752. *Phosphorus–Nitrogen Compounds. Part XIII.*[1] *Phenoxy- and* p-*Bromophenoxy-chlorocyclotriphosphazatrienes*

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The reaction between hexachlorocyclotriphosphazatriene and sodium phenoxide or sodium *p*-bromophenoxide in tetrahydrofuran has been investigated. All possible degrees of replacement $N_3P_3Cl_{6-n}(OAr)_n$ (n = 1—6; Ar = Ph or p-BrC_6H_4) were observed, thus providing the first example of this in the non-geminal replacement pattern of the cyclotriphosphazatriene system.

IN the partial replacement reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with a variety of reagents, geminal and non-geminal, patterns,[2,3] as well as combinations of these have been observed.[4-6] Although the nature of the primary products is sometimes

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[1] Part XII, R. Keat and R. A. Shaw, preceding Paper.
[2] S. K. Ray and R. A. Shaw, *J.*, 1961, 872.
[3] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.
[4] K. Hills and R. A. Shaw, *J.*, 1964, 130.
[5] R. Keat and R. A. Shaw, *J.*, 1965, 2215, and unpublished results.
[6] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, unpublished results.

rendered uncertain by *cis–trans*-isomerisations,[1,7,8] nevertheless a characteristic pattern is exhibited by each reaction which has been studied in sufficient detail.[4-6,9-11]

Earlier, we reported on the complete alcoholysis and phenolysis of chlorocyclophosphazenes;[12] here we discuss our findings on the replacement pattern of chlorine atoms by phenoxy- and *p*-bromophenoxy-groups in hexachlorocyclotriphosphazatriene.

The reactions between hexachlorocyclotriphosphazatriene, and the sodium aryloxides were carried out in tetrahydrofuran solution. Under our experimental conditions, it seems probable that the phenoxide ion (not solvated by tetrahydrofuran,[13] in contrast to the sodium ion [14]) will be a fairly reactive nucleophile towards 4-co-ordinated phosphorus atoms.

It seems that the initial reaction of hexachlorocyclotriphosphazatriene with sodium aryloxides is slower than with dimethylamine; however, differences in rate for successive replacement stages are smaller for the former than for the latter reagent. Thus, for example, when the hexachloride was allowed to react with eight equivalents of sodium phenoxide in tetrahydrofuran at −78° followed by warming to ambient temperature, all replacement stages were observed, with the tetraphenoxide ($n = 4$) predominating. Similar results were observed in dioxan just above the freezing point (11°) of this solvent. For good yields of the hexaphenoxy-derivative ($n = 6$) somewhat higher temperatures are preferred.[12] Even with stoicheiometric quantities of reagent, mixtures are obtained. By careful control of the reaction conditions, all possible degrees of replacement of phenoxychloro-derivatives, $N_3P_3Cl_{6-n}(OPh)_n$ (n = 1—6) could be isolated. Problems of separation are, however, considerably greater than with the other two most thoroughly investigated reactions.[5,11] Phenoxychlorophosphazenes were especially difficult to purify, since they proved to be low-melting solids or liquids. Evidence based on the preparation of dimethylamino-derivatives and their structural assignments,[15] shows that the replacement of chlorine atoms by phenoxy-groups under our experimental conditions follows predominantly a non-geminal scheme, giving both *cis*- and *trans*-isomers. The separation of one pure isomer was achieved with the tri-, $N_3P_3Cl_3(OPh)_3$, and tetra-phenoxy-derivatives, $N_3P_3Cl_2(OPh)_4$. In view of the importance of homogeneity, and heterogeneity, factors in the reactions of ambident nucleophiles [16] and, since chlorophosphazenes can be regarded as ambident electrophiles, we briefly examined the reaction of hexachlorocyclotriphosphazatriene with three equivalents of sodium phenoxide in light petroleum (b. p. 80—100°), in which this reagent was largely insoluble. Even at the boiling point of this solvent, the reaction proceeded extremely slowly. After 3 days, very little starting material remained, and the replacement pattern appeared to be similar to that obtained in tetrahydrofuran. The *p*-bromophenoxyphosphazenes, $N_3P_3Cl_{6-n}(p\text{-}OC_6H_4Br)_n$ (n = 1—6), appear to follow broadly the same course as the phenoxyphosphazenes; possessing higher melting points, they proved somewhat easier to purify.

Phenolysis and fluorination of hexachlorocyclotriphosphazatriene belong to the few examples, in which all degrees of replacement, $N_3P_3Cl_{6-n}Y_n$ (Y = OPh or F) (n = 1—6) are

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[7] R. Keat, R. A. Shaw, and C. Stratton, *J.*, 1965, 2223.

[8] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232.

[9] R. A. Shaw and F. B. G. Wells, *Chem. and Ind.*, 1960, 1189; K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J.*, 1964, 121.

[10] A. P. Carroll and R. A. Shaw, *Chem. and Ind.*, 1962, 1908; N. Boden, J. W. Emsley, J. Feeney, and H. Sutcliffe, *ibid.*, p. 1909.

[11] A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and R. F. M. White, *J.*, 1961, 1768; M. L. Heffernan and R. F. M. White, *ibid.*, p. 1382; G. Allen, M. Barnard, J. Emsley, N. L. Paddock, and R. F. M. White, *Chem. and Ind.*, 1963, 952.

[12] B. W. Fitzsimmons and R. A. Shaw, *J.*, 1964, 1735.

[13] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

[14] Cf. G. Wittig and E. Stahnecker, *Annalen*, 1957, **605**, 69; H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Amer. Chem. Soc.*, 1960, **82**, 2895; H. E. Zaugg, *ibid.*, p. 2903; *ibid.*, 1961, **83**, 837; H. D. Zook and T. J. Russo, *ibid.*, 1960, **82**, 1258; H. D. Zook and W. L. Gumby, *ibid.*, p. 1386.

[15] D. Dell, B. W. Fitzsimmons, and R. A. Shaw, unpublished results.

[16] Cf. N. Kornblum and A. P. Lurie, *J. Amer. Chem. Soc.*, 1959, **81**, 2705; D. Y. Curtin and D. H. Dybvig, *ibid.*, 1962, **84**, 225.

attainable in this chemical system. Whilst fluorination follows a geminal pattern, phenolysis yields, at least predominantly, non-geminal derivatives, thus providing the first example of all replacement stages in the latter pattern.

Lone-pair delocalisation of the electrons from the oxygen to the phosphorus atoms makes a ≡PCl•OPh grouping less susceptible to further nucleophilic attack than a $\equiv PCl_2$ grouping, thus giving rise to non-geminal derivatives. Independent physical evidence for this transfer of electrons to the ring (relative to the hexachloride) comes from basicity studies [17] as well as from the ultraviolet absorption spectra of the aryloxyphosphazenes.[15]

EXPERIMENTAL

Materials.—Hexachlorocyclotriphosphazatriene was recrystallised from light petroleum (b. p. 60—80°) to constant m. p. Diethyl ether, benzene, and light petroleum (b. p. 60—80°) were dried with sodium wire. Dioxan was purified by being boiled under reflux over sodium metal and then distilled from fresh sodium. Tetrahydrofuran was boiled under reflux over potassium hydroxide pellets and then distilled from sodium. Phenol and *p*-bromophenol were sublimed before use.

To prepare the sodium aryloxides, the required amount of sodium metal was cut into as small pieces as was conveniently possible and added to a solution of the phenol (~20% excess) in dry tetrahydrofuran. It is desirable to boil the solution in order to complete the reaction within a few hours.

Syntheses.—The reactions of hexachlorocyclotriphosphazatriene with sodium phenoxide. (a) *One equivalent.* Sodium (1·0 g., 43 mg.-atoms) was added to phenol (5·5 g., 59 mmoles) in tetrahydrofuran (100 ml.) and the solution added dropwise to a stirred solution of hexachlorocyclotriphosphazatriene (15·0 g., 43 mmoles) in tetrahydrofuran (200 ml.) at −78° during 1 hr. The solvent was removed *in vacuo* and the residue dissolved in light petroleum (100 ml.). The solution was washed successively with dilute hydrochloric acid, sodium hydrogen carbonate, and finally, several times with water. The extract was dried (Na_2SO_4) and, after evaporation of the solvent, a colourless oil remained (17·0 g., 94%), which slowly solidified (m. p. 40—48°). Molecular distillation at 60°/0·05 mm. gave *phenoxypentachlorocyclotriphosphazatriene*, m. p. 48° (63%) (Found: C, 18·3; H, 1·2; N, 10·8. $C_6H_5Cl_5N_3OP_3$ requires C, 17·8; H, 1·5; N, 10·4%).

(b) *Two equivalents.*—Sodium (2·0 g., 87 mg.-atoms) was added to phenol (19·0 g., 106 mmoles) in tetrahydrofuran (150 ml.) and the solution added dropwise to a stirred solution of hexachlorocyclotriphosphazatriene (15·2 g., 44 mmoles) in tetrahydrofuran (250 ml.) at −78° during 1 hr. The product was worked up to give a colourless oil (19·0 g.). Thin-layer chromatography with benzene–light petroleum (3 : 7) as eluant indicated the presence of two components in this product. A portion (2·63 g.) of the crude oil was chromatographed on silica gel (70 g.). Benzene–light petroleum (1 : 9) eluted *diphenoxytetrachlorocyclotriphosphazatrienes*, b. p. 130°/0·02 mm., $n_D^{25} = 1{\cdot}568$ (72%) (Found: C, 31·5; H, 2·2; Cl, 30·5; N, 9·1; P, 19·8. $C_{12}H_{10}Cl_4N_3O_2P_3$ requires C, 31·1; H, 2·2; Cl, 30·6; N, 9·1; P, 20·1%). Elution with benzene–light petroleum (2 : 3) yielded *triphenoxytrichlorocyclotriphosphazatrienes* [b. p. 160°/0·05 mm., $n_D^{25} = 1{\cdot}578$, (9·5%)] (Found: C, 41·4; H, 3·0; N, 7·8; P, 17·3. $C_{18}H_{15}Cl_3N_3O_3P_3$ requires C, 41·5; H, 2·9; N, 8·1; P, 17·9%). Attempts to crystallise these two liquid products by cooling them to −78°, or by cooling them to −78° followed by trituration with light petroleum, were unsuccessful.

Similar procedures were applied in the reactions described below. The compositions of the chromatographic eluting solvents are given in parentheses after each compoud.

(c) *Three equivalents.* Sodium (3·0 g., 130 mg.-atoms), phenol (14·6 g., 155 mmoles) in tetrahydrofuran (250 ml.), and hexachlorocyclotriphosphazatriene (15·0 g., 43 mmoles) in tetrahydrofuran (100 ml.) at −78° during 2 hr. gave a colourless oil (20 g.). Chromatography on silica gel yielded, as in (*b*), the diphenoxytetrachloro- [benzene–light petroleum (1 : 25)] (16%) and the triphenoxytrichloro-derivatives [benzene–light petroleum (1 : 5)] (57%). A total of 0·80 g. of this oily mixture of triphenoxy-isomers was placed on 40 thin-layer-chromatographic plates (20 × 20 cm.), coated with Kieselgel (Merck). When these were developed with

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[17] D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *Chem. and Ind.*, 1963, 164; *J.*, 1965, 2804.

ether–light petroleum (3 : 17) three spots were observed. The fastest-moving fraction contained about 5% of the material, with the remainder about equally distributed between the medium- and slow-moving fractions. Extraction yielded the slowest component as an oily solid which, on molecular distillation, gave *triphenoxytrichlorocyclotriphosphazatriene*, m. p. 68° (Found: C, 41·9; H, 3·1%). Details of the preparative thin-layer chromatography are described in Part IX [5] of this Series.

(d) *Four equivalents.* Sodium (2·1 g., 91 mg.-atoms), phenol (9·0 g., 96 mmoles) in tetrahydrofuran (250 ml.), and hexachlorocyclotriphosphazatriene (7·8 g., 22 mmoles) in tetrahydrofuran (250 ml.) at −78° during 1 hr. gave a colourless oil (11·0 g.). Chromatography on silica gel yielded *tetraphenoxydichlorocyclotriphosphazatriene* [benzene–light petroleum (3 : 7)] as a colourless oil (71%). After prolonged storage, partial crystallisation occurred. Separation of the crystalline part from the oil by hand-picking, followed by several recrystallisations from light petroleum, gave a pure *isomer* of m. p. 75°. The oil was purified by molecular distillation (180°/0·01 mm.) (Found for crystalline isomer: C, 49·7; H, 3·6; Cl, 12·2; N, 7·3; for oily isomers: C, 50·0; H, 3·4; N, 7·5%. $C_{24}H_{20}Cl_2N_3O_4P_3$ requires C, 49·7; H, 3·5; Cl, 12·3; N, 7·3%). Elution with benzene–light petroleum (1 : 1) yielded, after recrystallisation from light petroleum–ether (4 : 1), pentaphenoxychlorocyclotriphosphazatriene,[12] m. p. 67° (6%).

The reaction of hexachlorocyclotriphosphazatriene with four equivalents of sodium p-*bromophenoxide.* Sodium (0·8 g., 35 mg.-atoms) was added to *p*-bromophenol (7·9 g., 45 mmoles) in tetrahydrofuran (100 ml.) and the suspension of the reagent added dropwise to a stirred solution of hexachlorocyclotriphosphazatriene (3·0 g., 9 mmoles) in tetrahydrofuran (100 ml.) at room temperature during 1 hr. The reaction mixture was then boiled under reflux (2 hr.). When it was worked up as in (*a*) above, a viscous oil (4·81 g.) was obtained, which was chromatographed on silica gel (80 g.) with benzene–light petroleum mixtures as eluants (composition in parentheses). Elution of this gave eight fractions: (i) hexachlorocyclotriphosphazatriene, m. p. and mixed m. p. 113° (0·02 g., 1%); (ii) p-*bromophenoxypentachlorocyclotriphosphazatriene*, (1 : 9), m. p. 60° (after molecular distillation at 100°/0·01 mm.) (1·5%) (Found: C, 14·9; H, 0·8; N, 9·0%. $C_6H_4BrCl_5N_3OP_3$ requires C, 15·4; H, 0·9; N, 8·7%); (iii) *bis*-p-*bromophenoxytetrachlorocyclotriphosphazatrienes*, (3 : 17, early fractions) a viscous oil purified by molecular distillation (210°/0·01 mm.) (1·5%) (Found: C, 23·3; H, 1·3; N, 7·0%. $C_{12}H_8Br_2Cl_4N_3O_2P_3$ requires C, 23·2; H, 1·3; N, 6·8%); (iv) *tris*-p-*bromophenoxytrichlorocyclotriphosphazatriene* (3 : 17, remaining fractions), m. p. 129—130° (from light petroleum) (Found: C, 28·6; H, 1·7; N, 5·6%. $C_{18}H_{12}Br_3Cl_3N_3O_3P_3$ requires C, 28·5; H, 1·7; N, 5·5%): the mother-liquors from this recrystallisation yielded a mixture of solid isomers, m. p. 110—130°, which was indistinguishable by thin-layer chromatography from the pure isomer, m. p. 129—130° (Found: C, 28·7; H, 1·4; N, 6·1%): total yield of tris-isomers 15%; (v) *tetrakis*-p-*bromophenoxydichlorocyclotriphosphazatriene* (1 : 4), m. p. 87° (from light petroleum) (Found: C, 32·2; H, 2·1; N, 4·1. $C_{24}H_{16}Br_4Cl_2N_3O_4P_3$ requires C, 32·2; H, 1·8; N, 4·7%). The mother-liquors from this recrystallisation slowly solidified to give a mixture of tetrakis-isomers, m. p. 55—70°, which was indistinguishable by thin-layer chromatography from the pure isomer, m. p. 87°: total yield of tetrakis-isomers 12%; (vi) *pentakis*-p-*bromophenoxychlorocyclotriphosphazatriene*, (1 : 4 to 3 : 7), m. p. 106·5—108° (from light petroleum) (Found: C, 34·8; H, 2·2; N, 4·1%. $C_{30}H_{20}Br_5ClN_3O_5P_3$ requires C, 34·9; H, 1·9; N, 4·3%); (vii) *hexakis*-p-*bromophenoxycyclotriphosphazatriene*, (3 : 7 to 7 : 13), m. p. 175° [from light petroleum–chloroform (3 : 1)] (Found: C, 37·0; H, 2·3; N, 3·6%. $C_{36}H_{24}Br_6N_3O_6P_3$ requires C, 36·9; H, 2·1; N, 3·5%); (viii) p-*bromophenol*, (9 : 11 to 7 : 3), m. p. and mixed m. p. 64°. The yields of the *p*-bromophenoxychlorocyclotriphosphazatrienes reported here do not include the amount of product contained in the intermediate fractions, and are therefore lower than the true yields.

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