589. *The Reactivity of Organophosphorus Compounds. Part VI.*[1] N-*Chloroamidates.*

By J. I. G. Cadogan and W. R. Foster.

Various *N*-chloro-phosphor- and -phosphon-amidates, representatives of a new class of organophosphorus compounds, have been prepared. *N*-Aryl-*N*-chloro-derivatives have been shown to rearrange under heterolytic (Orton-type) and homolytic conditions to give nuclear chlorinated products. Ratios of isomerides and rates of rearrangement have been measured in some cases.

Although *N*-aryl-*N*-chloro-amides are well known in carbon chemistry, no reports of corresponding *N*-chloro-derivatives of phosphorus amides have appeared. Audrieth, Zimmer, and Zimmer's recent report [2] that they had failed to prepare such compounds leads us to describe the preparation and properties of various phosphorus *N*-chloroamides which we have recently investigated.

N-Aryl-*N*-chlorophosphoramidates such as diphenyl *N*-chloro-*N*-phenylphosphoramidate (I; R = Ar = Ph) are easily prepared by the reaction of t-butyl hypochlorite with the corresponding phosphoramidate in a methanolic solution of borax, a method used to convert acetanilide into *N*-chloroacetanilide.[3] *N*-Aryl-*N*-chlorophosphoramidates undergo the usual rearrangements in acid solution [4] to give nuclear-chlorinated derivatives, *e.g.*, diphenyl *N*-chloro-*N*-phenylphosphoramidate (I; R = Ar = Ph) rearranged in acetic acid in the presence of hydrochloric acid to a mixture of isomeric diphenyl *N*-chlorophenylphosphoramidates (II; R = Ph, Ar = C_6H_4Cl). The ratio of isomerides $[o/(m + p)]$ was determined in this and other cases by acid-hydrolysis to isomeric chloroanilines, which were analysed by gas–liquid chromatography. In this case the ratio was that expected from heterolytic chlorination. Similar results were obtained on rearrangement of diethyl *N*-chloro-*N*-phenylphosphoramidate (I; R = Et; Ar = Ph) in acetic–hydrochloric acid. The rearrangement of diphenyl *N*-chloro-*N*-phenylphosphoramidate (I; R = Ar = Ph) in acetic–hydrochloric acid in the presence of diphenyl *N*-*p*-tolylphosphoramidate (II; R = Ph; Ar = *p*-C_6H_4Me) was also carried out: hydrolysis of the product and analysis of the substituted anilines indicated the presence of chloro-*p*-toluidines (15%), showing intermolecular chlorination here, as in the carboxamide series.

Homolytic rearrangements of the *N*-chlorophosphoramidates have also been shown to occur readily. Irradiation with white light of a benzene solution of diethyl *N*-chloro-*N*-phenylphosphoramidate (I; R = Et, Ar = Ph), or reaction of this amidate with a catalytic amount of dibenzoyl peroxide in bromobenzene, led to homolytic chlorination of the nucleus, as revealed by the high (50%) yield of *o*-chloroaniline produced on acid hydrolysis. The large amount of *ortho*-substitution recalls the correspondingly high figure for

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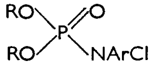
[1] Part V, Cadogan and Foster, preceding paper.

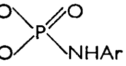
[2] Audrieth, Zimmer, and Zimmer, *J. prakt. Chem.*, 1959, **8**, 117.

[3] Chusty and Israelstam, *J. S. African Chem. Inst.*, 1956, **9**, 30.

[4] See Beard and Hickinbottom, *J.*, 1958, 2982.

benzene derivatives with free aryl radicals.[5] The ratio of isomerides (50% of *ortho*) produced by rearrangement of this amidate in boiling acetic acid indicates that homolytic chlorination occurs in this case also, even in the absence of free-radical initiators.


(I)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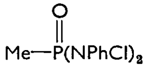
$Me{-}\overset{\overset{O}{\|}}{P}(NPhCl)_2$

(III)

The rates of rearrangement, induced by dibenzoyl peroxide, of diphenyl (I; R = Ar = Ph) and diethyl (I; R = Et; Ar = Ph) *N*-chloro-*N*-phenylphosphoramidate in bromobenzene were also measured. As expected, no significant differences were noted, but the rate contours showed autocatalytic characteristics, as in similar experiments with *N*-chloroacetanilide and related compounds.[6] The rearrangements in the acetanilide series appear to be considerably slower than those of the phosphoramidates. Qualitative observations indicated that *N*-aryl-*N*-chlorophosphoramidates were relatively stable on storage in daylight, *ca.* 3 or 4 days being needed for complete rearrangement. The compound believed to be *NN'*-dichloro-*P*-methyl-*NN'*-diphenylphosphonodiamidate (III), formed from the corresponding amidate, on the other hand, rearranged so rapidly that it could not be isolated.

EXPERIMENTAL

Gas–liquid chromatography was carried out as described in Part V.[1]

Preparation of Amidates.—t-Butyl hypochlorite was prepared by the method of Teeter *et al.*[7] The following amidates were prepared by inter-reaction of the appropriate chloridate and amine. Recorded values for m. p.s are given in parentheses; diethyl *N*-phenylphosphoramidate, m. p. 96° (96·5° [8]); diphenyl *N*-phenylphosphoramidate, m. p. 129—130° (128—129° [9]); diphenyl *N*-*p*-tolylphosphoramidate, m. p. 135° (134° [10]); ethyl *NN'*-diphenylphosphorodiamidate, m. p. 114·5° (114° [11]); *P*-ethyl-*NN'*-diphenylphosphonodiamidate, m. p. 147° (147° [12]); *ethyl* P-*ethyl*-N-*phenylphosphonamidate*, pale yellow, b. p. 134°/0·05 mm., m. p. 32° (Found: C, 56·1; H, 7·6. $C_{10}H_{16}NO_2P$ requires C, 56·3; H, 7·5%); diethyl *N*-*p*-chlorophenylphosphoramidate, m. p. 73° (76° [13]); 1-diphenoxyphosphinylpiperidine, m. p. 74·5° (70° [11]); diphenyl phosphoramidate, m. p. 150—152° (148—149° [9]); diethyl phosphoramidate, m. p. 52° (50—51° [14]); diphenyl *N*-cyclohexylphosphoramidate, m. p. 101—102° (101—102° [9]).

Preparation of N-*Chloroamidates.*—The method is exemplified by the following preparation of diphenyl *N*-chloro-*N*-phenylphosphoramidate. t-Butyl hypochlorite (5·25 g., 6 ml.) was added to diphenyl *N*-phenylphosphoramidate (11·0 g.) in 4% methanolic borax (200 ml.). After 5 min. the mixture was poured into water (1 l.), and the oil which separated was extracted with chloroform. The extracts were washed with water and dried ($MgSO_4$). Evaporation at 20 mm. left an almost colourless solid which on recrystallisation from light petroleum (b. p. 40—60°) gave colourless *diphenyl* N-*chloro*-N-*phenylphosphoramidate* (9 g.), m. p. 63·5—64·5° (Found: Active Cl, 10·5. $C_{18}H_{15}ClNO_3P$ requires Cl, 10·85%).

The following *N*-chloroamidates were similarly prepared: *Diethyl* N-*chloro*-N-*phenylphosphoramidate*, a yellow liquid (92%), n_D^{25} 1·5089 (Found: Active Cl, 13·0. $C_{10}H_{15}ClNO_3P$ requires Cl, 13·5%), which decomposed on storage to a solid from which was isolated diethyl *N*-*p*-chlorophenylphosphoramidate, m. p. and mixed m. p. 70°; the chloroamidate is 40% decomposed after 48 hr. at 25°. *Diphenyl* N-*chloro*-N-p-*tolylphosphoramidate*, yellow (95%), m. p. 62—63° (Found: Active Cl, 9·1. $C_{19}H_{17}ClNOP$ requires Cl, 9·5%). *Diethyl* N-*chloro*-p-*chlorophenylphosphoramidate*, a yellow liquid (96%), n_D^{25} 1·5170 (Found: Active Cl, 11·5.

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[5] Augood and Williams, *Chem. Rev.*, 1957, **57**, 123.
[6] Ayad, Beard, Garwood, and Hickinbottom, *J.*, 1957, 2981.
[7] Teeter, Bachmann, Bell, and Cowan, *Ind. Eng. Chem.*, 1949, **41**, 849.
[8] Foster, Overend, and Stacey, *J.*, 1951, 980.
[9] McCombie, Saunders, and Stacey, *J.*, 1945, 380.
[10] Michaelis and Schulze, *Ber.*, 1894, **27**, 2572.
[11] Michaelis, *Annalen*, 1903, **326**, 129.
[12] Cadogan, *J.*, 1957, 1079.
[13] Otto, *Ber.*, 1895, **28**, 613.
[14] Atherton, Openshaw, and Todd, *J.*, 1945, 660.

$C_{10}H_{14}Cl_2NO_3P$ requires 1Cl, 11·9%). *Ethyl* N-*chloro*-P-*ethyl*-N-*phenylphosphonamidate*, yellow liquid (93%), n_D^{25} 1·5164 (Found: Active Cl, 13·6. $C_{10}H_{15}ClNO_2P$ requires Cl, 14·3%), which slowly decomposed at room temperature (n_D^{25} 1·5207 after 3 hr.). *Diphenyl* N-*chloro*-N-*cyclohexylphosphoramidate*, a colourless liquid (98%), n_D^{16} 1·5508 (Found: Active Cl, 8·3. $C_{18}H_{21}ClNO_3P$ requires Cl, 9·7%), that is unstable (20% purity after 48 hr.) and was prepared in subdued light.

Attempts to prepare these compounds by reaction of t-butyl hypochlorite in the absence of borax but in ether or benzene gave impure products. Attempts to prepare pure samples of ethyl *NN'*-dichloro-*NN'*-diphenylphosphorodiamidate and *NN'*-dichloro-*P*-ethyl-*NN'*-diphenylphosphonodiamidate failed, due to their extreme instability; diphenyl phosphoramidate was recovered from the reaction mixture, but tars were also formed.

Rearrangement of Diphenyl N-*Chloro*-N-*phenylphosphoramidate*.—(i) *In acetic acid.* The *N*-chloroamidate (1 g.) in acetic acid (25 ml.) was boiled under reflux for 48 hr. The mixture was poured into water (100 ml.), and the product extracted in methylene chloride and dried ($MgSO_4$). Evaporation left an oil which on treatment with light petroleum (b. p. 40—60°) gave diphenyl *N-p*-chlorophenylphosphoramidate (0·25 g.) with m. p. and mixed m. p. 116° and the correct infrared spectrum.

(ii) *In acetic–hydrochloric acid.* The *N*-chloroamidate (3 g.) in acetic acid (20 ml.) was treated with 10N-hydrochloric acid (6 drops). The reaction was complete after 4 min. (starch–iodide paper). After neutralisation with solid sodium carbonate and addition of water (20 ml.) crude diphenyl *N-p*-chlorophenylphosphoramidate (2·8 g.; m. p. 90—104°, mixed m. p. 110°) separated. Hydrolysis of this product with boiling 4N-hydrochloric acid for 1½ hr. gave a mixture of monochloroanilines (90%).

Comparison of the gas–liquid chromatogram of this mixture with that of authentic mixtures showed its composition to be *o*-chloroaniline (13·5 ± 1%) and *m*- and *p*-chloroanilines (86·5 ± 1%). The *meta*- and *para*-isomers could not be resolved.

(iii) *In benzene under the influence of light.* The *N*-chloroamidate (3 g.) in benzene (25 ml.) was irradiated by white light (Crompton Spotlight; 150 w) for 72 hr. at room temperature. The excess of benzene was removed by distillation, the last traces being examined by gas–liquid chromatography for the presence of chlorobenzene. Only benzene was detected. The residual oil, on treatment with light petroleum (b. p. 40—60°), gave diphenyl *N-p*-chlorophenylphosphoramidate, m. p. 100—105°. Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave the pure product (0·4 g.), m. p. and mixed m. p. 116—117°. Repetition of the experiment with subsequent acid-hydrolysis of the residual oil, as described above, gave a mixture of anilines (*o*-chloroaniline 53%; *m*- and *p*-chloroaniline 46%; aniline *ca.* 2%).

Rearrangements of Other N-*Chloroamidates*.—*Diethyl* N-*chloro*-N-*phenylphosphoramidate*. Rearrangements as described above gave the following results: acetic–hydrochloric acid gave a mixture of diethyl chlorophenyl-amidates, from which was isolated the *para*-isomer (m. p. and mixed m. p. 72°). Hydrolysis gave *o*-chloroaniline (18%) and *m*- + *p*-chloroaniline (82%). Rearrangement of the *N*-chloroamidate in boiling acetic acid followed by acid-hydrolysis gave *o*-chloroaniline (50%) and *m*- + *p*-chloroaniline (50%). Irradiation by white light gave a similar mixture, from a portion of which was isolated diethyl *p*-chlorophenylphosphoramidate (m. p. and mixed m. p. 71—73°); hydrolysis of another portion gave *o*-chloroaniline (54%), *m*- + *p*-isomers (46%). Similar results (49, 51%) were obtained in a reaction catalysed by dibenzoyl peroxide in bromobenzene at 105°.

(ii) *Diethyl* N-*chloro*-N-p-*chlorophenylphosphoramidate*. Rearrangement of the amidate (1·3 g.) in acetic–hydrochloric acid gave *diethyl* N-2,4-*dichlorophenylphosphoramidate* (0·5 g.), m. p. 62—63° [from light petroleum (b. p. 60—80°)] (Found: C, 40·7; H, 4·79; N, 4·4; Cl, 30·0%; *M*, 257. $C_{10}H_{14}Cl_2NOP$ requires C, 40·3; H, 4·7; N, 4·70; Cl, 23·85%; *M*, 266). Hydrolysis of the amidate by 4N-hydrochloric acid gave 2,4-dichloroaniline, m. p. and mixed m. p. 58—59° (benzoyl derivative, m. p. and mixed m. p. 117°). Michaelis,[11] however, reported m. p. 105° for this 2,4-dichlorophenylphosphoramidate.

(iii) *Ethyl* N-*chloro*-P-*ethyl*-N-*phenylphosphonamidate*. Rearrangement in acetic–hydrochloric acid, followed by acid-hydrolysis, gave *o*-chloroaniline 17% and *m*- + *p*-chloroaniline 83%.

(iv) *Diphenyl* N-*chloro*-N-*phenylphosphoramidate in the presence of diphenyl* N-p-*tolylphosphoramidate*. Rearrangement of this *N*-chloroamidate in the presence of diphenyl *N-p*-tolylphosphoramidate (1 mol.) in acetic–hydrochloric acid followed by acid-hydrolysis gave a mixture of amines: *p*-toluidine + *o*-chloroaniline 31·5%, *m*- + *p*-chloroanilines 36·5%, 2-chloro-4-methylaniline + 3-chloro-4-methylaniline 15%, aniline 17%.

Rates of Rearrangement of N-*Chloroamidates.*—Dibenzoyl peroxide (0·05 mol.) was added to a 0·1M-solution of the *N*-chloroamidate in bromobenzene at 105°. Aliquot parts (10 ml.) were removed at intervals and dissolved in acetic acid and the amounts of positive chlorine were determined iodometrically. Control experiments were also carried out. Because the reactions were autocatalytic, first-order rate constants were calculated from the initial slopes of the curves. Diphenyl *N*-chloro-*N*-phenylphosphoramidate had $10^4k = 1·5$ (±0·5) sec.$^{-1}$; diethyl *N*-chloro-*N*-phenylphosphoramidate had $10^4k = 2·0$ (±0·5) sec.$^{-1}$.

KING'S COLLEGE, STRAND,
LONDON, W.C.2.

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