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N,N-DIHALOPHOSPHORAMIDES—XVI†

IONIC ADDITION OF DIETHYL N,N-DIBROMOPHOSPHOROAMIDATE (DBPA) TO ALKENES AND CYCLOALKENES‡

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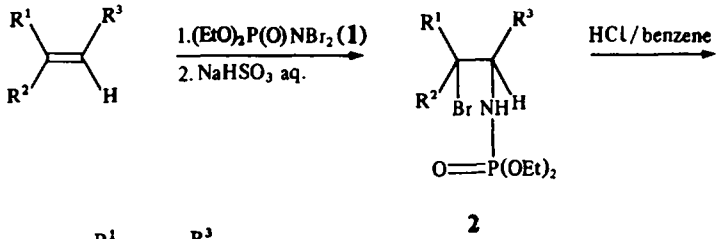
Abstract—The addition of DBPA to a variety of phenylethylenes, straight-chain terminal and nonterminal alkenes as well as cycloalkenes in the presence of boron trifluoride etherate has been investigated. It was found that the reaction proceeds smoothly at −20° by adding an olefin to the solution of equimolar amounts of DBPA and boron trifluoride etherate in tetrachloromethane. N-Bromoadducts (mixtures or single isomers depending upon the structure of the olefin) initially formed could be reduced *in situ* with sodium bisulphite solution to give the corresponding diethyl N-(β-bromoalkyl)phosphoroamidates which in turn afforded β-bromoamine hydrochlorides upon treatment with hydrogen chloride in benzene at room temperature. The regiospecificity typical for Markovnikov addition, as proven by NMR and MS evidence, was observed for unsymmetrical phenylethylenes. The addition of DBPA to (*E*)-1-phenylpropene, (*E*)-2-butene, and (*Z*)-2-butene was also found to proceed stereospecifically affording the corresponding anti-adducts. These results are fully compatible with an ionic addition pathway and can be rationalized by assuming the intermediate formation of an electrophilic complex between DBPA and boron trifluoride. The reaction offers a new approach to aminobromination of alkenes and cycloalkenes and makes possible an easy access to β-bromoamines, the convenient precursors of aziridines.

Direct functionalization of a C=C bond by free-radical or electrophilic addition of various pseudohalogens has been the subject of numerous studies during the last few years. In earlier papers of this series we have shown that diethyl N,N-dibromophosphoroamidate (DBPA, **1**) behaves as a pseudohalogen towards alkenes.[1-3] Thus, under homolytic conditions it reacts easily with phenylethylenes and α-olefins via a radical-chain mechanism, and gives diethyl N-(β-bromoalkyl)phosphoroamidates (**2**) which can be subsequently degraded to the corresponding β-bromoamine hydrochlorides (**3**) (Eq. 1):



(1)

2

3

R^1 = Ph, alkyl
R^2 = H, alkyl
R^3 = H, CH_3

Preparative applicability of free-radical DBPA addition to the synthesis of β-bromoamine hydrochlorides (**3**) directly from alkenes is restricted, however, only to some phenylethylenes and α-olefins affording the corresponding adducts (**2**) regiospecifically in high yields. Homolytic addition of DBPA to nonterminal alkenes and cycloalkenes occurs sluggishly and inevitably leads to complex and often intractable mixtures of compounds containing mainly allylic bromination and/or bromine addition products. This observation prompted us to investigate the possibility of heterolytic addition of DBPA to the double bond with the hope that such a process would make possible:

(i) effective functionalization of nonterminal alkenes and cycloalkenes; (ii) the synthesis of regioisomeric β-bromoamine hydrochlorides by changing the anti-Markovnikov addition pattern to the reversal one; (iii) stereospecific aminobromination of symmetrical di-

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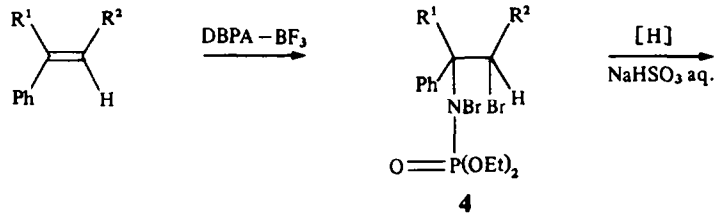
‡ Taken in part from Ph.D. thesis of K. Osowska-Pacewicka.

substituted alkenes in which two chiral centres are simultaneously created in the molecule upon addition. Such a dramatic change of the reaction mechanism seemed feasible providing the electrophilic character of the bromine atom in DBPA molecule could be sufficiently enhanced by external or internal factors. Experimental evidence proved that polarity of the reaction medium has practically no influence on the orientation of addition. Styrene taken as model substrate reacted rapidly with DBPA in typical dipolar aprotic solvents like dimethylformamide, nitromethane, and tetramethylurea even in the dark to give only the anti-Markovnikov adduct contaminated with considerable amounts of 1,2-dibromostyrene. The use of chloroform as solvent, which changes completely the mode of N,N-dibromobenzenesulphonamide addition to styrene,[4] did not also give the expected result. Although some amounts (up to 30%) of the Markovnikov adduct were formed its regioisomer was still the main component (~ 70%) of the mixture.

Clean heterolytic addition of DBPA to styrene was accomplished in the presence of stoichiometric amounts of boron trifluoride etherate using the preformed DBPA–BF_3 complex (*vide infra*) as a source of positive bromine. This observation was found to be of general character and the procedure optimized for styrene could be then extended for other phenylethylenes, alkenes, and cycloalkenes. The heterolytic additions of DBPA to styrene, (*E*)- and (*Z*)-1-phenylpropene, (*E*)- and (*Z*)-stillbene, 1,1-diphenylethylene, and α-methylstyrene have been examined. All reactions were carried out in tetrachloromethane by adding dropwise the hydrocarbon to an equimolar mixture of DBPA and boron trifluoride etherate at −20°. The reaction was rapid and exothermic and was virtually complete within 1 hr. Progress of the addition could be conveniently followed by paling of dark-red colour of the solution which finally acquired pale-yellow colouration. In all cases except α-methylstyrene the reaction proceeded according to the same general course outlined below (Eq. 2):

The formation of 1:1 adducts (**5**) was always observed. For α-methylstyrene in addition to (5 g) compound **6** was isolated from the reaction mixture in 29% yield. It is probably produced by allylic bromination of α-methylstyrene followed by DBPA addition to 3-bromo-2-phenylpropene thus formed. All phenylethylenes added DBPA regiospecifically in a Markovnikov fashion affording diethyl N-bromo-N-(β-bromoalkyl)phosphoroamidates (**4**). Upon reduction with 20% aqueous sodium bisulphite at 10° the initially formed unstable N-bromo adducts (**4**) could be quantitatively transformed *in situ* into stable diethyl N-(β-bromoalkyl)phosphoroamidates (**5a–g**). Structural assignments (exemplified below) were made by IR and ^{1}H-NMR spectroscopy using the characteristic absorption bands of NH and P=O bonds to determine the nature of the products, and the chemical shifts and splitting patterns of selected proton signals to establish the configurations of the products and the orientation of addition. The Markovnikov orientation of the adducts was further confirmed by means of mass spectroscopy. The isomer ratios were determined from the integral traces of appropriate absorption bands in the ^{31}P-NMR spectra of the mixtures. The NMR data are presented in Table 2. Crude compounds **5a–e** formed in relatively high yields were analytically pure. Crude adduct **5f** could be easily purified by column chromatography on silicagel. The mixture of **5g** and **6** was resolved by fractional crystallization from ether. The adducts **5c–e** were found to be diastereomeric mixtures of *erythro* and *threo* isomers.† Physical constants, yields, and elemental analysis data of **5a–g** are summarized in Table 1.

The addition of DBPA to numerous straight and branched-chain terminal and nonterminal alkenes as well as cycloalkenes has been also investigated. All reactions were carried out as for phenylethylenes by adding the hydrocarbon to the solution of preformed DBPA–BF_3 complex in tetrachloromethane at −20°. N-Bromo adducts formed as primary products were subsequently reduced *in situ* with 20% aqueous sodium



(2)

4

5a $R^1 = R^2 = H$
5b $R^1 = H, R^2 = CH_3$ (from *E* - isomer)
5c $R^1 = H, R^2 = CH_3$ (from *Z* - isomer)
5d $R^1 = H, R^2 = Ph$ (from *E* - isomer)
5e $R^1 = H, R^2 = Ph$ (from *Z* - isomer)
5f $R^1 = Ph, R^2 = H$
5g $R^1 = CH_3, R^2 = H$

6 (2)

†*Erythro* (*RS* and *SR*) and *threo* (*RR* and *SS*) configurations were ascribed to all racemic diastereomeric adducts on the basis of Cahn, Ingold, and Prelog convention.[5]

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

Compound no.	Yield %	M.p. (n_D^{20})	Remarks	Analyses % Required C	H	N	P	Found C	H	N	P
5a	92	90–91	—	42.9	5.7	4.2	9.2	42.8	5.6	4.2	8.7
5b	87	74–75	*erythro isomer*	44.5	6.0	4.0	8.9	44.6	6.1	4.1	8.6
5c	81	(1.5222)	*erythro*:*threo* 1:1	44.5	6.0	4.0	8.9	44.5	6.0	3.8	8.7
5d	25	155–157	*erythro*:*threo* 78:22	52.4	5.6	3.4	7.5	52.3	5.4	3.1	7.1
5e	30	149–153	*erythro*:*threo* 80:20	52.4	5.6	3.4	7.5	52.6	5.4	3.0	7.1
5f	42	91–92	—	52.4	5.6	3.4	7.5	52.5	5.5	3.5	7.4
5g	45	94–96	—	44.5	6.0	4.0	8.9	44.5	5.8	4.0	8.7
6	29	99–100	—	36.4	4.6	3.3	7.2	36.4	4.4	3.3	6.9

bisulphite to the corresponding diethyl N-(β-bromoalkyl)phosphoroamidates (**7–10**) (Scheme 1).

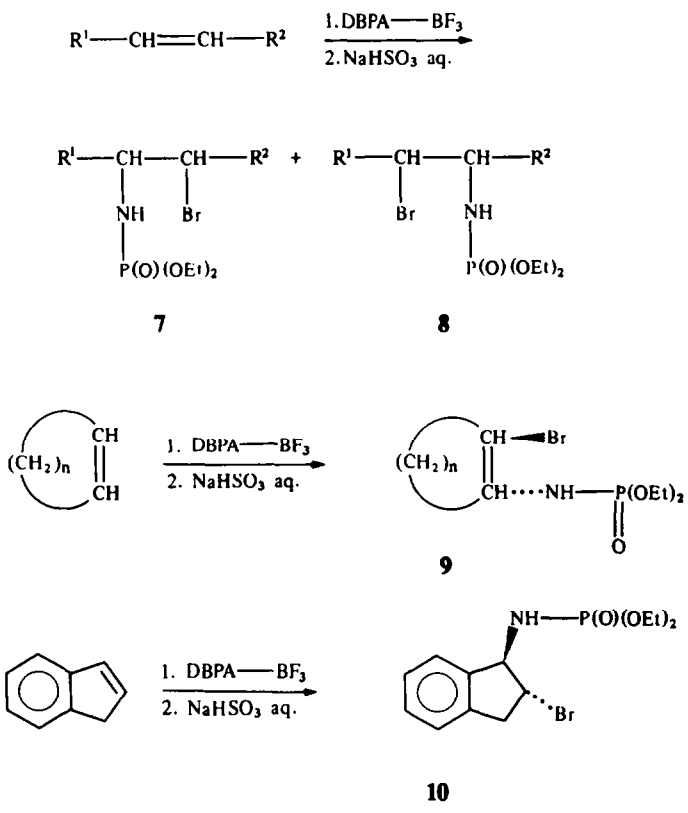
As determined by ^{31}P-NMR all additions to unsymmetrical alkenes were not regiospecific and afforded mixtures of both regioisomers. For α-olefins, like 1-pentene, and 1-hexene Markovnikov adducts were formed preferentially (Table 3) but nonterminal alkenes gave 1:1 mixtures. Regioisomeric adducts, easily distinguishable by ^{31}P-NMR, could not be resolved into individual compounds by column chromatography on silicagel. However, they could be successfully applied (after degradation with hydrochloric acid) for cyclization, both isomers giving the same aziridine. Stereospecific anti-addition was observed for (*E*)- and (*Z*)-2-butene and (*E*)-3-hexene (see proof of structure below). Branched-chain olefins, viz. isobutylene and 2-methyl-1-butene gave mixtures of products which were not identified. Sterically hindered olefins, like 3,3-dimethyl-2-butene did not react with DBPA–BF_3 complex in the sense of addition affording mixtures of bromine adducts and/or allylic bromination products exclusively. Yields, physical properties,

Table 2. Spectrometric data of diethyl N-(β-bromoalkyl)phosphoroamidates (**5a–g, 6**)

Compound no.	Characteristic IR absorption maxima[a] (KBr) (cm^{-1})	^{1}H-NMR assignments (CCl_4)[b] (δ in ppm from TMS; J in Hz)	^{31}P-NMR (δ in ppm from 85% H_3PO_4)
5a	3220m; 2990m; 2930m; 1475m; 1230s; 1160m; 1020s; 975m; 705m	1.00, 1.30 (2t, 6H, J = 7.2); 3.51 (d, 2H, J = 6.5); 3.72, 3.78 (2t, 1H, J = 6.5, J = 4.2); 4.05 (qu, 4H, J = 7.2); 7.01 (s, 5H)	7.75
5b	3220s; 2980m; 2950m; 1470m; 1230s; 1055s; 1030s; 970s; 705s	0.88, 1.30 (2t, 6H, J = 7.2); 1.68 (d, 3H, J = 6.0); 3.08–3.90 (m, 2H); 4.10 (qu, 4H, J = 7.2); 6.17 (t, 1H, J = 12.0); 7.03–7.55 (m, 5H)	7.75
5c	3220s; 3000m; 2920m; 1450m; 1220s; 1045s; 1025s; 965s; 700m	0.87, 1.30 (2t, 6H, J = 7.2); 1.52 (d, J = 6.0, *threo*); 1.69 (d, J = 6.0, *erythro*); 3.20–4.50 (m, 2H); 4.05 (qu, 4H, J = 7.2); 5.95 (t, 1H, J = 11.0); 7.05–7.55 (m, 5H)	7.75
5d		0.99, 1.21 (2t, 6H, J = 7.0); 3.30–5.05 (m, 4H); 4.49, 4.71 (2d, 1H, J = 5.0, J = 8.5); 5.22 (d, 1H, J = 5.0); 7.26 (bs, 10H)	6.50 *erythro* 7.50 *threo*
5e	3220s; 1220s; 1160m; 1070s; 1030s; 740s; 690m		6.50 *erythro* 7.50 *threo*
5f	3240m; 2800s; 1480m; 1440s; 1250m; 1140m; 1065s; 1020s; 740s; 685s	1.03 (t, 6H, J = 7.2); 3.73 (2q, 4H, J = 7.2, J = 2.5); 4.43 (s, 2H); 7.02 (m, 10H)	6.25
5g	3040s; 3000m; 2920w; 1450m; 1240s; 1065s; 1040s; 1015s; 965s; 705s	1.45, 1.72 (2t, 6H, J = 7.0); 2.13 (s, 3H); 4.05 (d, 2H, J = 5.5); 4.45 (qu, 4H, J = 7.0); 5.93 (d, 1H, J = 8.0); 7.45–7.97 (m, 5H)	6.50
6	3150m; 3000w; 2920m; 1480m; 1450m; 1245s; 1055s; 1040s; 980s; 700m	1.15 (t, 6H, J = 7.0); 3.80, 3.85 (2qu, 4H, J = 7.0); 4.02 (bs, 4H); 4.45 (d, 1H, J = 6.5); 7.07–7.57 (m, 5H)	5.50

[a] The most characteristic bands are only given. Abbreviations used: s, strong; m, medium; w, weak.

[b] Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet; b, broad; dist. t, distorted triplet.



Scheme 1.

and elemental analysis data of the phosphoroamidates (**7–10**) are listed in Table 3. Their IR and NMR spectral data are summarized in Table 4.

Proof of structure of DBPA–BF_3 *addition products.* All DBPA–BF_3 adducts to phenylethylenes, alkenes, and cycloalkenes (**5a–g**, **7–10**) could be satisfactorily analysed for C, H, N, and P. Their IR spectra (Tables 2 and 4) exhibited characteristic strong NH absorption bands in the region of 3140–3240 cm^{-1}, P=O bands at 1220–1240 cm^{-1}, and P—O—(C) bands within the range 1020–1040 cm^{-1} and 955–980 cm^{-1}. These spectral data are fully consistent with the anticipated phosphoroamidate structure. All regioisomeric adducts were recognized by ^{31}P-NMR spectroscopy, the isomer ratio being calculated from the area ratios of the respective P-signals in the spectra of crude reaction mixtures. Some reference phosphoroamidates with terminal carbon atom bearing the amidophosphoryl

Table 3. Diethyl N-(β-bromoalkyl)phosphoroamidates (from alkenes and cycloalkenes)

Compound no.	R^1	R^2	Yield %	M.p. (n_D^{20})	Remarks	Analyses							
						Required				Found			
						C	H	N	P	C	H	N	P
7a+8a	Bu^n	H	86	—	**7a:8a** = 70:30	38.0	7.3	4.4	9.8	37.7	7.2	4.6	9.5
7b+8b	Pr^n	H	82	—	**7b:8b** = 60:40	35.8	7.0	4.6	10.3	35.6	7.2	4.8	9.9
7c+8c	Pr^n	Me	70	—	**7c:8c** = 50:50	38.0	7.3	4.4	9.8	38.2	7.1	4.4	9.6
7d+8d	Et	Me	76	—	**7d:8d** = 50:50	35.8	7.0	4.6	10.3	36.1	6.8	4.7	9.9
7e	Et	Et	92	(1.4733)	*erythro* isomer[a]	38.0	7.3	4.4	9.8	37.9	7.2	4.4	9.6
7f	Me	Me	84	154–155	*erythro* isomer[b]	33.4	6.6	4.8	10.8	33.5	6.6	4.8	10.6
7g	Me	Me	89	134–136	*threo* isomer[c]	33.4	6.6	4.8	10.8	33.4	6.7	4.9	11.0
9a	n = 3		80	(1.4878)	—	39.0	6.4	4.7	10.3	38.7	6.3	4.8	10.0
9b	n = 4		80	79–81	—	38.2	6.7	4.8	9.6	38.4	6.8	4.6	9.3
9c	n = 5		79	73–75	—	40.3	7.1	4.3	9.4	40.3	7.0	4.2	9.6
9d	n = 6		27	(1.5058)	—	42.1	7.4	4.1	9.0	42.3	7.5	3.9	8.7
10	—		96	98–100	—	44.8	5.5	4.0	8.9	44.8	5.6	3.9	9.1

[a] From (*E*)-3-hexene.
[b] From (*E*)-2-butene.
[c] From (*Z*)-2-butene.

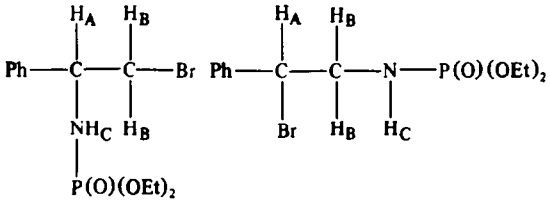
Table 4. Spectrometric data of diethyl N-(β-bromoalkyl)phosphoroamidates (7–10)

Compound no.	Characteristic IR absorption maxima (KBr or film) (cm^{-1})	^{1}H-NMR assignments (CCl_4) (δ in ppm from TMS, J in HZ)	^{31}P-NMR (δ in ppm from 85% H_3PO_4)
7a + 8a	3200m; 2960s; 1450m; 1220s; 1020s; 960s	0.92 (dist.t, 3H); 1.06–2.02 (m, 18H); 2.83–3.58 (m, 3H); 4.00 (qu, 4H, J = 7.5)	8.25, 9.25
7b + 8b	—	—	6.75, 7.50
7c + 8c	3220m; 2960m; 1450m; 1230s; 1050s; 1030s; 960s	0.90 (dist.t, 3H); 1.10–2.22 (m, 14H); 3.10 (bs, 1H, $W_{1/2}$ = 16.0); 3.95 (qu, 4H, J = 7.0)	7.75, 8.25
7d + 8d	—	—	6.00, 7.50
7e	3210m; 2975s; 1460m; 1235s; 1060s; 1030s; 970s	1.80 (dist.t, 6H); 1.13 (t, 6H, J = 7.0); 1.50–2.23 (m, 4H); 3.08 (m, 1H); 3.85–4.20 (m, 5H)	8.00
7f	3220s; 2930s; 1445s; 1380m; 1220m; 1080m; 1035s; 950m	1.25 (d, 3H, J = 7.0); 1.27 (t, 6H, J = 7.0); 1.65 (d, 3H, J = 7.0); 3.22 (m, 1H); 3.90–4.30 (m, 5H)	7.50
7g	3240s; 3000s; 1460m; 1240m; 1080m; 1020w; 960s	1.20 (d, 3H, J = 6.5); 1.30 (t, 6H, J = 7.0); 1.65 (d, 3H, J = 6.5); 3.28 (m, 1H); 3.80–4.30 (m, 5H)	8.00
9a	3220s; 2980s; 1440m; 1230s; 1025s; 960m	1.25 (t, 6H, J = 7.5); 1.50–2.50 (m, 7H); 3.52 (bs, 1H, $W_{1/2}$ = 22.0); 3.98, 4.03 (2qu, 4H, J = 7.5); 5.25 (t, 1H, J = 11.0)	8.25
9b	3185s; 2970m; 1245s; 1232s; 1140m; 1065m; 1040w; 996m; 970m; 690m	1.28 (t, 6H, J = 7.0); 1.30–2.65 (m, 9H); 3.00 (bs, 1H, $W_{1/2}$ = 25.0); 4.01 (qu, 4H, J = 7.0); 3.53 (t, 1H, J = 11.0)	8.50
9c	3160s; 2900s; 1460m; 1230s; 1050s; 1025s; 955s	1.28 (t, 6H, J = 7.0); 1.45–2.38 (m, 11H); 3.35 (bs, 1H, $W_{1/2}$ = 22.0); 3.95, 4.05 (2qu, 4H, J = 7.0); 5.58 (t, 1H, J = 11.0)	7.25
9d	3220m; 2920m; 1470m; 1440m; 1225s; 1050s; 1025s; 955s	1.28 (t, 6H, J = 7.0); 1.45–2.43 (m, 13H); 3.08 (bs, 1H, $W_{1/2}$ = 22.0); 3.98 (qu, 4H, J = 7.0); 4.85 (t, 1H, J = 11.0)	7.75
10	3140s; 2980m; 1480s; 1230s; 1120s; 1035s; 980s; 745s; 730s	1.20 (t, 6H, J = 7.0); ABMX system[a] (4H, δ_A = 3.50, δ_B = 3.05, δ_X = 4.22, J_{AB} = 16.0, J_{AM} = 7.0, J_{BM} = 6.5, J_{MX} = 6.5); 3.85 (qu, 4H, J = 7.0); 6.80–7.50 (m, 4H)	7.75

[a] First order treatment was applied.

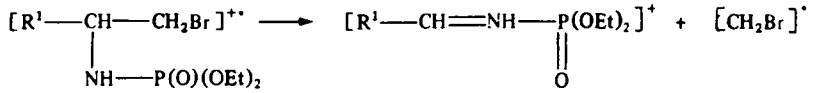
moiety were obtained, when necessary, by regiospecific, free-radical DBPA addition to the respective olefins.[1–3] The final unambiguous structural assignments, namely the location of the Br atom and the amidophosphoryl group, could be deduced from detailed inspection of the ^{1}H-NMR spectra of pure single isomers. Multiplicity of certain groups of protons, especially some splitting patterns due to long-range coupling with P atom were of particular diagnostic value for definite structural assignments. The Markovnikov orientation of some adducts could be also convincingly confirmed by means of mass spectroscopy. All mass spectra of the adducts derived from terminal alkenes displayed the base peaks at $m/z = M - CH_2Br$ which corresponds to the expected preferential α-cleavage fragmentation, in accord with the regioisomeric structure outlined below (Eq. 3):

Markovnikov-type adduct **5a** or its regioisomer **5a′**:



5a **5a′**

The NMR evidence is in accord only with the structure **5a**. In the ^{1}H-NMR spectrum of DBPA-styrene adduct (crystalline compound, m.p. 90–91°,



(3)

Such fragmentation pattern is impossible for regioisomeric, anti-Markovnikov adducts with the amidophosphoryl moiety at the terminal position.

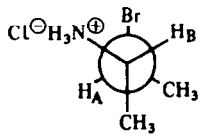
Definite structural assignment based on careful examination of the relevant ^{1}H-NMR spectrum is exemplified below for the DBPA-styrene adduct obtained under heterolytic conditions. For such a compound one can consider the structure of

$\delta_{^{31}P}$ = 7.75 ppm) the magnetically equivalent H_B protons appear as a doublet centred at 3.51 ppm. The downfield double triplet centred at 3.75 ppm integrating for one hydrogen and well resolved after deuteration of H_C proton is attributed to the H_A proton. Splitting of this signal evidently results from a long range coupling between benzylic H_A proton and P

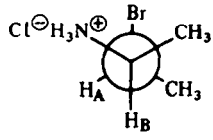
atom ($^3J_{PH}$ = 4.2 Hz). If the Br atom and amidophosphoryl group were reversed (regioisomer **5a'**) such a pattern would not be obtained and the benzylic H_A proton would display a downfield triplet with no further splitting by P atom. The remainder of the NMR spectrum exhibits two upfield triplets (6H) at 1.00 and 1.30 ppm derived from Me protons of two heterotopic EtO groups, and a symmetrical quintet of methylene protons centred at 4.05 ppm with $J_{HH} \approx {}^3J_{PH}$ = 7.2 Hz, all the signals being however of limited diagnostic value in distinguishing between the regioisomeric structures **5a** and **5a'**. This spectroscopic analysis could be verified experimentally by direct comparison of **5a** with an authentic specimen of **5a'** (oil, δ_{31P} = 8.3 ppm) obtained previously by an anti-Markovnikov, free-radical addition of DBPA to styrene.[2]

Diastereomeric (*E*)- and (*Z*)-2-butenes were selected as model compounds for studying stereochemistry of DBPA–BF_3 addition. Both crude adducts of DBPA–BF_3 complex to (*E*)- and (*Z*)-2-butenes **7a** and **7b** gave single signals in their ^{31}P-NMR spectra at $\delta_{H_3PO_4}(CCl_4)$ 7.5 and 8.0 ppm respectively.

This result suggested the formation of two distinct diastereoisomers *erythro* and *threo* produced by stereospecific anti-addition under heterolytic conditions. Direct assignment of stereochemistry could not be arrived at by ^{1}H-NMR due to the complex multiplicity patterns of the spectra. Detailed analysis was, however, possible for the ^{1}H-NMR spectra of the respective β-bromoamine hydrochlorides which could be readily obtained from the adducts **7a** and **7b** upon degradation with hydrochloric acid in benzene (*vide infra*).

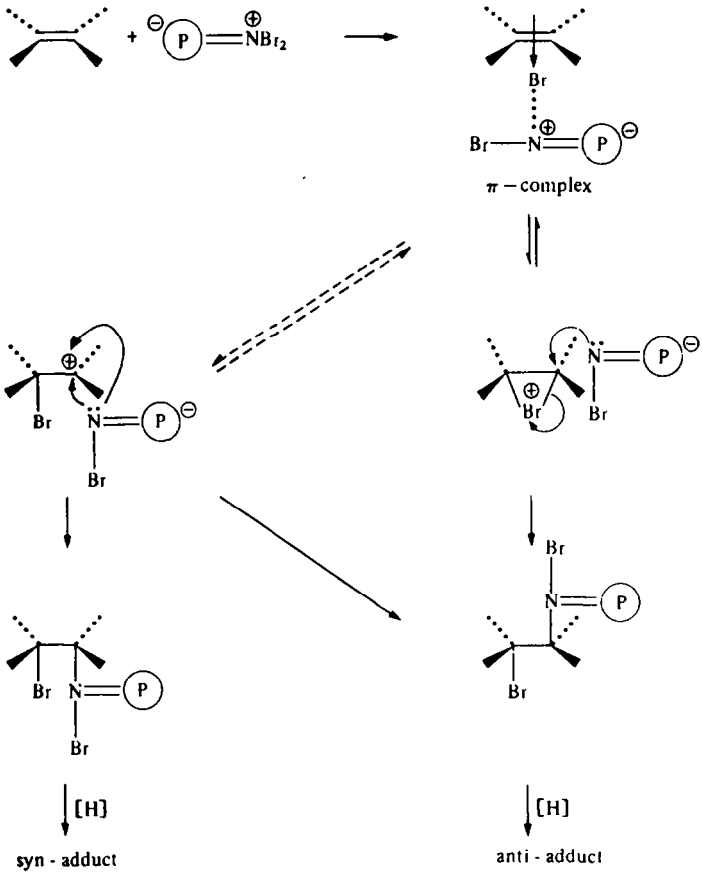


12c *threo*–isomer (from (*Z*)–2–butene)



12d *erythro*–isomer (from (*E*)–2–butene)

This treatment does not change the configuration on both chiral centres. The ^{1}H-NMR spectrum of the hydrochloride **12c** obtained from (*Z*)-2-butene exhibited the presence of two quintets integrating for one hydrogen each and centred at δ_{TMS} (D_2O) 3.87 and 4.65

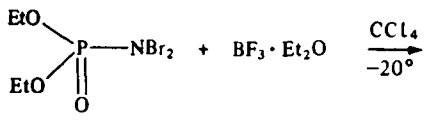


$\ominus P=\overset{\oplus}{N}Br_2 \equiv$ DBPA–BF_3 complex

Scheme 2.

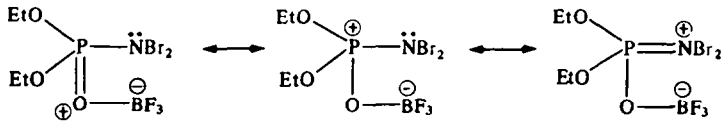
ppm ($J_{H_AH_B}$ = 6.6 Hz). These signals could be ascribed to methine protons H_A and H_B split by themselves and equally coupled to Me protons. In the ^{1}H-NMR spectrum of the hydrochloride **12d** obtained from (*E*)-2-butene the signals of methine protons H_A and H_B are displayed at δ_{TMS} (D_2O) 3.85 and 4.80 ppm as double quartets (J_{HH} = 6.6 Hz, $J_{H_AH_B}$ = 3.0 Hz). It is feasible to assume the antiperiplanar arrangement of vicinal protons H_A and H_B in the preferred conformation of *threo*-isomer **12c**. This would account for a relatively large coupling constant according to Karplus relationship. The synclinal arrangement of vicinal protons H_A and H_B in the preferred conformation of the *erythro*-isomer **12d** is in turn fully compatible with a low value of the respective coupling constant according to Karplus equation. Similar values (J_{HH} = 6.0 Hz and 3.5 Hz) have been reported by Hassner *et al.*[6] for *threo*- and *erythro*-3-chloro-2-aminobutene hydrochlorides respectively. This conformational analysis confirms the stereospecific anti-addition of DBPA–BF_3 complex to (*E*)- and (*Z*)-2-butenes leading to *erythro*- and *threo*-adducts **7a** and **7b** respectively. Additional evidence in support of this concept could be deduced from the ^{1}H-NMR spectrum of β-bromocyclohexylamine hydrochloride **12h** obtained by addition of DBPA–BF_3 complex to cyclohexene followed by degradation of the adduct. The configuration and conformation of this compound follows from the splitting pattern and large band-width (25 Hz) of the CHBr and $C\underline{H}NH_3^+$ proton signals, which are those expected for compounds existing predominantly in the di-equatorial conformation.[7]

Mechanism of DBPA–BF_3 *addition.* All DBPA–BF_3 additions to phenylethylenes, alkenes and cycloalkenes exhibit several characteristic features which are indicative of typical ionic reactions: (i) for phenylethylenes they follow regiospecifically affording Markovnikov adducts; (ii) for several alkenes and cycloalkenes they are stereospecific anti-addition processes; (iii) they are rapid at low temperature, insensitive to photolytic initiation and commence instantaneously without any induction period; (iv) they are strongly influenced by steric factors. All these phenomena can be rationalized in terms of heterolytic addition, with boron fluoride playing a role of an ionizing agent for DBPA molecule. It was found that the addition of an equimolar amount of boron trifluoride etherate to the solution of DBPA in tetrachloromethane changes the spectral characteristic of this reagent. The P=O absorption band in the IR spectrum (CCl_4, 0.25 mol) is shifted from 1275 cm^{-1} to 1235 cm^{-1} suggesting considerably diminished bond order of the phosphoryl group. The ^{31}P-NMR signal at δ = 10.75 ppm disappears and a new, ill-defined quartet at δ = 6.25 ppm (J = 10.7 Hz) is displayed in the spectrum. This spectral evidence strongly suggests the formation of a stable DBPA–BF_3 complex which is the resonance hybrid of three contributing structures (Eq. 4):



DBPA (1)

(4)



11a **11b** **11c**

Strongly enhanced electrophilic character of bromine atom in the complex (**11**), which is evident from the structure (**11c**), can induce heterolytic cleavage of N—Br bond and is responsible for ionic addition to the double bond (Scheme 2).

The formation of Markovnikov-type anti-adducts can be rationalized by assuming bromonium ion as a common intermediate although some contribution from an open carbonium ion (shown in Scheme 2 by a broken arrow) cannot be totally ignored. The lack of stereospecificity observed for the addition of DBPA–BF_3 complex to (*Z*)-1-phenylpropene as well as to (*E*)- and (*Z*)-stilbenes implies the parallel or alternative participation of this pathway. For phenylethylenes resonance stabilized benzylic-type open carbonium ions can be formed, paired with a phosphoroamidate counter ion, collapse of the intimate ion-pair occurring with overall syn- and/or anti-addition.

Degradation of DBPA–BF_3 *adducts.* All pure DBPA–BF_3 adducts were degraded to the corresponding β-bromoamine hydrochlorides **12** by means of gaseous hydrogen chloride in benzene. The reaction monitored by ^{31}P-NMR was complete after 24 hr at room temperature. The hydrochlorides **12** (Eq. 5) separated from the solution in pure form and could be easily isolated.

Yields, m.ps, and some spectroscopic data of **12** are summarized in Table 5. The addition of DBPA–BF_3 complex to alkenes and cycloalkenes followed by degradation of the adducts offers a convenient approach to β-bromoamine hydrochlorides which are not readily accessible by other methods.

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. All starting olefins purchased from Fluka, BDH or

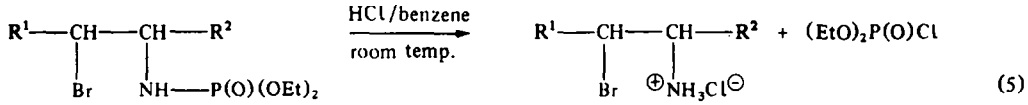


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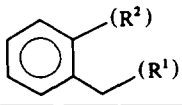
Table 5. β-Bromoamine hydrochlorides[a]

Compound no.	R^1	R^2	Yield %	M.p. (°)	IR (KBr) (cm^{-1})	^{1}H-NMR assignments (D_2O/CH_3COOH) (δ in ppm from TMS; J in Hz)
12a	H	Ph	99	176–8	2950s; 1590m; 1510s; 1450m; 1380m; 690s	4.03 (d, 2H, J = 7.0); 5.05 (t, 1H, J = 7.0); 7.73 (s, 5H)
12b	Me	Ph	76 *erythro*	182–4	2950s; 1590m; 1505s; 1450m; 1380m; 695s	1.76 (d, 3H, J = 6.0); 4.60–5.07 (m, 2H); 7.60 (s, 5H)
12c	Me	Me	68 *erythro*	164–6	2900s; 1600m; 1500m; 1375m	1.55 (d, 3H, J = 6.6); 1.92 (d, 3H, J = 6.6); 3.85 (2q, 1H, J = 6.6, J = 3.0); 4.80 (2q, 1H, J = 6.6, J = 3.0)
12d	Me	Me	57 *threo*	144–6	3000–2880s; 1590m; 1495s; 1380m	1.68 (d, 3H, J = 6.6); 2.02 (d, 3H, J = 6.6); 3.87 (qu, 1H, J = 6.6); 4.65 (qu, 1H, J = 6.6)
12e	Et	Et	64 *erythro*	157–9	2960–2840s; 1595m; 1510s; 1450m	1.30–1.71 (m, 6H); 2.00–2.66 (m, 4H); 3.80–4.18 (m, 1H); 4.83 (2q, 1H, J = 8.0, J = 3.0)
12f	$-(CH_2)_3-$		70	182–4	2980–2940s; 1560m; 1495m; 1445m	1.60–2.78 (m, 6H); 3.67–4.07 (m, 1H, $W_{1/2}$ = 20.0); 4.07–4.60 (m, 1H, $W_{1/2}$ = 20.0)
12g	$-(CH_2)_4-$		90	187–9	2840s; 1590m; 1520s; 1445m	1.43–3.03 (m, 8H); 3.48–4.00 (m, 1H, $W_{1/2}$ = 25.0); 4.18–4.73 (m, 1H, $W_{1/2}$ = 25.0)
12h	$-(CH_2)_5-$		66	152–4	2900s; 1585m; 1505m; 1445m	1.87–3.10 (m, 10H); 3.95–4.40 (m, 1H); 4.55–5.00 (m, 1H)
12i	$-(CH_2)_6-$		20	198–200	3100–2900s; 1580m; 1490m; 1390m	1.62–3.07 (m, 12H); 3.67–4.07 (m, 1H, $W_{1/2}$ = 18.0); 4.70–5.10 (m, 1H, $W_{1/2}$ = 18.0)
12j			78	201–3	2860s; 1590m; 1515s; 1450w; 1365w; 740s; 715m	ABMX system[b] (4H, δ_A = 4.15; δ_B = 3.61, δ_M = 5.00, δ_X = 5.38, J_{AB} = 17.0, J_{BM} = 6.0, J_{AM} = 7.0, J_{MX} = 5.5); 7.76 (m, 4H)

[a] The elemental analyses of all compounds (C, H, N) were fully consistent with the calculated values.
[b] First order treatment was applied.

E. Merck 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. M.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 using a Tesla BS 487C spectrometer in CCl_4 or D_2O/CF_3COOH using TMS as internal or external standards respectively. ^{31}P-NMR spectra were recorded at 24.3 MHz with a Jeol JNM-C-60HL spectrometer using 85% H_3PO_4 as external reference. Mass spectra were taken at 70 eV with a LKB 2091 spectrometer. All measurements were made on samples of analytical purity.

Diethyl phosphoroamidate was prepared by a modified procedure developed by Todd *et al.*[8] Dry ammonia gas was passed with stirring and external cooling (ice-water bath) through the soln of diethyl phosphite (138 g, 1 mol) in tetrachloromethane (500 ml) at such a rate to keep the temp of the exothermic reaction at 15–20°. After about 3 hr, when no more ammonia was absorbed, the inlet tube was detached and stirring was continued for additional 0.5 hr at room temp. Ammonium chloride was then filtered off with suction and washed with tetrachloromethane (2 × 100 ml). Crude phosphoroamidate obtained on evaporation of solvent was dissolved in hot tetrachloromethane (100 ml). Hot hexane (100 ml) was added to the soln and it was left overnight at room temp. Analytically pure diethyl phosphoroamidate (143.7 g, 94%) was filtered off and dried over P_2O_5. M.p. 53° (lit.: m.p. 50–51°;[8] 46–47°).[9]

Diethyl N,N-dibromophosphoroamidate (DBPA, 1) was synthesized as described previously[1] by bromination of diethyl phosphoroamidate with bromine at 0° in an aqueous soln containing equimolar amount of potassium carbonate. Addition of DBPA–BF_3 complex to phenylethylenes, alkenes, and cycloalkenes.

Boron trifluoride etherate (7.1 g 0.05 mol) was added dropwise with stirring to the soln of DBPA (15.55 g, 0.05 mol) in tetrachloromethane (100 ml) cooled to −20° (dry ice-acetone bath). Then the olefin (0.05 mol) was added at such a rate to maintain the temp of the strongly exothermic reaction at −20° (~ 0.5 hr). Cooling-bath was then removed and stirring was continued for additional 0.5 hr. The resulting pale-yellow soln was cooled to 10° and 20% aqueous soln of sodium bisulphite (30 ml) was added slowly at this temp. Tetrachloromethane (50 ml) was then added and the organic layer was separated, washed with water (2 × 50 ml), dried, and evaporated. The residual crude adducts were analytically pure when heated at 40–50°/0.1 mm for 1 hr to remove traces of solvent. Tables 1 and 3 show results, physical constants, and elemental analysis data. For (*E*)- and (*Z*)-stilbenes the addition was performed in usual way but at 20–25° (1 hr) to improve the

yield of adducts. For (*E*)- and (*Z*)-2-butenes the soln of DBPA–BF_3 complex, prepared as described immediately above, was satd with gaseous olefins at −20° until its colouration changed from red to yellow.

Degradation of DBPA *adducts with hydrogen chloride.* The slightly modified procedure described previously[3] was applied. Passing of dry HCl through the soln of the appropriate adduct (0.02 mol) in benzene (50 ml) for 1 hr at 20–25° followed by leaving it at room temp for 24 hr was found sufficient (^{31}P-NMR) for complete degradation. Analytically pure samples of β-bromoamine hydrochlorides **12** were obtained by dissolving crude compounds in ethanol and adding an excess of ether. The yields, m.ps, and spectroscopic characteristics of **12** thus obtained are summarized in Table 5.

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REFERENCES

[1] A. Zwierzak and S. Zawadzki, *Synthesis* 323 (1971).
[2] S. Zawadzki and A. Zwierzak, *Tetrahedron* **29**, 315 (1973).
[3] S. Zawadzki and A. Zwierzak, *Tetrahedron* **37**, 2675 (1981).
[4] M. S. Kharasch and H. M. Priestley, *J. Am. Chem. Soc.* **61**, 3425 (1939).
[5] M. Hanack, *Conformation Theory*, p. 333. Academic Press, New York (1965); see also: R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia* **12**, 81 (1956).
[6] A. Hassner, G. J. Matthews and F. W. Fowler, *J. Am. Chem. Soc.* **91**, 5046 (1969).
[7] H. Feltkamp and N. C. Franklin, *Angew. Chem.* **77**, 798 (1965); *Ibid.* Int. Ed. **4**, 774 (1965).
[8] F. R. Atherton, H. T. Openshaw and A. R. Todd, *J. Chem. Soc.* 660 (1945).
[9] J. E. Malowan, *Inorg. Synth.* **4**, 77 (1953).