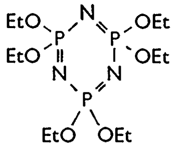
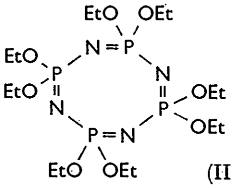
890. *Phosphorus–Nitrogen Compounds. Part XIV.*[1] *The Reaction of Benzoyl Chloride with Hexaethoxycyclotriphosphazatriene and Octaethoxycyclotetraphosphazatetraene*

By B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw

The reaction of hexaethoxycyclotriphosphazatriene with benzoyl chloride yields ethyl chloride, ethyl phosphenate, and 2,4,6-triphenyl-1,3,5-triazine. Octaethoxycyclotetraphosphazatetraene yields the same products. A reaction mechanism is proposed, and the reaction is compared with others in phosphorus nitrogen chemistry.

We recently reported[2] the reaction of benzoyl chloride with hexaethoxycyclotriphosphazatriene, (I), and octaethoxycyclotetraphosphazatetraene, (II), near 140°, the products from both of which are ethyl chloride, ethyl phosphenate, and 2,4,6-triphenyl-1,3,5-triazine, (III).


(I)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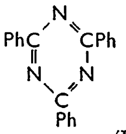
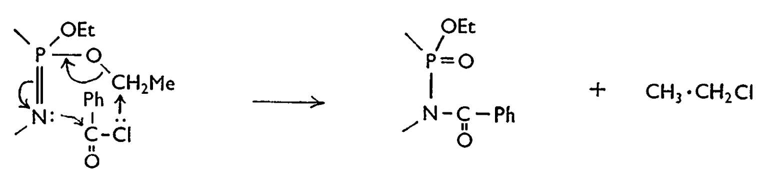

(III)

The initial step in the reaction of ethoxycyclophosphazenes with benzoyl chloride we believe to be nucleophilic attack by a ring nitrogen atom on the carbon atom of the carbonyl group yielding an *N*-benzoyloxophosphazane with the elimination of ethyl chloride.



Evidence for this initial step is that one mole of ethyl chloride is eliminated per phosphazene unit. That the reaction involves the phosphazene-ring nitrogen atom is demonstrated by the failure of 2,4,6-triethoxy-1,3,5-triethyl-2,4,6-trioxocyclotriphosphazane, where this structural feature is absent, to react with benzoyl chloride, even under somewhat

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[1] Part XIII, D. Dell, B. W. Fitzsimmons, and R. A. Shaw, *J.*, 1965, 4070.

[2] B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *Proc. Chem. Soc.*, 1962, 340.

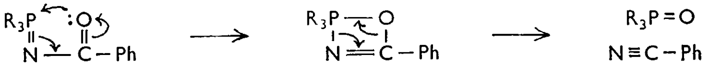
more drastic conditions. The mechanism proposed above is similar to that of the alkyl halide catalysed alkoxyphosphazene–oxophosphazane rearrangement.[3] An analogous reaction was described by Kabachnik and Gilyarov,[4] who studied the reaction of acetyl chloride with an alkoxymonophosphazene and showed the product to be an *N*-acyl-alkoxyoxophosphazane,

$$PhN{=}P(OR)_3 + Me{\cdot}COCl \longrightarrow PhN(COMe){\cdot}P(:O)(OR)_2$$

The reaction of the *N*-benzoyl derivative then proceeds by formation of ethyl phosphenate with concomitant splitting out of benzonitrile. The latter is known to trimerise in the presence of benzoyl chloride yielding 2,4,6-triphenyl-1,3,5-triazine.[5] Benzonitrile was found in the benzoyl chloride distilled from the reaction mixture, by gas–liquid chromatography.

A mechanism for the decomposition of the hypothetical oxophosphazane intermediate is suggested by consideration of the following reactions: that of hexachlorocyclotriphosphazatriene with sodium benzoate,[6] and the thermal decomposition of *N*-acylmonophosphazenes, $RC(:O)N:PR'_3$,[7–12] *N*-thioacylmonophosphazenes, $RC(:S)N:PR'_3$,[9] phosphazines, $R:N{\cdot}N:PR'_3$,[8,13] and phosphazides, $R{\cdot}N:N{\cdot}N:PR'_3$.[7,9,13,14]

Bezman and Reed[6] found that hexachlorocyclotriphosphazatriene reacted vigorously with sodium benzoate yielding benzonitrile, benzoic anhydride, and a phosphorus-containing compound believed to be a precursor of trisodium triphosphenate. They postulated an intermediate cyclic *N*-acyloxophosphazane, whose decomposition yields benzonitrile. Reactions of hexachlorocyclotriphosphazatriene with metal trifluoroacetates,[15,16] or with trifluororacetamide yields trifluoroacetonitrile,[16] in all cases. Monophosphazenes having unsaturated groups β to the nitrogen atom are frequently thermally unstable, and decompose with the elimination of a triply bonded molecule. Examples of this are given by the phosphazides,[7,9,13,14] the phosphazines,[8,13] the *N*-thioacylmonophosphazenes,[9] which have not been isolated but are believed to be intermediates in the reaction of tertiary phosphines with thioacyl azides, and the *N*-acylmonophosphazenes.[7–12] The thermal decomposition of *N*-acylmonophosphazenes provides a monomeric model of the final step of the benzoyl chloride reaction. It presumably proceeds by nucleophilic attack by the oxygen atom of the carbonyl group on the phosphorus atom.



Nucleophilic attack by carbonyl oxygen atoms on quinquevalent phosphorus atoms occurs in the decomposition of the intermediates of the Wittig reaction.[17]

A mechanism for the elimination of benzonitrile from an *N*-acyloxocyclophosphazane, involving nucleophilic attack by the carbonyl oxygen atom on phosphorus without the

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[3] B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J.*, 1964, 4459.

[4] M. I. Kabachnik and V. A. Gilyarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1956, 790.

[5] E. M. Smolin and L. Rapaport, " s-Triazines and Derivatives," Interscience, New York, 1959, p. 178.

[6] I. I. Bezman and W. R. Reed, *J. Amer. Chem. Soc.*, 1960, **82**, 2167.

[7] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.

[8] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

[9] L. Horner and A. Gross, *Annalen*, 1955, **591**, 117.

[10] A. V. Kirsanov, *Khim. i Prim. Fosfororgan Soedin., Akad. Nauk S.S.S.R. Kazansk. Filial., Trudy 1-oi Konf.*, 1955, 99 (*Chem. Abs.*, 1958, **52**, 251).

[11] A. V. Kirsanov, *Bull. Acad. Sci. U.S.S.R.*, 1954, 551.

[12] A. V. Kirsanov and R. G. Makirta, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 1033.

[13] G. Wittig and K. Schwarzenbach, *Annalen*, 1961, **650**, 1.

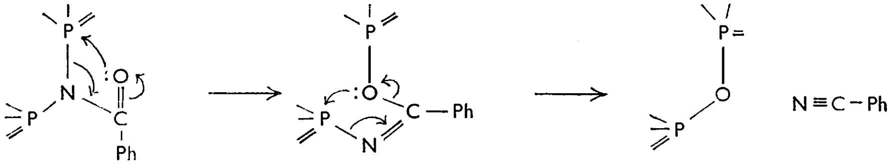
[14] H. Bock and W. Wiegräbe, *Angew. Chem. Internat. Ed.*, 1963, **2**, 484.

[15] A. B. Burg, quoted in ref. 6.

[16] T. J. Mao, R. D. Dresdner, and J. A. Young, *J. Inorg. Nuclear Chem.*, 1962, **24**, 53.

[17] S. Trippett, *Quart. Rev.*, 1963, **17**, 406.

necessity of an open-chain intermediate can now be drawn. Repetition of this process will give a phosphenate.



This mechanism is similar in some of its aspects to those proposed for the acid hydrolysis of the trisodium salt of trihydroxytrioxocyclotriphosphazane.[18]

In line with the observation that hexachlorocyclotriphosphazatriene resembles an acid chloride in its chemistry, it also undergoes reaction with hexaethoxycyclotriphosphazatriene at 150° with the formation of ethyl chloride and a polymeric phosphorus-containing material. Chlorodiphenylphosphine also reacts with hexaethoxycyclotriphosphazatriene at 140—175° with the formation of ethyl chloride (3 moles per mole of phosphazene), but the product, a white solid, rapidly hydrolyses and oxidises to give diphenylphosphinic acid.

EXPERIMENTAL

Ethyl chloride was identified by comparison of its infrared spectrum (gas cell) with that of an authentic sample. 2,4,6-Triphenyl-1,3,5-triazine was identified by infrared spectrum, m. p., mixed m. p., and elemental analysis.

Ethyl phosphenate* was isolated in a slightly impure state from these reactions, as the analytical figures show. The compound was identified by comparison of its infrared spectrum and refractive index with those given in the literature,[19] for triethyl triphosphenate, prepared by the action of ethyl iodide on trisilver triphosphenate in acetonitrile.

Reaction of Hexaethoxycyclotriphosphazatriene with Benzoyl Chloride.—Hexaethoxycyclotriphosphazatriene (7·02 g., 0·0173 mole) and benzoyl chloride (7·3 g., 0·052 mole) were heated together at 130—140° for 1 hr., the reaction mixture being swept out by a stream of dry nitrogen. Ethyl chloride (2·85 g., 0·044 mole) was evolved and collected in a cold-trap. Excess of benzoyl chloride (1·33 g., 0·0095 mole) was distilled out (b. p. 75°/11 mm.); this contained some benzonitrile (gas–liquid chromatography). On cooling the residue, 2,4,6-triphenyl-1,3,5-triazine, m. p. 239° crystallised out (Found: C, 81·6; H, 4·85; N, 13·1%; *M*, 300. Calc. for $C_{21}H_{15}N_3$: C, 81·6; H, 4·85; N, 13·6%; *M*, 309). The residue was dissolved in hot benzene, and on adding light petroleum, a heavy yellow oil was deposited. This was extracted three times with boiling benzene to remove impurities, giving ethyl phosphenate, n_D^{25} 1·4504 (lit.,[19] n_D^{21} 1·4435) (Found: C, 21·3; H, 5·8. Calc. for $C_2H_5O_3P$: C, 22·2; H, 4·6%).

Reaction of Octaethoxycyclotetraphosphazatetraene with Benzoyl Chloride.—Octaethoxycyclotetraphosphazatetraene (4·55 g., 0·0085 mole) was heated with benzoyl chloride (4·78 g., 0·034 mole) at 140—160° for 5 hr., the reaction mixture being swept out by a stream of dry nitrogen. Ethyl chloride (1·7 g., 0·026 mole) was evolved and 2,4,6-triphenyl-1,3,5-triazine, m. p. 239°, crystallised out of the reaction mixture on cooling.

Attempted Reaction of 2,4,6-*Triethoxy*-1,3,5-*triethyl*-2,4,6-*trioxocyclotriphosphazane with Benzoyl Chloride.*—2,4,6-Triethoxy-1,3,5-triethyl-2,4,6-trioxocyclotriphosphazane (0·86 g., 0·0021 mole) and benzoyl chloride (1·2 g., 0·0086 mole), when heated together at 170° for 2 hr. under nitrogen gave no ethyl chloride. Starting material, m. p. 74—75° (0·25 g., 30%) was recovered. The low recovery can be accounted for by the solubility of the compound in water used in the working up.

Reaction of Hexaethoxycyclotriphosphazatriene with Hexachlorocyclotriphosphazatriene.—Hexaethoxycyclotriphosphazatriene (6·32 g., 0·016 mole) and hexachlorocyclotriphosphazatriene (5·45 g., 0·016 mole) were dissolved in dry tetralin (50 ml.), and heated at 146° for 1 hr.

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* It is now known (G. Burkhardt, M. P. Klein, and M. Calvin, *J. Amer. Chem. Soc.*, 1965, **87**, 591), that this substance is probably a mixture of phosphenates.

[18] F. H. Pollard, G. Nickless, and R. W. Warrender, *J. Chromatog.*, 1962, **9**, 493.

[19] F. Cramer and H. Hettler, *Chem. Ber.*, 1958, **91**, 1181.

Ethyl chloride (1·2 g., 0·0185 mole) was evolved. A white solid (4·26 g.) was filtered off, and extracted in a Soxhlet apparatus with light petroleum to remove starting materials. The product was insoluble in the common solvents, and decomposed on attempted sublimation.

Reaction of Hexaethoxycyclotriphosphazatriene with Diphenylchlorophosphine.—Hexaethoxycyclotriphosphazatriene (5·0 g., 0·0124 mole) and diphenylchlorophosphine (13·3 ml., 0·074 mole) were heated together at 140—175° for 5 hr., the reaction mixture being swept out with a stream of nitrogen. Ethyl chloride (2·15 g., 0·033 mole) was evolved. The product, a white solid, rapidly hydrolysed and oxidised to give diphenylphosphinic acid.

The authors gratefully acknowledge the financial support (under P.L. 480) of the Agricultural Research Service of the U.S. Department of Agriculture.

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[*Received, January 29th,* 1965.]