56. *The Organic Chemistry of Phosphorus. Part IV.* The Thermal Decomposition of Tetra-aryloxyphosphorus Monohalides: A New Method for the Preparation of Aryl Halides.*

By D. G. Coe, H. N. Rydon, and B. L. Tonge.

The thermal decomposition of tetra-aryloxyphosphorus monohalides † to give aryl halides and triaryl phosphates forms the basis of a new and convenient method for the preparation of aryl halides from phenols by the following series of reactions :

$$\begin{aligned} 3\mathrm{ArOH} + \mathrm{PCl_5} &\longrightarrow \mathrm{(ArO)_3PCl_2} + 3\mathrm{HCl} \\ \mathrm{(ArO)_3PCl_2} + \mathrm{Ar'OH} &\longrightarrow \mathrm{(ArO)_3(Ar'O)PCl} + \mathrm{HCl} \\ \mathrm{(ArO)_3(Ar'O)PCl} + \mathrm{RHal} &\longrightarrow \mathrm{(ArO)_3(Ar'O)PHal} + \mathrm{RCl} \\ \mathrm{(ArO)_3(Ar'O)PHal} &\longrightarrow \mathrm{Ar'Hal} + \mathrm{(ArO)_3PO} \end{aligned}$$

where Ar′ contains a more powerfully electron-attracting substituent than does Ar.

Although one of the "text-book" reactions of organic chemistry, the formation of aryl halides by the action of phosphorus pentahalides on phenols[1,2]

$$\mathrm{ArOH} + \mathrm{PHal_5} \longrightarrow \mathrm{ArHal} + \mathrm{POHal_3} + \mathrm{HHal}$$

is of little preparative value, except in the case of nitrophenols,[3] owing to the formation of considerable amounts of by-products, notably triaryl phosphates, the reaction is,

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* Part III, Rydon and Tonge, *J.*, 1956, 3043.

† The names tetra-aryloxyphosphorus monohalide and triaryloxyphosphorus dihalide are used, for convenience, for the compounds having empirical formulæ $\mathrm{(ArO)_4PHal}$ and $\mathrm{(ArO)_3PHal_2}$, respectively, although these are known to have ionic structures (cf. Part III).

[1] Gerhardt and Laurent, *Annalen*, 1850, **75**, 79; Riche, *ibid.*, 1862, **121**, 357; Mayer, *ibid.*, 1866, **137**, 221; Henry, *Ber.*, 1869, **2**, 710; Beilstein and Kurbatov, *Annalen*, 1875, **176**, 33.

[2] Autenrieth and Geyer, *Ber.*, 1908, **41**, 146.

[3] Engelhardt and Latschinov, *Ber.*, 1870, **3**, 98; Clemm, *J. prakt. Chem.*, 1870, **1**, 154.

however, of considerable potential value and the present work was undertaken with the object of developing a satisfactory procedure using triaryloxyphosphorus dihalides † in place of phosphorus pentahalides :

$$\mathrm{(ArO)_3PHal_2 + Ar'OH \longrightarrow Ar'Hal + (ArO)_3PO + HHal}$$

It was clear, from the work of Autenrieth and Geyer [2] and from our own experience, that the reaction would have to be carried out in two stages, the dihalide being first treated with a phenol to produce a monohalide .

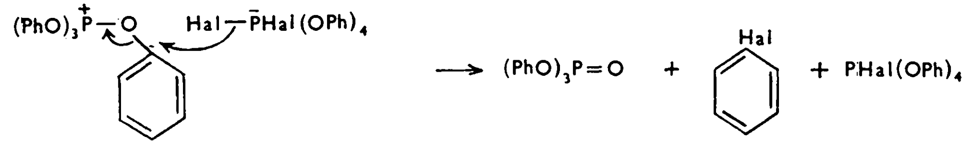
$$\mathrm{(ArO)_3PHal_2 + Ar'OH \longrightarrow (ArO)_3(Ar'O)PHal + HHal} \quad . \; . \; . \; . \; . \quad \text{(i)}$$

and this then being subjected to pyrolysis :

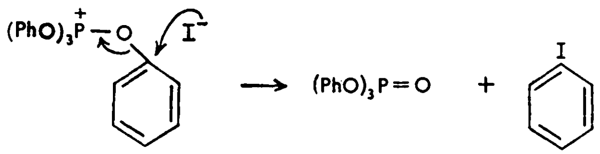
$$\mathrm{(ArO)_3(Ar'O)PHal \longrightarrow Ar'Hal + (ArO)_3PO} \quad . \; . \; . \; . \; . \; . \; . \quad \text{(ii)}$$

In preliminary experiments a number of triaryloxyphosphorus dichlorides,[4] prepared by the addition of chlorine to triaryl phosphites, were converted into tetra-aryloxyphosphorus monochlorides by reaction with a variety of phenols and the monochlorides were pyrolysed. The results, collected in Table 1 (p. 325), indicate that, in the decomposition of a mixed tetra-aryloxyphosphorus monochloride, the formation of a given aryl halide is favoured by the presence in that aryl group of an electron-attracting substituent. In addition to this electropolar influence there is also a statistical factor, tending to favour the formation of the aryl halide corresponding to the preponderating aryloxy-group; thus, pyrolysis of diphenoxy-di-(*p*-phenylphenoxy)phosphorus monochloride gave 4-chlorodiphenyl and chlorobenzene in the molar ratio 1·8 : 1, whereas pyrolysis of triphenoxy-*p*-phenylphenoxyphosphorus monochloride gave the same products in the molar ratio 0·8 : 1.

At this stage in our work the three pure tetraphenoxyphosphorus monohalides became available [4] and these were subjected to pyrolysis. All gave good yields of the halogenobenzene and triphenyl phosphate, establishing their decomposition as proceeding according to reaction (ii) above. For the monochloride and monobromide, which are known [4] to have the dimeric structure $\mathrm{[(PhO)_4P]^+[(PhO)_4PHal_2]^-}$, the mechanism of the reaction is clearly :



the tetraphenoxyphosphorus monohalide which is produced being, of course, available for further reaction in its dimeric, ionic form. The reaction with the monomeric iodide is analogous :



In both cases the formation of the aryl halide involves nucleophilic attack on one of the four benzene rings at its point of attachment to oxygen, and for a mixed tetra-aryloxy-compound this will lead, in agreement with the results summarised in Table 1, to preferential formation of the aryl halide containing the most powerfully electron-attracting substituent. The high yields of aryl halides obtained in suitable cases (see Tables 1, 2, and 3) indicate that the dimeric tetra-aryloxyphosphorus monohalides concerned have the structure $\mathrm{[(ArO)_3(Ar'O)P]^+[(ArO)_3(Ar'O)PHal_2]^-}$, rather than such alternatives as

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[4] Rydon and Tonge, *J.*, 1956, 3043.

$[(ArO)_2(Ar'O)_2P]^+[(Ar'O)_4PHal_2]^-$ or $[(ArO)_4P]^+[(ArO)_2(Ar'O)_2PHal_2]^-$, which could only give much reduced yields of Ar'Hal.

On the basis of these findings an experimental procedure has been developed which allows many phenols to be converted smoothly, and in good yield, into the corresponding aryl chlorides, bromides, and iodides (see Table 2). A triaryloxyphosphorus dichloride is first prepared by heating three mols. of a suitable phenol with phosphorus pentachloride :

$$3ArOH + PCl_5 \longrightarrow (ArO)_3PCl_2 + 3HCl$$

and is then converted into a mixed tetra-aryloxyphosphorus monochloride by heating with a second phenol, Ar'OH (cf. reaction i). Thermal decomposition (reaction ii) then yields the required aryl chloride, Ar'Cl. For the preparation of aryl bromides or iodides, the mixed tetra-aryloxyphosphorus monochloride is converted into the mono-bromide or -iodide, by halogen exchange with ethyl bromide or methyl iodide, and this is then subjected to thermal decomposition. It will be clear from the foregoing discussion that a good yield of the required halide, Ar'Hal, can only be expected if the corresponding phenol, Ar'OH, used in the second stage of the process, contains more strongly electron-attracting substituents than that, ArOH, used in the first stage. For this reason, *p*-*tert*.-butylphenol (commercially available at low cost) is more generally suitable as the first-stage phenol in preparative work than phenol itself, although phenol can be used satisfactorily in cases in which the second-stage phenol, Ar'OH, contains an electron-attracting substituent. The reaction fails with dihydric phenols.

The method has been applied successfully to the replacement of hydroxyl groups by halogen in a number of nitrogen heterocycles (see Table 3); it failed with 8-hydroxyquinoline and only two of the three hydroxyl groups in uric acid were replaced. In the heterocyclic series it seems that the new method succeeds only in those cases in which the phosphorus halides themselves may be used, but it gives better yields.

EXPERIMENTAL

Preliminary Experiments.—The following general procedure was used. Chlorine was passed, with stirring and cooling, into the appropriate triaryl phosphite until 1 mol. had been absorbed. The product was kept until it solidified, then the second phenol was added and the mixture heated at 120—140° for 72 hr. in an inert atmosphere. The mixture was then distilled, usually at atmospheric, but sometimes under reduced, pressure so that all material except the high-boiling phosphate residue passed over. Fractionation of the distillate gave the pure aryl halides which were suitably characterised.

The results are collected in Table 1.

TABLE 1. *Decomposition products of mixed tetra-aryloxyphosphorus monochlorides,* $(ArO)_3(Ar'O)PCl$.

Ar'	Products (% yield)	Ar'	Products (% yield)
	Ar = Ph		Ar = Ph
Ph	PhCl (88%)	*m*-$NO_2{\cdot}C_6H_4$	PhCl (42%); *m*-$Cl{\cdot}C_6H_4{\cdot}NO_2$ (54%)
p-$Me{\cdot}C_6H_4$	PhCl (67%)	*p*-$NO_2{\cdot}C_6H_4$	*p*-$Cl{\cdot}C_6H_4{\cdot}NO_2$ (68%)
p-$Ph{\cdot}C_6H_4$	PhCl (47%); *p*-$Ph{\cdot}C_6H_4Cl$ (37%)		
p-$Cl{\cdot}C_6H_4$	PhCl (43%); *p*-$C_6H_4Cl_2$ (18%)		Ar = *p*-C_6H_4Me
m-$CN{\cdot}C_6H_4$	PhCl (29%); *m*-$Cl{\cdot}C_6H_4{\cdot}CN$ (56%)	Ph	PhCl (66%)
o-$NO_2{\cdot}C_6H_4$	PhCl (7%); *o*-$Cl{\cdot}C_6H_4{\cdot}NO_2$ (45%)	*p*-$Cl{\cdot}C_6H_4$	*p*-$Me{\cdot}C_6H_4Cl$ (12%); *p*-$C_6H_4Cl_2$ (57%)

Two new triaryl phosphates were isolated as by-products, *viz., diphenyl* p-*tolyl phosphate*, b. p. 156—158°/0·002 mm., m. p. 18—20° (Found : C, 67·2; H, 5·2. $C_{19}H_{17}O_4P$ requires C, 67·1; H, 5·0%), and p-*chlorophenyl diphenyl phosphate*, b. p. 155—156°/0·0025 mm., n_D^{20} 1·5724 (Found : Cl, 10·0. $C_{18}H_{14}O_4ClP$ requires Cl, 9·8%).

Diphenyl phosphorochloridite (40·5 g.), in ether (70 ml.), was added dropwise with stirring to an ice-cold solution of *p*-phenylphenol (25·5 g.) and pyridine (12 g.) in ether (150 ml.). When addition was complete, the mixture was set aside for an hour, after which the pyridine hydrochloride was filtered off and washed with ether (200 ml.). Distillation of the combined ethereal solutions gave *diphenyl 4-diphenylyl phosphite* (49·2 g., 76%), b. p. 190—195°/0·015 mm. (Found: C, 74·8; H, 5·0. $C_{24}H_{19}O_3P$ requires C, 74·6; H, 5·0%). Conversion into the dichloride and reaction with *p*-phenylphenol by the general procedure gave chlorobenzene (30%), b. p. 130°, n_D^{20} 1·5280, and 4-chlorodiphenyl (55%), m. p. 69—73°.

Pyrolysis of Tetraphenoxyphosphorus Monohalides.—(a) *Chloride.* The monochloride (18·9 g.), prepared [4] from triphenyl phosphite (2 mols.) and chlorine (1 mol.), was distilled from a bath at 300°, giving chlorobenzene (4·6 g., 95%), b. p. 127—135°. The residue was triphenyl phosphate (13·6 g., 92%), m. p. 45—48° raised to 49° by recrystallisation from aqueous ethanol.

(b) *Bromide.* The monobromide (14·2 g.), distilled from a bath at 250°, gave bromobenzene (4·6 g., 92%), b. p. 154—160°, and triphenyl phosphate (9·4 g., 94%), m. p. 45—47°.

(c) *Iodide.* The monoiodide (35·2 g.) was similarly treated. The distillate was taken up in ether, washed with dilute alkali and water, dried, and redistilled, giving iodobenzene (11·1 g., 82%), b. p. 115—118°/100 mm. The residue, washed free from iodine, afforded triphenyl phosphate (18·4 g., 85%), m. p. 47—48° after recrystallisation from aqueous ethanol.

Preparation of Aryl Halides.—The general procedure was as follows. Phosphorus pentachloride (0·2 mole) was heated, with exclusion of moisture, for 4—5 hr. at 100° with phenol (0·6 mole) or at 120—140° with *p-tert.*-butylphenol (0·6 mole). The second phenol (0·2 mole if monohydric; 0·1 mole if dihydric) was added to the cooled product, which was then reheated as before.

For the preparation of aryl chlorides this crude tetra-aryloxyphosphorus monochloride was then decomposed by heating it at 250—350° for 10—20 min.; the chloride was isolated by distillation, usually under reduced pressure, and purified by redistillation or by recrystallisation.

For the preparation of aryl bromides or iodides the crude tetra-aryloxyphosphorus monochloride was refluxed for 2 hr. with ethyl bromide (0·4 mole) or methyl iodide (0·4 mole) before pyrolysis.

Details of preparations carried out in this way are given in Table 2.

TABLE 2. *Preparation of aryl halides.*

Phenol used in first stage (ArOH)	Phenol used in second stage (Ar′OH)	Pyrolysis temp.	Product (% yield); characterisation
PhOH	*p*-$NO_2\cdot C_6H_4\cdot OH$	200°	*p*-$NO_2\cdot C_6H_4Cl$ (91%); b. p. 128—132°/20 mm., m. p. 81—82° (lit., 83°)
,,	*p*-$NO_2\cdot C_6H_4\cdot OH$ *	200	*p*-$NO_2\cdot C_6H_4Br$ (77%); b. p. 135—140°/20 mm., m. p. 124—126° (lit., 126°)
,	*p*-$NO_2\cdot C_6H_4\cdot OH$ †	200	*p*-$NO_2\cdot C_6H_4I$ (53%); m. p. 171° (lit., 171·5°)
p-$Bu^t\cdot C_6H_4\cdot OH$ ‡	*p*-$NO_2\cdot C_6H_4\cdot OH$	250	*p*-$NO_2\cdot C_6H_4Cl$ (92%); m. p. 82°
,,	*p*-$NO_2\cdot C_6H_4\cdot OH$	250	*p*-$NO_2\cdot C_6H_4Cl$ (87%); m. p. 82—83°
,,	*p*-$NO_2\cdot C_6H_4\cdot OH$ *	250	*p*-$NO_2\cdot C_6H_4Br$ (82%); b. p. 120—125°/11 mm., m. p. 126°
,,	*p*-$NO_2\cdot C_6H_4\cdot OH$ †	250	*p*-$NO_2\cdot C_6H_4I$ (60%); m. p. 169—171°
,,	*o*-$NO_2\cdot C_6H_4\cdot OH$	250	*o*-$NO_2\cdot C_6H_4Cl$ (74%); m. p. 32° ((lit., 32—33°)
,,	*p*-$Cl\cdot C_6H_4\cdot OH$	300	*p*-$C_6H_4Cl_2$ (71%); b. p. 65—75°/20 mm., m. p. 53° (lit., 53°)
,,	*p*-$Cl\cdot C_6H_4\cdot OH$ *	250	*p*-$Cl\cdot C_6H_4Br$ (45%); b. p. 189—200°, m. p. 66—67° (lit., 67°)
,,	*p*-$Me\cdot C_6H_4\cdot OH$	360	*p*-$Me\cdot C_6H_4Cl$ (87%); b. p. 160—166°, n_D^{20} 1·5207 (lit., 1·5199)
,,	*p*-$Me\cdot C_6H_4\cdot OH$ *	300	*p*-$Me\cdot C_6H_4Br$ (51%); b. p. 180—188°, n_D^{20} 1·5505 (lit., 1·5490)
,,	α-$C_{10}H_7\cdot OH$	300	α-$C_{10}H_7Cl$ (60%), b. p. 116—118°/11 mm., n_D^{20} 1·6328 (lit., 1·6332)
,,	β-$C_{10}H_7\cdot OH$	300	β-$C_{10}H_7Cl$ (65%); b. p. 124—126°/10 mm., m. p. 55—56° (lit., 55—56°)
,,	*o*-$C_6H_4(OH)_2$	360	*p*-$Bu^t\cdot C_6H_4Cl$ (83%); b. p. 210—213°, n_D^{20} 1·5217 (lit., 1·5123)
,,	*m*-$C_6H_4(OH)_2$	360	*p*-$Bu^t\cdot C_6H_4Cl$ (44%); b. p. 211—214°
,,	*p*-$C_6H_4(OH)_2$	360	*p*-$Bu^t\cdot C_6H_4Cl$ (69%); b. p. 215—216°, n_D^{20} 1·5150

* Product treated with EtBr before pyrolysis.
† Product treated with MeI before pyrolysis.
‡ Commercial " butylphenol."

Preparation of Heterocyclic Chloro-compounds.—The procedure was as described for aryl halides, although a lower temperature usually sufficed for the final thermal decomposition. Various methods of working up were used, as indicated in Table 3, in which the details of the preparations are given.

TABLE 3. *Preparation of heterocyclic chloro-compounds.*

Heterocyclic compound used in second stage (Ar′OH)	Pyrolysis temp. and method of working up *	Product (% yield); characterisation
PhOH used in the first stage in all cases.		
2-Hydroxypyridine	250°; *b*	2-Chloropyridine (88%); b. p. 168—171° (lit., 170°)
3-Hydroxypyridine	150°; *b*	3-Chloropyridine (84%); b. p. 150—155°; picrate, m. p. 60° (lit., 60°); hydrochloride, m. p. 135° (lit., 135°)
2-Hydroxyquinoline	250°; *b*	2-Chloroquinoline (79%); b. p. 130—133°/9 mm.; picrate, m. p. 211—212° (lit., 212°)
Uracil	200°; *a*	2 : 4-Dichloropyrimidine (93%); b. p. 90—95°/20 mm., m. p. 62—63° (lit., 61—63°)
Barbituric acid	200°; *a*	2 : 4 : 6-Trichloropyrimidine (80%); b. p. 81—82°/8 mm.

* *a*, Product distilled from pyrolysis product. *b*, Cooled pyrolysis product treated with 2N-sodium carbonate and extracted with ether.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER, 1.

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