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N,N-DIHALOPHOSPHORAMIDES—XIV†

TWO-STEP AMINOBROMINATION OF PHENYLETHYLENES AND α-OLEFINS WITH DIETHYL N,N-DIBROMOPHOSPHOROAMIDATE (DBPA)‡

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Abstract—The addition of DBPA to several phenylethylenes and terminal olefins has been studied. The reaction was found to proceed in boiling dichloromethane and was spontaneously or photolytically initiated depending on the structure and reactivity of the reactants. *N*-Bromo adducts, formed upon addition, could be reduced *in situ* with sodium bisulphite solution to give the corresponding diethyl *N*-(β-bromoalkyl)phosphoroamidates. Degradation of the latter with hydrogen chloride in benzene at room temperature afforded β-bromoamine hydrochlorides in pure state and reasonable overall yield. The observed regiospecificity for anti-Markovnikov addition, as proven by NMR and MS, is fully consistent with the radical-chain mechanism proposed for the reaction. This two-step sequences offers an easy access to β-bromoamines, the convenient precursors for an aziridine synthesis.

Numerous synthetic procedures leading to ethylenimine and its derivatives have been described.[1] However, there is still a strong demand for new, simple and versatile synthesis of aziridines due to industrial and chemotherapeutic potentials of this important heterocyclic system. β-Haloamines (**1**) which cyclise spontaneously and exist in equilibrium with the respective aziridinium salts (**2**) can be considered as natural precursors of aziridines (**3**) (eqn 1):

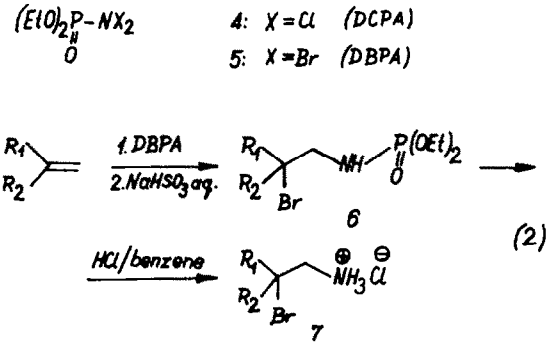
1 **2** **3** (1)

Limited preparative accessibility of **1** render them inappropriate starting materials for synthetic purposes.[2]

Some years ago we described[3,4] a simple two-step procedure leading to β-chloroamine hydrochlorides or β-chloro-α-aminoacid ester hydrochlorides involving the addition of diethyl N,N-dichlorophosphoramidate (DCPA, **4**) to phenylethylenes, α-olefins or α,β-unsaturated esters followed by degradation of the adducts with gaseous hydrogen chloride. In two earlier papers of this series[5,6] we have also reported about the adducts of diethyl *N,N*-dibromophosphoroamidate (DBPA, **5**) to styrene and isobutylene (**6**) as convenient precursors of the corresponding β-bromoamine hydrochlorides **7** (eqn 2)

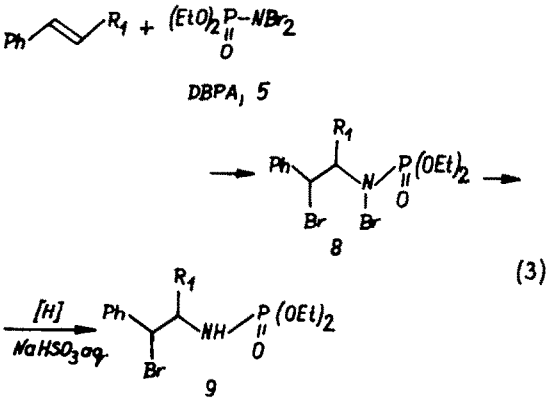
Recognized synthetic potential of **7** prompted us to publish the results of our studies on the preparation of these compounds by addition of DBPA (**5**) to some other phenylethylenes and α-olefins.

The addition of DBPA to styrene, (E)-1-phenylpropene, (Z)-1-phenylpropene, and α-methylstyrene has been examined. All reactions were carried out in boiling



(2)

dichloromethane by adding dropwise the hydrocarbon (in order to avoid its possible polymerization) to a solution of DBPA. After a short induction period the reaction was exothermic and complete within 1 hr. Progress of the addition could be easily followed by paling of dark-red DBPA colour. In all cases except α-methylstyrene the reaction proceeded according to the same general course outlined below (eqn 3):



(3)

9a : R_1 = H
9b : R_1 = CH_3 (from E-isomer)
9c : R_1 = CH_3 (from Z-isomer)

†Part XIII: K. Osowska and A. Zwierzak, *Synthesis* 577 (1979).

‡Presented in part on *XXVI IUPAC Congress*, Tokyo, 1977.

The formation of 1:1 adducts was always observed. Styrene and its analogues added DBPA 5 regiospecifically in an anti-Markovnikov fashion (see proof of structure below) affording diethyl *N*-bromo-*N*-(β-bromoalkyl)phosphoroamidates (**8**). Upon reduction with 20% aqueous sodium bisulphite at 10° the initially formed *N*-bromo adducts (**8**) were quantitatively reduced *in situ* to diethyl-*N*-(β-bromoalkyl)phosphoroamidates (**9a–c**). All crude compounds (**9a–c**) formed in high yields were analytically pure. Their physical constants, yields and elemental analysis data are summarized in Table 1. The adducts (**9b**) and (**9c**) were found to be diastereomeric mixtures of erythro and threoisomers† in the ratio 80:20 in both cases (see stereochemistry of DBPA addition below). Pure erythro-isomer could be easily isolated from such mixtures by crystallization from light petroleum.

Although the reaction between DBPA (**5**) and α-methylstyrene proceeded smoothly, the respective 1:1 adduct could not be isolated from the complex mixture of products formed under the above mentioned conditions. This was probably due to extensive allylic bromination of the hydrocarbon and/or consecutive solvolysis of the primary adduct containing tertiary benzylic bromine upon reduction and work-up. The addition of DBPA to several straight and branched-chain terminal olefins, *viz.* isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 1-hexene, and 1-octene has been investigated. All these compounds were found to be substantially less reactive towards DBPA than phenylethylenes. The phenomenon of spontaneous initiation was observed only in the case of isobutylene. Other olefins added DBPA relatively slowly in boiling dichloromethane but the reactions could be effectively accelerated by UV irradiation. It was recommended to apply photolytic initiation for less reactive straight-chain olefins. All additions were complete within 2–3 hr, which could be tested visually by disappearance of dark-red DBPA colour. Initially formed *N*-bromo adducts (**10**) were not isolated but reduced *in situ* with 20% aqueous sodium bisulphite to the corresponding diethyl *N*-(β-bromoalkyl-phosphoroamidates (**11**) (eqn 4). As determined by ^{31}P-NMR the formation of only one regioisomer† was always observed. Structural assignments based on ^{1}H-NMR and MS data (see proof of structure below) were fully consistent with the anti-Markovnikov addition pattern observed previously for phenylethylenes.

Crude adducts (**11a**) and (**11b**) were pure and could be satisfactorily analysed. Compounds (**11c–f**) were contaminated with considerable amounts (up to about 40%) of 1,2-dibromoalkanes, allylic bromination products, and other unidentified impurities. They underwent extensive decomposition on attempted distillation but could be easily purified by column chromatography on silicagel (solvent system: benzene–acetone–chloroform, 30:10:3) to give analytically pure samples. It is noteworthy that impure, crude adducts (**11c–f**) could be successfully applied for the preparation of β-bromoamine hydrochlorides (*vide infra*). Yields, physical properties, and

Table 1. Diethyl N-(β-bromoalkyl)phosphoroamidates

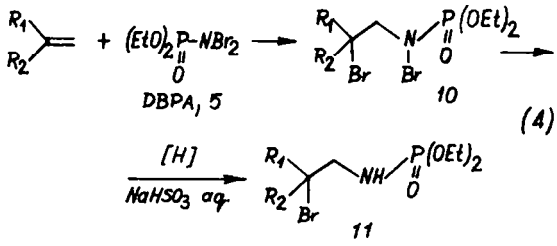
Compound No	Procedure/ duration hr	Yield %	n_D^{20}	Analyses % Required C	H	N	P	Found C	H	N	P
9a	A/0.5	93	1.5264	42.9	5.7	4.2	9.2	42.9	5.5	4.2	8.6
9b	A/1	89	–	44.5	6.0	4.0	8.9	44.3	5.8	4.1	8.9
9c	A/1	96	–	44.5	6.0	4.0	8.9	44.2	5.9	4.1	8.9
11a	B/0.5	97	1.4742	33.4	6.6	4.8	10.8	33.3	6.6	4.5	10.6
11b	B/1	96	1.4726	35.8	7.0	4.6	10.3	35.9	6.9	4.7	9.9
11c	B/3	48[a]	1.4712	35.3	7.0	4.6	10.3	35.8	7.1	4.9	9.6
11d	C/2	57[a]	1.4720	38.0	7.3	4.4	9.8	38.1	7.3	4.5	9.8
11e	C/3	47[a]	1.4762	38.0	7.3	4.4	9.8	38.3	7.2	4.2	9.6
11f	C/2	59[a]	1.4754	41.9	7.9	4.1	9.0	42.0	8.2	4.3	8.9

[a] Yields of pure adducts, isolated by column chromatography are given

†Erythro (RS and SR) and threo (RR and SS)-configurations were ascribed to both racemic diastereomeric adducts on the basis of Cahn, Ingold and Prelog convention.[7]

†Independent studies on ionic addition of DBPA to olefins[8] clearly indicate that regioisomeric adducts are easily distinguishable by ^{31}P-NMR.

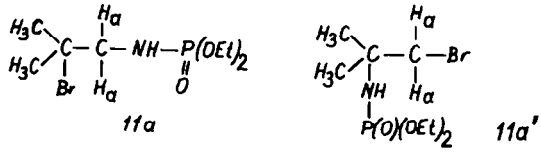
elemental analysis data of the phosphoroamidates (**11**) are listed in Table 1.



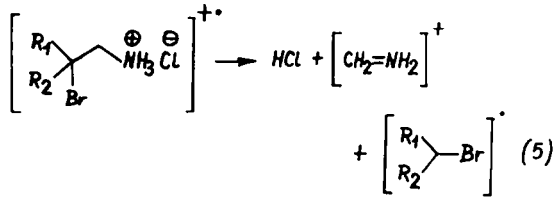
(4)

11a : $R_1 = R_2 = CH_3$
11b : $R_1 = CH_3$, $R_2 = C_2H_5$
11c : $R_1 = i\text{-}C_3H_7$, $R_2 = H$
11d : $R_1 = t\text{-}C_4H_9$, $R_2 = H$
11e : $R_1 = n\text{-}C_4H_9$, $R_2 = H$
11f : $R_1 = n\text{-}C_6H_{13}$, $R_2 = H$

All DBPA adducts to phenylethylenes and α-olefins (**9a–c, 11a–f**) were satisfactorily analysed for C, H, N, and P. Their IR spectra (Table 2) showed characteristic strong NH absorption bands in the region of 3170–3270 cm^{-1}, P=O bands at 1220–1240 cm^{-1}, and P–O–(C) bands within the range 1025–1040 cm^{-1}, which are fully consistent with the anticipated amidophosphoryl structure. Regioisomeric purity was evident from ^{31}P-NMR spectra examination (see above) and could be further confirmed by detailed analysis of their ^{1}H-NMR spectra. The final structural assignments, namely the positions of the Br atom and the amidophosphoryl moiety, could be deduced from careful inspection of the ^{1}H-NMR spectra by analysis of the chemical shifts, multiplicity and integration of the relevant groups of protons (see Table 2). Multiplicity of the methylene protons adjacent to nitrogen atom was of particular diagnostic value for definite structural assignments. This can be exemplified for DBPA–isobutylene adduct for which one can consider the structure of an anti-Markovnikov adduct (**11a**) or its regioisomer (**11a'**).



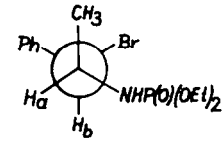
The NMR data are consistent only with the structure (**11a**). In the NMR spectrum of DBPA-isobutylene adduct the magnetically equivalent H_a protons absorbed as a broadened doublet at $\delta_{TMS}(CCl_4)$ 3.13 ppm integrating for two hydrogens. Splitting of this signal evidently resulted from a long range coupling between methylene protons H_a and P atom ($^3J_{PH} = 9.7$ Hz). If the Br atom and amidophosphoryl moiety were reversed (Formula 11a') such a pattern would not be observed and H_a protons would appear as a singlet with no further splitting by P atom. Other signals displayed in the NMR spectrum of DBPA–isobutylene adduct are in accord with the structure (**11a**) but do not allow to distinguish between the regioisomeric structures (**11a**) and (**11a'**) and therefore are of limited diagnostic value. Similar NMR analysis leads to unambiguous structural assignments for the adducts (**9a–c**) and (**11b**). It cannot, however, be applied for compounds (**11c–f**) which give rather complex spectral patterns, indistinguishable for both possible regioisomers. The anti-Markovnikov orientation of the adducts (**11c–f**) was unequivocally established by means of mass spectroscopy. The mass spectra of β-bromoamine hydrochlorides (**15e–h**) obtained from (**11c–f**) by degradation with gaseous HCl (*vide infra*), showed preferential α-cleavage fragmentation to yield $[CH_2{=}NH_2]^+$ ions, $m/e = 30$, in accord with the regiospecificity shown below (eqn 5):



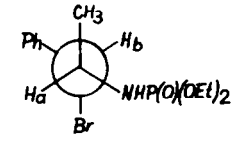
(5)

Such fragmentation pattern could not be obtained for β-bromoamine hydrochlorides with the amino function at the nonterminal, secondary or tertiary position.

Diastereomeric (E)- and (Z)-1-phenylpropenes were suitably selected for studying sterochemical course of DBPA addition. Both crude adducts of DBPA to (E)- and (Z)-1-phenylpropene (**9b**) and (**9c**) have superimposable IR and NMR spectra, suggesting that they are identical mixtures of erythro- and threo-isomers. Their ^{31}P-NMR spectra displayed in each case two distinct signals at $\delta_{H_3PO_4}$ (CCl_4) 7.0 and 7.5 ppm. Integration of these signals allowed to establish the ratio of both diastereoisomers which was found to be 80:20 (erythro:threo-adduct). Assignment of stereochemistry was arrived at by careful ^{1}H-NMR spectra examination. The spectra exhibited the presence of two partially overlapping doublets of different intensities centered at $\delta_{TMS}(CCl_4)$ 4.99 ppm ($J_{H_aH_b} = 10.6$ Hz, higher intensity signal) and 5.04 ppm ($J_{H_aH_b} = 6.2$ Hz, lower intensity signal) which could be assigned to the benzylic proton H_b in both diastereoisomers on the basis of integration, multiplicity and chemical shifts.



12a erythro-isomer



12b threo-isomer

It is feasible to assume the synclinal arrangement of vicinal protons H_a and H_b in the preferred conformation of erythro-isomer (**12a**). This would account for a smaller vicinal coupling constant of the higher-field doublet according to Karplus relationship. The higher value of vicinal coupling constant of the lower-field doublet is consistent in turn with preferable antiperiplanar arrangement of H_a and H_b in the threo-isomer (**12b**). Erythro-configuration of the main constituent of the adducts (**9b**) and (**9c**) could be also corroborated by chemical means. Pure erythro-adduct (isolated from the mixture **9b** or **9c**) was cyclised in the presence of sodium ethoxide to the corresponding *N*-phosphorylated aziri-

Table 2. Characteristic IR absorption maxima and ^{1}H-NMR spectral assignments of diethyl N-(β-bromoalkyl) phosphoroamidates

Compound No.	Characteristic IR absorption maxima (film)[a] (cm^{-1})	^{1}H-NMR assignments[b] (δ in ppm from TMS; J in Hz)
9a	3200m; 2980m;2910m;1455s;1225s;1120m;1025s; 960s;700s	1.20,1.26(2t,6H,J=7.0);3.15-4.00(m,2H);3.80, 3.91(2q,4H,J=7.0),4.45-4.85(bs,1H);4.95(t;1H, J=7.3); 7.10-7.60(m;5H)
9b,c	3170s;2995m;2930m;1480m;1220s;1140m;1060s 1035s; 965s; 700s	1.05-1.45(m;9H);3.25-3.95(m);3.86(q,4H;J=7.0); 4.99(d;1H,J=10.6threo;J=6.2erythro);7.05-7.60 (m,5H)
11a	3200s; 2970s;2910m;1455m;1370m;1220s;1155m; 1030s; 960s	1.30(t,6H,J=7.3); 1.75,1.85(2s,6H);3.13(bd, J=9.7);4.00(q,4H,J=7.3);4.60-5.15(bt,1H)
11b	3220s;2982s;2935s;1460m;1240s;1060s;1037s; 972s	1.05(t,3H,J=7.6);1.31(t,6H,J=7.6);1.50-2.15(m,2H); 1.70(s,3H);3.17(bd,2H,J=8.4);4.00(q,4H,J=7.6); 4.50-5.15(bs,1H)
11c	3240s;2995s;1450s;1395m;1375m;1230s;1060s; 1037s; 970s	1.25,1.37(dd,6H,J=7.3);1.74(t,6H,J=7.3);2.50-3.10 (m,1H);3.90-4.15(m,2H);5.30(q,5H,J=7.3)
11d	3240s;2995s;1480m;1450m;1400m;1370s;1230s; 1030s;965s	1.05(s,9H);1.27(t,6H;J=7.2);2.80-3.60(m,2H);3.98 (q,5H,J=7.2)
11e	3270s;3000s;2970s;1465m;1445m;1238s;1032s; 965s	0.71-1.05(m,3H);1.29(t,6H,J=7.0);1.25-2.10(m,6H); 2.88-3.38(m,2H);3.98(q,5H;J=7.0);4.75-5.20(bt,1H)
11f	3260m;2970s;1465m;1240s;1060s;1040s;970s	0.69-1.05(m,3H);1.28(t,6H,J=7.1);1.15-2.20(m,10H); 2.88-3.38(m,2H);3.98(q,5H,J=7.1);4.80-5.30(bs,1H)

[a] Only characteristic absorption bands are included. Abbreviations used: s, strong; m, medium.

[b] Abbreviations used: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quintet; m, multiplet; b, broad.

Table 3. β-Bromoamine hydrochlorides[a]

Compound No	Yield[b] %	M.p.[c] °C	Characteristic IR absorption maxima (KBr)[d] cm^{-1}	NMR assignments (D_2O) (δ in ppm from HMDS, J in Hz)
15a	82	158–9	3000–2700s; 1600m; 1500s; 1445m 758s; 700s	3.82, 3.95, 5.60 (ABX system, J_{AB}=13.6; J_{AX}=6.6; J_{BX}=8.7), 5.00 (s); 7.47–7.80 (m, 5H)
15b	40[e] {74% erythro, 26% threo}	165–6	3000–2800s; 1590s, 1510s; 1450m; 1390m; 750s, 700s	3.70–4.40 (m); 5.31 (d; threo, J_{AB}=10.3); 5.47 (d, erythro; J_{AB}=6.5) 4.92 (s); 1.28 (d, 3H, J=7.2 threo); 1.52 (d, 3H, J=7.2 erythro); 7.55 (bs, 5H)
15c	58	151–3	3000–2750s; 1580s, 1505s, 1450s, 1375m, 1142s, 1130s, 850m	1.82 (s, 6H); 3.33 (s, 2H); 4.71 (s)
15d	57	133–5	3000–2800s, 1590m, 1505m, 1450m, 1390m, 1145m, 1130m	1.05 (t, 3H, J=7.2); 1.78 (s, 3H); 1.60–2.22 (m, 2H); 3.40 (s, 2H); 4.72 (s).
15e	33	160–2	3000–2800s, 1600m, 1490s, 1390m, 1160m, 1325m, 880m	3.54, 3.41, 4.30 (ABX system, 3H, J_{AB}=13.7, J_{AX}=-2.5, J_{BX}=-9.9), 0.99, 1.04 (dd, 6H, J=6.5); 1.55–2.40 (m, 1H); 4.75 (s).
15f	84	205–7	3000–2800s, 1590m, 1520m, 1400m, 1370m, 1220m, 898m	3.19, 2.84, 3.74 (ABX system, 3H, J_{AB}=14.1; J_{AX}=-2.2, J_{BX}=-11.8), 0.65 (s, 9H); 4.29 (s)
15g	42	174–6	3000–2800s; 1595m; 1500m; 1460m, 1400m, 1235m; 870w, 720w	3.91, 3.70, 4.57 (ABX system, 3H, J_{AB}=14.0, J_{AX}=-1.7, J_{BX}=-11.3); 1.10–1.50 (bt, 3H); 1.50–2.08 (m, 4H), 2.08–2.50 (m, 2H); 5.05 (s)
15h	36	134–6	3000–2850s, 1600m; 1510m, 1465m, 1400m, 1155w, 900w, 724w	3.88, 3.65, 4.71 (ABX system, 3H, J_{AB}=14.0, J_{AX}=-2.9, J_{BX}=-9.5); 1.10–1.41 (bt, 3H); 1.41–2.06 (m, 8H); 2.06–2.56 (m, 2H); 5.05 (s)

[a] The elemental analyses of all compounds (C, H, N, P) were fully consistent with the calculated values.

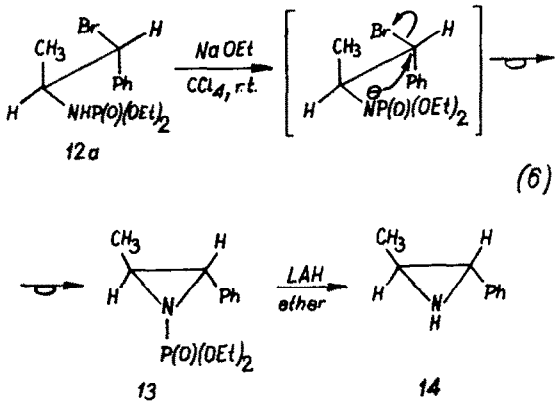
[b] In respect to the starting olefin. The adducts 9 and 11 were not isolated.

[c] Crystallized from ethanol. All compounds decomposed on melting.

[d] Only the most characteristic bands are given.

[e] Degraded for 5 hr at 60–65° in chloroform solution.

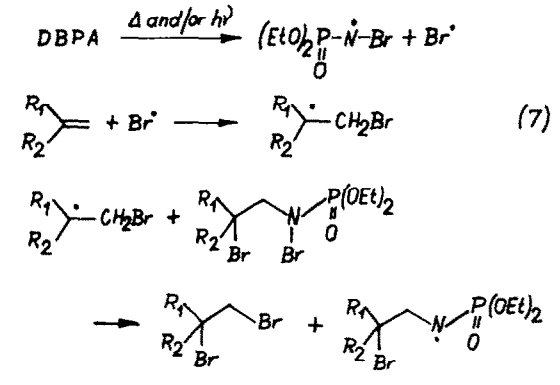
dine (13) affording *trans*-2-methyl-3-phenylaziridine (14), identical with the compound described by Brois and Beardsley,[9] upon reduction with LAH in ether[10] (eqn 6):



(6)

The formation of *trans*-aziridine (14) unambiguously confirms erythro-configuration of the starting adduct (12a).

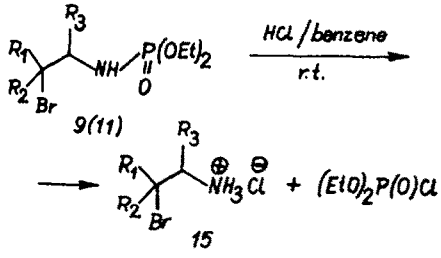
Mechanism of DBPA addition to phenylethylenes and α-olefins. All DBPA additions to phenylethylenes and α-olefins exhibit several characteristic features which are indicative of spontaneously initiated or thermally induced free-radical chain reactions: (i) they follow regiospecifically affording anti-Markovnikov adducts; (ii) thermal and/or photolytic initiation is required for less reactive olefins; (iii) the reaction rates are markedly increased by UV irradation but practically independent on the polarity of solvent; (iv) the addition to non-terminal olefins, e.g. 1-phenylpropene, is non-stereospecific. All these phenomena can be plausibly interpreted in terms of free-radical reaction pathways, fully analogous to those suggested for the addition of diethyl N,N-dichlorophosphoroamidate (DCPA) to phenylethylenes[3] and α-olefins.[4] The formation of substantial amounts of 1,2-dibromoalkanes during the addition of DBPA 5 to α-olefins can be explained by the following Scheme (eqn 7):



(7)

One cannot exclude, however, the direct bromination of olefins with molecular bromine produced by thermal decomposition of DBPA.

Degradation of DBPA adducts. Synthesis of β-bromoamine hydrochlorides. All DBPA adducts to phenylethylenes (9a–c) and α-olefins (11a–f) could be easily and effectively degraded to the corresponding β-bromoamine hydrochlorides (15) by means of gaseous hydrogen chloride in benzene at room temperature. It was neither necessary nor desirable to purify crude adducts before degradation because the hydrochlorides (15) separated from the solution in pure form and all impurities left in the mother liquor. Overall yields of β-bromoamine hydrochlorides (15) (in respect to the olefin used for functionalization) were within the range 35–80% which seems reasonable from the preparative point of view. Melting points and spectroscopic data of (15) are collected in Table 3.



15a : R_1 = Ph, R_2 = R_3 = H
15b : R_1 = Ph, R_2 = H, R_3 = CH_3
15c : R_1 = R_2 = CH_3, R_3 = H
15d : R_1 = CH_3, R_2 = C_2H_5, R_3 = H
15e : R_1 = i-C_3H_7, R_2 = R_3 = H
15f : R_1 = t-C_4H_9, R_2 = R_3 = H
15g : R_1 = n-C_4H_9, R_2 = R_3 = H
15h : R_1 = n-C_6H_{13}, R_2 = R_3 = H

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. Light petroleum refers to the fraction boiling at 40–60°. All starting olefins were freshly distilled just before use and were at least 99% pure (GC). All extracts were dried over $MgSO_4$ and evaporated under reduced press. B.ps (taken in capillaries) are uncorrected. IR spectra were recorded for liquid films or KBr pellets using a Specord 71 IR (C.Zeiss) spectrophotometer. ^{1}H-NMR spectra were measured at 80 MHz with a Tesla BS 487C spectrometer in CCl_4 or D_2O using TMS or DSS as internal standards respectively.^{31}P-NMR spectra were recorded at 24.3 MHz with a Jeol JNM-C-60 HL spectrometer using 85% H_3PO_4 as external reference. All measurements were made on samples of analytical purity. Column chromatography was performed on Silicagel (100–200 mesh).

Diethyl N,N-dibromophosphoroamidate (DBPA, 5) was prepared as described previously[5] by bromination of diethyl phosphoroamidate with elemental bromine at 0° in an aqueous solution containing equimolar amount of potassium carbonate.

Addition of DBPA (5) to phenylethylenes and α-olefins

Method A. The olefin (0.05 mole) was added dropwise with stirring to the soln of DBPA (15.55 g, 0.05 mole) in dichloromethane (50 ml) preheated to 30° at such a rate to maintain gentle reflux of the soln. Stirring was then continued for the indicated time (Table 1) at reflux temp. The resulting pale-yellow soln was colled to 10° and 20% aqueous soln of sodium bisulphite (50 ml) was then added slowly at this temp. Dichloromethane (50 ml) was then added and the organic layer was separated, washed with water (3 × 30 ml), dried, and evaporated. The residual crude adducts (9a–c) were analytically pure when heated at 40–50°/0.1 mm for 1 hr to remove traces of solvent. Table 1 shows results and analyses.

Method B. The soln of DBPA (15.55 g, 0.05 mole) in dichloromethane (15 ml) was added dropwise to dichloromethane (50 ml) saturated with gaseous olefin at such a rate to maintain a pale-yellow colouration of the reacting mixture. The addition of DBPA to isobutylene occured at room temp. For the adducts (11b and 11c) the reaction was carried out in boiling di-

chloromethane. After the addition had been completed (see Table 1 for the indicated time) the products were worked-up as described above for the method A. Crude adducts (**11a** and **11b**) were analytically pure when kept at 40–50°/0.1 mm for 1 hr to remove traces of solvent. Pure adduct (**11c**) could be isolated by column chromatography, if necessary, or degraded in crude form.

Method C. A soln of an appropriate olefin (0.05 mole) in dichloromethane (40 ml) was placed in a quartz flask and refluxed gently with stirring. A soln of DBPA (15.55 g, 0.05 mole) in dichloromethane (15 ml) was slowly added dropwise while the mixture was continuously irradiated by a UV lamp. After the indicated time (Table 1) the product was worked-up as described previously for the methods A and B. Crude adducts (**11d–f**) were purified by column chromatography or degraded without isolation.

Erythro-Diethyl N-(*β-bromo-β-phenylpropyl*)*phosphoroamidate* (**12a**)

Crude adduct (**9b** 15.5 g) was twice recrystallized from light petroleum (300 ml) to give 6.3 g of pure erythro-isomer, m.p. 90–91°. (Found: C, 44.2; H, 5.9; N, 4.1; P, 8.9; $C_{13}H_{21}BrNO_3P$ requires: C, 44.5; H, 6.0; N, 4.0; P, 8.9%). The IR spectrum (CCl_4) showed characteristic bands at: 3220 (NH), 3010s (CH aromat.), 1460s (CH_3), 1260s, 1240s (P=O), 1060s, 1040s, 970s (P–O–(C)), 700s cm^{-1}. The ^{1}H-NMR spectrum (CCl_4) showed signals at: δ = 1.04–1.50 (m, 9H, CH_3–CH_2–O, CH_3–CH), 3.20–4.17 (m, 5H, CH_3–CH_2–O, –NH–CH), 4.28–4.62 (bt, 1H, NH), 4.98 (d, 1H, J_{HH} 6.5 Hz, –CH–Br), 7.0–7.55 (m, 5H, arom. protons). The ^{31}P-NMR spectrum (CCl_4) displayed one signal at δ = 7.2 ppm (from H_3PO_4).

trans-N-(*Diethoxyphosphoryl*)-2-*methyl*-3-*phenylaziridine* (**13**)

A soln of sodium ethoxide (prepared from 0.78 g, 0.017 mole of sodium dissolved in 14 ml of ethanol) was added dropwise with stirring and occasional external cooling to a soln of pure erythro-adduct (**12a** 5.95 g, 0.017 mole) in dichloromethane (25 ml) at 10°. Stirring was then continued for 1 hr at room temp. The resulting mixture was washed with water (3 × 25 ml), dried, and evaporated to give 4.45 g (97.5%) of analytically pure aziridine (**13**) as colourless oil, n_D^{20} 1.5026. (Found: C, 57.5; H, 7.5; N, 5.4; P, 11.0; $C_{13}H_{20}NO_3P$ requires: C, 58.0; H, 5.2; 7.4; P, 11.5%). The IR spectrum (CCl_4) showed characteristic absorption maxima at: 3010s (CH aromat.), 1399m (CH_3), 1275s, 1253s (p=O), 1065s, 1045s, 972s (P–O(C)), 700s cm^{-1}. The ^{1}H-NMR spectrum (CCl_4) showed signals at: δ = 1.20, 1.27 (2t, 6H, J_{HH} 7.5 Hz, CH_3–CH_2–O), 1.56 (d, 3H, J_{HH} 5.5 Hz, CH_3–CH–), 2.22–3.02 (m, 1H, CH–CH_3), 3.26 (dd, 1H, J_{HH} 3.0 Hz, $^3J_{PH}$ 15.5 Hz, CH–Ph), 3.99, 4.08 (2qt, 4H, $J_{HH} \approx {}^3J_{PH}$ 7.5 Hz, CH_3–CH_2–O), 7.16 (s, 5H, arom. protons). The ^{31}P-NMR spectrum (CCl_4) showed signal at δ = 11.0 ppm (from H_3PO_4).

trans-2-*Methyl*-3-*phenylaziridine* (**14**)[10]

A soln of *trans*-arizidine (**13**) (4.05 g, 0.015 mole) in ether (20 ml) was added dropwise with stirring to a suspension of LAH (1.5 g) in ether (20 ml) at such a rate as to maintain gentle reflux. Stirring was continued at room temp. for 1.5 hr. 20% Aqueous sodium hydroxide (6 ml) was then added. Inorganic salts were filtered off and washed with ether (2 × 30 ml). The filtrate was combined with washings, dried over NaOH and K_2CO_3, and evaporated to give 1.8 g (90%) of crude aziridine (**14**), which was analytically pure when heated at 40°/0.8 mm to remove traces of volatile impurities. Colourless liquid of characteristic mushroom odour, n_D^{20} 1.5418. (Found: C, 81.1; H, 8.2; N, 10.3; $C_9H_{11}N$ requires: C, 81.2; H, 8.3; N, 10.5%). The IR spectrum showed characteristic absorption maxima at: 3275s (NH), 3010s (CH aromat.), 2990s (CH_3), 1500s (Ph), 1385m (CH_3), 1215m (aziridine ring), 1085m (NH), 850s (aziridine ring def.?), 745, 700s cm^{-1}. The ^{1}H-NMR spectrum (CCl_4) showed signals at: δ = 0.89 (s, 1H, NH), 1.23 (d, 3H, J_{HH} 5.2 Hz, CH_3), 1.87 (dq, 1H, J_{CH_3-H} 5.2 Hz, J_{HH} 2.8 Hz, CH_3–CH–), 2.45 (d, 1H, J_{HH} 2.8 Hz, Ph–CH–), 7.08 (s, 5H, aromat. protons) and was identical with that reported by Brois and Beardsley.[9]

Degradation of DBPA adducts with hydrogen chloride

β-Bromoamine hydrochlorides (**15**). Dry, gaseous HCl was passed slowly through the soln of the appropriate crude DBPA adduct (**9a–c**, **11a–f**, 0.02 mole) in benzene (50 ml). The reaction was carried out at 20–25° for 4–5 hr. The soln saturated with HCl was left overnight at room temp. The excess of HCl and some solvent was then removed *in vacuo*. Anhydrous ether (50 ml) was added to the residue. The crystalline precipitate was filtered off, washed with ether, and crystallized from ethanol. The yields, m.p.'s and spectroscopic characteristics of *β*-bromoamine hydrochlorides (**15**) thus obtained are summarized in Table 3.

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