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N,N-DIHALOPHOSPHORAMIDES—VI*

SYNTHESIS AND SOME PREPARATIVE APPLICATIONS OF DIALKYL N,N-DIBROMO-PHOSPHOROAMIDATES

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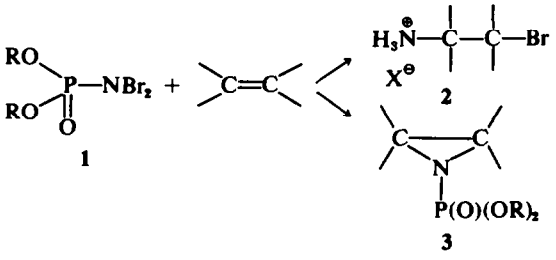
Abstract—O,O'-Dialkyl N,N-dibromophosphoroamidates, a novel pseudohalogen-type reagent has been prepared by direct bromination of O,O'-dialkyl phosphoroamidates in aqueous potassium carbonate. The preparative usefulness of these compounds in the synthesis of N-phosphorylated 2-phenylaziridines has been demonstrated.

Recently, various N,N-dihaloamides, particularly N,N-dichlorourethane (DCU) and N,N-dichlorosulphonamides, have proven of significant value for the facile one-step functionalization of unsaturated compounds.[2]

Although a lot of work on addition of N,N-dichloroamides to olefins has been done and the preparative usefulness of these and related reactions has been firmly established, the relevant data concerning the behaviour of N,N-dibromoamides are limited to a few examples only. It has been reported[3,4] that N,N-dibromoderivatives of aromatic sulphonamides react with styrene to form 1-phenyl-1-arylsulphonamido-2-bromoethanes. However, recent investigation of the addition of N,N-dibromobenzenesulphonamide to norbornylene[5] as well as the results obtained by Ueno *et al.* on the addition of the same reagent to cyclohexene[6] and cyclopentene[7] have shown that the reactions are not straightforward and clean but afford a complex mixture of products.

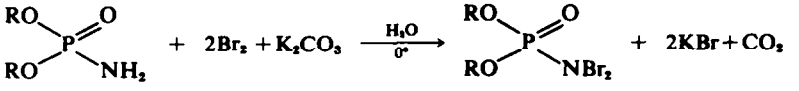
In the light of our findings on addition of diethyl N,N-dichlorophosphoroamidate (DCPA) to phenylethylenes[8] dialkyl N,N-dibromophosphoroamidates (1) seemed to be very promising as new pseudohalogen-type reagents for the preparation of β-bromoamines (2), and particularly for the synthesis of N-phosphorylated aziridines (3) directly from unsaturated compounds:



The purpose of this work is to investigate the reality of the synthetic projects outlined above.

Here we present the preparation of dialkyl N,N-dibromophosphoroamidates (1), a novel class of organophosphorus pseudohalogens, and some preliminary results pertinent to their preparative applicability.

Dialkyl N,N-dibromophosphoroamidates (1) have not been hitherto described except the compound $[(EtO)_2P(O)NBr_2]_3.NaBr$ which was obtained recently by Pinchuk *et al.*[9] from the reaction of diethyl N,N-dichlorophosphoroamidate and sodium bromide. We have found that free diethyl N,N-dibromophosphoroamidate (DBPA; 1, R = Et) of analytical purity can be readily obtained in excellent yield (94%) by direct bromination of diethyl phosphoroamidate. The reaction using elemental bromine was carried out in K_2CO_3 aq. at 0° (Eq. 1).



(1)

Use of the stoichiometric amount of K_2CO_3 to neutralize the hydrobromic acid as it was formed rendered the reaction practically irreversible and

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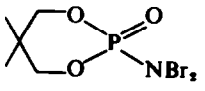
almost quantitative. DBPA, which is insoluble in the aqueous system, separated as an orange-red sirupy oil having a sharp, characteristic odour resembling elemental bromine. As determined by ^{31}P NMR, it was analytically pure and contained no unreacted diethyl phosphoroamidate. Samples of crude DBPA thus prepared could be stored in the dark at 0–5° without any appreciable symptoms of decomposition. Similarly to DCPA[10] diethyl N,N-dibromophosphoroamidate exhibited typical behaviour of positive halogen containing reagents. It reacted instantaneously and quantitatively with acidified KI aq liberating free iodine. It was also found, as expected, to add easily in an anti-Markovnikov fashion to a variety of unsaturated compounds.[11] The chemical reactivity of DBPA towards unsaturated compounds, (examined in our Laboratory) makes it an attractive organophosphorus halogenoid of significant synthetic utility.

Structural analogues of DBPA, *viz.* di-*n*-propyl N,N-dibromophosphoroamidate (1, R = *n*-Pr), diisopropyl N,N-dibromophosphoroamidate (1, R = *i*-Pr), di-*n*-butyl N,N-dibromophosphoroamidate (1, R = *n*-Bu), di-*t*-butyl N,N-dibromophosphoroamidate (1, R = *t*-Bu), and 2-(N,N-dibromoamino)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (4) have been synthesized by the same experimental procedure (Eq. 1) starting from the corresponding phosphoroamidates.



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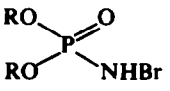

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The first three compounds, which are orange-red sirupy oils, were contaminated with considerable amounts (up to 30% as determined by ^{31}P NMR) of unidentified, phosphorus containing impurities, possibly the corresponding dialkyl N-bromophosphoramidates (5). This assumption, (discussed later) is based on experimental evidence involving the almost quantitative transformation of crude 1 into N-phosphorylated 2-phenylaziridines (6). No unreacted dialkyl phosphoroamidates were detected (^{31}P NMR) in respective samples of 1. Di-*t*-butyl N,N-dibromophosphoroamidate and cyclic N,N-dibromophosphoroamidate (4) are pale-yellow crystalline solids, the former being extremely unstable even when stored in the dark over KOH.

Bromination of diethyl phosphoramidate carried out in the presence of sodium or lithium carbonate afforded in both cases yellow water insoluble solids (m.p. 118–120° and 108–112° respectively) for which the structures $(DBPA)_3$, NaBr and $(DBPA)_3$. LiBr have been anticipated on the basis of elemental analysis data.[1]

Physical constants, yields, elemental analysis and spectral data of dialkyl N,N-dibromophosphoroamidates (1) and of the cyclic analogue 4 are in the Table. All structural assignments are unequivocally supported by IR and NMR spectral data which are in all cases fully consistent with the relevant structures.

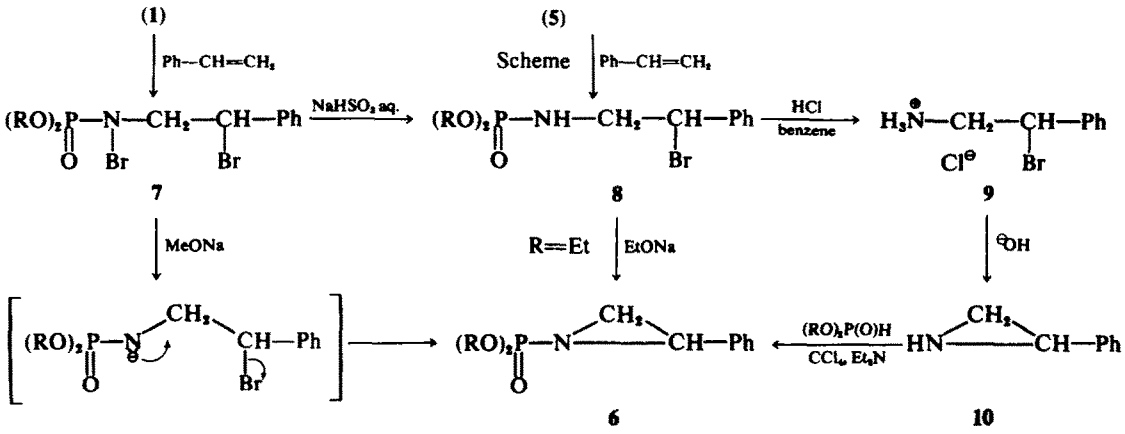
Some reactions of diethyl N,N-dibromophosphoroamidate (DBPA; 1, R = Et) and its structural analogues are visualized on the Scheme. Styrene was used as a model unsaturated hydrocarbon to exemplify those chemical transformations which may be of interest as potential synthetic procedures and can simultaneously deliver the final proof of structure for N-phosphorylated 2-phenylaziridines (6) prepared directly from 1 and the olefin. According to our preliminary report[1] the anti-Markovnikov addition of DBPA to styrene affords diethyl N-bromo-N-(β-bromo-β-phenylethyl)phosphoroamidate (7, R = Et) which can be subsequently reduced to 8 (R = Et) and then degraded by means of gaseous HCl to yield β-bromo-β-phenylethylamine hydrochloride (9) in good yield.* The preparative usefulness of 9 as starting material for the synthesis of 2-phenylaziridine 10 is obvious. Phosphorylation of 10 by conventional methods gives rise to the formation of the corresponding N-phosphorylated derivative 6. In the search for a simpler and more effective approach to 6 we turned our attention to the possibility of direct cyclization of the primarily formed adducts (7). These adducts were easily produced when styrene was added dropwise to a boiling dichloromethane solution of 1. All reactions were rapid, exothermic and complete within 30 min. It was neither necessary nor desirable to isolate the products. On treatment with two molar equivalents of methanolic NaOMe at room temp they could be directly transformed into N-phosphorylated 2-phenylaziridines (6). Products of NMR purity have been obtained in all cases. They could not be, however, purified by distillation *in vacuo* without any appreciable loss of material due to the partial thermal decomposition. Considerable amounts of impurities present in some N,N-dibromophosphoroamidates (1, R = *n*-Pr, *i*-Pr, *n*-Bu), as mentioned previously, did not affect the yield of crude 6 which was almost quantitative in all cases. It seems therefore reasonable to assume the structure of the corresponding N-bromoamides (5) for the contaminants. If this is the case, one can expect the formation of 8 on addition of 5 to styrene. As proven by an independent experiment, cycliza-

*The structure of 8 (R=Et) is evident from its ^1H NMR spectrum[1] exhibiting the presence of a downfield triplet ($\delta = 4{\cdot}95$, $J_{HH} = 7{\cdot}5$ Hz) for a methine proton. If the Br atom and amino group were reversed, as claimed by Kharasch and Priestley[3] for N,N-dibromosulphonamide-styrene adducts, such a pattern would not be obtained. In this case the ^1H NMR spectrum would display the presence of a downfield *double* triplet for the methine proton, owing to coupling with the adjacent methylene protons and P atom.

Table 1. N,N-Dibromophosphoramides

Compd.	Yield %	m.p. °C	n^{30}	Analyses, Calc. / Found C%	H%	P%	N%	Characteristic IR absorption bands[a] cm^{-1}	^{1}H-NMR[b] δ, J(Hz)	^{31}P-NMR δ (from H_3PO_4)
1, R = Et	94	—	1·5244	15·4 15·55	3·2 3·1	10·0 9·8	4·5 4·85	1250s (P=O); 1161s (Et—O—(P)); 1094s 1024s, 970s (P—O—(C))	1·443, 1·457 (2t, 6H, J_{HH} 7·1, CH_3); 4·26 (2q. 4H, J_{HH} 7·1, J_{PH} 8·3, CH_2—CH_3)	−10·7 (pure)
1, R = *n*-Pr	94	—	1·5120	21·2 23·4	4·1 4·4	9·1 8·7	4·1 4·5	1240s (P=O), 1016s (P—O—(C)); 542s, 515s (N—Br?)	1·06 (t, 6H, J_{HH} 6·9, CH_3—CH_2); 1·79 (st. 4H, J_{HH} 6·9, —CH_2—CH_2—O); 4·05qt. 4H, J_{HH} 6·9, —CH_2—O)	−10·5 19% impurities δ = −9·3
1, R = *i*-Pr	94	—	1·5040	21·2 22·9	4·1 4·6	9·1 9·0	4·1 4·4	1390s, 1380s (CH_3) 1255vs (P=O); 1012 vs (P—O—(C)); 548s 526s (N-Br?)	1·42 (d, 12H, J_{HH} 6·5, CH_3); 4·32–5·10 (m, 2H, —CH—O)	−8·5 (28% impurities δ = −7·2)
1, R = *n*-Bu	94	—	1·5024	26·2 26·4	4·9 4·9	8·45 8·5	3·8 4·0	1246vs (P=O); 1030vs (P—O—(C)); 545m, 518m (N—Br?)	1·00 (t. def., 6H, CH_3) 1·17–2·47 (m, 8H, —CH_2—CH_2—); 4·20 (qt. def., 4H, —CH_2—O)	−10·6 (29% impurities δ = −9·3)
1, R = *t*-Bu	78	88–89	—	26·2 27·2	4·9 5·0	8·45 8·35	3·6 4·0	1399w, 1373m (CH_3); 1242vs (P=O); 992vs (P—O—(C)); 557m, 535w (N-Br?)[c]	1·52 (s, 18H, CH_3)	−0·75 (pure)
4	85	132–136	—	18·6 18·8	3·1 3·1	9·6 9·2	4·3 4·3	1477w (CH_3); 1278 vs (P=O); 1052s, 1007s, 985m (P—O—(C)), 506s, 490m (N-Br?)[c]	0·90 (s, 3H, CH_3 eq.); 1·31 (s, 3H, CH_3 ax.); 3·55–4·27 (m, 4H, ring protons)[d]	−1·80[e] (pure)

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak;
[b] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; st, sextet; m, multiplet; def., ill-defined signal; ax., axial; eq., equatorial
[c] KBr disc
[d] $CDCl_3$ soln.
[e] Acetone soln.



tion of 8 can readily occur under basic conditions to give the same N-phosphorylated 2-phenylaziridine (6) as prepared directly from 1:

Structures of N-phosphorylated 2-phenylaziridines (6) have been unambiguously confirmed by their ^1H NMR spectra examination. All spectra exhibited a typical AMX pattern additionally split by the P atom for the aziridine ring protons. The values of $^3J_{PH}$ long-range coupling constants for these protons were found within the region of 15·0–20·0 Hz, which is compatible with the literature[12]. IR spectra and elemental analysis were also in good agreement with the proposed structures.

Molecular-type compound $(DBPA)_3.NaBr$ was found to add to styrene almost quantitatively but at a higher temperature (refluxing benzene) than the free 1, (R = Et). The lithium bromide–$(DBPA)_3$ complex produced, however, a mixture consisting upon reduction of 60% of adduct 8 and 40% of styrene dibromide.

EXPERIMENTAL

Light petroleum refers to the fraction boiling at 60–80°. All extracts were dried over $MgSO_4$ and evaporated under reduced press. B.p.'s and m.p.'s (taken in capillaries) are uncorrected. IR spectra were recorded for liquid films unless otherwise stated using an UR-10 spectrophotometer (C. Zeiss, Jena). ^1H NMR spectra were measured at 60 MHz with a Jeol JNM-C-60 HL spectrometer using TMS as internal standard. ^{31}P NMR spectra were recorded at 24·3 MHz with the same spectrometer using 85% H_3PO_4 as external reference. CCl_4 solns were used unless otherwise stated.

Dialkyl phosphoroamidates were prepared conventionally by the action of gaseous ammonia on the corresponding dialkyl phosphites in benzene-CCl_4 soln.[13]

Di-t-butyl phosphoroamidate. A stream of gaseous ammonia dried over KOH was passed through a soln of di-*t*-butyl phosphite[14] (87·0 g, 0·45 mole) in CCl_4 (200 ml) at 50–55° with efficient stirring. After 14 hr the soln was evaporated to dryness and the resulting solid (NH_4Cl + amide) extracted continuously with benzene for 10 hr. Evaporation of the extract afforded 56·3 g (60%) of crude amide, m.p. 134–137°. On recrystallization from light petroleum an analytically pure sample was obtained, with m.p. 136–137° (lit.[14]: m.p. 122–125° dec.). (Found: C, 45·8; H, 9·5; N, 6·7; P, 14·7: $C_8H_{20}NO_3P$ requires: C, 45·9; H, 9·6; N, 6·7; P, 14·8%). The IR spectrum (KBr disc) showed characteristic bands at: 3355s (NH), 3268s (NH), 3157s (NH), 1396m (CH_3), 1372s (CH_3), 1258s (P=O), 1232s (P=O), 1184s (P—O—(C)), 1048s (P—O—(C)), 1024s (P—O—(C)), 990vs (P—O—(C) cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) showed signals at: $\delta = 1{\cdot}50$ (s, 18H, CH_3), 3·40 (s, 2H, NH_2). The ^{31}P NMR spectrum ($CHCl_3$) showed signal at $\delta = -1{\cdot}42$ ppm (from 85% H_3PO_4 as external reference).

2-Amino-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan was prepared as described previously.[10]

Preparation of $(DBPA)_3.NaBr$ *and* $(DBPA)_3$. LiBr as well as addition of DBPA to styrene and degradation of the reduced adduct (8, R = Et) to 2-bromo-2-phenylethylamine hydrochloride (9) were described in the preliminary communication.[1]

Preparation of N,N-*dibromophosphoramides* (1), (4). *General procedure.* Bromine (16·0 g, 0·1 mole) was added dropwise with stirring and external cooling (ice-salt bath) to a soln of the corresponding phosphoroamidate (0·05 mole) in water (60 ml) at 0°. The resulting mixture was stirred for 30 min at 0° and finally for 1 hr at 20°. CH_2Cl_2 (40 ml) was then added, the organic layer separated, and the aqueous phase extracted with CH_2Cl_2 (3 × 20 ml). Combined extracts were water washed (2 × 20 ml), dried, and evaporated to an oil from which residual solvent was removed to give crude 1 as orange-red, syrupy oil. Synthesis of di-*t*-butyl N,N-dibromophosphoroamidate (1, R = *t*-Bu) was carried out for 1 hr at 0–5°. Yellow ppt was filtered off, washed with cold water (3 × 15 ml) and dried in the dark in a vacuum desiccator over KOH. Cyclic N,N-dibromophosphoroamidate (4) was obtained by the standard procedure, but isolated from the reaction by filtration of the pale-yellow ppt followed by washing with cold water (3 × 15 ml) and drying *in vacuo* over KOH.

Addition of diethyl N,N-*dibromophosphoroamidate* (1, R = Et) *to styrene.* N-(*Diethoxyphosphoryl*)-2-*phenylaziridine* (6, R = Et). A soln of styrene (5·2 g, 0·05 mole) in CH_2Cl_2 (15 ml) was added dropwise with stirring to the boiling soln of DBPA (15·55 g, 0·05 mole) in CH_2Cl_2 (60 ml). The soln was refluxed gently for 30 min, cooled to room temp and treated with 15% methanolic NaOMe (0·1 mole). Stirring was continued for 1 hr at room temp. NaBr ppt was filtered off and washed with CH_2Cl_2 (3 × 50 ml). The soln was water washed (3 × 30 ml), dried,

and evaporated to give crude N-(diethoxyphosphoryl)-2-phenylaziridine (11·9 g, 93%) of NMR purity. Distillation *in vacuo* afforded pure **6** (R = Et) as colourless oil, (72%) b.p. 112–114°/0·15 mm (bath temp 145–150°), n_D^{20} – 1·5078, (Found: C, 56·2; H, 7·1; N, 5·6; P, 11·8; $C_{12}H_{18}NO_3P$ requires: C, 56·5; H, 7·1; N, 5·5; P, 12·15%). The IR spectrum showed characteristic bands at 1470m (CH_3—C as.), 1395m (CH_3—C sym.) 1270s (P=O), 1195m and 1158m (P—O—Et), 1035vs (P—O—(C)), 790s (aziridine ring def.?) cm^{-1}. The ^1H NMR spectrum showed signals at: δ = 1·22, 1·30 (2*t*, 6H, J_{HH} 7·3 Hz, $^4J_{PH}$ 0·6 Hz, CH_3—CH_2), AMXY (Y=P) system (24 lines, 3H, δ_A = 2·02, δ_M = 2·57, δ_X = 3·40, J_{AM} = 2·0 Hz, J_{AX} 3·4 Hz, J_{MX} 6·3 Hz, J_{AP} 15·3 Hz, J_{MP} 18·8 Hz, J_{XP} 16·5 Hz, aziridine ring protons), 4·04, 4·10 (2dq, 4H, $^3J_{PH}$ 8·4 Hz, J_{HH} 7·3 Hz, CH_3—CH_2—O), 7·24 (br. s, 5H, arom. protons).

Addition of di-n-propyl N,N-*dibromophosphoroamidate* (**1**, R = *n*-Pr) *to styrene.* N-(*Di-n-propoxyphosphoryl*)-2-*phenylaziridine* (**6**, R = *n*-Pr). The reaction was carried out and the product was worked-up as described above to give crude **6** (R = *n*-Pr) (98%) of NMR purity. Distillation *in vacuo* afforded analytically pure material as a colourless oil, b.p. 123–124°/0·1 mm, n_D^{20} 1·4992, 75·5% (Found: C, 59·3; H, 7·6; N, 5·4; P, 10·4; $C_{14}H_{22}NO_3P$ requires: C, 59·4; H, 7·8; N, 4·95; P, 10·95%). The IR spectrum showed characteristic bands at: 1468m (CH_3—C as.), 1392m (CH_3—C sym.), 1271s (P=O), 1000vs, br (P—O—(C)), 860m, br (aziridine ring def.?) cm^{-1}. The ^1H NMR spectrum showed signals at: δ = 0·65–1·12 (m, 6H, CH_3—CH_2—), 1·20–1·90 (m, 4H, —CH_2—CH_2—), AMXY (Y=P) system (24 lines, 3H, δ_A = 2·08, δ_M = 2·57, δ_X = 3·41, J_{AM} 1·8 Hz, J_{AX} 3·3 Hz, J_{MX} 6·2 Hz, J_{AP} 15·3 Hz, J_{MP} 18·9 Hz, J_{XP} 16·2 Hz, aziridine ring protons), 3·96, 4·00 (2dt, 4H, J_{HH} 6·6 Hz, $^3J_{PH}$ 7·8 Hz, —CH_2—O), 7·20 (s, 5H, arom. protons).

Addition of diisopropyl N,N-*dibromophosphoroamidate* (**1**, R = *i*-Pr) *to styrene.* N-(*Diisopropoxyphosphoryl*)-2-*phenylaziridine* (**6**, R = *i*-Pr). The same experimental procedure as before was applied. Usual work-up of the reaction gave crude **6** (R = *i*-Pr) of NMR purity (97%). Distillation *in vacuo* afforded analytically pure product as colourless oil, b.p. 115–116°/0·1 mm, n_D^{20} 1·4942, 63%. (Found: C, 59·2; H, 7·6; N, 5·3; P, 10·6; $C_{14}H_{22}NO_3P$ requires: C, 59·4; H, 7·8; N, 4·95; P, 10·95%). The IR spectrum showed characteristic bands at: 1470s (CH_3—C as.) 1388s and 1380s (CH_3—C sym.), 1268vs (P=O), 1000vs, br (P—O—(C)), 794s (aziridine ring def.?) cm^{-1}. The ^1H NMR spectrum showed signals at: δ = 1·19, 1·21, 1·25, 1·29 (4d, 12H, J_{HH} 6·4 Hz, $((CH_3)_2CH$—), AMXY (Y=P) system (24 lines, 3H, δ_A = 1·99, δ_M = 2·55, δ_X = 3·36, J_{AM} 1·9 Hz, J_{AX} 3·3 Hz, J_{MX} 6·2 Hz, J_{AP} 15·0 Hz, J_{MP} 19·0 Hz, J_{XP} 16·5 Hz, aziridine ring protons), 4·27–5·10 (m, 2H, J_{HH} 6·4 Hz, $^3J_{PH}$ 7·6 Hz, $((CH_3)_2CH$—O—), 7·17 (s, 5H, arom. protons).

Addition of di-n-butyl N,N-*dibromophosphoroamidate* (**1**, R = *n*-Bu) *to styrene.* N-(*Di-n-butoxyphosphoryl*)-2-*phenylaziridine* (**6**, R = *n*-Bu). The experiment carried out as described above followed by usual work-up of the reaction gave crude **6** (R = *n*-Bu) of NMR purity (98·5%). Distillation *in vacuo* afforded analytically pure product as pale-yellow oil, b.p. 137–138°/0·05 mm, n_D^{20} 1·5000, (55%). (Found: C, 61·5; H, 8·15; N, 4·5; P, 9·7; $C_{16}H_{26}NO_3P$ requires: C, 61·7; H, 8·4; N, 4·5; P, 10·0%). The IR spectrum showed characteristic bands at: 1468s (CH_3—C as.), 1390s (CH_3—C sym.), 1270vs and 1239s (P=O), 1025vs, br (P—O—(C)), 850m and 798m (aziridine ring def.?) cm^{-1}. ^1H NMR spectrum showed signals at: δ = 0·60–1·08 (m, 6H, CH_3), 1·08–1·80 (m, 8H, —CH_2—CH_2—), AMXY (Y=P) system (24 lines, 3H, δ_A = 2·01, δ_M = 2·57, δ_X = 3·35, J_{AM} = 1·9 Hz, J_{AX} 3·4 Hz, J_{MX} 6·3 Hz, J_{AP} 15·6 Hz, J_{MP} 19·2 Hz, J_{XP} 16·8 Hz, aziridine ring protons), 3·68–4·42 (m, 4H, J_{HH} 6·3 Hz, —CH_2—O—), 7·17 (s, 5H, arom. protons).

Addition of $(DBPA)_3$.NaBr *to styrene.* A soln of styrene (1·90 g, 0·018 mole) in benzene (10 ml) was added dropwise at reflux temp to a stirred suspension of $(DBPA)_3$.NaBr (6·20 g, 0·006 mole) in the same solvent (30 ml). Stirring was continued for 30 min until the soln became pale-yellow. The mixture was then cooled to room temp, diluted with benzene (40 ml) and treated with 20% sodium pyrosulphate aq (60 ml). The organic layer was separated, water washed (2 × 20 ml), dried, and evaporated. Oily residue was heated at 40–45°/0·2 mm for 1 hr to give diethyl N-(2-*bromo*-2-*phenylethyl*)-*phosphoroamidate* (**8**, R = Et) as a pale-yellow oil, n_D^{20} 1·5276, 6·0 g (99%). IR and ^1H NMR spectra of this product were superimposable with those of **8** (R = Et) prepared from styrene and pure DBPA.

Addition of $(DBPA)_3$.LiBr *to styrene.* The reaction was carried out as described immediately above using the same molar proportions of starting materials. Orange solid (5·6 g) was obtained after work-up of the reaction mixture and identified (^1H NMR) as a mixture of 58% **8** (R = Et) and 42% styrene dibromide.

Cyclization of 2-*bromo*-2-*phenylethylamine hydrochloride* (**9**). 2-*Phenylaziridine* (**10**). The modified procedure[15] used for cyclization of 2-chloro-2-phenylethylamine hydrochloride was applied. The mixture of 2-bromo-2-phenylethylamine hydrochloride (**9**) (40·0 g, 0·169 mole) and 10% NaOH aq (300 ml) was heated at 60–70° for 2 hr. Excess solid KOH was added and the product distilled with steam. The distillate was saturated with KOH and ether extracted (4 × 50 ml). On evaporation of solvent colourless oil (15·0 g, 75%) of NMR purity was obtained. n_D^{20} 1·5646 (lit.[16]: n_D^{20} 1·5588). The ^1H NMR spectrum showed signals at: δ = 1·08 (br. s, 1H, NH), AMX system (12 lines, 3H, δ_A = 1·43, δ_M = 1·83, δ_X = 2·62, J_{AM} = 0·6 Hz, J_{MX} = 6·3 Hz, aziridine ring protons), 6·99 (s, 5H, arom. protons).

Cyclization of diethyl N-(2-*bromo*-2-*phenylethyl*)-*phosphoroamidate* (**8**, R = Et). N-(*Diethoxyphosphoryl*)-2-*phenylaziridine* (**6**, R = Et). Equimolar amounts of 20% ethanolic NaOEt was added dropwise with stirring at room temp to a soln of diethyl N-(2-bromo-2-phenylethyl)-phosphoroamidate (10·1 g, 0·03 mole). When the exothermic reaction had subsided the soln was refluxed for 1 hr. NaBr ppt was filtered off and washed with EtOH. The soln was evaporated, the residue diluted with benzene (70 ml) and water washed (3 × 20 ml). Solvent was then removed and crude aziridine **6** (R = Et) distilled *in vacuo* to give colourless oil, 5·1 g (67%), b.p. 116–118°/0·15 mm n_D^{20} 1·5076. IR and ^1H NMR spectrum of this material were superimposable with those of N-(diethoxyphosphoryl)-2-phenylaziridine (**6**, R = Et) prepared directly from styrene and diethyl N,N-dibromophosphoroamidate.

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