Tetrahedron. Vol. 26, pp. 3527 to 3537. Pergamon Press 1970. Printed in Great Britain

N,N-DIHALOPHOSPHORAMIDES—II*

THE ADDITION OF DIETHYL N,N-DICHLOROPHOSPHOROAMIDATE (DCPA) TO PHENYLETHYLENES

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(*Received in the UK* 16 *March* 1970; *Accepted for publication* 7 *April* 1970)

Abstract—The addition of DCPA to a variety of phenylethylenes has been examined. After a short induction period the reaction proceeds rapidly and exothermically to give high yields of N-chloro adducts, which afford the corresponding phosphoroamide derivatives upon reduction with sodium pyrosulphite solution. Addition of DCPA to methylstyrenes as well as *trans*-stilbene is nonstereospecific and in the latter case evidently subject to steric retardation. The reaction with 1,1-di(*p*-methoxyphenyl)ethylene takes a different path to give 1,1-di(*p*-methoxyphenyl)-2-chloroethylene as the major product. Some of the DCPA addition products easily undergo degradation by means of hydrogen chloride in benzene solution affording the corresponding β-chloroamines in good yields. The complete selectivity for anti-Markovnikov addition, as shown by NMR evidence, reflects the enhanced stability of the benzyl radicals assumed as intermediates in the reaction, for which a spontaneous initiated radical-chain mechanism is proposed. Spectral data pertinent to the proof of structures are presented.

THE addition of various N,N-dihaloamides to unsaturated compounds has been extensively studied.[1] The reactions have been reported to give anti-Markovnikov adducts with terminal olefins[2] and α, β-unsaturated compounds.[3] With the isomeric 2-butenes,[4] *trans*-3-hexene[2] and *trans*-stilbene[2] mixtures of the *erythro* and *threo* isomers are formed. The initial adducts, β-chloro-N-chlorocarbamates or β-chloro-N-chlorosulphonamides, were not isolated but were reduced to the β-chloroalkyl derivatives with either sodium bisulphite[2] or potassium iodide followed by thiosulphate solution.[4]

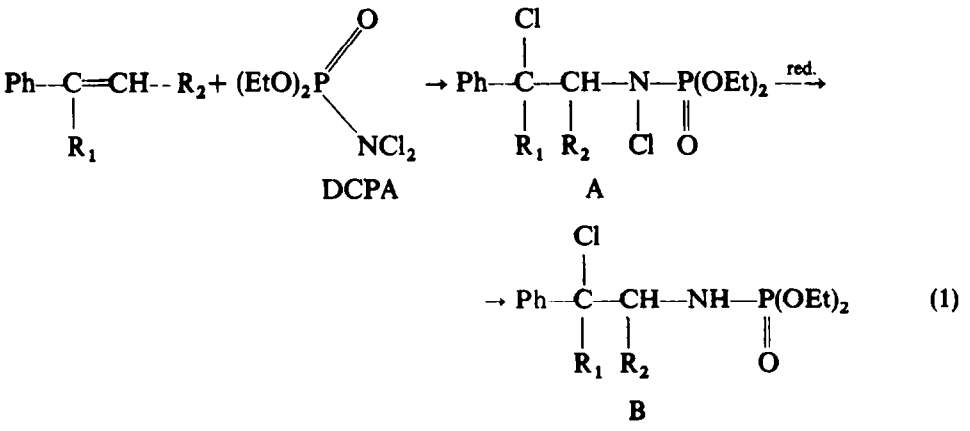
We have described[1] the preparation of diethyl N,N-dichlorophosphoroamidate (DCPA) and some of its structural analogues. In the present paper we report: (a) the reaction of DCPA with a variety of phenylethylenes, (b) proof of structure of the addition products together with some suggestions pertinent to the reaction mechanism, and (c) the synthetic utility of the addition products in the preparation of β-chloroamines directly from unsaturated compounds.

Addition of DCPA to phenylethylenes

The addition of DCPA to styrene, α-methylstyrene, *cis*- and *trans*-β-methylstyrenes, 1,1-diphenylethylene, *trans*-stilbene, and 1,1-di(*p*-methoxyphenyl)ethylene has been

* Part I: A. Zwierzak and A. Koziara, *Tetrahedron* **26**, 3521 (1970). Paper CILIX on organophosphorus compounds.

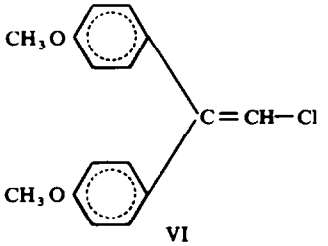
examined. In all cases except the last one, the reaction followed the same general course outlined below (Eq. 1):



(1)

Styrene and its analogues added DCPA in anti-Markovnikov fashion (see proof of structure below) affording diethyl N-chloro-N-(β-chloroalkyl)phosphoroamidates (A). All initially obtained adducts were N-chloro derivatives; the chlorine attached to nitrogen still had a positive halogen character, which could be demonstrated iodometrically. Washing the benzene solution of the adduct (A) with 20% aqueous sodium pyrosulphite at low temperature (0–10°) reduced it to the corresponding diethyl N-(β-chloroalkyl) phosphoroamidate (B, compounds I–V). After reduction the crude compounds (I–V) were further purified by distillation *in vacuo* or crystallization. Compounds II and III were found to be analytically pure in the crude state. Physical constants, yields, elemental analysis, and some IR spectral data of the compounds I–V are listed in Table 1.

Three addition procedures were employed, the choice depending on the reactivity of the unsaturated compound. In the case of styrene and its methyl analogues the hydrocarbon was added dropwise to a benzene solution of DCPA at 60–80° (method a). After a short induction period the reaction was rapid, exothermic, and complete within 1 hr. Yields of isolated, analytically pure diethyl N-(β-chloroalkyl)-phosphoroamidates (B, 1–V) were in the range of 70–80%. Addition of DCPA to 1,1-diphenylethylene and its *p*-methoxy derivative could be readily effected by dropping the reagent into a benzene solution of an olefin at 30–50° (method b). The reaction occurred very rapidly with strong exothermic effect giving rise to the formation of an adduct (IV) or, unexpectedly, a side-chain vinylic chlorination product (VI).



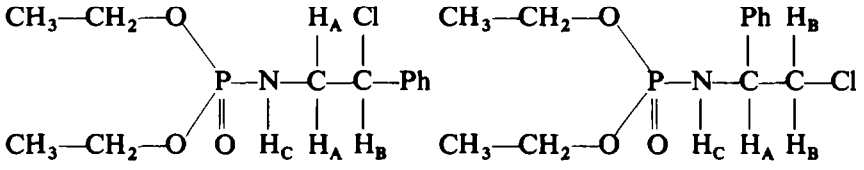
VI

trans-Stilbene reacted with DCPA extremely slowly, as anticipated on steric grounds, and required a reaction time of 4 hr in refluxing benzene (method c) for complete disappearance of olefin. The crystalline reaction product was isolated in 33·5% yield.

Proof of structure of addition products

All diethyl N-(β-chloroalkyl)phosphoroamidates (I–V) listed in Table 1 had acceptable elemental analysis and IR spectra. The final structural assignments, namely, the location of the Cl atom and the amido group (—$NHP(O)(OEt)_2$) were made from NMR spectra by analysis of the chemical shifts and multiplicity of the relevant protons, particularly those adjacent to N atom (H_A). Table 2 lists the NMR spectral assignments for all protons for various phosphoroamidates (I–V) except the amide ones. Signals of aromatic protons, which appear as complex multiplets, are also not included into the Table. As determined by integration, the NH signals overlap with those of the CH_2—O groupings. Rather complex patterns were usually observed also for H_A protons. Exchange of the amide protons with deuterium oxide reduced the multiplicity of H_A signals and rendered the correct structural assignments possible.

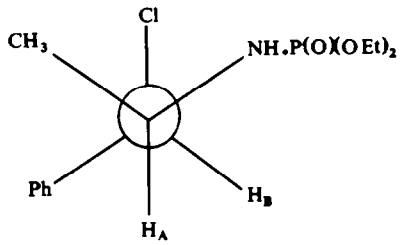
Detailed examination of the NMR spectrum of DCPA-styrene adduct (I) is given below to exemplify the general way of related establishments. Addition of DCPA to styrene followed by reduction could yield the anti-Markovnikov product (I), or its isomer (I′):



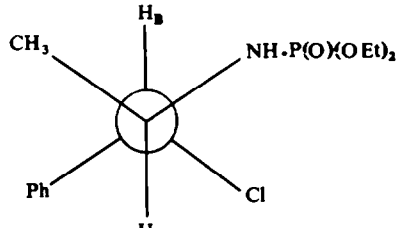
The NMR data are consistent only with the structure (I). The benzylic protons, H_B (1H) appears at 5·03 τ as a triplet owing to splitting by two protons H_A. Because of magnetic symmetry the protons H_A (2H) are equivalent and appear as a double doublet (centered at 6·64 τ) resulting from splitting of H_A by both the benzylic proton, H_B and by P atom ($J_{P-NH-CH_A}$ = 10·4 c/s). This pattern is observed after exchange of the amide proton (H_C) with deuterium oxide. If the Cl atom and amido group were reversed (formula I′), such a pattern would not be obtained. NMR spectrum of the compound I′ would display on deuteration a downfield doublet (2 H) for two protons, H_B and a double triplet for the benzylic proton, H_A (1 H), owing to coupling with H_B and P atom.

The structure of the addition product of DCPA to α-methylstyrene (II) was demonstrated by NMR and confirmed by chemical evidence. It has been found that degradation of II with hydrogen chloride leads to the corresponding β-chloroamine hydrochloride (Table 3) with the chlorine being benzylically located, as proved by its quantitative solvolytic replacement in water at room temperature.

The adducts of DCPA with *cis*- and *trans*-β-methylstyrenes have in both cases identical, but very complex NMR spectra, suggesting that they are mixtures of *erythro* and *threo* isomers (IIIa and IIIb).



IIIa—erythro



IIIb—threo

The spectra exhibit the presence of two well-defined downfield doublets centered at 5·07 τ (J = 5·5 c/s) and 4·89 τ (J = 4·5 c/s) which can be assigned to the benzylic proton H_B in both stereoisomers (IIIa and IIIb) on the basis of integration, multiplicity and chemical shifts. It is apparent from the values of vicinal coupling constants that a higher-field signal with larger splitting can be associated with *trans*-coplanar arrangement of vicinal protons (H_A and H_B) corresponding to the *threo*-isomer (IIIb). Integration of the relative amounts of the respective signals allowed a calculation of the isomer ratio, which was found to be 87:13 (*erythro*:*threo* adduct) prepared from *cis*-β-methylstyrene, and 82:18, from *trans*-β-methylstyrene respectively. Similar observation has been reported by Schrage,[4] who found that, independently on the geometric configuration of the olefin, the same amounts of N-chlorourethane as well as N,N-dichlorourethane adducts were formed with 2-butene.

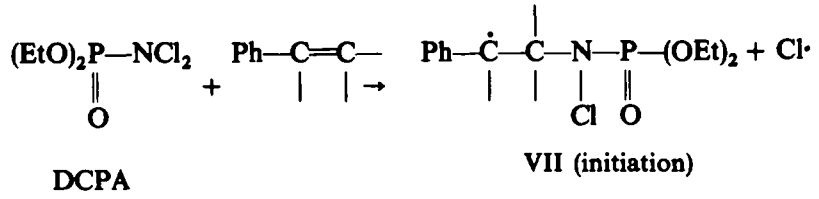
The appearance of two upfield triplets in the spectrum of the *trans*-stilbene adduct (V) centered at 9·00 τ (~ 3 H) and 8·80 τ (~ 3 H), clearly indicates the existence of two nonequivalent Me groups, probably due to the presence of both stereoisomers in an approximately equimolar ratio.

The structure of vinylic chlorination product, proposed for the compound VI, was unambiguously confirmed by direct comparison with an authentic specimen of VI prepared by an independent method.[6]

Mechanism of reaction of DCPA with phenylethylenes

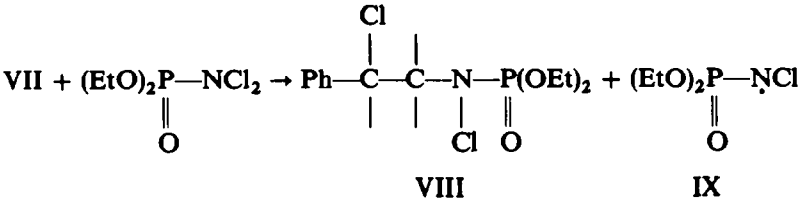
The reaction of DCPA with phenylethylenes has several characteristic features of a free-radical chain reaction: (a) an induction period is usually observed followed by a rapid, exothermic reaction; (b) the reaction is evidently catalysed by light or UV irradiation and free-radical inhibitors, such as hydroquinone and t-butylcatechol, markedly slow down the reaction rate;* (c) the addition proceeds in anti-Markovnikov fashion and is nonstereospecific. However, contrary to the expectations, neither vinyl polymerization nor allylic chlorination was observed in any of the addition reactions. The failure to obtain stereoselective addition with *trans*-stilbene and β-methylstyrenes argues against a possible concerted, completely synchronous mechanism. The exothermicity displayed by almost all reactions and lack of initiators required for the addition are characteristic of a spontaneous initiated radical-chain reaction. Such phenomenon of spontaneous initiation has been observed by Walling[7] and by Poutsma.[8,9] In the case of N,N-dichlorocarbamates reacting with dienes this mechanistic approach has been also suggested by Daniher and Butler.[10] The probable steps for the chain are presented below.

* Pure styrene was found to give 97% of crude adduct (I) with DCPA. Small additives of hydroquinone or t-butylcatechol under comparable conditions reduced the yield of (I) to 72·5% and 68·5% respectively.

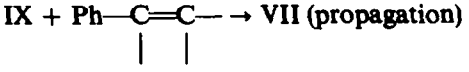


DCPA VII (initiation)

(2)

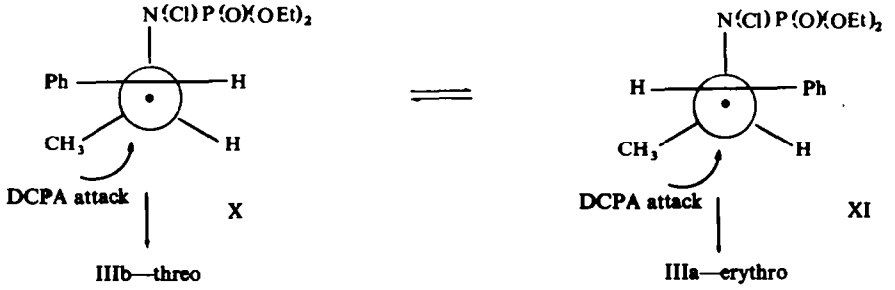


VIII IX



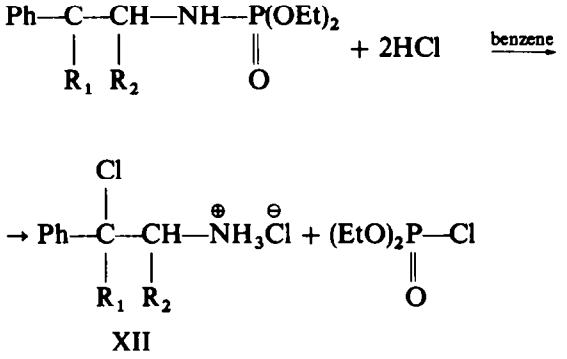
As no vinyl polymerization takes place, the propagation step to form the final 1:1 adduct (VIII) from the radical adduct (VII) is probably a much faster process than the polymerization propagation step. For similar reasons allylic chlorination does not occur because the reaction of VII with DCPA successively competes with allylic hydrogen abstraction. The complete selectivity for anti-Markovnikov addition which has been observed in all cases evidently reflects the enhanced stability of the intermediate benzyl radical (VII). The same selectivity was also proved for the addition of DCPA to straight-chain and branched-chain terminal olefins.[11] The statement recently reported by Pincuk *et al*,[12] who claim the exclusive formation of the Markovnikov terminal olefines—DCPA adducts, seems to be erroneous in the light of our findings. The authors, however, neither describe the reactions in detail nor present any conclusive proof of structure.

The nonstereospecific nature of the products from *trans*-stilbene and β-methylstyrenes results from free rotation of the intermediate radical (VII). The composition of *erythro-threo* mixture of IIIa and IIIb obtained from *cis*- and *trans*-β-methylstyrenes is *independent* of the geometric configuration of the olefin. The explanation, similar to that suggested by Schrage[4] and assuming the existence of dynamic equilibrium between the radical intermediates X and XI, is offered to account for this phenomenon.



Degradation of DCPA-phenylethylene addition products

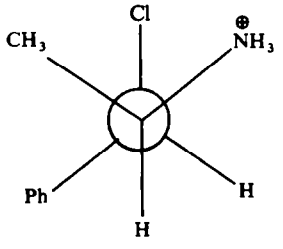
All DCPA-phenylethylenes addition products except the compounds IV and V can be readily degraded by means of gaseous hydrogen chloride in benzene to form the corresponding β-chloroamine hydrochlorides (XII) in reasonable yields (50–85%). The reaction (3) carried out according to the previously described procedure affords additional chemical evidence to prove the structures of the adducts and can be also successively used as a convenient synthetic route to β-chloroamines.



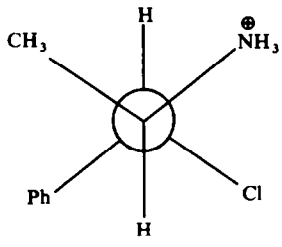
(3)

Physical properties, yields, elemental analysis, and NMR data relevant to structures of the corresponding β-chloroamine hydrochlorides (XII) are summarized in Table 3.

The same mixture of α-methyl-β-chloro-β-phenylethylamine hydrochlorides consisting of 76% *erythro* and 24% *threo* isomers is produced on degradation of *cis*- and *trans*-β-methylstyrene adducts. This assignment, consistent with the previously discussed data for the starting phosphoroamidates (IIIa and IIIb) is based upon NMR spectroscopy. Two downfield doublets centered at 4·69 τ (J = 9·6 c/s) and at 4·41 τ (J = 4·6 c/s) have been ascribed to C<u>H</u>—Cl signals in the *threo* (XIII) and *erythro* (XIV) isomers respectively. The proposed correlation results from the application of the Karplus equation to predict the values of relevant coupling constants for both stereoisomers. Their most stable conformers are represented by the formulas XIII and XIV.

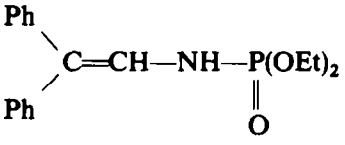


XIII—erythro



XIV—threo

The degradation takes a completely different course in the case of the relatively unstable 1,1-diphenylethylene adduct (IV). The product does not arise from P—N bond rupture, but from elimination and has been assigned the structure of enamide XV.



XV

The assignment is based upon elemental analysis and NMR spectral data. In the NMR spectrum of XV the signal for the vinylic proton appears as a downfield double doublet centered at 3·35 τ (1H) coupled to phosphorus (J = 6·5 c/s) and to the amide proton (J = 12·5 c/s). The latter coupling as well as the NH signal (appearing as a triplet due to approximately equal coupling with both the vinylic proton and phosphorus) may be removed by treating the sample with deuterium oxide. The formation of an extensively conjugated π-electron system can support the driving force for the elimination leading to XV.

trans-Stilbene adduct (V) does not undergo any change under the influence of hydrogen chloride. This lack of reactivity is possibly due to steric retardation but unfavourable electronic reasons cannot be excluded.

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. Phenylethylenes were freshly distilled before use and free from inhibitors. Light petroleum refers to the fraction boiling at 60–80°. All extracts were dried over $MgSO_4$ and evaporated under reduced press. B.ps and m.ps (taken in capillaries) are uncorrected. NMR spectra were obtained on Varian A-60 spectrometer in $CDCl_3$ or D_2O solns using TMS or DSS as internal standards, respectively. IR spectra were recorded using an UR-10 spectrophotometer (C. Zeiss, Jena). Measurements were made on samples of analytical purity. The purity of cis- and trans-β-methylstyrenes was determined by glpc which was carried on a Giede III gas chromatograph at 110° using a 1 m column packed with 30% Silicone Gum on Chromosorb W.

cis-β-Methylstyrene was obtained by decarboxylation of *trans*-α-methylcinnamic acid carried out in quinoline soln at 210–220° in presence of Cu powder as catalyst, yield 34%, b.p. 75–76°/40 mm, n_D^{25} – 1·5398 (Lit.[13]: b.p. 64·5°/20 mm, n_D^{25} – 1·5400). As determined by GLPC, the product contained 97·5% of *cis* isomer and only traces of *trans* isomer (retention times relative to *o*-xylene: 1·75 for *cis* and 2·1, for *trans* isomer).

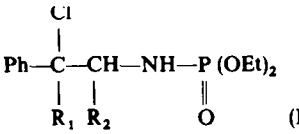
trans-β-Methylstyrene was prepared by dehydration of phenylethylcarbinol by means of $KHSO_4$, yield 56%, b.p. 76–77°/23 mm, n_D^{25} 1·5468 (Lit.[13]: b.p. 73·5°/20 mm, n_D^{25} – 1·5473). The material was contaminated (GLPC) with about 4% of *cis* isomer.

1,1-Di-(*p*-methoxyphenyl)ethylene was synthesized according to Pfeiffer and Wizinger,[14] yield 50%, m.p. 142·5–143·5° (from benzene-MeOH 5:1).

1,1-Di(*p*-methoxyphenyl)2-chloroethylene was obtained by chlorination of 1,1-di(*p*-methoxyphenyl-ethylene with sulphuryl chloride in CCl_4 soln at room temp,[6] yield 70%, m.p. 79–80°. (Lit.[6]: m.p. 78°). The IR spectrum (CCl_4) showed characteristic bands at: 1601s (C=C conjugated), 1241vs (Ph—O—C), and 831s (*p*-disubst. benzene) cm^{-1}.

Addition of DCPA to phenylethylenes

Method a. The olefin (0·05 mole) was added dropwise with stirring to the soln of DCPA (11·1 g, 0·05 mole) in benzene (25 ml) at 35–60°. After addition of about ⅓ of the olefin a spontaneous, strongly exothermic reaction started. The rest of the olefin was added at such a rate to maintain the mixture at the indicated temp (Table 1). Stirring was then continued at this temp for additional 1–2 hr. The resulting soln was colourless or pale-yellow. A 20% aqueous soln of sodium pyrosulphite (50 ml) was then added at 0–5° with efficient external cooling (ice-salt bath) and the organic layer was separated. The aqueous phase was extracted with ether (2 × 20 ml) and combined organic layers were then washed with 20% NaCl aq (2 × 20 ml), dried, and evaporated. The residue was purified by high-vacuum distillation or heated at 50–70°/0·01–0·05 mm for 1–2 hr to remove traces of solvent. Table 1 shows results and analyses.

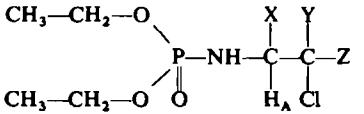


(B)

Unsaturated compd.	Addition product (B); R_1, R_2	Method (reaction) temp)	Yield %	B.p./mm[a] [m.p.]°C	n_D^{20}	Analyses, *Calcd* Found C%	H%	P%	N%	Characteristic IR absorption bands cm^{-1}
Ph—CH=CH_2	(I); $R_1 = R_2 = H$	a (~ 80°)	67	135–6°/0·01 (175–180)	1·5097	*49·4* 50·0	*6·6* 6·7	*10·6* 11·0	*4·8* 4·9	3220 w(NH), 1245s (P=O), 1170s (Et—O—(P)), 1064s, 1037s (P—O—(C))[d]
Ph—C(CH_3)=CH_2	(II); $R_1 = CH_3$, $R_2 = H$	a (55–60°)	77 (crude)	(90)/0·01[b]	1·5180	*51·1* 51·3	*6·9* 7·1	*10·1* 10·45	*4·6* 5·3	3425w, 3215w (NH), 1264s (P=O), 1170s (Et—O—(P)), 1061s, 1038s (P—O—(C))[d]
Ph—CH=CH—CH_3 (*cis*)	(IIIa)-*erythro* (87%) (IIIb)-*threo* (13%) $R_1 = H$, $R_2 = CH_3$	a (65–70°)	67 (crude)	—	—	*51·1* 51·2	*6·9* 6·85	*10·1* 10·0	*4·6* 4·9	3420w, 3205w(NH), 1240s, 1263s (P=O), 1152s (Et—O—(P)), 1062s, 1040s (P—O—(C))[d]
Ph—CH=CH—CH_3 (*trans*)	(IIIa)-*erythro*(82%) (IIIb)-*threo* (18%) $R_1 = H$, $R_2 = CH_3$	a (65–70°)	80 (crude)	—	—	*51·1* 50·7	*6·9* 6·6	*10·1* 10·0	*4·6* 4·6	3420w, 3205w(NH), 1240s, 1263s (P=O), 1152s (Et—O—(P)), 1062s, 1040 (P—O—(C))[d]
$(Ph)_2C$=CH_2	(IV); R_1 = Ph, $R_2 = H$	b (50–55°)	59[c]	[59–60] from light petroleum	—	*58·8* 58·4	*6·3* 6·5	*8·4* 8·6	*3·8* 3·9	3420w, 3075w NH, 1265s (P=O),1170 m (Et—O—(P)) 1065s, 1040s (P—O—(C))[e]
Ph—CH=CH—Ph *trans*	(V); $R_1 = R_2$ = Ph *erythro* + *threo* ~ 1:1	c (~ 80°)	33·5	[170–2] (crude)	—	*58·8* 58·8	*6·3* 6·2	*8·4* 8·6	*3·8* 3·8	3210m NH, 1220s (P=O) 1163m (Et—O—(P)), 1070s, 1036s (P—O—(C^b))[f]

[a] Bath temp given in parenthesis; [b] Evaporated in vacuo; [c] Unstable compound; [d] Liquid film; [e] CCl_4 soln; [f] Nujol mull; Abbreviations used: s, strong; m; medium; w, weak.

TABLE 2. NMR SPECTRAL ASSIGNMENTS OF DIETHYL N-(β-CHLOROALKYL)-PHOSPHOROAMIDATES



Compd No	X	Y	Z	Chemical shifts (J, c/s)						Remarks
				$\tau(CH_3)$	JCH_3–CH_2	$\tau(CH_2)$	JP—O–CH_2	$\tau(CH_A$[a]$)$	JP—NH–CH_A	
I	H_A	H_B	Ph	8·75t	7·0	6·03q	7·0	6·70 6·58 dd	10·4	$\tau(H_B)$ – 5·03t
II	H_A	CH_3	Ph	8·74t	7·4	6·05q	7·4	6·55d	7·8	τ (Y) – 8·02s
IIIa	CH_3	H_B	Ph	8·71t	7·0	5·62– – 6·65m	—	5·62– – 6·65m	—	τ (X) – 8·85d; $J(CH_A—CH_3)$ = 6·5 $\tau(H_B)$ – 4·89d; $J(CH_A—CH_B)$ = 4·5
IIIb	CH_3	H_B	Ph	8·71t	7·0	5·62– – 6·65m	—	5·62– – 6·65m	—	τ (X) – 8·85d; $J(CH_A—CH_3)$ = 6·5 $\tau(H_B)$ – 5·07; $J(CH_A—CH_B)$ = 5·5
IV	H_A	Ph	Ph	8·80t	7·0	6·15q	7·0	6·05d	5·8	τ (NH) – 6·6–7·15 bs
V	Ph	H_B	Ph	9·00t 8·80t [b]	7·0	5·80– – 6·70m	—	5·50 5·35 dd	9·5	$\tau(H_B)$ – 4·80d; $J(CH_A—CH_B)$ = 5·7

[a] NH proton was exchanged by deuterium on treatment with D_2O in $CDCl_3$ soln. As determined by integration, it overlapped with the CH_2 signal before deuteration and was not visible;

[b] Signals assigned to *threo* and *erythro* isomers.

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

TABLE 3. β-CHLOROAMINE HYDROCHLORIDES AND OTHER DEGRADATION PRODUCTS OF I–IV

Starting amide	Reaction conditions	Degradation product	Yield %	M.p. °C	Analyses: *Calcd.* / Found C%	H%	N%	P%	NMR assignments[a] (τ in ppm from DSS; *J* in c/s)
I	3hr room temp	Ph—CH(Cl)—CH_2—$\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	85	163–163·5 dec.[b] (from EtOH)	*50·0* 49·9	*5·7* 5·5	*7·3* 7·2	—	6·43d(CH_2); 4·71t(CH); 2·54bm(H aromat.); *J*(CH—CH_2) = 7·4
II	2hr, room temp	Ph—$C(CH_3)$(Cl)—CH_2—$\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	59	130–132 dec (from EtOH)	*52·4* 52·9	*6·45* 6·4	*6·9* 6·9	—	7·89s(CH_3); 6·23s(CH_2); 2·12–2·82 m (H aromat.)
IIIa + IIIb	5hr, 80°	Ph—CH(Cl)$CH(CH_3)\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$ *76% erythro + 24% threo*	48	158–175 dec. (crude)	*52·4* 52·6	*6·45* 6·2	*6·9* 7·15	—	8·51d(CH_3); 6·12–6·57m (*CH*—CH_3); *J*(CH—CH_3) = 7·0; threo-isomer: 4·69d (*CH* − Cl); *J*(CH − CH) = 9·6 erythro-isomer: 4·41d(*CH*—Cl); *J*(CH − CH) = 4·6
IV	2hr, room temp	$(Ph)_2C$=CH—NH—P(O)$(OEt)_2$ XV	48·5	76·5–78·5 (from benzene-light petroleum 1:3)	*65·25* 65·3	*7·0* 6·9	*4·2* 4·3	*9·3* 9·3	8·66t(CH_3); 5·88q(CH_2); 3·29, 3·40dd (= CH); 5·01t(NH); *J*(CH_3CH_2; H) = 7·0; *J*(P—O—CH_2) = 7·3; *J*(P—NH—CH) = 6·5; *J*(CH—NH) ≈ *J*(P—NH) = 12·5

[a] NMR spectra were run in D_2O for β-chloroamine hydrochlorides and in $CDCl_3$ soln (with TMS as internal reference) for the compound (XV); [b] Lit.[5]: M.p. 162–164° dec.; Abbreviations: s. singlet; d, doublet; t, triplet; m, multiplet: dd, double doublet.

Methoa b. DCPA (11·1 g, 0·05 mole) was added dropwise with stirring to the soln of olefin (0·05 mole) in benzene (25 ml) heated to 30–40°. The addition was carried out at such a rate to keep the temp of the exothermic reaction at 50–55°. Stirring was continued for a further 15–30 min and the product was worked-up as described immediately above for the method (a).

Method c. The mixture of olefin (0·025 mole), DCPA (5·55 g, 0·025 mole), and benzene (25 ml) was refluxed for 4 hr. The product was worked-up as described previously.

Reaction of DCPA with 1,1-di(*p*-methoxyphenyl)ethylene.

. The method (b) was applied, but heating at 50–55° was prolonged to 2 hr. Usual work-up of the mixture followed by evaporation of the solvent yielded an oil, which crystallized on standing. Colourless plates (63%), m.p. 80–80·5° obtained on recrystallization from MeOH, were identified as VI. (Found: C, 69·4; H, 6·0; $C_{16}H_{15}O_2Cl$ requires: C, 69·8; H, 5·5%). The product was identical (IR, m.m.p.) with an authentic specimen of this compound.

Reactions of DCPA with styrene in presence of free-radical inhibitors

The mixture of DCPA (5·55 g, 0·025 mole), styrene (2·6 g, 0·025 mole), and hydroquinone (0·0025 mole) or t-butylcatechol (0·0025 mole) was refluxed for 1 hr in benzene (50 ml). The product was worked-up in the usual way. The yield of crude adduct (I) was found to be 72·5% in presence of hydroquinone, and 68·5%, when t-butylcatechol was used as inhibitor. Blank experiment carried out under the same conditions but without an inhibitor afforded the crude adduct (I) in 97% yield.

Degradation of diethyl N(β-chloroalkyl)phosphoroamidates (I–V) by means of hydrogen chloride

Dry, gaseous HCl was passed through the conc. (ca. 25%) benzene soln of diethyl N(β-chloroalkyl)-phosphoroamidate. The temps and reaction times are indicated in Table 3. The soln saturated with HCl was left overnight at room temp. The excess of HCl was then removed *in vacuo*. The crystalline ppt was filtered off, washed with benzene, and crystallized from a suitable solvent. Table 3 presents the results, elemental analyses, and NMR spectral data of the degradation products. *trans*-Stilbene-DCPA adduct (V) was found to be unreactive towards gaseous HCl even in refluxing benzene.

Solvolysis of α-chloro-β-phenylethylamine hydrochloride

α-Chloro-β-phenylethylamine hydrochloride (1·0 g, 0·005 mole) was dissolved in water (10 ml) and left at room temp for 3 days. Evaporation of water left a theoretical amount of colourless, crystalline residue, m.p. 147–148°, identified as pure α-hydroxy-β-phenylethylamine hydrochloride. (Found: C, 57·4; H, 7·6; N, 7·7; $C_9H_{14}NOCl$ requires: C, 57·6; H, 7·5; N, 7·5%). The IR spectrum (KBr disc) showed characteristic bands at: 3300s (OH), 2850s (NH_3^+), 1560 (NH_3^+ as. def.) cm^{-1}. The NMR spectrum (in D_2O with DSS as internal reference) showed signals at: 8·31 τ (s, CH_3), 6·62 τ (s, CH_2), 5·28 τ (s, NH_3^+, OH?), 2·68 τ – 2·25 τ (m, arom. protons).

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