol. Meanwhile 1.04 g. (0.045 g.-atom) of sodium was mixed with 20 ml. of absolute ethanol. When the sodium had completely dissolved, 160 ml. of water was added to the ethoxide solution, the mixture chilled to 0–5° and added to the phosphonium salt slurry. The bright red phosphinemethylene formed immediately but, as the mixture warmed to room temperature over a period of 30 minutes, there was a color change to orange and a heavy orange oil formed. This oil was taken up in three 50-ml. portions of benzene and the combined benzene extracts were dried over calcium sulfate. After partially concentrating the benzene, orange-yellow crystals (0.5 g.) melting at 177–178°¹⁷ were obtained and identified by infrared and microanalytical data as *p,p'*-dinitrobenzyl (0.005 mole).

Anal. Calcd. for C₁₄H₁₂N₂O₄: C, 61.76; H, 4.44; N, 10.29; mol. wt., 272.26. Found: C, 61.15; H, 4.53; N, 10.01; mol. wt., 291.3.

The filtrate of the *p,p'*-dinitrobenzyl was freed of benzene and distilled under reduced pressure; 2 g. of *p*-nitrotoluene¹⁶ (b.p. 195° (19 mm.)) was obtained. The tarry distillation residue was extracted with benzene, treated with charcoal, filtered and concentrated. Treatment of this concentrate with petroleum ether gave 4.3 g. of triphenylphosphine oxide (m.p. 153–154°).

b. Formation in Anhydrous Ammonia.—Commercial sodium amide (4.0 g., 0.10 mole) was added to 1 liter of liquid ammonia and stirred until it dissolved. *p*-Nitrobenzyltriphenylphosphonium bromide (47.8 g., 0.10 mole) was introduced and the resulting bright red mixture stirred for 2 hours at –33°. At the end of this time the ammonia was allowed to evaporate under a slow flow of nitrogen. The residual red solid was taken up in hot benzene and filtered to remove sodium bromide. The benzene filtrate deposited red crystals which when filtered and dried weighed 12.0 g. (33% yield) and decomposed at 171–172°. Concentration of this filtrate yielded an additional crop of crystals which was stored in solvent in order to prevent decomposition. The yield of phosphinemethylene, therefore, was actually well above 50%. Infrared analysis showed little or no –NO₂ from *p*-nitrotoluene (1350, 1520 cm.⁻¹) but showed strong –NO₂ at 1585 and 1260 cm.⁻¹. There were additional peaks at 1090, 915 and at 785 and 826 cm.⁻¹. The ultraviolet spectrum showed absorption in the visible region at λ₅₀₅ mμ and λ shoulder 340 mμ; λ_{max} 273 mμ and λ_{max} 267 mμ. Nuclear magnetic resonance measurements of the phosphinemethylene in benzene gave a value of –13 p.p.m. relative to 85% phosphoric acid for the phosphorus atom.¹⁸ Microanalytical results indicated that the phosphinemethylene has partially complexed with the benzene solvent.

Anal. Calcd. for C₂₅H₂₀PNO₂·C₆H₆: C, 78.2; H, 5.50; N, 2.94; P, 6.50. Calcd. for C₂₅H₂₀PNO₂: C, 75.55; H, 5.07; N, 3.52; P, 7.79. Found: C, 76.59; H, 5.18; N, 3.18; P, 6.16.

This partial complexation of the triphenyl-*p*-nitrobenzylidene phosphorane with benzene was further confirmed by gas-liquid chromatography.

Alcohol Decomposition of Triphenyl-*p*-nitrobenzylidene phosphorane.—Triphenyl-*p*-nitrobenzylidene phosphorane was recrystallized from ethylene dichloride-petroleum ether. It was collected on a sintered glass plate, washed with cold petroleum ether, dried under reduced pressure for 2 hours and then stored under nitrogen for a short time before use.

(17) Lit. m.p. 179–180° for *p,p'*-dinitrobenzyl (A. Stelling and R. Fittig), *Ann. Chem.*, **137**, 260 (1866).

(18) In benzene, the phosphorus nuclear magnetic resonance of triphenylphosphine is +5.9 and triphenylphosphine oxide is –24 p.p.m.

Samples of this recrystallized phosphinemethylene (and in two cases the phosphinemethylene as obtained from benzene) were then allowed to react with butanol, ethanol and deuterated alcohols.¹⁹ For each reaction the dry triphenyl-*p*-nitrobenzylidene phosphorane was weighed in a rubber capped flask and small volumes (5–15 ml.) of alcohol were added by syringe. After standing for several days at room temperature these samples were analyzed by mass spectrometry. The accuracy of this analytical data was checked by a mixture of ethanol, diethyl ether and *p*-nitrotoluene of known concentrations.

Anal. Known: C₂H₅OH, 0.1580 mole; C₂H₅OC₂H₅, 0.0456 mole; CH₃C₆H₄NO₂, 0.0080 mole. Found: C₂H₅OH, 0.1580 mole; C₂H₅OC₂H₅, 0.044 mole, CH₃C₆H₄NO₂, 0.0095 mole.

Since triphenyl phosphine oxide is not sufficiently volatile to give a spectrum suitable for a mass spectrometric standard, its concentration in these reactions was calculated by difference assuming: (1) There were no components present other than those listed. (2) The concentrations of alcohols did not change during the reaction and therefore were used as internal standards.

These reaction mixtures were also analyzed by gas-liquid chromatography using a 2-meter diisodecyl phthalate column at 50° for the methanol and ethanol reactions and at 125° for the butanol reactions. The results of both analytical methods are summarized in Table II. It should be noted concerning the reactions of ethanol-*d* that preliminary analyses by mass spectrometry of mixtures of: (1) ethanol-*d* and *p*-nitrotoluene and (2) ethanol-*d* and *p*-nitrotoluene in the presence of triphenyl-*p*-nitrobenzylidene phosphorane showed that *p*-nitrotoluene did not undergo ordinary deuterium exchange with ethanol-*d*.

Reaction of *p*-Nitrobenzyltriphenylphosphonium Bromide with Deuterium Oxide.—*p*-Nitrobenzyltriphenylphosphonium bromide (0.02 mole, 9.5 g.) was mixed with 100 g. of deuterium oxide. The solid phosphonium salt did not go into solution. The mixture was heated to 50° and kept at this temperature for 3 hours. It was then cooled to room temperature and allowed to stand for 2 days. A sample of the phosphonium salt was withdrawn at the end of this time and analyzed by infrared spectroscopy. Comparison of the spectrum of this material with that of pure *p*-nitrobenzyltriphenylphosphonium bromide showed no deuterium exchange.

Approximately 100 ml. of freshly distilled dimethylformamide (b.p. 152–154°, *n*_D²⁰ 1.4272) was added to the original phosphonium salt-deuterium oxide mixture, and it was gently warmed. When solution was complete the mixture was cooled to room temperature and allowed to stand for 2 days. The excess dimethylformamide then was removed and the solid phosphonium salt precipitated. After drying, infrared analysis of this salt showed strong absorption bands at 2100 and 2200 cm.⁻¹, indicative of carbon-deuterium bonds. This spectrum also indicated that if any CH₂ remained, it was in amounts less than 10%. The melting point of the deuterated *p*-nitrobenzyltriphenylphosphonium bromide was 289–290°.

Reaction of Butyltriphenylphosphonium Bromide with Sodium Alkoxides. **a. Sodium Ethoxide.**—Sodium (1.6 g., 0.07 g.-atom) was allowed to react with 77.9 g. of absolute ethanol and the solution was cooled to room temperature. Butyltriphenylphosphonium bromide (27.4 g., 0.07 mole) was added all at once to the ethoxide solution and the mixture was refluxed overnight. No gases were evolved during this time. The mixture was cooled and filtered to remove sodium bromide, and the filtrate concentrated to yield 8.4 g. (0.021 mole) of unreacted phosphonium salt. The filtrate residue was extracted with hot hexane to give 5.4 g. (0.021 mole) of butyldiphenylphosphine oxide (m.p. 85°).

Anal. Calcd. for C₁₈H₁₈PO: C, 74.40; H, 7.41; P, 11.99. Found: C, 74.47; H, 7.47; P, 12.07.

The original reaction mixture was analyzed by gas-liquid chromatography and found to contain 3.3 weight per cent. benzene (0.026 mole). No diethyl ether was found in the reaction mixture.

b. Sodium Ethoxide.—The reaction of butyltriphenylphosphonium bromide with anhydrous sodium ethoxide (see a above) was repeated using larger quantities of phosphonium

(19) C₂H₅OD and CD₃OH were obtained from Merck & Co. Ltd. The butanol and ethanol used contained less than 0.05% by weight water as determined by Karl Fisher analysis.

salt (100 g., 0.25 mole), sodium (5.8 g., 0.25 g.-atom) and ethanol (200 g.). Samples of this reaction mixture were taken after 0.5, 2.5, 24, 48 and 120 hr. of refluxing and analyzed by gas-liquid chromatography using an Apiezon column at 145°. A small quantity of benzene was resolved after 30 minutes, but no diethyl ether was detected after 120 hours of reaction. After 24 hours a shoulder appeared on this benzene peak. This shoulder increased when water was added to the reaction sample. After refluxing for 120 hr. the reaction mixture was cooled, filtered and analyzed by mass spectrometry. Approximately 0.07 mole of benzene along with 0.03 mole of butyldiphenylphosphine oxide was found. No ether was detected by either mass spectrometry or infrared analysis.

c. **Sodium Ethoxide and Water.**—Butyltriphenylphosphonium bromide (40 g., 0.10 mole) was treated with sodium (2.3 g., 0.10 g.-atom) in 150 ml. of absolute ethanol under the same conditions as the previous experiment, with the exception that a few milliliters of water was introduced. After refluxing for 24 hr., the clear orange-yellow reaction liquid was distilled at atmospheric pressure. The low boiling distillation cuts (63–78°) were examined by infrared spectroscopy which found them to contain benzene. The distillation residue was extracted with hot benzene and the benzene extract filtered to remove sodium bromide. Upon concentration of the benzene to dryness, 21.1 g. of a crystalline solid was obtained melting at 86–88°. The solid represents 0.082 mole of butyldiphenylphosphine oxide.

d. **Sodium Butoxide.**—Sodium (2.3 g., 0.10 g.-atom) was allowed to react with butanol (100 ml.) and butyltriphenylphosphonium bromide (40 g., 0.10 mole) under the same conditions as the three previous experiments. After 28 hr. of refluxing the mixture was cooled and filtered to remove sodium bromide. The reaction mixture was analyzed by mass spectrometry which found 0.0258 mole of benzene and 0.0026 mole of dibutyl ether plus 0.00645 mole of butyldiphenylphosphine oxide. Upon concentration of the reaction filtrate, 15.3 g. (0.038 mole) of butyltriphenylphosphonium bromide was recovered plus a brown viscous sirup which would not crystallize. Analysis by mass spectrometry of the small volume of gas (450 cc.) displaced during this reaction showed trace amounts of hydrocarbons up to C₈.

Reaction of Tetramethylenebis-(triphenylphosphonium Bromide) with Sodium Butoxide.—Sodium (4.6 g., 0.2 g.-atom) was dissolved in 300 g. of butanol and 74.0 g. (0.1 mole) of tetramethylenebis-(triphenylphosphonium bromide) was added. This mixture was refluxed for 48 hr., then cooled and filtered. A sample of the filtrate was analyzed by gas-liquid chromatography, but showed only a peak for butanol. The filtrate was stripped to half its original volume and 23.0 g. (47.5% yield) of tetramethylenebis-(diphenylphosphine oxide) melting at 260–261° was obtained.²⁰ The

structure of this compound was further confirmed by infrared analysis.

Reaction of Tetrabutylphosphonium Bromide with Sodium Butoxide. a. **At Atmospheric Pressure.**—Tetrabutylphosphonium bromide (8.7 g., 0.025 mole) was dissolved in 60 ml. of butanol under nitrogen. Sodium (0.5 g., 0.022 g.-atom) was dissolved in an additional 60 ml. of butanol, and the butoxide solution was added to the phosphonium salt. The mixture was refluxed overnight. No gas was evolved during this time. The reaction mixture was analyzed by gas-liquid chromatography, using a 2-meter diisodecyl phthalate column at 125°; only butanol could be detected. This mixture was analyzed by mass spectrometry and contained 0.0063 mole of tributylphosphine, < 0.0075 mole of tributylphosphine oxide, < 0.000121 mole of octane and < 0.00242 mole of dibutyl ether. The original reaction mixture was filtered to remove sodium bromide and the filtrate was stripped to dryness. The residual sirup would not crystallize. It was analyzed for unreacted tetrabutylphosphonium bromide by means of a Volhard titration and 0.0112 mole was found.

b. **At High Pressure.**—Sodium (5.8 g., 0.25 g.-atom) was dissolved in 500 g. of butanol and mixed with 87 g. (0.25 mole) of tetrabutylphosphonium bromide in a stirred 1-liter autoclave. The reactants were heated for 24 hours at 200° and an average pressure of 12 atm. A gas sample was taken after 5 hours of reaction and analyzed by mass spectrometry. Trace quantities of butane and butene (14.4 mole per cent. butane and 22.0 mole per cent. butene in the gas sample) were found. The autoclave was cooled after 24 hr. and the reaction mixture was filtered. The filtrate was analyzed by gas-liquid chromatography. An Apiezon column at 152° resolved only butanol and dibutyl ether. The filtrate was also analyzed by mass spectrometry which found 0.14 mole of tributylphosphine oxide, 0.035 mole of dibutyl ether and 0.0021 mole of octane.

Reaction of Tetraethylphosphonium Iodide with Sodium Ethoxide.—Tetraethylphosphonium iodide (8.5 g., 0.031 mole) was mixed with 20 ml. of absolute ethanol under nitrogen. Sodium (0.7 g., 0.031 g.-atom) was dissolved in an additional 30 ml. of ethanol and the ethoxide solution was added to the phosphonium salt. The mixture was refluxed overnight. No gases were evolved.

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(20) Lit. m.p. 257° (see ref. 7).

STAMFORD, CONN.

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH DEPT., AGRICULTURAL DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

Phosphorothioates. I. The Reaction of Phosphorochloridothioates with Carboxylate and *t*-Butoxide Anions

BY BERNARD MILLER

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Acetate and trimethylacetate ions react with O,O-diphenyl phosphorochloridothioate with second-order kinetics to give mixed anhydrides, which react extremely rapidly with carboxylate ions to form O,O-diphenyl phosphorothioate anions and carboxylic anhydrides. Potassium *t*-butoxide reacts with O,O-diphenyl phosphorochloridothioate in a similar manner with the consumption of two moles of base. The published report of the preparation of O-acetyl O,O-diethyl phosphorothioate by the reaction of sodium acetate with O,O-diethyl phosphorochloridothioate could not be confirmed.

Introduction

Recently, Zemlyanskii and Malinovskii¹ reported the preparation of a series of acylated phos-

phorothioates by the reaction of carboxylic acid salts and O,O-diethyl phosphorochloridothioate (I) in ethanol solution. Among the compounds prepared in this manner was O-acetyl O,O-diethyl phosphorothioate (II) which was reported to be a water-soluble solid, m.p. 64°.

(1) N. I. Zemlyanskii and M. S. Malinovskii, *Zhur. Obshechei Khim.*, **26**, 1677 (1956).