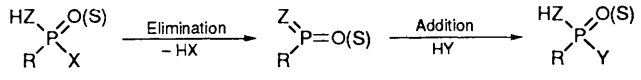
Nucleophilic Substitution in Benzylic Thiophosphinyl and Thiophosphonyl Chlorides: the Contribution of Elimination–Addition Pathways with Methylenethioxophosphorane (Thiophosphene) Intermediates[1]

Michael P. Coogan and Martin J. P. Harger*
Department of Chemistry, The University, Leicester, UK LE1 7RH

For the reactions of $ArCH_2P(S)(Ph)Cl$ and $ArCH_2P(S)(NMe_2)Cl$ with Et_2NH, changing $ArCH_2$ from benzyl to 4-nitrobenzyl increases the rates of substitution by factors of 80 and $>10^3$, respectively, and reduces markedly the ability to discriminate between competing Et_2NH and Me_2NH nucleophiles. With Et_2ND, the nitrobenzyl substrates give products that contain deuterium in the benzylic methylene group. These observations point to substitution by elimination–addition, with a three-coordinate methylenethioxophosphorane (thiophosphene) intermediate, for the nitrobenzyl compounds.

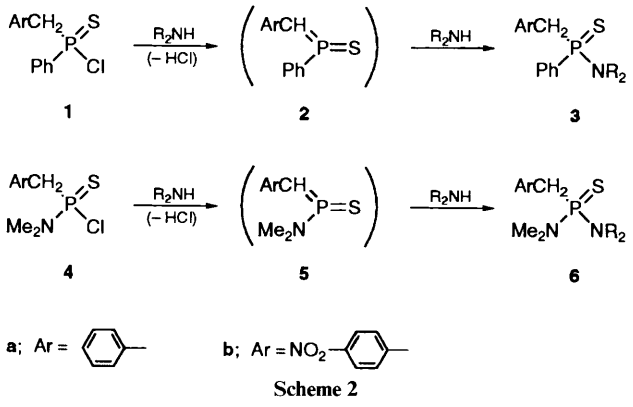
Nucleophilic substitution at a phosphoryl (P=O) or thiophosphoryl (P=S) centre is generally associative and S_N2-like, albeit that the five-coordinate species in $S_N2(P)$ is likely to be an intermediate, not just a transition state.†[2,3] Dissociative S_N1-like reactions are uncommon, presumably because phosphorylium ($R_2\overset{+}{P}{=}O$) and thiophosphorylium ($R_2\overset{+}{P}{=}S$) cations are difficult to form.[4–6] The need to form a cation can be circumvented if one of the ligands (HZ) on phosphorus can lose a proton: then dissociative substitution is possible by an elimination–addition (EA) mechanism (Scheme 1; X = leaving



Scheme 1

group).[3,7] Although this requires a three-coordinate P^V species to be formed as intermediate, it can be the preferred pathway for nucleophilic substitution when ligand HZ is highly acidic, *i.e.* when Z is oxygen[8] or sulfur.[9] For moderately acidic ligands where Z is nitrogen, the EA mechanism can sometimes compete with $S_N2(P)$, especially when steric factors discourage associative reaction and the nucleophile is reasonably basic.[10] Even if Z is just carbon, nucleophilic substitution by EA should still be possible in principle. This type of reaction is well known for sulfonyl compounds, forming sulfene intermediates,[11] and for carbonyl compounds, forming ketenes,[12] but for phosphoryl and thiophosphoryl compounds it seems hardly to have been considered.[13,14] Prompted by this neglect, we have looked for evidence of an EA mechanism in the substitution reactions of the 4-nitrobenzyl thiophosphinyl and thiophosphonyl chlorides **1b** and **4b** with amines (Scheme 2). As substrates these have the basic essentials for reaction by EA, *i.e.* a good leaving group (Cl) on phosphorus and a ligand (4-nitrobenzyl) with a reasonably acidic C–H bond. For our present purposes they also have the benefit of a P=S group. They should therefore react by $S_N2(P)$ less readily than the corresponding P=O compounds,[15] so any tendency to react by EA should be revealed more clearly. To allow comparisons to be made, the unsubstituted-benzyl compounds **1a** and **4a** were also included in our study. Lacking the NO_2 group, these will be markedly less acidic and the EA mechanism will be correspondingly less likely.

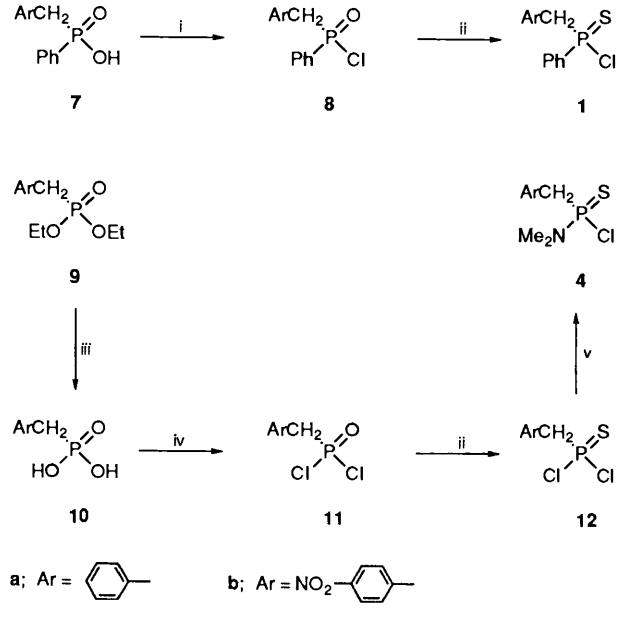
† By $S_N2(P)$ we mean associative bimolecular nucleophilic substitution at phosphorus, regardless of whether the mechanism is concerted (like S_N2 at tetrahedral carbon) or stepwise (addition–elimination with a five-coordinate intermediate).



Scheme 2

Results and Discussion

Preparative Experiments.—The phosphonic acid **10b** (Scheme 3) was prepared by acid-catalysed hydrolysis of the ester **9b** obtained by heating 4-nitrobenzyl bromide with $(EtO)_3P$ (Arbusov reaction), and was converted into the phosphonic



Scheme 3 *Reagents:* i, $(COCl)_2$; ii, $PSCl_3$, DMF (catalyst), heat; iii, conc. HCl, heat; iv, $SOCl_2$, DMF (catalyst), heat; v, 2 Me_2NH ($-Me_2\overset{+}{N}H_2\ Cl^-$)

Table 1 Times for 50% completion of reactions with Me_2NH and Et_2NH (0.6 mol dm^{-3} in CH_2Cl_2) at 33 °C

Substrate	$t_{\frac{1}{2}}$ (Me_2NH)	$t_{\frac{1}{2}}$ (Et_2NH)
13	4 min	13.5 h
4a	9 min	25.5 h
4b	0.4 min	1.1 min

dichloride **11b** using $SOCl_2$ [DMF (dimethylformamide) catalyst; reflux temperature]. Attempts to exchange the oxygen atom for sulfur by heating with $PSCl_3$ (b.p. 125 °C) were not at first successful, but when a small amount of DMF (0.1 mol equiv.) was introduced the transformation of **11b** to **12b** (δ_P 40.7→79.8) was essentially complete in 14 h using a sixfold excess of the reagent. This method of O–S exchange has the advantage that both the excess of the $PSCl_3$ and the $POCl_3$ byproduct can be removed simply by evaporation under reduced pressure. Controlled addition of Me_2NH (2 mol equiv.) to the phosphonothioic dichloride in CH_2Cl_2 gave the 4-nitrobenzyl phosphonamidothioic chloride **4b**. The unsubstituted-benzyl substrate **4a** was obtained in a similar way from the known phosphonic dichloride **11a**.

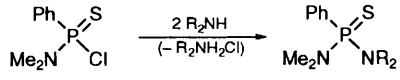
The phosphinic acids **7a** and **7b** were prepared from benzyl chloride or 4-nitrobenzyl bromide and $PhP(OEt)_2$ by heating (Arbusov reaction) followed by hydrolysis. They reacted rapidly with oxalyl chloride (no catalyst) at room temperature to give the phosphinic chlorides **8a** and **8b**, and exchange of oxygen for sulfur as before gave the phosphinothioic chlorides **1a** and **1b**.

All four substrates reacted with Me_2NH and Et_2NH to give the expected substitution products **3a**, **3b**, **6a** and **6b** (R = Me or Et).

Reactivity.—To ascertain their reactivity, the reactions of the phosphinic substrates **1a** and **1b** with Et_2NH were monitored by ^{31}P NMR spectroscopy. Using a large excess of the amine as a 0.6 mol dm^{-3} solution in CH_2Cl_2 at 33 °C, the reaction of **1a** (δ_P 87.2→71.2) was seen to reach *ca.* 85% completion during 1 h ($t_{\frac{1}{2}}$ 22 min). By contrast, the reaction of the nitro compound **1b** (δ_P 84.3→70.2) was >90% complete inside a minute ($t_{\frac{1}{2}}$ *ca.* 17 s). It is not known by how much the NO_2 group in **1b** enhances the reactivity of the P atom towards associative nucleophilic attack, but since it is isolated from the P=S group its effect is unlikely to be large. The observed 80-fold increase in reactivity therefore suggests that a pathway other then $S_N2(P)$, possibly an EA mechanism, may be making an important contribution.

The substrates **4a** and **4b** have an NMe_2 group on phosphorus in place of the Ph group in **1a** and **1b**. We could not predict how this would affect their EA reactivity, but substantially reduced $S_N2(P)$ reactivity seemed very likely. We were therefore hopeful that they would afford clearer evidence of reaction by EA, by displaying behaviour more dramatically in contrast with that expected for $S_N2(P)$. The reactions of **4a** and **4b** with Et_2NH, and also with Me_2NH, were examined as before by ^{31}P NMR spectroscopy (0.6 mol dm^{-3} R_2NH in CH_2Cl_2; T = 33 °C). Table 1 shows the halflives ($t_{\frac{1}{2}}$) for these reactions and also, by way of reference, for the corresponding reactions of the non-benzylic substrate **13** (Scheme 4) which cannot possibly react by EA.

Three features of the results in Table 1 are particularly noteworthy. First, the Me_2N group on phosphorus does indeed reduce the reactivity of the unsubstituted-benzyl compound **4a** [$S_N2(P)$] quite markedly: with Et_2NH it is 70 times less reactive than **1a**. By contrast, the nitro compounds **1b** and **4b** differ in reactivity with Et_2NH by a factor of only four. Second, when



13 **14**

Scheme 4

the amine is changed from Me_2NH to Et_2NH the rate decreases 200-fold for **13** [which can only react by $S_N2(P)$] and 170-fold for **4a**, but for the nitro compound **4b** the rate decreases only by a factor of 2.5–3. This shows that **4b** can undergo substitution by a mechanism that is relatively insensitive to the bulk of the amine. That will surely be the case for EA (Scheme 2), since in the rate limiting step the amine is required only to act as a base, not as a nucleophile. Third, when the substrate is changed from **4a** to the nitro compound **4b**, the rate of reaction with Et_2NH increases by a factor of more than a thousand. An increase of this magnitude is inconceivable for $S_N2(P)$, but not for EA if the benzylic C atom has considerable carbanion character in the rate-limiting elimination stage.

There is one way, other than by influencing the acidity of the benzylic C–H bond, that a nitro substituent might enhance the reactivity of the substrates **1b** and **4b**. This is by making them susceptible to electron transfer from the amine. In a number of cases, 4-nitrobenzyl compounds ($ArCH_2X$) have been found to undergo rapid nucleophilic substitution as their radical anions,[16] by an $S_{RN}1$ mechanism. Since our substrates do not have the leaving group on the benzylic C atom, it is difficult to see how an $S_{RN}1$ mechanism could possibly be involved. However, to make sure, we carried out the reaction of **4b** with Et_2NH in the presence of the powerful electron acceptor 1,4-dinitrobenzene (0.5 mol equiv.), a known inhibitor of $S_{RN}1$. The rate was unaffected, confirming that the high reactivity of **4b** is not due to the nitro substituent acting as an electron acceptor.

Competition Experiments.—Having examined the reactions of our substrates with individual nucleophiles it seemed likely that a study of their behaviour with competing nucleophiles would be revealing. Accordingly, each of the substrates was added to CH_2Cl_2 containing an equimolar mixture of Me_2NH and Et_2NH (20 mol equiv.; each amine 0.6 mol dm^{-3}) and, with the aid of authentic samples, the products were analysed by ^{31}P NMR spectroscopy. The unsubstituted-benzyl substrates **1a** and **4a** and the non-benzylic substrate **13** gave entirely the product **3a**, **6a** or **14** having R = Me, resulting from attack of Me_2NH; no trace of the Et_2NH-derived product (R = Et) could be detected (≤1%). This is reasonable if the reactions proceed by a sterically-sensitive associative mechanism [$S_N2(P)$], and it is what would be predicted from the rates of reaction with the individual amines ($k_{Me_2NH} > 100\ k_{Et_2NH}$ for **4a** and **13**). Of more interest were the reactions of the nitro compounds **1b** and **4b**. These gave a substantial amount of the product **3b** or **6b** having R = Et, the NMe_2 : NEt_2 product ratio being 82:18 for **1b** and 70:30 for **4b**. This relative lack of selectivity is important for two reasons. First, it provides support for the involvement of a methylenethioxophosphorane (thiophosphene) in product formation. Being three-coordinate and trigonal at phosphorus, this will be both highly reactive and sterically accessible; a relative lack of discrimination between Me_2NH and Et_2NH is therefore to be expected. Second, it confirms that EA is important in the reactions of the nitro compounds with Me_2NH as well as with Et_2NH. The NEt_2 product must be formed by EA, because Et_2NH cannot compete with Me_2NH in $S_N2(P)$ (see above). But it is inconceivable that the thiophosphene intermediate is trapped less efficiently by Me_2NH than it is by Et_2NH. It follows that, in the competition experiments, at least 18% of **1b** and 30% of

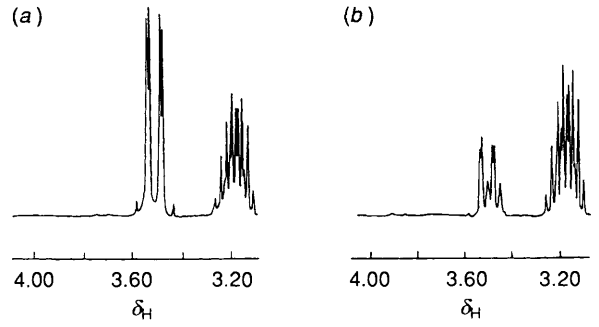


Fig. 1 ^{1}H NMR signal (300 MHz) of the benzylic methylene group of product **6b** (R = Et) (δ 3.51) from the reaction of substrate **4b** (*a*) with Et_2NH, (*b*) with Et_2ND [half of the (symmetrical) signal of the NEt_2 methylene groups of the product (δ 3.17, 2 H) is included for reference]

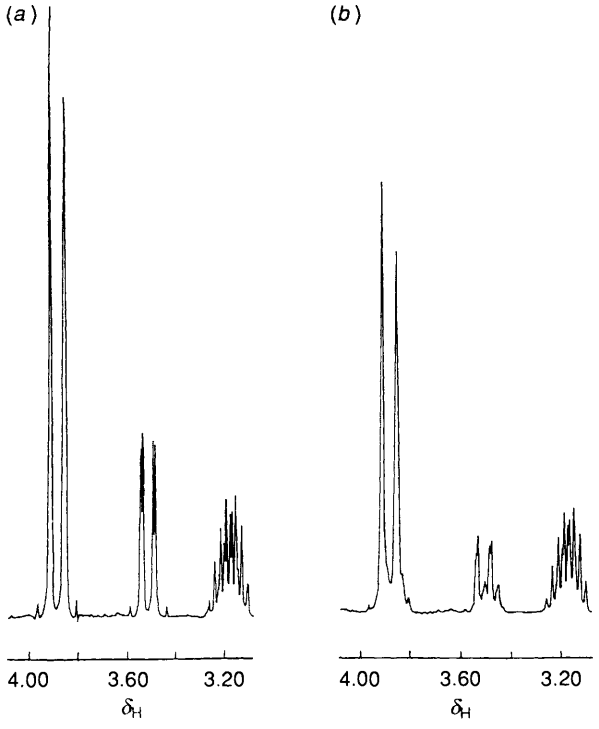


Fig. 2 ^{1}H NMR signals (300 MHz) of the benzylic methylene groups of substrate **4b** (δ 3.88) and product **6b** (R = Et) (δ 3.51) in (*a*) a mixture (2.5:1) of the undeuteriated compounds, (*b*) the mixture obtained by quenching the reaction of **4b** with Et_2ND at *ca.* 28% completion [half of the (symmetrical) signal of the NEt_2 methylene groups of the product (δ 3.17) is included for reference]

4b is converted into the NMe_2 product by the EA mechanism and not more than 64% of **1b** and 40% of **4b** reacts with Me_2NH by $S_N2(P)$. In fact the thiophosphene will almost certainly show at least some preference for reaction with the less hindered nucleophile (Me_2NH), in which case the extent to which the NMe_2 product is formed by EA will actually exceed the estimates above. The greater contribution of the EA mechanism for **4b** is, apparently, not so much because the NMe_2 group assists thiophosphene formation as because it retards the alternative $S_N2(P)$ mechanism.

Deuterium Incorporation.—The evidence so far accords well with an EA mechanism, but is largely circumstantial. More direct evidence was therefore sought, using Et_2ND as the nucleophile; if the product is formed *via* a thiophosphene it should incorporate deuterium at the benzylic C atom. Accordingly, the nitro compound **4b** was treated with Et_2ND ($\geqslant$90 atom % D) (10 mol equiv.; 0.6 mol dm^{-3} in CH_2Cl_2; T = 33 °C; 4 min, 96% completion) and the product **6b** (R = Et) was examined spectroscopically. In the ^{1}H NMR spectrum, the signal for the benzylic methylene group (δ 3.51; diastereotopic H atoms coupled to P) was seen to be altered by the use of Et_2ND [Fig. 1(*b*), *cf.* 1(*a*) for product from Et_2NH reaction] and the integral indicated a composition 0.85 H/1.15 D. This certainly shows that deuterium is incorporated, but the level of incorporation imples that some molecules contain not just one D atom but two. The mass spectrum (low resolution) confirmed the presence of an appreciable amount of [$^2H_2$]-product [ratio m/z 315:316:317 = 15:56.5:28.5, *cf.* 87:11:2 for the product obtained using Et_2NH (ions containing D in place of H not resolved from those containing ^{13}C in place of ^{12}C)]. A control experiment [**6b** (R = Et) + Et_2ND] showed that only a little of the observed deuterium could have been incorporated by H–D exchange in the product once it was formed, so by implication there must have been considerable exchange in the substrate before it underwent substitution. This was verified by an experiment in which reaction was quenched (dil. HCl) after 1 min (*ca.* 60% completion). The mass spectrum of the remaining substrate indicated that about three-quarters of the molecules had become deuteriated [m/z 278 (M^+ for ^{35}Cl molecule) reduced from 62.5% of the molecular ion cluster (m/z 278–282) to 13.5%], a fair proportion with more than one D atom [m/z 280, 25% of the molecular ion cluster (21% [$^2H_2$]substrate with ^{35}Cl and 4% [$^2H_0$]substrate with ^{37}Cl or ^{34}S)]. Such extensive H–D exchange in the substrate obviously makes deuterium in the product inadequate as evidence for its formation *via* a thiophosphene. It is, nonetheless, very important: it shows either that the benzylic C–H bonds in the substrate are acidic enough for the carbanion to be formed rapidly, in which case substitution by EA is likely, or that the thiophosphene is indeed formed, by reversible elimination.

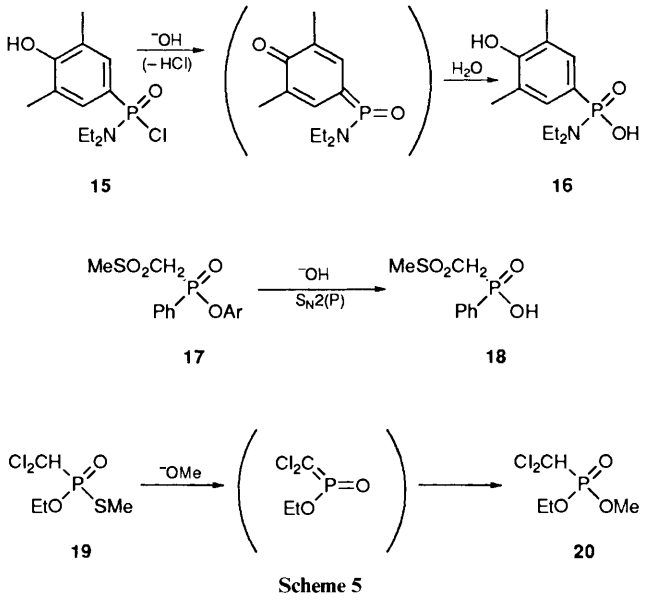
In an attempt to minimise exchange in the substrate, the experiment was repeated with quenching after just 15 s (*ca.* 28% completion). The mass spectrum of the substrate–product mixture showed that about half the substrate molecules now contained deuterium [m/z 278 reduced to 33.5% of the molecular ion cluster], with few having more than one D atom. Unfortunately the product molecular ion was of such low abundance that reliable information on its deuterium content could not be obtained.* In the ^{1}H NMR spectrum of the substrate–product mixture [Fig. 2(*b*), *cf.* 2(*a*) for undeuteriated substrate–product mixture of the same composition (2.5:1)] the integrals of the benzylic methylene groups indicated a composition 1.55 H/0.45 D for the substrate (in agreement with the mass spectrum) and 1.05 H/0.95 D for the product. Given that most of the product will have been formed from substrate containing considerably less deuterium than is present at the time of quenching (H–D exchange less advanced), that deuterium may be lost in the elimination stage, and that the Et_2ND was < 100 atom % D, it seems clear that in general a D atom is incorporated actually during the transition from substrate to product, *i.e.* that substitution does proceed *via* a thiophosphene intermediate.†

* Mass spectrometry should have been the ideal technique for our study of deuterium incorporation, giving an accurate measure of the relative amounts of $ArCH_2X$, ArCHDX and $ArCD_2X$ (the last of these cannot, of course, be seen in the ^{1}H NMR spectrum). Unfortunately, both the substrates and products gave molecular ions of low relative abundance and showed a disposition to ion–molecule reactions. The latter is potentially serious as $(M + H)^+$ would not be distinguished from M^+ containing a D atom. We have included only results obtained under conditions where ion–molecule reactions appeared to be of negligible importance, but we still consider the ^{1}H NMR results to be more reliable, albeit that they lack high precision.

† We are grateful to a referee for pointing out the potential value of deuterium-coupled ^{13}C NMR spectra in assessing the extent of deuterium incorporation.

The reactions of two of the other substrates with Et_2ND were also briefly examined (^1H NMR only). Predictably, the nitro compound **1b** (reaction time 10 min; 100% completion) gave product **3b** (R = Et) that was extensively deuteriated (benzylic methylene *ca.* 1.0 H/1.0 D). More surprisingly, the much less reactive unsubstituted-benzyl substrate **4a** also gave product [**6a** (R = Et)] containing some deuterium. Analysis of the substrate–product mixture from a reaction quenched (after 6 h) at 12% completion suggested a benzylic methylene composition of 1.7 H/0.3 D for the substrate and 1.6 H/0.4 D for the product. This may indicate that some of the product is formed *via* a thiophosphene [in additon to $S_N2(P)$ reaction of deuteriated substrate] but we are not confident that our measurements of the low levels of deuterium are very accurate. Qualitatively, there is no doubt that some deuterium was incorporated, and that in itself is significant: if the benzylic hydrogen is acidic enough to be replaced by deuterium, substitution by EA must presumably be feasible. Whether EA can successfully compete with $S_N2(P)$ remains, for the present, uncertain.

Conclusion.—It is, perhaps, surprising that the possibility of dissociative EA substitution involving methyleneoxophosphorane (phosphene) or methylenethioxophosphorane (thiophosphene) intermediates (Scheme 1, Z = C) has attracted so little attention. Related substitution reactions (Scheme 1, Z = O, S, N) have been, and continue to be, the focus of much activity, and there is good evidence for the formation of phosphenes and thiophosphenes in other types of reaction,[17] *e.g.* oxidation,[18] rearrangement[19] and fragmentation.[20] There has recently (since our preliminary communication[1]) been one report of a substitution involving a phosphene intermediate (Scheme 5; **15**→**16**), but an even more recent study could find



Scheme 5

no evidence for an EA mechanism in the alkaline hydrolysis of the phenolic esters **17** (Scheme 5; **17**→**18**).[14] Some years before that, Hall *et al.*[13] considered the possibility of an EA mechanism for the reaction of a dichloromethylphosphonate with methoxide (Scheme 5; **19**→**20**). This substitution is unusual in that the SMe group is replaced with retention of configuration at phosphorus. However, as the authors point out, it is difficult to see how a planar phosphene intermediate could be responsible for retention of configuration.

For the reactions of our nitro compounds **1b** and **4b** with Et_2NH the evidence for EA seems overwhelming: high reactivity, low selectivity, and incorporation of deuterium all point to the same conclusion. As in the EA reactions of sulfinyl, sulfonyl and carbonyl substrates,[21,22] the elimination stage is either E1cB or reversible E2 with an E1cB-like transition state. 4-Nitrobenzyl is obviously not a typical alkyl group, but in other respects our substrates are not unusual. With nucleophiles more basic than Et_2NH, it is probable that thiophosphenes will play a part in quite a few substitutions at thiophosphoryl centres. For phosphoryl compounds this seems less likely. With P=O in place of P=S, the neighbouring C–H bond will have essentially the same acidity,[23] but the three-coordinate P^V intermediate may be considerably less stable (relative to the substrate or its conjugate base). This, together with the greater ease of $S_N2(P)$ at a P=O centre,[15] may mean that only in exceptional circumstances will the dissociative EA mechanism make any significant contribution.

Experimental

M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were recorded at 90 MHz on a Varian EM 390 spectrometer or (where indicated) at 300 MHz on a Bruker AM-300 (Me_4Si internal standard; coupling constants given in Hz), and ^{31}P NMR spectra (^1H decoupled) were recorded at 36.2 MHz on a JEOL JNM-FX90Q spectrometer (positive chemial shifts downfield from external 85% H_3PO_4). Mass spectra were obtained in EI mode using VG 16-B (routine spectra), 12-253 (deuterium analyses) and ZAB-E (high resolution spectra) spectrometers, the last two at the SERC Mass Spectrometry Service Centre (Swansea). Me_2NH and Et_2NH were dried over KOH and CH_2Cl_2 was distilled from CaH_2. Light petroleum refers to the fraction b.p. 60–80 °C unless otherwise indicated, ether to diethyl ether, and DMF to *N*,*N*-dimethylformamide. Phenylphosphonothioic dichloride was commercial material (Aldrich), and diethyl phenylphosphonite was prepared from phenylphosphonous dichloride (reaction with EtOH–pyridine in light petroleum).

4-Nitrobenzyl(phenyl)phosphinic acid (**7b**). Diethyl phenylphosphonite (7.33 g, 37 mmol) and 4-nitrobenzyl bromide (7.13 g, 33 mmol) were stirred together under a stream of dry nitrogen. The flask was placed in an oil bath at 80 °C, the temperature was raised to 100 °C (vigorous reaction), and heating was continued for a further 0.5 h. On cooling, ethyl 4-nitrobenzyl(phenyl)phosphinate was obtained as a solid; a sample crystallised from ether had m.p. 101–102 °C; *m*/*z* 305 (M^+, 1.5%), 275 (40), 169 (20, $M^+ - CH_2Ar$) and 141 (100, $M^+ - CH_2Ar - C_2H_4$); $\delta_P(CDCl_3)$ 38.1; $\delta_H(CDCl_3)$ 8.03 (2 H, d, J_{HH} 8), 7.75–7.25 (5 H, m), 7.24 (2 H, dd, J_{PH} 2, J_{HH} 8), 3.97 (2 H, m), 3.35 (2 H, d, J_{PH} 18) and 1.29 (3 H, t, J_{HH} 7). The crude ester was hydrolysed by stirring with conc. hydrochloric acid (40 cm^3) at 125–130 °C (bath temp.) overnight. After cooling, the product was collected by filtration, washed with water, and crystallised from ethanol–water (15:1) (90 cm^3; insoluble impurity removed by hot filtration) to give 4-nitrobenzyl(phenyl)phosphinic acid **7b** (7.79 g, 85%), m.p. 176–178 °C; $\delta_P(CDCl_3)$ 38.9; $\delta_H(CDCl_3)$ 7.89 (2 H, d, J_{HH} 9), 7.6–7.2 (5 H, m), 7.09 (2 H, dd, J_{PH} 2, J_{HH} 9), 6.90 (2 H, s, OH + 0.5 H_2O) and 3.18 (2 H, d, J_{PH} 18) (Found: C, 55.8; H, 4.15; N, 4.9. $C_{13}H_{12}NO_4P$ requires C, 56.3; H, 4.4; N, 5.05%).

Benzyl(phenyl)phosphinic acid (**7a**). Ethyl benzyl(phenyl)phosphinate (5.0 g, 19.2 mmol)[24] was hydrolysed with conc. hydrochloric acid (18 cm^3) as above to give benzyl(phenyl)phosphinic acid **7a** (3.69 g, 83%), m.p. 177–179 °C (from ethanol) (lit.,[25] 178–180 °C); $\delta_P(CDCl_3)$ 41.2; $\delta_H(CDCl_3)$ 10.75 (1 H, s), 7.6–6.8 (10 H, m) and 3.08 (2 H, d, J_{PH} 18).

4-Nitrobenzylphosphonic acid (**10b**). 4-Nitrobenzyl bromide (9.7 g, 45 mmol) was stirred with triethyl phosphite (9.0 g, 54 mmol) under a gentle stream of dry nitrogen. The flask was placed in an oil bath at 80 °C, the temperature was raised to

110 °C, and heating was continued for a further 1.5 h. The excess phosphite was evaporated (100 °C/20 mmHg) leaving diethyl 4-nitrobenzylphosphonate **9b**, $\delta_H(CDCl_3)$ 8.12 (2 H, d, J_{HH} 9), 7.47 (2 H, dd, J_{PH} 2, J_{HH} 9), 4.04 (4 H, dq, J_{PH} 7, J_{HH} 7), 3.26 (2 H, d, J_{PH} 22) and 1.28 (6 H, t, J_{HH} 7). Without purification, this was hydrolysed by stirring with conc. hydrochloric acid (95 cm^3) at 130 °C (bath temp.) for 5.5 h. After cooling, 4-nitrobenzylphosphonic acid **10b** (9.3 g, 95%) was collected by filtration, m.p. 210–213 °C. The m.p. was considerably lower than expected (lit.,[26] 232–234 °C), but was not increased significantly by crystallisation (m.p. 212–215 °C from propan-2-ol). Also, the salt formed with Na_2CO_3 in D_2O was pure by NMR [δ_P 17.8; δ_H (referenced to Me_2CO, δ 2.00) 7.96 (2 H, d, J_{HH} 9), 7.32 (2 H, dd, J_{PH} 2, J_{HH} 9) and 2.94 (2 H, d, J_{PH} 21)].

Phosphinothioic chlorides. (*a*) Oxalyl chloride (0.51 g, 4.0 mmol) was gradually added to a stirred suspension of 4-nitrobenzyl(phenyl)phosphinic acid **7b** (0.55 g, 2.0 mmol) in CH_2Cl_2 (4 cm^3) (gas evolved). After a further 0.5 h the resulting solution (δ_P 49.9) was evaporated to dryness, giving the phosphinic chloride **8b**. To this was added $PSCl_3$ (2.0 g, 12.0 mmol) and DMF (6 mg), and the mixture was stirred at 130 °C for 20 h. All volatile material was removed *in vacuo* and the resulting solid was purified by filtration of a CH_2Cl_2 solution through silica gel. Crystallisation from CH_2Cl_2–light petroleum gave 4-nitrobenzyl(phenyl)phosphinothioic chloride **1b** (0.53 g, 84%), m.p. 134–135 °C; *m/z* 311, 313 (M^+, 80%), 175, 177 ($M^+ - CH_2Ar$, 100) and 139 (40); $\delta_P(CDCl_3)$ 83.7; $\delta_H(CDCl_3)$ 8.05 (2 H, d, J_{HH} 9), 8.0–7.4 (5 H, m), 7.23 (2 H, dd, J_{PH} 3, J_{HH} 9), 3.95 (1 H, d, J_{PH} 17) and 3.93 (1 H, d, J_{PH} 14) (Found: C, 49.8; H, 3.3; N, 4.4. $C_{13}H_{11}ClNO_2PS$ requires C, 50.1; H, 3.6; N, 4.5%).

(*b*) Benzyl(phenyl)phosphinic acid **7a** was converted into the phosphinic chloride **8a** and thence into benzyl(phenyl)-phosphinothioic chloride **1a** as in (*a*) above except that the product, m.p. 42–43 °C, could not be satisfactorily recrystallised; *m/z* 266, 268 (M^+, 100), 231 ($M^+ - Cl$, 10), 175, 177 ($M^+ - CH_2Ph$, 25) and 91 (55); $\delta_P(CDCl_3)$ 86.9; $\delta_H(CDCl_3)$ 8.0–7.35 (5 H, m), 7.3–6.9 (5 H, m) and 3.86 (2 H, d, J_{PH} 15) (Found: M^+, 266.0086. $C_{13}H_{12}ClPS$ requires *M*, 266.0086).

Phosphonothioic dichlorides. (*a*) 4-Nitrobenzylphosphonic acid **10b** (1.74 g, 8.0 mmol) was stirred with thionyl chloride (20 cm^3) and a catalytic amount of DMF (12 mg), and the mixture was heated (bath temp. 75 °C) until a clear solution was obtained (1.5–2 h). Volatile material was evaporated under reduced pressure to give the phosphonic dichloride **11b** (a solid), $\delta_P(CDCl_3)$ 42.0; $\delta_H(CDCl_3)$ 8.22 (2 H, d, J_{HH} 9), 7.57 (2 H, dd, J_{PH} 4, J_{HH} 9) and 4.05 (2 H, d, J_{PH} 19). This was heated with $PSCl_3$ (8.2 g, 48 mmol) and DMF (40 mg) at 130–140 °C (bath temp.). Further portions of DMF (10 mg) were added after 2 h and 12 h; reaction was essentially complete (δ_P 40.7→79.8) after 14 h. Volatile material ($POCl_3$ and excess of $PSCl_3$) was removed *in vacuo* and the product was extracted from the residue using several portions of hot light petroleum (b.p. 60–80 °C). The extracts, on cooling, gave crystals of 4-nitrobenzylphosphonothioic dichloride **12b** (1.41 g, 66%), *m/z* 269, 271, 273 (M^+, 55%) and 136 ($ArCH_2^+$, 100); $\delta_P(CDCl_3)$ 79.7; $\delta_H(CDCl_3)$ 8.20 (2 H, dd, J_{PH} 2, J_{HH} 9), 7.55 (2 H, dd, J_{PH} 5, J_{HH} 9) and 4.21 (2 H, d, J_{PH} 16). The analytical sample was purified by distillation, b.p. 120 °C (oven temp.)/0.2 mmHg, and recrystallisation from light petroleum, m.p. 73.5–74 °C (Found: C, 31.1; H, 2.2; N, 4.9. $C_7H_6Cl_2NO_2PS$ requires C, 31.1; H, 2.2; N, 5.2%).

(*b*) Benzylphosphonic dichloride **11a** (1.88 g, 9.0 mmol)[27] was heated with $PSCl_3$ (10.0 g, 59 mmol) and DMF (35 mg) at 140–145 °C for 5 h (δ_P 43.0→84.3). Volatile material was removed *in vacuo* and the residue was distilled to give benzylphosphonothioic dichloride **12a** (1.76 g, 87%), b.p. 120 °C (oven temp.)/1.0 mmHg; $\delta_P(CDCl_3)$ 85.5 (small impurity at 75.6) (lit.,[28] 85.3); $\delta_H(CDCl_3)$ 7.4–7.3 (5 H, m) and 4.08 (2 H, d, J_{PH} 15). A sample crystallised from light petroleum (b.p. 40–60 °C) had m.p. 22–23 °C.

Phosphonamidothioic chlorides. (*a*) Dimethylamine (108 mg, 2.4 mmol) in CH_2Cl_2 (3 cm^3) was added dropwise over 20 min to a stirred solution of 4-nitrobenzylphosphonothioic dichloride **12b** (324 mg, 1.2 mmol). After a further 1 h, voltatile material was evaporated and the residue, dissolved in CH_2Cl_2, was washed with water. Crystallisation from CH_2Cl_2–ether–light petroleum afforded *N,N*-dimethyl-*P*-(4-nitrobenzyl)phosphonamidothioic chloride **4b** (259 mg, 78%), m.p. 123–124 °C; *m/z* 278, 280 (M^+, 25%), 243 (10), 142, 144 ($M^+ - CH_2Ar$, 100) and 44 (90); $\delta_P(CDCl_3)$ 91.5; $\delta_H(CDCl_3$; 300 MHz) 8.21 (2 H, dd, J_{PH} 1, J_{HH} 9), 7.53 (2 H, dd, J_{PH} 3, J_{HH} 9), 3.88 (2 H, d, J_{PH} 17.5; slight non-equivalence of H atoms evident) and 2.89 (6 H, d, J_{PH} 16.5) (Found: C, 38.7; H, 4.3; N, 10.0. $C_9H_{12}ClN_2O_2PS$ requires C, 38.8; H, 4.3; N, 10.05%).

(*b*) Benzylphosphonothioic dichloride **12a** was similarly converted into *N,N*-dimethyl-*P*-benzylphosphonamidothioic chloride **4a** (64%), crystallised from ether–light petroleum, m.p. 61–62 °C; *m/z* 233, 235 (M^+, 15%), 198 (10), 142, 144 ($M^+ - CH_2Ph$, 20), 91 ($PhCH_2^+$, 100) and 44 (80); $\delta_P(CH_2Cl_2)$ 95.9; $\delta_H(CDCl_3$; 300 MHz) 7.40–7.27 (5 H, m), 3.80 (2 H, ABP, δ_A 3.85, δ_B 3.75, J_{AP} 17, J_{BP} 17, J_{AB} 15) and 2.86 (6 H, d, J_{PH} 16) (Found: C, 46.4; H, 5.6; N, 5.9. $C_9H_{13}ClNPS$ requires C, 46.25; H, 5.6; N, 6.0%).

(*c*) Phenylphosphonothioic dichloride was similarly converted (at 0 °C) into *N,N*-dimethyl-*P*-phenylphosphonamidothioic chloride **13** (97%), b.p. 115 °C (oven temp.)/0.5 mmHg (lit.,[29] 105 °C/0.1 mmHg); *m/z* 219, 221 (M^+, 45%), 184 (35), 143, 145 (60) and 44 (100); $\delta_P(CDCl_3)$ 89.5; $\delta_H(CDCl_3)$ 8.1–7.3 (5 H, m) and 2.73 (6 H, d, J_{PH} 18).

Phosphinothioic amides and phosphonothioic diamides. The compounds below were obtained from the reactions of phosphinothioic chlorides **1a** and **1b** and phosphonamidothioic chlorides **4a**, **4b** and **13** with Me_2NH or Et_2NH in CH_2Cl_2 after removal of the amine hydrochloride byproduct by washing with water or filtering through silica gel.

Amide **3a** (R = Me), crystallised from light petroleum–ether, m.p. 93.5–94.5 °C; *m/z* 275 (M^+, 25%) and 184 ($M^+ - CH_2Ph$, 100); $\delta_P(CDCl_3)$ 75.7; $\delta_H(CDCl_3)$ 7.8–6.75 (10 H, m), 3.54 (2 H, d, J_{PH} 15) and 2.53 (6 H, d, J_{PH} 14).

Amide **3a** (R = Et), crystallised from light petroleum–ether, m.p. 61–62 °C; *m/z* 303 (M^+, 20%) and 212 ($M^+ - CH_2Ph$, 100); $\delta_P(CDCl_3)$ 71.7; $\delta_H(CDCl_3)$ 7.85–6.85 (10 H, m), 3.57 (1 H, d, J_{PH} 15), 3.55 (1 H, d, J_{PH} 13), 3.04 (4 H, m) and 1.07 (6 H, t, J_{HH} 7) (Found: C, 67.1; H, 7.4; N, 4.65. $C_{17}H_{22}NPS$ requires C, 67.3; H, 7.3; N, 4.6%).

Amide **3b** (R = Me), m.p. 70 °C; *m/z* 320 (M^+, 10%) and 184 ($M^+ - CH_2Ar$, 100); $\delta_P(CDCl_3)$ 74.6; $\delta_H(CDCl_3)$ 7.90 (2 H, d, J_{HH} 9), 7.85–7.25 (5 H, m), 7.02 (2 H, dd, J_{PH} 3, J_{HH} 9), 3.65 (1 H, d, J_{PH} 17), 3.62 (1 H, d, J_{PH} 15) and 2.55 (6 H, d, J_{PH} 15) (Found: M^+, 320.0745. $C_{15}H_{17}N_2O_2PS$ requires *M*, 320.0748).

Amide **3b** (R = Et), crystallised from light petroleum–ether, m.p. 79–80 °C; *m/z* 348 (M^+, 15%) and 212 ($M^+ - CH_2Ar$, 100); $\delta_P(CDCl_3)$ 70.5; $\delta_H(CDCl_3)$ 7.91 (2 H, d, J_{HH} 9), 7.85–7.25 (5 H, m), 7.09 (2 H, dd, J_{PH} 3, J_{HH} 9), 3.70 (1 H, d, J_{PH} 16), 3.67 (1 H, d, J_{PH} 14), 3.09 (4 H, m) and 1.12 (6 H, t, J_{HH} 7) (Found: M^+, 348.1061. $C_{17}H_{21}N_2O_2PS$ requires *M*, 348.1061).

Diamide **6a** (R = Me), b.p. 140 °C (oven temp.)/0.3 mmHg; *m/z* 242 (M^+, 30%), 151 ($M^+ - CH_2Ph$, 100), 108 (20) and 91 (50); $\delta_P(CDCl_3)$ 86.6; $\delta_H(CDCl_3)$ 7.27 (5 H, br s), 3.37 (2 H, d, J_{PH} 15) and 2.52 (12 H, d, J_{PH} 12) (Found: M^+, 242.1007. $C_{11}H_{19}N_2PS$ requires *M*, 242.1007).

Diamide **6a** (R = Et), b.p. 145 °C (oven temp.)/0.3 mmHg; *m/z* 270 (M^+, 20%), 179 ($M^+ - CH_2Ph$, 95), 108 (50) and 91 ($PhCH_2^+$, 100); $\delta_P(CDCl_3)$ 85.1; $\delta_H(CDCl_3)$ 7.45–7.15 (5 H, m), 3.38 (2 H, d, J_{PH} 15), 3.05 (4 H, m), 2.51 (6 H, d, J_{PH} 13)

and 0.90 (6 H, t, J_{HH} 7) (Found: M^+, 270.1320. $C_{13}H_{23}N_2PS$ requires M, 270.1320).

Diamide **6b** (R = Me), crystallised from light petroleum, m.p. 76–77 °C; *m/z* 287 (M^+, 10%), 151 ($M^+ - CH_2Ar$, 100) and 108 (25); $\delta_P(CDCl_3)$ 84.9; $\delta_H(CDCl_3)$ 8.11 (2 H, dd, $J_{PH} < 1$, J_{HH} 8), 7.47 (2 H, dd, J_{PH} 3, J_{HH} 8), 3.47 (2 H, d J_{PH} 15) and 2.53 (12 H, d, J_{PH} 12) (Found: C, 46.2; H, 6.35; N, 14.4. $C_{11}H_{18}N_3O_2PS$ requires C, 46.0; H, 6.3; N, 14.6%).

Diamide **6b** (R = Et), crystallised from light petroleum, m.p. 88–90 °C; *m/z* 315 (M^+, 2%), 179 ($M^+ - CH_2Ar$, 100) and 108 (60); $\delta_P(CDCl_3)$ 83.1; $\delta_H(CDCl_3$; 300 MHz) 8.16 (2 H, dd, J_{PH} 1, J_{HH} 9), 7.55 (2 H, dd, J_{PH} 2.5, J_{HH} 9), 3.51 (2 H, ABP; δ_A 3.52, δ_B 3.495, J_{AP} 15.4, J_{BP} 15.7, J_{AB} 13.5), 3.17 (2 H, m), 3.00 (2 H, m), 2.57 (6 H, d, J_{PH} 12.5) and 0.97 (6 H, t, J_{HH} 7) (Found: C, 49.55; H, 7.0; N, 13.2. $C_{13}H_{22}N_3O_2PS$ requires C, 49.5; H, 7.0; N, 13.3%).

Diamide **14** (R = Me) crystallised from light petroleum (b.p. 40–60 °C), m.p. 44–45 °C (lit.,[30] 47 °C); *m/z* 228 (M^+, 45) and 151 (100); $\delta_P(CDCl_3)$ 82.5; $\delta_H(CDCl_3)$ 8.05–7.75 (2 H, m), 7.50–7.35 (3 H, m) and 2.57 (12 H, d, J_{PH} 12).

Diamide **14** (R = Et), b.p. 140 °C (oven temp.)/0.3 mmHg; *m/z* 256 (M^+, 25) and 72 (100); $\delta_P(CDCl_3)$ 80.0; $\delta_H(CDCl_3)$ 8.10–7.75 (2 H, m), 7.50–7.30 (3 H, m), 3.17 (4 H, dq, J_{PH} 12, J_{HH} 7), 2.52 (6 H, d, J_{PH} 14) and 0.98 (6 H, t, J_{HH} 7) (Found: C, 55.7; H, 8.65; N, 10.7. $C_{12}H_{21}N_2PS$ requires C, 56.2; H, 8.3; N, 10.9%).

Reactivity Studies.—A 10 mm NMR tube containing an anhydrous 0.6 mol dm^{-3} CH_2Cl_2 solution of Me_2NH or Et_2NH (1.0 cm^3) was placed in the probe of the ^{31}P NMR spectrometer maintained at 33 °C. The substrate (0.06 mmol) was added and the transformation of substrate (δ_P 84–96) to product (7–17 ppm up field) was monitored, using peak areas (height × half-height width) to deduce the extent of conversion. For the slowest reactions (**4a** and **13** with Et_2NH) the tube was transferred to a thermostatted bath (T 33 °C) between each recording. For the very fast reactions of the nitro compounds **1b** and **4b**, only one or two spectra could be recorded before the reaction was complete, and only approximate values of $t_{\frac{1}{2}}$ could be obtained. For all the other reactions, data from 6–10 spectra recorded over 1–2 halflives were used to construct first-order plots; from the slopes of the lines, values of the apparent first-order rate constant (and thence $t_{\frac{1}{2}}$) were deduced. In one case (**4b** with Et_2NH) it was shown that the presence of 1,4-dinitrobenzene (5 mg; 0.03 mmol) had no perceptible effect on the rate of reaction.

Competition Experiments.—The substrate (0.06 mmol) was added to a CH_2Cl_2 solution (1.1 cm^3) containing equimolar amounts of Me_2NH and Et_2NH (each amine 0.6 mol dm^{-3}) at 33 °C. When reaction was complete the NMe_2 : NEt_2 product ratio was measured (**1b**, 4.6 : 1; **4b**, 2.4 : 1), or the absence of the NEt_2 product established (**1a**, **4a**, **13**; 1% would have been detected), using ^{31}P NMR spectroscopy.

Deuterium Incorporation Studies.—Et_2ND was first prepared as follows: a solution of Et_2NH (0.73 g, 10 mmol) in CH_2Cl_2 (5 cm^3) was shaken with D_2O (>95 atom % D) (0.30 g, 15 mmol), the layers were separated, and the organic layer was dried over anhydrous K_2CO_3. The procedure was repeated three more times and the amine solution was finally dried over 4 Å molecular sieve (D_2O—washed prior to activation), diluted with CH_2Cl_2 to *ca.* 0.6 mol dm^{-3} amine [^1H NMR; ratio $Et_2ND(H):CH_2Cl_2$ = 1 : 23; ratio $Et_2NH:Et_2ND \leqslant 1:9$], and stored at −40 °C until used.

The substrate **4b** (19.5 mg, 0.07 mmol) was added to the above solution (1.1 cm^3) at *ca.* 33 °C. At the appropriate time (t = 240, 60 or 15 s) the reaction mixture was poured with stirring into ice-cold water (*ca.* 1.2 cm^3) containing a slight excess of HCl (relative to unreacted amine). The layers were separated, the aqueous layer was extracted with CH_2Cl_2, and the combined organic portions were dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was examined spectroscopically. Using ^1H NMR spectroscopy (300 MHz) the extent of substrate-to-product conversion was determined from the integrals of the NMe_2 signals, and the H/D composition of the benzylic methylene groups was deduced by comparing the integrals of their signals with those of the NMe_2 groups. The substrate–product mixtures were also examined by mass spectrometry (EI; low resolution). In a control experiment the (undeuteriated) product **6b** (R = Et) was treated with Et_2ND in the same way (t = 240 s); no incorporation of deuterium was apparent in the ^1H NMR spectrum (benzylic methylene integral 2.0 H) but the mass spectrum suggested the composition 1.95 H/0.05 D.

The reaction of substrate **4a** with Et_2ND was studied in the same way except that after the appropriate period (6 h) the reaction mixture was simply evaporated and the substrate–product mixture separated from amine hydrochloride by extraction into light petroleum.

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