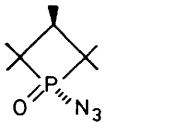
N-Chloro- and *NN*-Dichloro-derivatives of Some Phosphinic Amides: Preparation and Reactions with Anthracene, Anisole, and Triphenylarsine

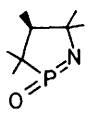
By **Martin J. P. Harger** * and **Michael A. Stephen**, Department of Chemistry, The University, Leicester LE1 7RH

1-Amino-2,2,3,4,4-pentamethylphosphetan 1-oxide (5) and di-t-butylphosphinic amide (9) can be converted into the *N*-monochloro- and *NN*-dichloro-derivatives with t-butyl or sodium hypochlorite. The *N*-monochloro-amides partially disproportionate in solution. They can be prepared conveniently by evaporation of the solvent from a solution containing equimolar amounts of the appropriate amide and *NN*-dichloroamide. The *N*-monochloro- and *NN*-dichloro-derivatives of (5) are reduced to the amide by sodium methoxide in methanol; no rearrangement (ring-expansion) is observed. They react with anthracene to give 9-chloro- and 9,10-dichloro-anthracene and with anisole to give chloroanisole (mainly the *para*-isomer). Triphenylarsine reacts with the *NN*-dichloroamide to give (after reductive work-up) an arsoranylideneamine, which can also be prepared from the amide (5) and diacetoxytriphenylarsorane.

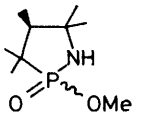
An azidophosphetan oxide such as (1) decomposes with loss of nitrogen on photolysis in methanol. The major product is a 1,2-azaphospholidone [*e.g.* (3)] resulting from addition of methanol to the intermediate monomeric metaphosphonamidate [*e.g.* (2)] formed by migration of a ring-carbon atom from phosphorus to nitrogen.[1,2] Requiring a non-photochemical method of achieving this type of ring expansion we considered thermolysis of azidophosphetan oxides. However, we found that (1), like other phosphinic azides,[3] is remarkably stable towards heat; *e.g.* in benzene solution it decomposes only very slowly (days) even at 200 °C.[4] In a solvent such as methanol, which would trap efficiently any monomeric metaphosphonamidate that might be formed, phosphinic azides will generally suffer solvolytic displacement of azide ion more readily than they will thermolyse with loss of nitrogen. We have therefore turned to derivatives of the aminophosphetan oxide (5). In particular, we hoped that the *N*-chloro- (6) and *NN*-dichloro- (7) derivatives would, with suitable reagents, undergo ring expansion with formal loss of HCl and Cl_2, respectively. Although this hope has not been realised, some interesting chemistry has emerged.



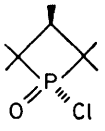
(1)



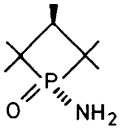
(2)



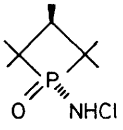
(3)



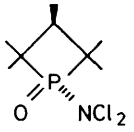
(4)



(5)



(6)



(7)

RESULTS AND DISCUSSION

Reaction of *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (4)[5] with ammonia in ethanol gave the amide (5) having an n.m.r. spectrum consistent with it being a single stereoisomer. Since (4) is known to react with a variety of nucleophiles with retention of configuration at phosphorus[6] it is assumed that the NH_2 group in (5) is, like the Cl atom in (4), *trans* to the 3-Me group.

The amide (5) reacts readily with t-butyl hypochlorite in dichloromethane at room temperature. Using two molar equivalents of hypochlorite the product is a pale yellow crystalline solid, m.p. 87—89 °C, having an i.r. spectrum (Nujol) in which no N–H group is apparent; the n.m.r. spectrum and elemental analysis accord with the *NN*-dichloroamide structure (7). The same product is obtained when the amide (5) in dichloromethane is shaken with an excess of aqueous sodium hypochlorite, or when chlorine is bubbled through a solution of (5) in an aqueous acetate buffer.

When only one molar equivalent of t-butyl hypochlorite in dichloromethane is used, the amide (5) gives a different product. This is colourless, m.p. 125—130 °C, and has a peak at 2 680 cm^{-1} in the i.r. spectrum (Nujol mull) indicative, perhaps, of a P(O)NHCl group. Elemental analysis supports the *N*-monochloroamide structure (6), as does the conversion of the compound into the dichloroamide (7) with t-butyl hypochlorite or sodium hypochlorite, and into the amide (5) with aqueous sodium metabisulphite. In spite of all this, the ^1H n.m.r. spectrum of the compound in CH_2Cl_2 or $CDCl_3$ clearly contains too many methyl resonances to be compatible with structure (6).

With a view to clarifying the situation, we decided to examine di-t-butylphosphinic amide (9) [the acyclic analogue of (5)] and its *N*-chlorinated derivatives. Anticipating that the bulky alkyl groups in $Bu^t_2P(O)Cl$ would hinder its reaction with ammonia, we prepared the amide by treating Bu^t_2PCl with ammonia and then oxidising (H_2O_2) the aminophosphine.

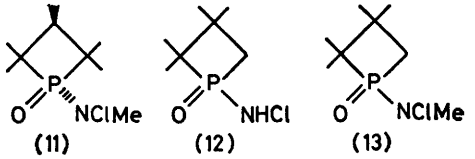
Di-t-butylphosphinic amide reacts with an excess of t-butyl hypochlorite in dichloromethane or aqueous sodium hypochlorite to give a product, m.p. 40—41 °C, which is readily characterised as the *NN*-dichloroamide (10). The product formed with one molar equivalent of t-butyl hypochlorite has m.p. 52—54 °C, $\nu_{max.}$ (Nujol mull) 2 705 cm^{-1}, and is converted into the *NN*-dichloro-

amide with more t-butyl hypochlorite. Here again, however, the ^1H and ^{31}P n.m.r. spectra in CH_2Cl_2 are too complex to be ascribed simply to the *N*-monochloroamide (8). Thus the ^1H n.m.r. spectrum indicates the presence of three types of P–Bu^t group, at δ 1.49, 1.34, and 1.25 (ratio *ca.* 1 : 2 : 1; all d, J_{PH} 14 Hz), and three ^{31}P n.m.r. signals (δ_P −80.6, −63.8, and −55.0 p.p.m.) confirm the presence of three distinct compounds. Comparing this data with that for the amide (9) (δ_H 1.24, δ_P −55.0) and the *NN*-dichloroamide (10) (δ_H 1.48, δ_P −80.6) the explanation becomes obvious: the *N*-monochloroamide (8) (δ_H 1.34, δ_P −63.8) disproportionates in solution, to the extent of *ca.* 50% (at 20 °C).

$$\underset{(8)}{2Bu^t_2P(O)NHCl} \rightleftharpoons \underset{(9)}{Bu^t_2P(O)NH_2} + \underset{(10)}{Bu^t_2P(O)NCl_2}$$

Confirmation of the equilibrium shown above came from mixing equal amounts of the amide (9) and the dichloroamide (10) in dichloromethane: not only was the ^1H n.m.r. spectrum identical to that of a solution of the monochloroamide (8), but on removal of the solvent solid (8) separated out. This is reminiscent of the preparation of *N*-monochlorocarbamates (ROCONHCl) by mixing of the appropriate amide and *NN*-dichloroamide,[7] while analogous disproportionations have been noted for *N*-chlorosulphonamides [8] and *N*-bromocarbamates.[9] Monochloro-derivatives of primary phosphinic amides do not seem to have been examined before although $Ph_2P(O)NCl_2$ has been reported,[10a] as have some *NN*-dichlorophosphoramidates [$(RO)_2P(O)NCl_2$].[10]

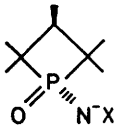
Returning to *N*-monochloroaminophosphetan oxide (6), it can similarly be established that disproportionation (*ca.* 70% at 20 °C) occurs in solution, and that this is responsible for the unexpectedly complex ^1H n.m.r. spectrum. For the monochloro-amide (11) the presence of an *N*-methyl group precludes disproportionation and the n.m.r. spectrum is now quite straightforward. Similarly, the *N*-monochloroaminotetramethylphosphetan oxide (12) in solution gives rise to a complex n.m.r. spectrum whereas that of the *N*-methyl analogue (13) is relatively simple.



(11) (12) (13)

We have experienced no problems in the preparation and handling of *N*-chlorinated phosphinic amides but we would draw attention to the recent report [11] of an explosion during the attempted chlorination of a dialkyl phosphoramidate.

Our original intention was to use the *N*-chlorinated amides (6) and (7) as sources of the anion (14). This, we hoped, would undergo Hofmann-like rearrangement with loss of chloride; the resulting cyclic metaphosphonamidate (2) could then be trapped with suitable reagents. However, the *NN*-dichloroamide (7) reacts with one molar equivalent of sodium methoxide in methanol to give the *N*-monochloroamide (6) (87%) and with two



(14) X = Cl
(15) X = H

equivalents of sodium methoxide to give the parent amide (5) (87%). The amide (5) (86%) is also the product when the *N*-monochloroamide (6) reacts with one equivalent of sodium methoxide. Products of ring expansion were not isolated in these experiments, nor in others using different bases (Et_3N, Bu^{t}OK, NaH) and solvents (benzene, dioxan, tetrahydrofuran, t-butyl alcohol).

While it is possible that the monochloroamide does not form the anion (14), preferring to give up positive chlorine and form the anion (15), there seems no reasonable alternative to (14) as an intermediate in the reduction of the dichloroamide. Apparently the anion (14) has little, if any, tendency to rearrange.

Nucleophilic displacement of NCl_2^- by methoxide, such as has been observed with *NN*-dichlorocarboxamides [12] was not an important reaction of the dichloroamide (7) but it might be with less-hindered phosphinic *NN*-dichloroamides.

The apparent ease with which the *NN*-dichloroamide (7) is dehalogenated by reagents such as sodium methoxide suggested that it might be able to chlorinate reactive aromatic substrates. This possibility was examined by heating (7) (3 molar equivalents) with anthracene in benzene solution: 9,10-dichloroanthracene was isolated in 49% yield.

Using equimolar amounts of the reactants and following the reaction by g.l.c., it could be seen that anthracene is rapidly consumed (*ca.* 90% after 0.5 h), that 9-chloroanthracene is the principal product in the early stages ($\leqslant$1 h), and that the proportion of 9,10-dichloroanthracene increases with time, implying that it is formed *via* the monochloro-compound. After 3.5 h a mixture of mono- and di-chloroanthracene (86% total) was isolated, with the dichloro-compound accounting for 58 mol % of the mixture (by g.l.c.). Mixtures of mono- and di-chloroanthracene were also obtained using the *NN*-dichloroamides (10) and $Pr^i_2P(O)NCl_2$.

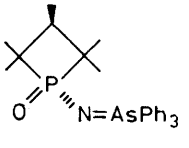
From the yields of the chloroanthracenes, it is clear that more than one chlorine can be acquired from each molecule of the dichloroamide (7), and indeed it was found that the monochloroamide (6) also forms 9-chloro- and 9,10-dichloro-anthracene when heated with anthracene in benzene. It does not necessarily follow that (6) acts as a chlorinating agent, since in solution it is in equilibrium with the dichloroamide (and amide), but the following observation suggests that it may. The *N*-methyl-*N*-chloro-amide (11) cannot disproportionate but

it too reacts with anthracene in boiling benzene to give a mixture of 9-chloro- and 9,10-dichloro-anthracene.

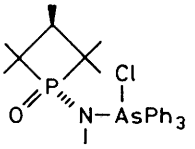
Anthracene would be expected to undergo chlorination rapidly (relative to benzene) and at the 9- and 10-positions by an electrophilic mechanism,[13] but a homolytic mechanism should also be considered in view of the known high reactivity of the 9-position in anthracene towards methyl,[14] trichloromethyl,[15] and benzoyloxy [16] radicals.

Anisole, like anthracene, is attacked very readily by electrophiles [17] but differs little from benzene in its reactivity towards radicals.[18] When anisole was heated (42 h) with the *NN*-dichloroamide (7) in benzene, chloroanisole (42% by g.l.c.; largely the *para*-isomer) was formed, but not chlorobenzene. Since benzene was present in great excess (>100-fold relative to anisole) it is clear that the chlorinating species has a much greater affinity for anisole. That being so, the chlorination of anisole appears to be electrophilic rather than homolytic, and the same is probably true for anthracene. The precise nature of the electrophile is open to conjecture.

Following the suggestion [19] that a phosphoryl nitrene is formed in the reactions of diethyl *NN*-dibromophosphoramidate, $(EtO)_2P(O)NBr_2$, with zinc, we looked briefly at the reaction of the *NN*-dichloroamide (7) with zinc in the presence of the nitrene trap triphenylarsine.[20] A mixture of the reactants in dichloromethane was heated for 15 h; after reductive work-up (aqueous metabisulphite) and chromatography the crystalline *N*-phosphinoylarsoranylideneamine (16) was isolated in 46% yield. Although (16) is formally derived by the trapping of a phosphinyl nitrene with triphenylarsine, it seems unlikely that a nitrene is actually involved since we find that the reaction proceeds just as well in the absence of zinc. A likely route to the arsoranylideneamine is *via* the arsorane (17) and reduction by zinc or metabisulphite. This would be analogous to the reported formation of an arsoranylideneamine when *NN*-dichlorotoluene-*p*-sulphonamide is treated with triphenylarsine and the product reduced with copper.[21]



(16)



(17)

The arsoranylideneamine (16) can be prepared in higher yield (70—71%) directly from the amide (5), by reaction with lead tetra-acetate and triphenylarsine in dichloromethane or with diacetoxytriphenylarsorane in benzene.[22] The latter reagent can also be used to prepare *N*-(di-isopropylphosphinoyl)- and *N*-(di-t-butylphosphinoyl)-triphenylarsoranylideneamines from the respective phosphinic amides. Nitrenes are unlikely to be involved in these reactions. An alternative route to the di-t-butylphosphinoyl compound involves heating di-t-butylphosphinic azide with triphenylarsine and copper powder at 165 °C. In this case a nitrene–copper complex may be involved; certainly no reaction occurs at 165 °C when copper is absent.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with Perkin-Elmer 237 and 257 instruments, and ^1H n.m.r. spectra with Varian T-60 and JEOL JNM-PS-100 spectrometers, tetramethylsilane as internal standard. ^{31}P N.m.r. chemical shifts (δ_P) were obtained by decoupling 60-MHz ^1H n.m.r. spectra using an NMR Specialities HD 60 heteronuclear decoupler and noting the irradiating frequency; they are quoted in p.p.m. relative to external 85% phosphoric acid. Mass spectra were recorded with an A.E.I. MS9 instrument. G.l.c. analyses were performed on a Pye 104 flame-ionisation chromatograph fitted with 1.5 m × 4 mm internal diameter glass columns packed with the stated stationary phase coated on silanised 100—120 mesh diatomite C 'Q.' Petroleum refers to the fraction of b.p. 60—80 °C unless otherwise indicated. Aqueous sodium hypochlorite contained 10—14% free chlorine. t-Butyl hypochlorite was prepared by the method of Mintz and Walling [23] and used without purification. Reactions of *N*-chloroamides were carried out in an atmosphere of dry nitrogen.

1-Amino- and 1-(*N*-methylamino)-2,2,3,4,4-pentamethylphosphetan 1-oxides, and all compounds derived from them, have been assigned the configuration in which the amino-group is *trans* to the 3-Me group for the reasons stated (see Results and Discussion section) but without additional experimental verification (**CAUTION**: An explosion has been reported [11] during the attempted chlorination of a phosphoramidate).

r-1-*Chloro*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (4) (60%), m.p. 72—74.5 °C (lit.,[5] 72—75 °C) (from petroleum); $\delta(CDCl_3)$ 1.75 (1 H, dq, J_{PH} 4, J_{HH} 7 Hz), 1.34 (6 H, d, J_{PH} 20 Hz), 1.31 (6 H, d, J_{PH} 21 Hz), and 0.93 (3 H, dd, J_{PH} 1.5, J_{HH} 7 Hz), was prepared by published procedures.[5]

Di-t-butylchlorophosphine (46%), b.p. 74—78 °C at 0.5 mmHg (lit.,[24] 48 °C at 0.3 mmHg); $\delta(CDCl_3)$ 1.18 (d, J_{PH} 12 Hz) was obtained by the method of Scherer and Schieder.[24]

1-*Chloro*-2,2,3,3-*tetramethylphosphetan* 1-*oxide* was prepared by the method previously described.[1]

Di-isopropylphosphinic Acid.—Based on the method of Christen and van der Linde,[25] a solution (*ca.* 3M) of the Grignard reagent from 2-bromopropane (246 g, 2.0 mol) was cooled (0—5 °C) while thiophosphoryl chloride (91 g, 0.54 mol) in ether (100 ml) was added over 3 h. The mixture was stirred overnight and then poured slowly onto crushed ice (400 g) and 2M sulphuric acid (650 ml) added cautiously. The organic layer was separated and the aqueous phase extracted with ether (2 × 300 ml). The combined organic extracts were concentrated to a viscous liquid (crude tetra-isopropyldisphosphine disulphide), which was oxidised by addition of 30% nitric acid (330 ml), during which time the temperature was kept below 80 °C, and then heating of the mixture at 100 °C for 1 h. The solution was transferred to an evaporating basin and heated on a steam-bath to drive off unchanged nitric acid, water being added repeatedly to replace that lost by evaporation. The material so obtained was dissolved in water (1.0 l) and the solution heated to 80 °C while lead monoxide (*ca.* 400 g) was added (to pre-

cipitate sulphate ions) until the solution was alkaline to litmus. The precipitated lead sulphate was filtered off and washed with water (1.0 l). Soluble lead salts in the combined filtrate and washing were precipitated completely by passing hydrogen sulphide through the solution. The mixture was filtered and the filtrate concentrated, first on a rotary evaporator and then *in vacuo* at 100 °C. Distillation gave di-isopropylphosphinic acid (30.2 g, 0.20 mol, 37%) which after crystallisation from petroleum had m.p. 48—50 °C (lit.,[26] 47.5—49.5 °C); $\delta(CDCl_3)$ 12.2 (1 H, s), 2.2—1.5 (2 H, m), and 1.13 (12 H, dd, J_{PH} 16, J_{HH} 7 Hz).

Di-isopropylphosphinic Chloride.—Thionyl chloride (4.3 g, 36 mmol) was added dropwise with stirring to di-isopropylphosphinic acid (2.7 g, 18 mmol) in benzene (30 ml). The mixture was boiled under reflux for 1.5 h, concentrated on a rotary evaporator, and freed from the last traces of thionyl chloride by addition, and evaporation, of a fresh portion of benzene. Distillation afforded di-isopropylphosphinic chloride (2.85 g, 16.9 mmol, 94%), b.p. (oven temp.) 68—78 °C at 1.0 mmHg (lit.,[25] 50 °C at 0.2 mmHg); $\nu_{max.}$ (liquid film) 1 230 cm^{-1} (P=O); $\delta(CDCl_3)$ 2.30 (2 H, d × septet, $J_{PH} \approx J_{HH} \approx 7$ Hz), 1.29 (6 H, dd, J_{PH} 19, J_{HH} 7 Hz), and 1.26 (6 H, dd, J_{PH} 19, J_{HH} 7 Hz).

r-1-*Amino*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide* (5).—*r*-1-Chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (50 g, 0.26 mol) in ether (300 ml) was added dropwise to a stirred and cooled solution of ammonia (18 g, 1.06 mol) in ethanol (100 ml). After a further 2 h at room temperature the mixture was filtered and the filtrate washed with a small volume of aqueous potassium carbonate and dried ($MgSO_4$). The residue remaining after evaporation of the solvent was crystallised from benzene to give *r*-1-amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (37 g, 0.21 mol, 81%), m.p. 162—163 °C (lit.,[1] 162—163 °C); *m/e* 175 (M^+); $\nu_{max.}$ (Nujol) 3 360, 3 230, 3 120, and 1 555 (NH_2), and 1 180 and 1 155 cm^{-1} (P=O); $\delta_H(CDCl_3)$ 3.0br (2 H, s, NH_2), 1.58 (1 H, dq, J_{PH} 4, J_{HH} 7 Hz), 1.23 (6 H, d, J_{PH} 18 Hz), 1.19 (6 H, d, J_{PH} 19 Hz), and 0.87 (3 H, dd, J_{PH} 2, J_{HH} 7 Hz); δ_P −50.8 (Found: C, 54.9; H, 10.0; N, 8.4. Calc. for $C_8H_{18}NOP$: C, 54.8; H, 10.35; N, 8.0%).

1-*Amino*-2,2,3,3-*tetramethylphosphetan* 1-*Oxide*.—This was prepared as previously described.[1]

r-1-(N-*Methylamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide*.—*r*-1-Chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (20 g, 0.10 mol) in dichloromethane (100 ml) was added dropwise with stirring to an ethanolic solution of methylamine (30 ml of 30% w/w $MeNH_2$). The mixture was stirred for a further 1 h and filtered. The filtrate was washed with 5% aqueous sodium carbonate and dried ($MgSO_4$). After removal of volatile material, crystallisation from benzene afforded r-1-(N-*methylamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (13.0 g, 0.069 mol, 69%), m.p. 146—148 °C; *m/e* 189 (M^+), 174 ($M^+ - CH_3$), 119 ($M^+ - C_5H_{10}$), 112, 97, 78, and 72; $\nu_{max.}$ (Nujol) 3 180 (NH), and 1 185 and 1 165 cm^{-1} (P=O), $\delta_H(CDCl_3)$; 2.72 (3 H, d, J_{PH} 10 Hz), *ca.* 2.6br (1 H; exchanges with D_2O), 1.58 (1 H, dq, J_{PH} 3, J_{HH} 7 Hz), 1.25 (6 H, d, J_{PH} 17 Hz), 1.19 (6 H, d, J_{PH} 18 Hz), and 0.86 (3 H, dd, J_{PH} 2, J_{HH} 7 Hz) (Found: C, 57.3; H, 10.8; N, 7.9. $C_9H_{20}NOP$ requires C, 57.1; H, 10.7; N, 7.4%).

1-(N-*Methylamino*)-2,2,3,3-*tetramethylphosphetan* 1-*Oxide*.—This was similarly prepared from the appropriate chloro-compound in 89% yield. After crystallisation from benzene–petroleum (b.p. 40—60 °C) (1 : 3) it had m.p. 94—97 °C; $\nu_{max.}$ (Nujol) 3 210 (NH) and 1 190 and 1 150 cm^{-1} (P=O); $\delta_H(CDCl_3)$ 3.23br (1 H, exchanges with D_2O), 2.75 (3 H, dd, J_{PH} 11, J_{HH} 4 Hz, collapses to d, J 11 Hz with D_2O, N–Me), 2.32 (2 H, d, J_{PH} 15 Hz), 1.25 (3 H, d, J_{PH} 19 Hz), 1.17 (3 H, d, J_{PH} 20 Hz), 1.17 (3 H, s), and 1.13 (3 H, s) (Found: C, 54.4; H, 10.2; N, 8.0. $C_8H_{18}NOP$ requires C, 54.8; H, 10.35; N, 8.0%).

Di-t-butylphosphinic Amide (9).—Di-t-butylchlorophosphine (27 g, 0.15 mol) in dichloromethane (200 ml) was added dropwise with stirring to dry liquid ammonia (30 ml) maintained at −40 °C. The mixture was allowed to warm to room temperature and stirred for 1 h, filtered, and the resulting solution oxidised at 0—10 °C by the dropwise addition of 30% hydrogen peroxide (50 ml) over a period of 1 h. Stirring was continued at room temperature for 1 h, the organic layer separated, washed with water (20 ml), dried ($MgSO_4$), and the solvent evaporated off to yield, after crystallisation from benzene, *di-t-butylphosphinic amide* (13.0 g, 0.073 mol, 49%), m.p. 199—200 °C; *m/e* 177 (M^+) and 121 ($M^+ - C_4H_8$); $\nu_{max.}$ (Nujol) 3 350, 3 240, 3 140, and 1 570 (NH_2), and 1 140 cm^{-1} (P=O); $\delta_H(CDCl_3)$ 2.7 (br, 2 H) and 1.24 (18 H, d, J_{PH} 14 Hz); δ_P −55.0 (Found: C, 54.4; H, 11.5; N, 7.8. $C_8H_{20}NOP$ requires C, 54.2; H, 11.4; N, 7.9%).

Di-isopropylphosphinic Amide.—Di-isopropylphosphinic chloride (15.8 g, 0.094 mol) in dichloromethane (100 ml) was added dropwise with stirring to liquid ammonia (50 ml) over a period of 1 h. The mixture was allowed to warm up to room temperature, stirred for a further 1 h, and filtered. The filtrate was washed with water (20 ml) and dried ($MgSO_4$). Evaporation of the solvent and crystallisation from petroleum gave *di-isopropylphosphinic amide* (13.8 g, 0.093 mol, 98%), m.p. 135—137.5 °C; *m/e* 149 (M^+), 107, and 106; $\nu_{max.}$ (Nujol) 3 300, 3 230, 3 120, and 1 575 (NH_2), and 1 170 and 1 150 cm^{-1} (P=O); $\delta(CDCl_3)$ 3.03 (2 H, br s), 2.3—1.6 (2 H, m), 1.17 (6 H, dd, J_{PH} 16, J_{HH} 6 Hz), and 1.13 (6 H, dd, J_{PH} 16, J_{HH} 6 Hz) (Found: C, 48.2; H, 10.7; N, 9.5. $C_6H_{16}NOP$ requires C, 48.3; H, 10.8; N, 9.4%).

r-1-(NN-*Dichloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide* (7).—*Method A*. A solution of *r*-1-amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (1.3 g, 7.43 mmol) in dichloromethane (20 ml) was stirred while t-butyl hypochlorite (1.75 g, 16.1 mmol) in dichloromethane (20 ml) was added dropwise. After a further 1 h, volatile material was removed under reduced pressure and the residue triturated with petroleum (b.p. 40—60 °C) and crystallised from n-heptane to give pale yellow r-1-(NN-*dichloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (1.65 g, 6.76 mmol, 91%), m.p. 87—89 °C; $\nu_{max.}$ (Nujol) 1 245 and 1 205 cm^{-1} (P=O); $\delta_H(CH_2Cl_2)$ 1.78 (1 H, dq, J_{PH} 5, J_{HH} 7 Hz), 1.35 (12 H, d, J_{PH} 19 Hz), and 0.93 (3 H, dd, J_{PH} 2, J_{HH} 7 Hz); δ_P −77.2; $\delta_H(C_6H_6)$ includes 1.10 (6 H, d, J_{PH} 19 Hz), 1.04 (6 H, d, J_{PH} 19 Hz), and 0.45 (3 H, dd, J_{PH} 2, J_{HH} 7 Hz) (Found: C, 39.6; H, 6.7; Cl, 29.1. $C_8H_{16}Cl_2NOP$ requires C, 39.4; H, 6.6; Cl, 29.05%).

Method B. A solution of *r*-1-amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (4.5 g, 25.7 mmol) in dichloromethane (135 ml) was stirred vigorously with aqueous sodium hypochlorite (180 ml) for 0.75 h. The organic layer was separated, washed with water (50 ml), and dried ($MgSO_4$). The solvent was evaporated and the residue crystallised from n-heptane to give the *NN*-dichloroamide (4.0 g, 16.4 mmol, 64%), m.p. 86—89 °C.

Method C. A solution of *r*-1-amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (5.33 g, 30.5 mmol) in water (120 ml) buffered with acetic acid (0.56 g) and sodium

acetate (5.6 g) was stirred and chlorine bubbled through until no more solid deposited and the liquid was green.[10b] After a further 0.5 h the solid was filtered off, washed with water, and dried *in vacuo* (P_2O_5). Crystallisation gave the *NN*-dichloroamide (4.54 g, 18.6 mmol, 61%), m.p. 85—87 °C.

Method D. *r*-1-(*N*-Chloroamino)-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0.50 g, 2.4 mmol) in dichloromethane (2 ml) was treated with t-butyl hypochlorite (0.30 g, 2.8 mmol) in dichloromethane (2 ml) as in method A to give the *NN*-dichloroamide (0.55 g, 2.3 mmol, 95%), m.p. 86—88 °C.

Method E. *r*-1-(*N*-Chloroamino)-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0.432 g, 2.06 mmol) in dichloromethane (20 ml) was treated with aqueous sodium hypochlorite (30 ml) as in method B (reaction time 1.5 h) to give the *NN*-dichloroamide (0.462 g, 1.89 mmol, 92%), m.p. 87—89 °C.

Di-t-butylphosphinic NN-*Dichloroamide* (10).—This was prepared from di-t-butylphosphinic amide by methods A (94% yield) and B (83% yield) and from di-t-butylphosphinic *N*-chloroamide by method D (96% yield), using petroleum (b.p. 40—60 °C) at low temperatures for crystallisation, m.p. 40—41 °C; $\nu_{max.}$ (melt) 1 230, 1 210, and 1 180 cm^{-1} (P=O); $\delta_H(CH_2Cl_2)$ 1.48 (d, J_{PH} 15 Hz); δ_P −80.6 (Found: C, 39.3; H, 7.5; N, 5.8; Cl, 28.7. $C_8H_{18}Cl_2NOP$ requires C, 39.0; H, 7.4; N, 5.7; Cl, 28.8%).

Di-isopropylphosphinic NN-*Dichloroamide*.—This was prepared from di-isopropylphosphinic amide by method A (87% yield), using petroleum (b.p. 40—60 °C) at low temperatures for crystallisation, m.p. 32—35 °C; $\delta(CDCl_3)$ 2.47 (2 H, m) and 1.33 (12 H, dd, J_{PH} 16, J_{HH} 7 Hz) (Found: C, 33.1; H, 6.7; N, 6.05; Cl, *ca.* 35.5. $C_6H_{14}Cl_2NOP$ requires C, 33.05; H, 6.5; N, 6.4; Cl, 32.5%).

r-1-(N-*Chloro*-N-*methylamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide* (11).—This was prepared from *r*-1-(*N*-methylamino)-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide by methods A (99% yield) and B (86%; reaction time 4 h) with crystallisation from ether–petroleum (b.p. 40—60 °C); it was colourless and had m.p. *ca.* 65 °C (decomp.); $\nu_{max.}$ (Nujol) 1 240, 1 200, and 1 160 cm^{-1} (P=O); $\delta(CDCl_3)$ 3.12 (3 H, d, J_{PH} 12 Hz), 1.77 (1 H, dq, J_{PH} 5, J_{HH} 7 Hz), 1.33 (6 H, d, J_{PH} 18 Hz), 1.28 (6 H, d, J_{PH} 18 Hz), and 0.89 (3 H, dd, J_{PH} 2, J_{HH} 7 Hz). Satisfactory elemental analysis could not be obtained.

1-(N-*Chloro*-N-*methylamino*)-2,2,3,3-*tetramethylphosphetan* 1-*Oxide* (13).—t-Butyl hypochlorite (4.34 g, 40 mmol) in methanol (10 ml) was added with stirring to 1-(*N*-methylamino)-2,2,3,3-tetramethylphosphetan 1-oxide (3.50 g, 20 mmol) in methanol (20 ml). After a further 1 h, volatile material was removed under reduced pressure and the residue crystallised from petroleum (b.p. <40 °C) to give 1-(N-*chloro*-N-*methylamino*)-2,2,3,3-*tetramethylphosphetan* 1-*oxide* (3.16 g, 15 mmol, 75%), m.p. 42—44 °C; $\nu_{max.}$ (Nujol) 1 240 and 1 220 cm^{-1} (P=O); $\delta(C_6H_6)$ 2.82 (3 H, d, J_{PH} 12 Hz, N-Me), 2.20 (2 H, d, J_{PH} 15 Hz), 1.20 (3 H, d, J_{PH} 19 Hz), 0.97 (3 H, d, J_{PH} 20 Hz), and 0.85 (6 H, slightly br s); $\delta(CHCl_3)$ 3.12 (3 H, d, J_{PH} 12 Hz), 2.50 (2 H, d, J_{PH} 15 Hz), 1.33 (3 H, d, J_{PH} 20 Hz), 1.23 (3 H, d, J_{PH} 20 Hz), and 1.17 (6 H, slightly br s). A satisfactory elemental analysis could not be obtained.

r-1-(N-*Chloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide* (6).—t-Butyl hypochlorite (0.68 g, 6.27 mmol) in dichloromethane (20 ml) was added dropwise over 0.5 h to a cold, stirred solution of *r*-1-amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (1.075 g, 6.14 mmol) in dichloromethane (50 ml). After a further 0.5 h at room temperature, volatile material was evaporated and the residue triturated with petroleum to give r-1-(N-*chloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (1.2 g, 5.7 mmol, 93%), m.p. 125—130 °C; *m/e* 211 and 209 (M^+, 4%), 196 and 194 (M^+ − Me), and 175 (M^+ + H − Cl, 100%); $\nu_{max.}$ (Nujol) 2 680 (NH) and 1 190, 1 180, and 1 160 cm^{-1} (P=O) (Found: C, 46.2; H, 8.3; N, 6.6; Cl, 17.3. $C_8H_{17}ClNOP$ requires C, 45.8; H, 8.2; N, 6.7; Cl, 16.9%). The ^1H n.m.r. spectrum ($CDCl_3$) had signals at δ 1.31 (d, J_{PH} 18 Hz), 1.29 (d, J_{PH} 18 Hz), and 0.89 (dd, J_{PH} 2, J_{HH} 7 Hz) in addition to those due to the amide [δ 1.26 (d, J_{PH} 18 Hz), 1.22 (d, J_{PH} 19 Hz), and 0.89 (dd, J_{PH} 2, J_{HH} 7 Hz)] and the *NN*-dichloroamide [δ 1.36 (d, J_{PH} 19 Hz), 1.34 (d, J_{PH} 19 Hz), and 0.93 (dd, J_{PH} 2, J_{HH} 7 Hz)]; the relative intensities of the signals indicated *ca.* 70% disproportionation of the *N*-chloroamide. Heteronuclear decoupling indicated δ_P −56.6 for the *N*-chloroamide.

The *N*-chloroamide (6), m.p. 124—130 °C (one sample had m.p. 132—134 °C), was also obtained in 95% yield by mixing solutions of the amide (0.174 g, 1.0 mmol) and the dichloroamide (0.244 g, 1.0 mmol) in dichloromethane (6 ml each), stirring for 1 h, evaporating off volatile material, and triturating with petroleum.

Di-t-butylphosphinic N-*Chloroamide* (8).—This was obtained in 97% yield by both the methods employed above for the preparation of the *N*-chloroamide (6). It had m.p. 52—54 °C; $\nu_{max.}$ (Nujol) 2 705 (NH) and 1 160 cm^{-1} (P=O). The ^1H n.m.r. spectrum (CH_2Cl_2) had a signal at δ 1.34 (d, J_{PH} 14 Hz) in addition to those due to the amide [δ 1.25 (d, J_{PH} 14 Hz)] and the *NN*-dichloroamide [δ 1.49 (d, J_{PH} 14 Hz)]; the relative intensities of the signals indicated *ca.* 50% disproportionation of the *N*-chloroamide. Heteronuclear decoupling indicated δ_P −63.8 for the *N*-chloroamide.

1-(N-*Chloroamino*)-2,2,3,3-*tetramethylphosphetan* 1-*oxide* (12) (64%), $\nu_{max.}$ 2 680 (NH), 1 230, 1 200, 1 150, and 1 125 cm^{-1}, was prepared from the amide and t-butyl hypochlorite (1.1 mol equiv.) but it had a ^1H n.m.r. spectrum too complex to analyse (disproportionation) and was not further characterised.

Reactions with Sodium Methoxide in Methanol.—Sodium methoxide (0.055 g, 1.02 mmol) in methanol (5 ml) was added dropwise with stirring to a solution of *r*-1-(*NN*-dichloroamino)-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0.246 g, 1.01 mmol) in methanol. After 6.5 h the solvent was evaporated and the residue extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated to give the *N*-monochloroamide (6) (0.184 g, 0.88 mmol, 87%), m.p. 126—130 °C (from petroleum), i.r. spectrum as for authentic (6).

By the same method but with 2 mol equiv. of sodium methoxide the dichloroamide (7) afforded the amide (5) (87%), m.p. 162—163 °C (from benzene), i.r. and n.m.r. spectra identical to those of the authentic amide.

Similarly, using the *N*-monochloroamide (6) and 1 mol equiv. of sodium methoxide, the amide (5) (86%), m.p. 162—163 °C, was obtained.

Chlorination of Anthracene.—(i) *With* r-1-(NN-*dichloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (7). (*a*) The dichloroamide (7) (0.619 g, 2.54 mmol) and anthracene (0.148 g, 0.83 mmol) were heated in benzene (7 ml) for 21 h. The reaction mixture was washed with 20% aqueous sodium metabisulphite and the washing extracted with benzene. The combined organic portions were

chromatographed on silica; elution with petroleum gave 9,10-dichloroanthracene (0.100 g, 0.405 mmol, 49%), m.p. 209—211 °C (from acetone) (lit.,[27] 210 °C); *m/e* 250, 248, and 246 (ratio 1 : 6 : 9; M^+); $\nu_{max.}$ (Nujol) 950 and 750 cm^{-1}; $\delta(CDCl_3)$ 8.7 (4 H, m) and 7.8 (4 H, m).

(*b*) The dichloroamide (7) (1.53 g, 6.3 mmol) and anthracene (1.22 g, 6.8 mmol) were heated in benzene (45 ml) for 4 h. The mixture was filtered and the solvent evaporated. The residue was crystallised three times from acetone to give 9,10-dichloroanthracene (0.070 g). Chromatography of the crystallisation mother-liquors on Kieselguhr and elution with petroleum (b.p. 40—60 °C) afforded a small sample of pure 9-chloroanthracene (0.030 g), m.p. 103—104 °C (from ethanol) (lit.,[28] 104—106 °C); *m/e* 214 and 212 (ratio 1 : 3; M^+); $\nu_{max.}$ (Nujol) 940, 890, 770, 735, and 725 cm^{-1}; $\delta(CDCl_3)$ 8.6 (3 H, m), 8.15 (2 H, m), and 7.7 (4 H, m).

(*c*) The dichloroamide (7) (0.503 g, 2.05 mmol) and anthracene (0.350 g, 1.97 mmol) were heated in benzene (25 ml) and the progress of the reaction was monitored by g.l.c. (3% APL at 250 °C), measuring the relative areas of the peaks due to anthracene (t_R 3.9 min), 9-chloroanthracene (t_R 7.3 min), and 9,10-dichloroanthracene (t_R 13.1 min). After 3.5 h the bulk of the reaction mixture (corresponding to 1.74 mmol anthracene) was washed with 20% aqueous sodium metabisulphite and chromatographed on Kieselguhr. Elution with petroleum (b.p. 40—60 °C) gave a mixture (0.348 g) of 9-chloroanthracene and 9,10-dichloroanthracene (ratio 0.61 : 1 w/w by g.l.c. with calibrated detector response) representing yields of 36 and 50%, respectively.

(ii) *With di-t-butylphosphinic* NN-*dichloroamide* (10). An experiment similar to (i) (*c*) gave 9-chloroanthracene (54%) and 9,10-dichloroanthracene (27%) after heating for 72 h.

(iii) *With di-isopropylphosphinic* NN-*dichloroamide*. An experiment similar to (i) (*c*) above gave 9-chloroanthracene (50%) and 9,10-dichloroanthracene (26%) after heating for 72 h.

(iv) *With* r-1-(N-*chloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (6). Using 2.3 mol equiv. of the chloroamide in an experiment similar to (i) (*c*) and heating for 20 h, 9-chloroanthracene (29%) and 9,10-dichloroanthracene (60%) were produced.

(v) *With* r-1-(N-*methyl*-N-*chloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (11). Using 2.1 mol equiv. of the *N*-methylchloroamide in an experiment similar to (i) (*c*), with heating for 22.5 h, there were produced 9-chloroanthracene (55%) and 9,10-dichloroanthracene (41%).

Chlorination of Anisole.—(a) *With* r-1-(NN-*dichloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (7). The dichloroamide (0.488 g, 2.0 mmol) and anisole (0.226 g, 2.09 mmol) were heated in benzene (30 ml) for 41 h. G.l.c. examination (3% OV 17 at 115 °C) with *p*-dichlorobenzene as internal standard indicated the presence of *p*-chloroanisole (t_R 7.1 min) and *o*-chloroanisole (t_R 8.2 min) in a combined yield of 42% and a ratio of *ca.* 10 : 1. The major product was isolated by preparative g.l.c. (10% E30) and its identity confirmed by comparison of its n.m.r. spectrum with that of an authentic sample of *p*-chloroanisole. It was not possible to establish the complete absence of *m*-chloroanisole because (using an authentic sample) it was only partly resolved from the *p*-isomer by g.l.c. and by n.m.r. (MeO signals), but chlorobenzene was shown to be absent (1% relative to anisole would have been detected on 3% OV 17 at 80 °C).

(b) *With* r-1-(N-*chloroamino*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (6). In an experiment similar to the one above, *o*- and *p*-chloroanisoles were detected in a combined yield of 13.5%.

N-*Phosphinoylarsoranylideneamines.*— N-(2,2,t-3,4,4-*Pentamethylphosphetan*-r-1-*yl*)*triphenylarsoranylideneamine* P-*Oxide* (16). *Method A.* *r*-1-(*NN*-Dichloroamino)-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0.486 g, 2.0 mmol) and triphenylarsine (0.611 g, 2.0 mmol) were heated in dichloromethane for 12 h. The mixture was washed with 20% aqueous sodium metabisulphite (15 ml) and water, and dried ($MgSO_4$). A portion (equivalent to 0.97 mmol *NN*-dichloroamide) was chromatographed on alumina. Elution with 2% methanol in ether afforded the *arsoranylideneamine* (16) (0.237 g, 0.49 mmol, 51%), m.p. 199—201 °C (from petroleum); *m/e* 479 (M^+), 409 ($M^+ - C_5H_{10}$), and 306 (Ph_3As^+); $\nu_{max.}$ (Nujol) 1 150, 1 080, and 1 065 cm^{-1}; $\delta(CDCl_3)$ 7.8—7.6 (6 H, m), 7.5—7.3 (9 H, m), *ca.* 1.65 (1 H, m), 1.09 (6 H, d, J_{PH} 17 Hz), 1.03 (6 H, d, J_{PH} 17 Hz), and 0.79 (3 H, dd, J_{PH} 2, J_{HH} 7 Hz) (Found: C, 64.9; H, 6.35; N, 3.1. $C_{26}H_{31}AsNOP$ requires C, 65.1; H, 6.5; N, 2.9%). The same product was obtained in comparable yield when the reaction was carried out in the presence of active zinc.[29]

Method B. r-1-Amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0.176 g, 1.0 mmol), lead tetra-acetate (0.89 g, 2.0 mmol), and triphenylarsine (0.617 g, 2.0 mmol) were heated in dichloromethane (25 ml) for 22 h. The mixture was filtered and the filtrate washed with water (20 ml) and aqueous sodium hydrogen carbonate (2 × 20 ml), dried (Na_2SO_4), and chromatographed to give the arsoranylideneamine (16) (0.339 g, 0.71 mmol, 71%), m.p. 199.5—201.5 °C (from petroleum).

Method C. *r*-1-Amino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0.175 g, 1.0 mmol) and diacetoxytriphenylarsorane [22] (0.634 g, 1.5 mmol) were heated in benzene (10 ml) for 2 h. Chromatography gave the arsoranylideneamine (16) (0.337 g, 0.70 mmol, 70%), m.p. 199—201 °C (from petroleum).

N-(*Di-isopropylphosphinoyl*)*triphenylarsoranylideneamine* (73%).—This was prepared from di-isopropylphosphinic amide by method C above; it had m.p. 100.5—102 °C (from petroleum); $\delta(CDCl_3)$ 7.8—7.6 (6 H, m), 7.45—7.2 (9 H, m), 2.3—1.4 (2 H, m), 1.10 (6 H, dd, J_{PH} 16, J_{HH} 7 Hz), and 0.98 (6 H, dd, J_{PH} 15, J_{HH} 7 Hz) (Found: C, 63.8; H, 6.6; N, 3.05. $C_{24}H_{29}AsNOP$ requires C, 63.6; H, 6.45; N, 3.1%).

N-(*Di-t-butylphosphinoyl*)*triphenylarsoranylideneamine* (25%).—This was prepared from di-t-butylphosphinic amide by method C (toluene solvent), m.p. 174—175.5 °C (from petroleum); *m/e* 424 ($M^+ - C_4H_9$) and 306 (Ph_3As^+); $\nu_{max.}$ (Nujol) 1 135, 1 080, and 1 065 cm^{-1}; $\delta(CDCl_3)$ 7.8—7.6 (6 H, m), 7.4—7.2 (9 H, m), and 1.08 (18 H, d, J_{PH} 13 Hz) (Found: C, 64.9; H, 6.95; N, 2.9. $C_{26}H_{33}AsNOP$ requires C, 64.9; H, 6.9; N, 2.9%).

The same product (0.140 g, 0.29 mmol, 46%) was obtained by heating a mixture of di-t-butylphosphinic azide [30] (0.127 g, 0.63 mmol), triphenylarsine (0.378 g, 1.2 mmol), and copper powder (0.60 g) at 165 °C for 8 h and chromatographing the crude product. The azide did not decompose when heated at 165 °C in the absence of copper, nor was the arsoranylideneamine formed when the azide and triphenylarsine were heated at 165 °C in the absence of copper.

We thank the S.R.C. for a Research Studentship.

[9/700 *Received*, 8*th May*, 1979]

REFERENCES

[1] M. J. P. Harger, *J.C.S. Perkin I*, 1974, 2604.
[2] J. Wiseman and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1974, **96**, 4262.
[3] R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, 1965, **30**, 3860; F. Weissbach and W. Jugelt, *J. prakt. Chem.*, 1975, **317**, 394.
[4] M. J. P. Harger, unpublished observation.
[5] J. J. McBride, E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833; Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 934.
[6] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465; S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200; S. E. Cremer, *Chem. Comm.*, 1970, 616; J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713; J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502.
[7] S. C. Czapf, H. Gottlieb, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, 1973, **38**, 2555 and references therein.
[8] F. G. Soper, *J. Chem. Soc.*, 1924, 1899; J. C. Morris, J. A. Salazar, and M. A. Wineman, *J. Amer. Chem. Soc.*, 1948, **70**, 2036; T. Higuchi, K. Ikela, and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 546.
[9] C. Bachand, H. Driguez, J. M. Paton, D. Touchard, and J. Lessard, *J. Org. Chem.*, 1974, **39**, 3136.
[10] (*a*) L. N. Markovskii, A. M. Pinchuk, and T. V. Kovalevskaya, *J. Gen. Chem. USSR*, 1970, **40**, 509; (*b*) A. Zwierzak and A. Koziara, *Tetrahedron*, 1970, **26**, 3521.
[11] B. J. Walker, *Chem. Brit.*, 1979, **15**, 65.
[12] R. E. White and P. Kovacic, *J. Amer. Chem. Soc.*, 1975, **97**, 1180.
[13] R. O. C. Norman, 'Principles of Organic Synthesis,' Methuen, 1968, p. 359; R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds', Elsevier, 1965, pp. 87, 219—221.
[14] M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.
[15] E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.
[16] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 1952, 2695.
[17] G. Kohnstam and D. L. H. Williams in 'The Chemistry of the Ether Linkage,' ed. S. Patai, Interscience, 1967, ch. 3, pp. 81—166.
[18] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon, 1960, pp. 57, 101, and 105.
[19] A. Zwierzak and S. Zawadzki, *Tetrahedron*, 1973, **29**, 3899.
[20] J. I. G. Cadogan and I. Gosney, *J.C.S. Perkin I*, 1974, 460.
[21] A. Schönberg and E. Singer, *Chem. Ber.*, 1969, **102**, 2557.
[22] J. I. G. Cadogan and I. Gosney, *J.C.S. Perkin I*, 1974, 466.
[23] M. J. Mintz and C. Walling, *Org. Synth.*, Coll. Vol. 5, 184.
[24] O. J. Scherer and G. Schieder, *Chem. Ber.*, 1968, **101**, 4184.
[25] P. J. Christen and L. M. van der Linde, *Rec. Trav. Chim.*, 1959, **78**, 543.
[26] P. C. Crofts and G. M. Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3379.
[27] Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1962, 1725.
[28] D. C. Nonhebel, *Org. Synth.*, 1963, **43**, 15.
[29] R. D. Rieke, S. J. Uhm, and P. M. Hudnall, *J.C.S. Chem. Comm.*, 1973, 269.
[30] M. A. Stephen, Ph.D. Thesis, University of Leicester, 1978.