Reactions of Bromonitroalkenes with Tervalent Phosphorus. Part II.[1] Reaction in Methanol

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The reactions of β-bromo-β-nitrostyrenes with triphenylphosphine in methanol have been investigated with a view to obtaining evidence for the site of initial attack. Some ion-pair hydrolysis products were obtained, but the major products from 2-phenyl- and 2-(4-methylphenyl)-1-bromo-1-nitroethylene were the novel rearranged benzylideneaminomethylphosphonium salts (7a and b), which were identified both from their spectra and by chemical degradation. With β-bromo-β-nitrostyrenes containing electron-withdrawing groups, triphenyl(triphenylphosphoranylideneamino)phosphonium bromide and α-formyl-α-phosphoniobenzylides were obtained: similar products were formed in the reaction of 1-chloro-2-nitrophenylethylene, and for this reason a common intermediate is proposed. Both azirine and oxaziridine intermediates are suggested to explain the formation of the foregoing products; the results of reactions in methan[^{2}H]ol support one of the proposed mechanisms.

β-BROMO-β-NITROSTYRENES undergo deoxygenation with triphenylphosphine in aprotic solvents to give high yields of (cyanomethyl)phosphonium salts (1) and triphenylphosphine oxide.[1] In an attempt to gain further information about the site of initial attack we have repeated these reactions in methanol, and in other protic solvents, where protons are readily available to trap the ion pair (3), ultimately as the debrominated nitro-compound (4) and methyltriphenylphosphonium bromide.

In some cases the methylphosphonium salt, the debrominated nitro-compound (4), and triphenylphosphine oxide were isolated from reactions in methanol (see Table). In addition to methyltriphenylphosphonium bromide, reactions with 1-bromo-1-nitroprop-1-ene also yielded isopropenyltriphenylphosphonium bromide (5).

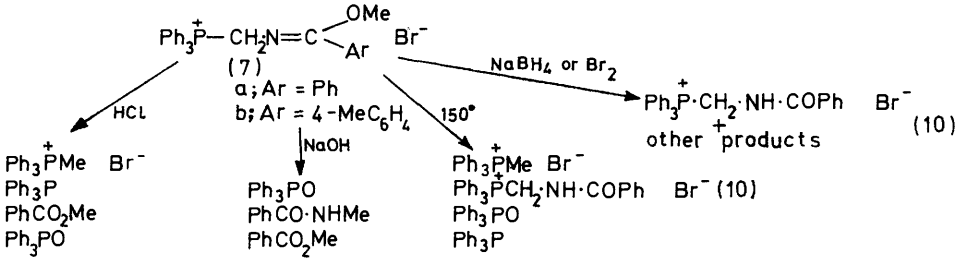
In general these yields are low and nitroalkenes (2) having electron-withdrawing substituents give different types of product, although extra stabilisation of the ion pair (3) might be expected. The reaction of β-bromo-β-nitrostyrene (2a) in benzene containing diethyl malonate gave a mixture of α-cyanobenzyltriphenylphosphonium bromide, triphenylphosphine oxide, β-nitrostyrene, and the salt (6). The last two products presumably arise from reactions of the ion pair (3) with diethyl malonate, although in this case the reaction observed in aprotic solvents [1] is not completely suppressed.

In addition to the low yield of methyltriphenylphosphonium bromide, the reaction of β-bromo-β-nitrostyrene

[1] Part I, C. J. Devlin and B. J. Walker, *J.C.S. Perkin I*, 1973, 1428.

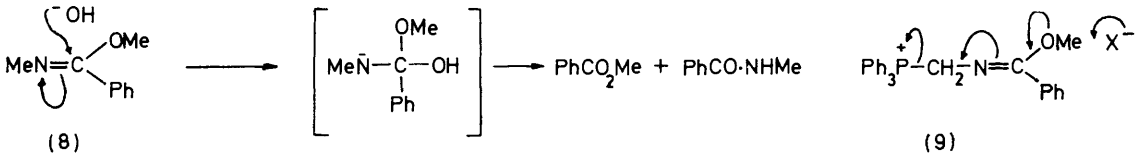
with triphenylphosphine in methanol gave another phosphonium salt (7a). An analogous salt (7b) was obtained from a similar reaction of β-bromo-β-nitro-4-methylstyrene with triphenylphosphine. The i.r. spectrum of the salt (7a) showed that it contained no nitro-group but did have methoxy- (2750) and >C=N- (1655 cm^{-1}) systems. Although the mass spectrum did not show a molecular ion, intense peaks at *m/e* 105, 96, and 94 suggested fragmentation to benzoyl and methyl bromide. The presence of a methoxy-group was confirmed by a three-proton singlet at τ 6·44 in the n.m.r. spectrum, which also showed a two-proton doublet (*J* 8 Hz) at τ 4·14. The low-field position of the latter resonance suggests a methylene group adjacent to positively charged phosphorus, although the coupling constant (J_{PH}) is low.[2]

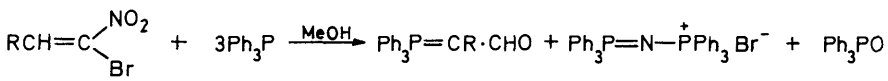
On the basis of these spectral data the salt (7a) was tentatively identified as (α-methoxybenzylideneaminomethyl)triphenylphosphonium bromide and this structure was confirmed by chemical degradation (Scheme 1). Under conditions of basic hydrolysis initial reaction presumably leads to triphenylphosphine oxide and the imine (8), the latter undergoing further hydrolysis to give a mixture of *N*-methylbenzamide and methyl benzoate. The triphenylphosphine and methyltriphenylphosphonium salt formed by acidic hydrolysis could arise by nucleophilic attack at the methoxy carbon atom (9) and expulsion of phosphine, which could then react with the methyl fragment. Vacuum pyrolysis at 150 °C, reduction with borohydride in methanol at 0 °C, and refluxing in chloroform containing bromine, all gave a new salt (10) together with low yields of other products. The structure (10) was assigned on the basis of amide carbonyl i.r. absorption and a two-proton doublet of doublets (J_{PH} 3, J_{NH} 6 Hz) at τ 4·59 in the n.m.r. spectrum, which collapsed to a doublet (J_{PH} 3 Hz) * on shaking with D_2O and to a broad singlet on irradiation at the NH frequency (τ 0·04).†

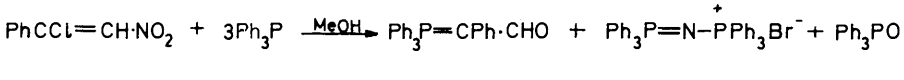


SCHEME 1

The structure (10) was confirmed by synthesis from *N*-(bromomethyl)benzamide ‡ and triphenylphosphine. Samples of (10) prepared in this way showed no detectable differences in i.r. and n.m.r. spectra from those obtained from salt (7a). However, samples of (10) obtained by the latter route generally had a lower m.p. and were less crystalline than those prepared by quaternisation, although the nature of any impurities present was never determined. Attempts to convert the amide salt (10) into the ethoxy-analogue of salt (7a) by reaction with







‡ The prepared sample of *N*-(bromomethyl)benzamide (see ref. 26) gave a mass spectrum with no molecular ion and showing a bromine-containing impurity (*m/e* 226 and 228); however quaternisation with triphenylphosphine gave the salt (10), which had spectral characteristics identical with those of the corresponding chloride synthesised from triphenylphosphine and pure *N*-(chloromethyl)benzamide.

* An unusually low J_{PCH} value was also observed for (7a).

† The NH absorption is a well resolved triplet, in spite of the ^{14}N quadrupole moment, and PCNH coupling is apparently absent.

[2] G. Marvel, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 261.

triethyloxonium tetrafluoroborate were unsuccessful, although the last reagent has been used to convert amides into imino-ethers [3]; increased difficulty in the alkylation of compounds containing a positive centre is not unexpected.

Different types of product were obtained from the reaction of triphenylphosphine with β-bromo-β-nitrostyrenes containing electron-withdrawing substituents. 2-(3-Nitrophenyl)- and 2-(4-nitrophenyl)-1-bromo-1-nitroethylene (2; R = 3- or 4-$O_2N{\cdot}C_6H_4$) each reacted with 3 mol. equiv. of triphenylphosphine in methanol to give triphenylphosphine oxide, (triphenylphosphoranylideneamino)phosphonium bromide (12), and the corresponding phosphonium ylide (11). A similar reaction took place with 2-(3-chlorophenyl)-1-bromo-1-nitroethylene (2e) to give (12) but only traces of the formyl ylide (11e) were isolated. A significant amount of methyl 3-chlorobenzoate was isolated from this reaction, a possible source of which is the rearranged salt (7; Ar = 3-ClC_6H_4), especially since this should be particularly susceptible to hydrolysis through the effect of the 3-chlorophenyl group.*

1-Chloro-2-nitro-1-phenylethylene and triphenylphosphine undergo a closely related reaction in methanol to give the formyl ylide (11a), the iminophosphine (12), and triphenylphosphine oxide. A similar reaction in nitromethane gave (12) and phosphine oxide but α-formylbenzyltriphenylphosphonium chloride was formed in place of the corresponding ylide.

The formyl ylides (11) were identified on the basis of their spectra; all showed carbonyl i.r. absorption at *ca.* 1600 cm^{-1} and molecular ions in their mass spectra; their n.m.r. spectra have been discussed elsewhere.[4] An authentic sample of α-formylbenzyltriphenylphosphorane (11a) [5] was prepared from the reaction of triphenylphosphine with 2-bromo-2-phenylacetaldehyde, followed by treatment of the phosphonium salt obtained with base.

The introduction of further electron-withdrawing substituents into the nitroalkene (2) caused another change in reaction path. 2-(2,4-Dinitrophenyl)-1-bromo-1-nitroethylene and triphenylphosphine in methanol gave triphenylphosphine oxide and traces of the cyano-ylide [13; R = 2,4-$(NO_2)_2C_6H_3$] together with a compound identified as (2,4-dinitrophenyl)acetamide on the basis of its n.m.r. and mass [6] spectra. Traces of a red compound, which was not identified, were also obtained. A summary of all the products isolated from the reactions of various bromonitroalkenes with triphenylphosphine in methanol is given in the Table.

The formation of salt (7) is most easily rationalised [7] in terms of an intermediate azirine (14) (Scheme 2). Support for this mechanism is available both from the reaction of α-chloronitroalkanes with triphenylphosphine,[8] which appears to proceed *via* an oxime derivative related to (15), and from the analogy of the rearrangement of (15) with the Neber rearrangement.[9] Initial attack of phosphine, illustrated as taking place on oxygen, could take place on halogen, although in the latter case rapid further reaction would be required since under the reaction conditions methanolysis of the ion pair is a further available pathway.

Rearrangement of the azirine (14) would apparently take place *via* the antiaromatic [10] anion (16), although the high energy of such a species may be reduced by the phosphorus 3*d* orbitals accepting electrons from the

Products (%) from the reaction of triphenylphosphine with 1-bromo-1-nitroalkenes

$$RCH{=}CBr{\cdot}NO_2 + 3Ph_3P \xrightarrow{MeOH} \text{products}$$

R	Ph_3PO	$Ph_3P{:}CR{\cdot}CN$ (13)	$Ph_3\overset{+}{P}MeBr^-$ * A	B	$Ph_3\overset{+}{P}{\cdot}CH_2{\cdot}N{:}{-}CR{\cdot}OMe\ Br^-$ (7)	$RCH{:}CH{\cdot}NO_2$ (4)	$Ph_3P{:}CR{\cdot}CHO$ (11)	$Ph_3P{:}N{\cdot}\overset{+}{P}Ph_3$ (12)	Miscellaneous
a; Ph	77	13	24	26	55	Trace			
b; 4-MeC_6H_4	73	19	28	30	47	21			
c; 4-$MeO{\cdot}C_6H_4$	53 †		43	100		40			
d; 3-$NO_2{\cdot}C_6H_4$	52	3					60	58	
e; 3-ClC_6H_4	70	3	12	18			2	48	Ph_3P (17%) RCO_2Me (11%)
f; Me	75		31	50					Ph_3P (10%) Salt (5) (31%)
g; 4-$NO_2{\cdot}C_6H_4$	47	Trace					62	42	
h; 2,4-$(NO_2)_2$-C_6H_3	114	6							$RCH_2{\cdot}CO{\cdot}NH_2$ (9%)

* A, Actual yield of salt; B, yield of salt as a percentage of total salts + ylides isolated. † Yield of oxide calculated on the assumption that 1 mole of alkene (2c) gives 1 mole of oxide. The yield of oxide in all other cases is calculated on the assumption that 1 mole of alkene (2) gives 2 moles of oxide. The yield of all other products is calculated on the assumption that 1 mole of alkene (2) gives 1 mole of product.

* Traces of (7; Ar = 3-ClC_6H_4) were detected in some reactions.

[3] L. A. Paquette, *J. Amer. Chem. Soc.*, 1964, **86**, 4096; S. Petersen and E. Tietze, *Annalen*, 1959, **623**, 166.

[4] C. J. Devlin and B. J. Walker, *Tetrahedron*, 1972, **28**, 3501.

[5] A hydrated form of ylide (11a) has been reported: H. J. Bestmann in ' Newer Methods of Preparative Organic Chemistry,' vol. V, ed. W. Foerst, Academic Press, Germany, 1968, p. 27.

[6] H. Budzikiewicz, C. Djerassi, and D. H. Williams, in ' Mass Spectroscopy of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 336.

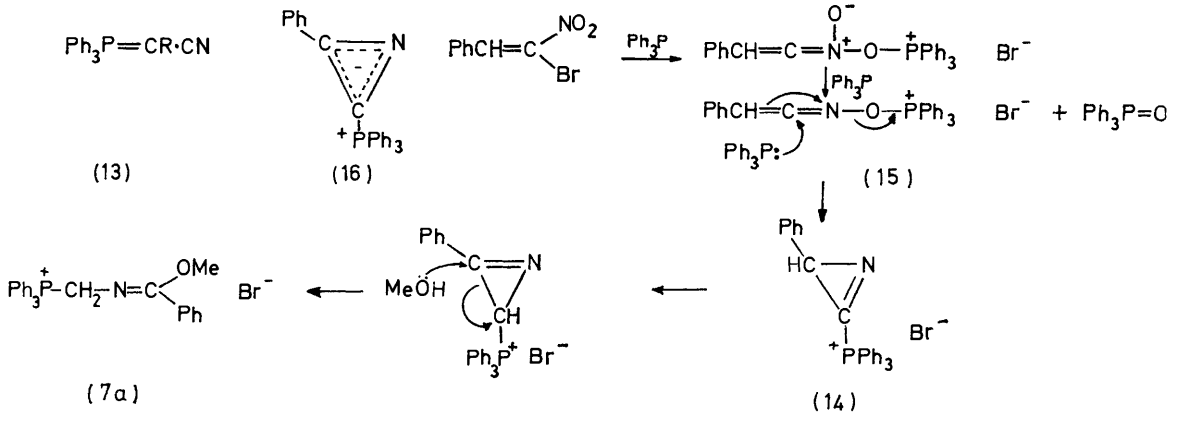
[7] C. J. Devlin and B. J. Walker, *Chem. Comm.*, 1970, 917.

[8] M. Ohno and N. Kawake, *Tetrahedron Letters*, 1966, 3935.

[9] C. O'Brien, *Chem. Rev.*, 1964, **64**, 81.

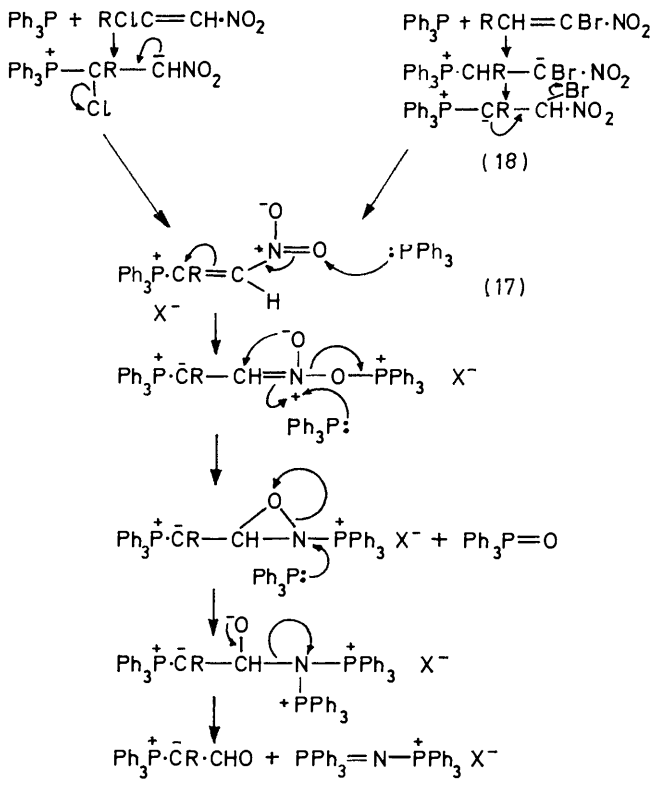
[10] R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, 1967, **89**, 4383.

ring.[11] The salt (7a) obtained from reactions in methan-[^{2}H]ol had both methylene protons replaced by deuterium atoms in accord with this mechanism, whereas samples of the salt (7a) did not undergo exchange of their methylene protons during several days in methan[^{2}H]ol.



SCHEME 2

The formation of the formyl ylides (11) and the iminophosphine (12) from bromonitrostyrenes carrying electron-withdrawing substituents is more difficult to rationalise. However, the isolation of similar products from the reaction of 1-chloro-2-nitro-1-phenylethylene and triphenylphosphine in methanol suggested that a common intermediate might be involved. In addition, the formation of α-formylbenzyltriphenylphosphonium bromide in a similar reaction of 1-chloro-2-nitro-1-phenylethylene in nitromethane indicated that the source of the aldehyde oxygen atom was the nitroalkene rather than the solvent, and probably excludes mechanisms related to the Nef reaction.[12] In view of this we tentatively suggest the mechanism outlined in Scheme 3, in which the 2-nitrovinylphosphonium salt (17) is the common intermediate. A reasonable route to (17) from 1-chloro-2-nitro-1-phenylethylene involves an addition–elimination reaction, and phosphines are known[13] to react with activated vinyl halides to give vinyl phosphonium salts in high yield. The formation of (17) from β-bromo-β-nitrostyrenes could involve a similar initial addition followed by proton transfer to give the ylide (18), which could eliminate bromide to give (17). Only styrenes containing electron-withdrawing groups give formyl ylides with triphenylphosphine and this supports the foregoing mechanism since the stability of the ylide (18) is presumably important in the proton-transfer step.



SCHEME 3

EXPERIMENTAL

M.p.s were taken on a Kofler hot-stage apparatus. I.r., mass, and n.m.r. spectra were obtained with a Perkin-Elmer 457, an A.E.I. MS-902, and a Varian HA-100 spectrometer (tetramethylsilane as internal reference), respectively.

Halogenonitroalkenes.— *1-Chloro-2-nitro-1-phenylethylene.*[14a] Phenylacetylene (26·3 g, 0·26 mol) in carbon tetrachloride (37 ml) at 0° was added to nitrosyl chloride[14b] (35·04 g, 0·535 mol) in carbon tetrachloride (37 ml) at −40 to −60° with stirring during 2 h. This solution was stirred at or below 0° for 4 days and then at room temperature for 2 days. The solvent was then removed under reduced pressure (bath temp. 25—30°) to leave a reddish oil. This oil crystallised from hot light petroleum (b.p. 30—40°) to give, overnight at 0 °C, yellow crystals, m.p. 49—51°. This solid was distilled under reduced pressure, the fraction of b.p. 99—102° at 2·0 mmHg being collected. One crystallisation from light petroleum (b.p. 40—60°) gave *trans*-1-chloro-2-nitro-1-phenylethylene (8·3 g, 18%), m.p. 51—52°

[11] See M. A. Battiste and C. T. Sprouse, *Tetrahedron Letters*, 1969, 3165.

[12] N. Kornblum, R. K. Blackwood, and J. W. Powers, *J. Amer. Chem. Soc.*, 1957, **79**, 2507.

[13] G. Pattenden and B. J. Walker, *J. Chem. Soc.* (*C*), 1969, 531.

[14] (*a*) I. Owai, K. Tomita, and J. Ido, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 118 (*Chem. Abs.*, 1965, **62**, 14,541f); (*b*) J. R. Morton and H. W. Wilcox, *Inorg. Synth.*, 1953, **4**, 48.

(lit.,[14a] 55—56°); $\nu_{max.}$ (KBr) 1630, 1525, and 1340 cm^{-1}; τ (CCl_4) 2·57(s); *m/e* 185(1%), 184(1), 183(2), 182(1), 155(11), 148(15), 127(27), 125(58), 105(41), 102(100), 101(33), and 93(33). Other halogenonitroalkenes were prepared as previously described.[1]

Reactions of Halogenonitroalkenes with Triphenylphosphine. —(*a*) 1-Bromo-1-nitro-2-phenylethylene (2a) (2·96 g, 0·013 mol) in methanol (150 ml) was added to triphenylphosphine (10·48 g, 0·040 mol) in methanol (1 l) in one portion at room temperature. The solution was stirred for 24 h. The methanol was removed under reduced pressure without heating. Ethyl acetate–ether (5 : 1; 400 ml) was added and the mixture was then put aside for 6—8 h. The solution was decanted and the yellow oily solid was washed with ethyl acetate (50 ml) and ether (3 × 150 ml) and triturated to give a whitish solid (4·6 g), m.p. 175—178°, consisting of methyltriphenylphosphonium bromide and the salt (7a) in the ratio 1 : 2·3, respectively (n.m.r.) (actual yields of 24 and 55%, respectively). Three recrystallisations from chloroform–ethyl acetate gave (*β-methoxybenzylideneaminomethyl)triphenylphosphonium bromide* (7a) (0·9 g), m.p. 188—190°; $\nu_{max.}$ (KBr) 2750, 1650, 1435, 1310, 1270, 1100, 740, 710, and 685 cm^{-1}; *m/e* 277(2%), 262(100), 183(50), 152(7), 108(3), 105(40), 96(50), and 94(50); τ ($CDCl_3$) 2·25 (15H, m), 2·55 (5H, m), 4·14 (2H, d, J_{PH} 8 Hz), and 6·44 (3H, s) (Found: C, 66·1; H, 5·3; Br, 16·7; N, 2·9; P, 6·6. $C_{27}H_{25}BrNOP$ requires C, 66·1; H, 5·1; Br, 16·3; N, 3·1; P, 6·3%).

The ethyl acetate–ether solution and washings were reduced in volume (to 50 ml) and chromatographed on alumina (600 g). Elution with ether gave traces of β-nitrostyrene;[15] elution with ether–ethyl acetate (1 : 1) gave α-cyanobenzyltriphenylphosphorane (13) (0·54 g, 13%), m.p. 203—204°. Elution with ethyl acetate gave triphenylphosphine oxide (5·6 g, 77%), m.p. and mixed m.p. 153—154°.

(*b*) 1-Bromo-2-(4-methylphenyl)-1-nitroethylene (2b) (1·45 g, 0·006 mol) in methanol (225 ml) was added to triphenylphosphine (4·18 g, 0·018 mol) in methanol (450 ml) in one portion at room temperature. The solution was stirred for 24 h. The methanol was then removed under reduced pressure to give an oil, to which was added ethyl acetate–ether (5 : 1, 300 ml). After 14 h, the solvent was decanted from the yellow oily solid, which was washed with ethyl acetate (150 ml) and then ether (2 × 150 ml), and recrystallised from chloroform–ethyl acetate to give a white solid (2·0 g), m.p. 175—178°. The i.r. spectrum indicated that it contained methyltriphenylphosphonium bromide and (α-methoxy-4-methylbenzylideneaminomethyl)triphenylphosphonium bromide (7b); this was confirmed by its n.m.r. spectrum: τ ($CDCl_3$) 2·22 (m), 2·62 (m), 4·15 (d, J_{PH} 8 Hz, P·CH_2·N), 6·44 (s, OMe), 6·74 (d, J_{PH} 14 Hz, P·CH_3), and 7·62 (s, C_6H_4·CH_3), which indicated yields of 28 and 47%, respectively.

The ethyl acetate–ether extract and washings were reduced in volume (to 75 ml) and chromatographed on activated alumina (400 g). Elution with ether gave 1-(4-methylphenyl)-2-nitroethylene (2b)[16] (0·21 g, 21%), m.p. and mixed m.p. 100—101°. Elution with ether–ethyl acetate (1 : 1) gave α-cyano-4-methylbenzyltriphenylphosphorane (13b) (0·44 g, 19%), m.p. 213—214°. Elution with ethyl acetate gave triphenylphosphine oxide (2·44 g, 73%), m.p. and mixed m.p. 153—154°.

(*c*) 1-Bromo-2-(4-methoxyphenyl)-1-nitroethylene (2c), by the same procedure, gave methyltriphenylphosphonium bromide (43%), m.p. 225° (lit.,[17] 227—229°); τ ($CDCl_4$) 2·24 (15H, m) and 6·74 (3H, d, J_{PH} 14 Hz), 1-(4-methoxyphenyl)-2-nitroethylene (4c)[18] (40%), m.p. and mixed m.p. 87—88°, and triphenylphosphine oxide (53%), m.p. and mixed m.p. 153—154°.

(*d*) 1-Bromo-1-nitro-2-(4-nitrophenyl)ethylene (2g) (3·55 g, 0·013 mol) in methanol (450 ml) was added to triphenylphosphine (10·22 g, 0·039 mol) in methanol (1400 ml) at room temperature in one portion. The solution was stirred at room temperature for 30 h. The methanol was removed under reduced pressure without heating. Addition of ethyl acetate (600 ml) and ether (160 ml) to the residual red oil gave pinkish crystals of triphenyl(triphenylphosphoranylideneamino)phosphonium bromide (12)[19] (3·4 g, 42%), m.p. 252—253°. One recrystallisation gave white crystals, m.p. and mixed m.p. 255—256° (from methanol–ether); $\nu_{max.}$ (KBr) 3020, 1480, 1435, 1280—1260 (band), 1100, 990, 745, 720, and 685 cm^{-1}; *m/e* 277, 272, and 262; τ ($CDCl_3$) 2·44 (m, aromatic) (Found: C, 70·5; H, 5·3; Br, 13·1; N, 2·4; P, 9·8. Calc. for $C_{36}H_{30}BrNP_2$: C, 69·9; H, 4·9; Br, 12·9; N, 2·3; P, 10·0%).

The ethyl acetate–ether filtrate was reduced in volume (to 50 ml) under reduced pressure and chromatographed on activated alumina (900 g). Elution with ether–ethyl acetate (1 : 1) gave traces of a red oil, $\nu_{max.}$ 2145 cm^{-1} (C≡N) and mass spectrometry confirmed that this contained α-cyano-4-nitrobenzyltriphenylphosphorane (13 g), *m/e* 422. Elution with ethyl acetate gave triphenylphosphine oxide (4·0 g, 47%), m.p. and mixed m.p. 153—154°. Elution with ethyl acetate containing methanol (3%) gave *α-formyl-4-nitrobenzylidenetriphenylphosphorane* (11 g) (3·4 g, 62%), m.p. 222—227°, which afforded yellow crystals (2·6 g), m.p. 228—229° (from ethyl acetate); $\nu_{max.}$ (KBr) 2750, 1610, 1570, 1500, 1440, 1340, 1305, 1290br, 1190, 1150, 1100, 995, 850, 750, 710, and 690 cm^{-1}; *m/e* 425·118 (100%) (M^+, $C_{26}H_{20}NO_3P$ requires 425·118), 424 (91), 480·115(4) ($C_{26}H_{19}NO_2P$ requires 408·115), 396(8), 378·141(18) ($C_{26}H_{21}NP$ requires 378·141), 349(3), 277(12), 262(14), 201(12), 185(14), 185(14), 183(43), 165(10), 153(6), 108(17), 77(4), and 76(9) (Found: C, 73·1; H, 5·0; N, 3·6; P, 7·8. $C_{26}H_{20}NO_3P$ requires C, 73·4; H, 4·7; N, 3·3; P, 7·3%).

(*e*) 1-Bromo-2-nitro-2-(3-nitrophenyl)ethylene (2d), by the same procedure, over 30 h, gave triphenyl(triphenylphosphoranylideneamino)phosphonium bromide (12) (58%), m.p. and mixed m.p. 255—256°, α-cyano-3-nitrobenzyltriphenylphosphorane (13d)[1] (3%), triphenylphosphine oxide (52%), and *α-formyl-3-nitrobenzylidenetriphenylphosphorane* (11d) (60%), m.p. 157—158°, as yellow crystals from ethyl acetate; $\nu_{max.}$ (KBr) 2750, 1610, 1580, 1530, 1480, 1440, 1370, 1350, 1340, 1100, 990, 870, 790, 760, 750, 730, 710, and 690 cm^{-1}; *m/e* 425(100%), 4·8(5), 396(7), 378(17), 351(5), 349(5), 277(25), 262(15), 201(19), 183(58), 165(13), 152(10), 108(19), 77(7), and 76(19) (Found: C, 72·9; H, 4·6; N, 3·1; P. 7·6. $C_{26}H_{20}NO_3P$ requires C, 73·4; H, 4·7; N, 3·3; P, 7·3%).

(*f*) 1-Bromo-2-(3-chlorophenyl)-1-nitroethylene (2e), by the same procedure over 48 h, gave a mixture, m.p. 220—230°, of methyltriphenylphosphonium bromide and triphenyl(triphenylphosphoranylideneamino)phosphonium bromide (12) in the ratio 1 : 4 (n.m.r. spectrum) (actual

[15] D. E. Worrall, *Org. Synth.*, Coll. Vol. I, 1941, p. 413.
[16] D. E. Worrall, *J. Amer. Chem. Soc.*, 1938, **60**, 2841.
[17] W. Foerst in 'Newer Methods of Preparative Organic Chemistry,' Academic Press, London, 1964, p. 141.
[18] K. W. Rosenmund, *Ber.*, 1909, **42**, 4778.
[19] V. R. Appel and A. Hauss, *Z. anorg. Chem.*, 1961, **311**, 290.

yields 12 and 48%, respectively). Three recrystallisations from chloroform–ethyl acetate gave pure (12), m.p. and mixed m.p. 255—256°.

Chromatography gave triphenylphosphine (17% of total used) and methyl *m*-chlorobenzoate (11%) on elution with ether. Triphenylphosphine was isolated as methyltriphenylphosphonium iodide, m.p. and mixed m.p. 182—183°. Elution with ether–ethyl acetate (1 : 1) gave 3-chloro-α-cyanobenzyltriphenylphosphorane (13e) (3%), m.p. and mixed m.p. 195—198°, and elution with ethyl acetate gave triphenylphosphine oxide (70%), m.p. and mixed m.p. 153—154°. Elution with ethyl acetate containing 3% methanol gave *3-chloro-α-formylbenzylidenetriphenylphosphorane* (11e) (2%), m.p. 178—179° (off-white crystals from ethyl acetate); $\nu_{max.}$ (KBr) 3010, 2760, 1585, 1560, 1460, 1420, 1325, 1245, 1170, 1140, 1100, and 1020 cm^{-1}; *m/e* 416(38), 415(55), 414(100), 413(94), 397(4), 385(16), 351(7), 277(9), and 262(28) (Found: C, 75·0; H, 4·6; Cl, 8·7. $C_{26}H_{20}ClOP$ requires C, 75·3; H, 4·8; Cl, 8·6%).

(*g*) 1-Bromo-1-nitroprop-1-ene (2f), by the same procedure, over 3 days, gave a mixture, m.p. 180—190°, shown (n.m.r.) to consist of equal proportions of methyltriphenylphosphonium bromide and isopropenyltriphenylphosphonium bromide (5) (actual yields 31% each); τ ($CDCl_3$) 2·22 (m), 3·10 (d, J_{PH} 48 Hz), 3·90 (d, J_{PH} 22 Hz), 6·76 (d, J_{PH} 14 Hz, P·CH_3), and 7·70 (d, J_{PH} 14 Hz, P·C·CH_3) [identical with the spectrum from equal quantities of authentic methyltriphenylphosphonium bromide [17] and isopropenyltriphenylphosphonium bromide (5) [20]].

Chromatography gave triphenylphosphine (10% of the total used), identified as methyltriphenylphosphonium iodide, m.p. and mixed m.p. 182—183°, and triphenylphosphine oxide (75%), m.p. and mixed m.p. 153—154°.

(*h*) 1-Chloro-2-nitro-1-phenylethylene, by the same procedure, over 44 h, gave white crystalline triphenyl(triphenylphosphoranylideneamino)phosphonium chloride (40%), m.p. 270—273° (lit.,[21] 269—271°); $\nu_{max.}$ (KBr) 3020, 1480, 1435, 1330—1240br, and 1110 cm^{-1}; τ ($CDCl_3$) 2·22 (m); *m/e* 277, 276, and 262 (Found: C, 74·8; H, 5·6; Cl, 6·1; N, 2·4; P, 11·1. Calc. for $C_{36}H_{30}ClNP_2$: C, 75·3; H, 5·2; Cl, 6·2; H, 2·4; P, 10·8%).

Chromatography gave triphenylphosphine oxide (49%), m.p. and mixed m.p. 153—154°, eluted with ethyl acetate. Further elution with the same solvent containing 2% methanol gave off-white crystals of *α-formylbenzylidenetriphenylphosphorane* (11a) (39%), m.p. 157—158° (from ethyl acetate); $\nu_{max.}$ (KBr) 3060, 2740, 1600, 1560, 1490, 1440, 1340, 1320, 1290, 1210, 1150, and 1105 cm^{-1}; *m/e* 380(100), 379(90), 363(3), 351(13), 203(3), 277(5), 262(7), 185(6), 183(35), 165(19), 152(8), 108(17), 91(7), and 77(8) (Found: C, 82·1; H, 5·5; P, 8·2. $C_{26}H_{21}OP$ requires C, 82·0; H, 5·5; P, 8·2%).

(*i*) 1-Chloro-2-nitro-1-phenylethylene reacted with triphenylphosphine (3 mol. equiv.) in nitromethane, under the same conditions, to give a mixture, m.p. 170—180°, of α-formylbenzyltriphenylphosphonium chloride (ν_{CO} at 1610br cm^{-1}) and triphenyl(triphenylphosphoranylideneamino)-phosphonium chloride (1330—1250br cm^{-1}). This solid was dissolved in chloroform and shaken with aqueous 5N-sodium hydroxide for 5 min. The dried chloroform layer was evaporated to give a mixture of salt and ylide. Extraction of the residue with hot ethyl acetate gave α-formylbenzylidenetriphenylphosphorane (11a), m.p. 157—158°. The remainder had m.p. and mixed m.p. 270—273° (from methanol–ether). Calculations showed that the solid originally isolated contained α-formylbenzyltriphenylphosphonium chloride and triphenyl(triphenylphosphoranylideneamino)phosphonium chloride in the ratio 10 : 11 (actual yields 49 and 31%, respectively).

Chromatography on activated alumina gave triphenylphosphine oxide (64%), m.p. and mixed m.p. 153—154°.

(*j*) 1-Bromo-2-(2,4-dinitrophenyl)-1-nitroethylene (2h) (2·23 g, 0·007 mol) in methanol (100 ml) was added in one portion to triphenylphosphine (5·50 g, 0·021 mol) in methanol (400 ml) at 0—5° with vigorous stirring. A deep red colour developed and within 5 min a red solid was precipitated. Stirring was continued for 3 h. The solid was filtered off, washed with cold ethyl acetate (10 ml), and recrystallised from ethyl acetate to give red crystals (1·3 g), m.p. 165—168° (decomp.) (Found: C, 63·5; H, 4·0; N, 9·1; P, 9·5. Calc. for $C_{18}H_{13}N_2O_3P$: requires C, 64·3; H, 3·9; N, 8·3; P, 9·2%); $\nu_{max.}$ (KBr) 1600, 1565, 1480, 1440, 1340, 1310, 1260, 1100, and 1075 cm^{-1}; *m/e* 277(100%), 262(6), 207(5), 201(16), 199(16), 185(7), 183(13), 108(2), 107(22), 77(15), and 51(10); τ ($CDCl_3$) 1·42 (d, *J* 2 Hz), 1·52 (d, *J* 2 Hz), 2·38 (m), 2·68 (d, *J* 9 Hz) and 3·00 (d, *J* 9 Hz) (ratio 6 : 13 : 127 : 6 : 3).

The red filtrate was evaporated to dryness under reduced pressure without heating and the residue was chromatographed on activated alumina (500 g). Elution with ether–ethyl acetate (1 : 1) gave *α-cyano-2,4-dinitrobenzyltriphenylphosphorane* (13 h) (0·2 g, 6%) as yellow crystals (from ethyl acetate), m.p. 218—220°; $\nu_{max.}$ (KBr) 2150, 1600, 1520, 1475, 1430, 1345, 1315, 1300, 1100, 735, 720, and 695 cm^{-1}; *m/e* 422(9%), 421(100) (*M* − NO_2), 420(55), 377(20), 376(45), 277(4), 262(16), 196(28), 194(55), 163(5), 108(16), and 77(5) (Found: C, 67·3; H, 4·2; N, 8·8. $C_{26}H_{18}N_3O_4P$ requires C, 66·8; H, 3·9; N, 9·0%).

Further elution with ether–ethyl acetate (1 : 1) gave triphenylphosphine oxide (4·4 g, 114%), m.p. and mixed m.p. 153—154°. Elution with ethyl acetate gave red tarry products; elution with ethyl acetate containing 3% methanol gave a red solid, 2,4-dinitrophenylacetamide (0·14 g, 9%), m.p. 168—174° (lit.,[22] 180°; yellow); $\nu_{max.}$ (KBr) 3300, 3100, 1660, 1565, 1520, 1380, and 1350 cm^{-1}; *m/e* 181(100%) (*M* − $OCNH_2$), 179(100) (*M* − NO_2), 164(85), 150(43), 133(17), 124(12), 122(17), 107(8), 106(12), 105(17), 102(14), 90(50), 78(30), 75(43), 63(64), 44(43), and 43(5); τ [$(CD_3)_2SO$] 1·30 (2H, s), 2·02 (1H, d, *J* 2 Hz), 2·18 (1H, d, *J* 10 Hz), 2·80 (1H, dd, *J* 10 and 2 Hz), and 5·50 (2H, masked by H_2O impurity in solvent).

Reaction of 1-Bromo-1-nitro-2-phenylethylene (2a) *with Triphenylphosphine in the presence of Diethyl Malonate.*—To triphenylphosphine (2·1 g, 0·008 mol) in benzene (100 ml) containing diethyl malonate (10 ml) was added 1-bromo-1-nitro-2-phenylethylene (0·61 g, 0·0027 mol) in benzene (50 ml). The yellow solution was stirred for 48 h at room temperature to give a crystalline precipitate (0·215 g), m.p. 197—200°. The n.m.r. [τ ($CDCl_3$) 8·7 (t), 5·8 (q)] and i.r. [$\nu_{max.}$ (KBr) 2660, 1610, and 1580 cm^{-1}] spectra suggested that this was a mixture of salts (1) and (6) and this was supported by its mass spectrum (*m/e* 377 and 420).

The filtrate was reduced in volume (to 10 ml), and chromatographed on alumina (100 g). Elution with ether gave β-nitrostyrene [15] (0·04 g); elution with ethyl acetate gave

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triphenylphosphine oxide (1·1 g), m.p. and mixed m.p. 154—155°.

Synthesis of α-Formylbenzylidenetriphenylphosphorane (11a).—(a) *α-Bromophenylacetaldehyde.*[23] To *cis*-β-Methoxystyrene [24] (11·3 g, 0·085 mol) in ether (50 ml) at −20° was added bromine (13·6 g, 4·34 ml, 0·85 mol) during 10 min with stirring. The solution was then immediately poured into aqueous 10% sodium hydrogen carbonate (100 ml) at 0° and the mixture was stirred at this temperature for 2 h. The ether layer was washed with water (100 ml), dried, and evaporated under reduced pressure. Fractional distillation, under dry nitrogen, gave an oil, α-bromophenylacetaldehyde (6·8 g, 40%), b.p. 83—84° at 2 mmHg (lit.,[23] 82—85° at 2 mmHg, 48%) which deteriorated in air.

(b) *α-Formylbenzyltriphenylphosphonium bromide.* To α-bromophenylacetaldehyde (4·98 g, 0·025 mol) in benzene (50 ml) at 5—10° was added triphenylphosphine (6·55 g, 0·025 mol) in benzene (200 ml) at 5—10° in one portion. The solution was allowed to reach room temperature and left at this temperature for 2 h. The solvent was decanted from the oil which, when washed with ethyl acetate (200 ml) and ether (200 ml), gave a semicrystalline solid. Recrystallisation from chloroform–ethyl acetate gave white crystals of *α-formylbenzyltriphenylphosphonium bromide* (6·2 g, 54%), m.p. 233—237°. A sample obtained by three recrystallisations from nitromethane–ethyl acetate had m.p. 235—237°; ν (KBr) 2760, 2550br, 1610br, 1440, 1355, 1250, and 1110 cm^{-1}; *m/e* 380(100%), 379(100), 351(21), 277(6), 262(9), 201(10), 185(9), 183(44), 165(21), 108(14), 91(6), 82(12), 81(4), 80(12), and 79(4); τ ($CDCl_3$) 1·76 (1H, d, J_{PH} 32 Hz), 2·40 (15H, m), and 2·90 (5H, m) (Found: C, 67·4; H, 4·7; Br, 17·1; P, 6·9. $C_{26}H_{22}BrOP$ requires C, 67·7; H, 4·8; Br, 17·4; P, 6·7%).

(c) *α-Formylbenzylidenetriphenylphosphorane* (11a). α-Formylbenzyltriphenylphosphonium bromide (3·2 g, 0·007 mol) in chloroform (50 ml) was shaken with aqueous 5N-sodium hydroxide (50 ml) for 5 min. The chloroform layer was washed with water (2 × 50 ml), dried, and evaporated to give an oil which crystallised from ethyl acetate to give off-white crystals of α-formylbenzylidenetriphenylphosphorane (11a) (1·4 g, 54%), m.p. 157—158°, identical (i.r., mass, and n.m.r. spectra) with the compound obtained from the reaction of 1-chloro-2-nitro-1-phenylethylene with triphenylphosphine in methanol.

Decomposition of (α-Methoxybenzylideneaminomethyl)triphenylphosphonium Bromide (7a).—(a) *Acidic hydrolysis.* To the salt (7a) (2·0 g) was added 5N-hydrochloric acid (70 ml). The solution was stirred at room temperature for 12 h. A sweet smell developed on addition of the acid and some white solid precipitated after a few hours. Extraction with ether (200 ml) followed by drying and evaporation gave a sweet-smelling oil (1·1 g) which showed two spots on t.l.c. Chromatography on silica gel (150 g) (elution with ether) gave an oil (0·6 g) which was shown, by g.l.c. (Carbowax-1540 column at 100°), to contain methyl benzoate (0·3 g) and by t.l.c. to contain triphenylphosphine (0·2 g) (isolated as the salt, methyltriphenylphosphonium iodide, m.p. and mixed m.p. 182—183°). Further elution, with ethyl acetate, gave triphenylphosphine oxide (0·2 g), m.p. and mixed m.p. 153—154°.

Extraction of the acidic solution with chloroform (200 ml) followed by drying and evaporation gave a white oil (0·9 g). Extraction of this oil with ethyl acetate (50 ml) gave triphenylphosphine oxide (0·1 g); crystallisation of the residual sticky solid from chloroform–ethyl acetate eventually gave methyltriphenylphosphonium bromide (0·09 g), m.p. and mixed m.p. 226—227°.

(b) *Alkaline hydrolysis.* To the salt (7a) (2·0 g) was added aqueous 5N-sodium hydroxide (50 ml) and the resulting solution was stirred for 2 h. A whitish sticky solid was precipitated in the first hour. Extraction with ether, drying, and evaporation gave a whitish oil from which triphenylphosphine oxide (0·3 g) crystallised when the oil dissolved in the minimum of ether. G.l.c. of the filtrate indicated traces of methyl benzoate, and chromatography on silica gel (100 g) gave, on elution with ether, *N*-methylbenzamide (0·1 g), m.p. 74—76° (lit.,[25] 78—79°); $\nu_{max.}$ (KBr) 3320, 1630, and 1550 cm^{-1}; τ ($CDCl_3$) 2·16 (2H, dd), 2·64 (3H, m), 3·10br (1H, s), and 7·00 (3H, d); *m/e* 135 (55%) (M^+), 134(17), 105(100), and 77(60). Further elution with ethyl acetate, gave triphenylphosphine oxide (0·1 g), m.p. and mixed m.p. 153—154°.

(c) *Pyrolysis.* The salt (7a) (0·5 g) was maintained at 150° in a sublimation apparatus at 0·05 mmHg for 4 h. The residue (0·3 g) showed three spots on t.l.c., two of which were due to triphenylphosphine and phosphine oxide and the other to salt products. The residue was washed free of phosphine and phosphine oxide with ethyl acetate (25 ml) to leave an oily solid. N.m.r. spectroscopy indicated that this contained methyltriphenylphosphonium bromide and another salt (10). Semicrystalline *(benzamidomethyl)triphenylphosphonium bromide* (10) (0·06 g) was obtained by four successive recrystallisations from chloroform–ether; m.p. 205—208° (lit.,[7] m.p. 166—167°); $\nu_{max.}$ (KBr) 3220, 1665, 1530, 1485, 1430, 1270, and 1110 cm^{-1}; τ ($CDCl_3$) 0·04 (1H, t), 2·0—2·5 (17H, m), 2·60—2·72 (3H, m), and 4·59 (2H, dd, J_{PH} 3, J_{NH} 6 Hz); *m/e* 262(100%), 183(80), 152(15), 108(72), 107(26), 105(70), 77(80), and 51(50) (Found: C, 64·8; H, 5·0; Br, 17·0; N, 2·8; P, 6·6. $C_{26}H_{23}BrNOP$ requires C, 65·6; H, 4·8; Br, 16·8; N, 2·9; P, 6·5%).

Synthesis of (Benzamidomethyl)triphenylphosphonium Halides.—N-*(Bromomethyl)benzamide.*[26] To *N*-(hydroxymethyl)benzamide [27] (7·55 g, 0·05 mol) in ether (30 ml) at 0 °C was added phosphorus pentabromide (21·55 g, 0·05 mol) in portions during 30 min with vigorous stirring. During the addition dry nitrogen was passed into the flask and the reagent was stored under ether (20 ml), which was added to the flask when addition was complete. The yellow solution was stirred for a further 2 h, while it warmed to room temperature. Filtration and washing with ether (10 ml) and light petroleum (b.p. 40—60°) (10 ml) gave *N*-(bromomethyl)benzamide (6·0 g, 56%), m.p. 101—104° (lit.,[26] 105—107°; 80%, yellow) from dioxan–ether; $\nu_{max.}$ (KBr) 3280, 1655, and 1525 cm^{-1}; τ ($CDCl_3$) 2·1—2·2 (2H, m), 2·3—2·7 (3H, m), and 4·34 (2H, deformed d). The mass spectrum contained no parent peak, but showed extraneous peaks of equal intensity at *m/e* 228 and 226 with a base peak at 134 and a smaller peak at 105.

N-*(Chloromethyl)benzamide.*[26] To *N*-(hydroxymethyl)-benzamide (7·55 g, 0·05 mol) in ether (10 ml) at 0° was added phosphorus pentachloride (10·4 g, 0·05 mol) during 30 min

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[24] K. Auwers, *Ber.*, 1911, **44**, 3514.
[25] H. E. Franck and R. Adams, *J. Amer. Chem. Soc.*, 1921, **43**, 651.
[26] H. Bohme, R. Broese, A. Dick, F. Eiden, and D. Schunemann, *Chem. Ber.*, 1959, **92**, 1599.
[27] A. Einhorn, E. Bischkopff, and B. Szelinski, *Annalen*, 1905, **343**, 223.

with vigorous stirring. Care was taken to exclude moisture and a work-up similar to the foregoing gave *N*-(chloromethyl)benzamide (4·29 g, 47%), m.p. 80—84° (lit.,[26] 87—88°; 77%) (from carbon tetrachloride–acetonitrile); $\nu_{max.}$ (KBr) 3300, 1655, and 1525 cm^{-1}; τ ($CDCl_3$; 60 MHz) 2·0—2·4 (2H, m), 2·4—2·9 (3H, m), and 4·5—5·2 (2H, deformed d); *m/e* 171(8%), 169(25) (M^+), 135(3), 134(25), 133(14), 105(100), 77(100), and 51(57).

(Benzamidomethyl)triphenylphosphonium bromide (10). To a stirred solution of *N*-(bromomethyl)benzamide (6·0 g, 0·028 mol) in ethyl acetate (250 ml) was added (in one portion, at room temperature) triphenylphosphine (7·87 g, 0·03 mol) in ethyl acetate (70 ml). The solution became cloudy and after 1 h an oil separated. The solution was stirred for 6 h, and was then decanted from an oil, which was well washed with hot ethyl acetate (3 × 50 ml). Trituration gave a white solid, m.p. 204—220°, which fumed slightly and from which white crystals of the title compound (7·2 g, 54%) were obtained by one recrystallisation from chloroform–ethyl acetate; m.p. 234—236° (Found: C, 65·5; H, 5·0; Br, 16·8; N, 2·8; P, 6·5. Calc. for $C_{26}H_{23}BrNOP$: C, 65·6; H, 4·8; Br, 16·8; N, 2·9; P, 6·5%). The i.r., mass, and n.m.r. spectra of this compound were identical with those for a salt that resulted from pyrolysis, bromination, and reduction of salt (7a).

(Benzamidomethyl)triphenylphosphonium chloride. To a stirred solution of *N*-(chloromethyl)benzamide (3·4 g, 0·02 mol) in ethyl acetate (150 ml) at room temperature was added, in one portion, triphenylphosphine (6·55 g, 0·025 mol) in ethyl acetate (50 ml). The solution was set aside for 12 h, during which a crystalline solid was precipitated. This was filtered off, washed with hot ethyl acetate (3 × 50 ml), and recrystallised from chloroform–ethyl acetate to give white crystals of the *title compound* (6·0 g, 69%), m.p. 230—231° (Found: C, 72·4; H, 5·3; Cl, 8·2; P, 7·3. $C_{26}H_{23}ClNOP$ requires C, 72·3; H, 5·3; Cl, 8·2; P, 7·2%); $\nu_{max.}$ (KBr) 3200—2900br,w, 1650, 1530, 1485, 1440, 1285, and 1110 cm^{-1}; *m/e* 262(100%), 185(9), 183(80), 152(13), 108(45), 107(30), 105(55), 77(69), and 51(35); τ ($CDCl_3$) −0·64 (1H, t, NH), 2·00—2·56 (17H, m), 2·56—2·82 (3H, m), and 4·64 (2H, dd, J_{PH} 3, J_{HH} 6 Hz).

Triethyloxonium Tetrafluoroborate[28] *Treatment of (Benzamidomethyl)triphenylphosphonium Bromide.*—To a stirred solution of triethyloxonium tetrafluoroborate (1·89 g, 0·01 mol) in methylene chloride (25 ml) under nitrogen at room temperature was added (benzamidomethyl)triphenylphosphonium bromide (10) (4·76 g, 0·01 mol) in the same solvent, dropwise during 15 min. The solution was stirred at room temperature for 18 h, then aqueous 5% sodium carbonate (20 ml) was added and stirring was continued for 30 min. The organic layer was separated, washed with water (50 ml), dried, and evaporated to give an oil consisting of triphenylphosphine and phosphine oxide (t.l.c.) and unchanged salt (10), which was isolated by three successive recrystallisations from chloroform–ethyl acetate (1·9 g; m.p. 230—235°).

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[28] H. Meerwein, *Org. Synth.*, 1966, **46**, 113.