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N,N-DIHALOPHOSPHORAMIDES—X†

THE ADDITION OF DIETHYL N,N-DICHLOROPHOSPHOROAMIDATE (DCPA) TO α-OLEFINS AND α,β-UNSATURATED ESTERS

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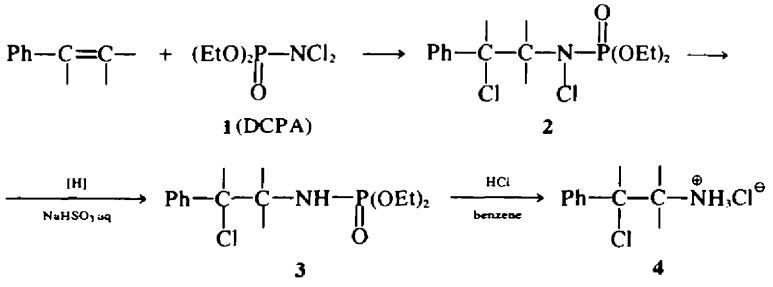
Abstract—The addition of DCPA to several α-olefins and α,β-unsaturated esters has been studied. The reaction was found to proceed in boiling benzene and was evidently accelerated by UV irradiation. N-Chloro adducts, formed in reasonable yields, afforded the corresponding diethyl N-(β-chloroalkyl) phosphoroamidates upon reduction with sodium bisulphite solution. β-Chloroamine hydrochlorides or α-chloro-β-aminoacid ester hydrochlorides could be produced from the latter compounds by P–N bond cleavage with hydrogen chloride in benzene. The full regioselectivity for anti-Markovnikov addition, as proven by NMR evidence, is in accord with the photolytically initiated radical-chain mechanism proposed for the reaction. This reaction offers an easy, two-step approach to aminochlorination of a double bond in α-olefins and α,β-unsaturated esters.

Modern synthetic chemistry offers a variety of methods for introducing oxygen functions into organic molecules. The available repertory is, however, much more limited when the introduction of nitrogen functions is required, in particular for regio- and stereospecific bifunctionalization. The use of nitrogen radicals as synthetic intermediates,[1] extensively studied in recent years, provides a ready access to the variety of nitrogen-containing bifunctional structures.

Some years ago we have described[2] a simple aminochlorination of phenylethylenes by means of free-radical anti-Markovnikov addition of diethyl N,N-dichlorophosphoroamidate (DCPA) to a double bond, followed by reduction and subsequent degradation of the corresponding N-chloro adducts (eqn 1). DCPA seems to present paper their simple and effective preparation from α-olefins and α,β-unsaturated esters.

Addition of DCPA to α-olefins. The addition of DCPA to a variety of straight- and branched-chain terminal olefins, viz. ethylene, isobutylene, 1-hexene, 1-octene and 3,3-dimethyl-1-butene has been examined. In contrast to phenylethylenes all the above mentioned olefins added DCPA much more slowly and the phenomenon of spontaneous initiation was never observed. All reactions were carried out in refluxing benzene and had to be initiated and/or accelerated by UV irradiation. Depending on the olefin used the reaction was usually complete within 3–5 hr and this could be recognized by the disappearance or paling of greenish-yellow DCPA colour. All reactions following according to the eqn (2), in an anti-Markovnikov fashion

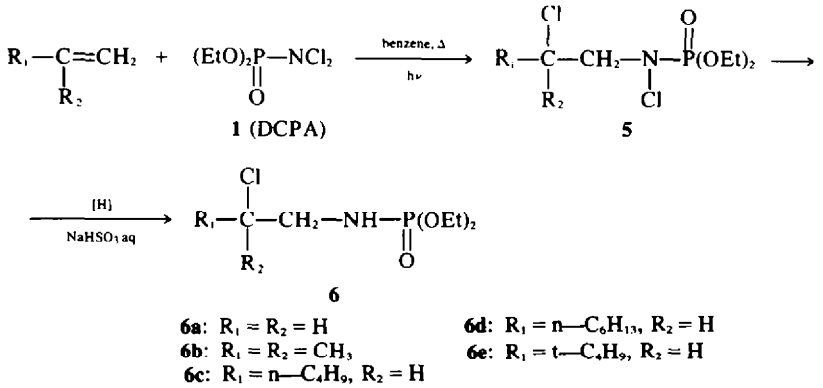


(1)

be a reagent of choice for such functionalization of a double bond because a phosphoryl group, in contrast to acyl or sulphonyl moiety, can be readily removed from nitrogen under very mild anhydrous conditions.[3] β-Chloroamine hydrochlorides thus obtained have been recently found useful[4] as starting materials for the preparation of 2-oxazolidones, an important class of heterocyclic compounds which has attracted considerable attention.[5,6] Having in mind the possible synthetic utility of β-chloroamine hydrochlorides, we wish to report in the (see proof of structure below), were regiospecific and afforded diethyl N-chloro-N-(β-chloroalkyl) phosphoroamidates **5**.

Upon treatment with 20% aqueous sodium bisulphite at 0–5° the preliminary formed N-chloro adducts **5** were reduced to diethyl N-(β-chloroalkyl) phosphoroamidates **6a–e**. All crude compounds **6b–e** were purified by distillation *in vacuo* to give analytically pure samples. Physical constants, yields, and elemental analysis data of the phosphoroamidates **6b–e** are listed in Table 1. The addition of DCPA to ethylene in boiling benzene proceeded extremely sluggishly. Only minute amounts of diethyl N-β-chloroethyl phosphoroamidate **6a** (identified by compari-

†Part IX: A. Zwierzak and J. Brylikowska, *Synthesis* 712 (1975).



(2)

6a: $R_1 = R_2 = H$ **6d**: $R_1 = n\text{—}C_6H_{13}$, $R_2 = H$
6b: $R_1 = R_2 = CH_3$ **6e**: $R_1 = t\text{—}C_4H_9$, $R_2 = H$
6c: $R_1 = n\text{—}C_4H_9$, $R_2 = H$

Table 1. Diethyl N-(β-chloroalkyl)phosphoroamidates and N-phosphorylated α-chloro-β-aminoacid esters

Compound No.	Yield %	B.p./mm[a]	n_D^{20}	Analyses % Required C	H	N	P	Found C	H	N	P
6 b	61	76–78/0.05 /110–115/	1.4473	39.4	7.9	5.75	12.7	39.4	7.9	6.1	12.8
6 c	55	110–112/0.05 /145–150/	1.4552	-	-	5.15	11.4	-	-	5.3	11.2
6 d	57	114–115/0.01 /145–150/	1.4634	48.1	9.1	4.7	10.3	47.7	9.3	4.9	10.2
6 e	66	128–130/0.1 /190–200/	1.4680	44.3	8.4	5.15	11.4	44.05	8.15	5.6	11.4
8 a	45[b]	111–112/0.05 /145–150/	1.4536	37.5	6.65	4.9	10.8	37.7	6.8	5.1	11.05
8 b	61	110–112/0.07 /150–155/	1.4559	37.5	6.65	4.9	10.8	37.4	7.2	5.3	10.6
8 c	53	112–115/0.1 /160–170/	1.4550	37.5	6.65	4.9	10.8	37.6	6.4	4.8	10.9

[a] Bath temp given in parenthesis

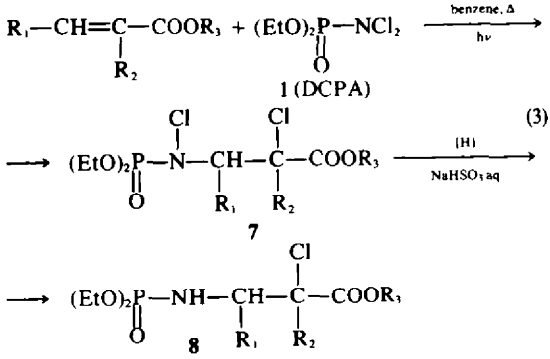
[b] Crude product obtained in 85% yield decomposed partially during distillation .

son with authentic sample of this compound) were detected (TLC) in the reaction mixture after its work-up with sodium bisulphite solution. Other adducts were formed in reasonable yields (Table 1) albeit some of them were contaminated in crude state with considerable amounts of side-products arising from allylic monochlorination.

Addition of DCPA to α,β-unsaturated esters. It was found that DCPA reacts with typical vinyl monomers, such as ethyl acrylate, methyl methacrylate and methyl crotonate, at a rate comparable to that of α-olefins. This result is consistent with the generally accepted conclusion that radical reactions are less sensitive to polar effects than are ionic reactions. All additions were carried out with uninhibited monomers by refluxing stoichiometric amounts of both reactants in benzene within 3–5 hr with continuous irradiation (UV) of the mixture. Vinyl polymerization was not observed in any of the addition reactions. The formation of N-phosphorylated α-chloro-β-aminoacid esters **8a–c** upon reduction of the primarily formed N-chloro adducts 7 (eqn 3) has been unequivocally established in all cases.

Regiospecificity of the addition and the relevant structure of adducts is evident from careful inspection of their NMR spectra (see below and Table 2). Yields, physical properties and elemental analysis data of the phosphoramidates **8a–c** are summarized in Table 1.

Proof of structure of DCPA addition products. All products resulting from addition of DCPA to α-olefins or



(3)

8a: $R_1 = R_2 = H$, $R_3 = Et$ **8c**: $R_1 = R_3 = Me$, $R_2 = H$
8b: $R_1 = H$, $R_2 = R_3 = Me$

α,β-unsaturated esters followed by reduction (**6b–e**, **8a–c**) were satisfactorily analysed for C, H, N and P. Their IR spectra (Table 2) showed characteristic NH bands in the region of 3130–3210 cm^{-1}, P=O bands at 1225–1242 cm^{-1}, and P–O–Et bands within the range 1025–1033 cm^{-1}. The final structural assignments, namely the exact location of the Cl atom and the amidophosphoryl moiety, could be deduced from detailed examination of their NMR spectra. Analysis of the chemical shifts and multiplicity of the relevant protons, particularly methylene protons adjacent to N atom, provided unambiguous arguments in support of the proposed structures. All spectra were examined after

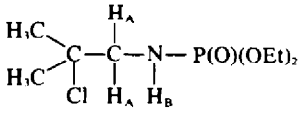
Table 2. Characteristic IR absorption maxima and NMR spectral assignments of diethyl Na(β-chloroalkyl)phosphoramidates and N-phosphorylated α-chloro-β-aminoacids esters

Compound No	Characteristic IR absorption maxima (film)[a] (cm^{-1})	NMR assignments[b] (δ in ppm from TMS; J in Hz)
6b	3160m (N-H), 1230s (P=O), 1027s (P-O-(C))	δ = 1.33 (t, 6H, J_{H-H} = 7.0, CH_3-CH_2-O), δ = 1.6(s, 6H,$(CH_3)_2$C-), δ = 3.11 (d, 2H, $^3J_{P-H}$ = 8.6, -CH_2-N-P); δ = 4.09(qt, 4H, $J_{H-H} \approx {}^3J_{P-H}$ = 7.0, CH_3-CH_2-O).
6c	3164m (N-H), 1227s (P=O), 1176m (Et-O-(P)), 1032s (P-O-(C)).	Part of A_3B_2 system: δ = 0.92(m, 3H, CH_3-CH_2-), δ = 1.18-2.5(m, 6H, $CH_3(CH_2)_3$-), δ = 1.34(t, 6H, J_{H-H} = 7.0, CH_3- CH_2-O), δ = 2.82-3.43 (m,1H,-CH-Cl), δ = 4.05(qt, 6H, $J_{H-H} \approx {}^3J_{P-H}$ = 7.0, CH_3-CH_2-O overlapping with CH_2-NH-).
6d	3130m (N-H), 1227s (P=O), 1032s (P-O-(C))	Part of A_3B_2 system: δ = 0.89(m, 3H, CH_3-CH_2), δ = 1.08-2.4(m, 10H, $CH_3(CH_2)_5$-), δ = 1.33(t, 3H, J_{H-H} = 7.0, CH_3-CH_2-O), δ = 2.86-3.7(m, 3H, CH_2-CH-Cl), δ = 4.07(qt, 4H, $J_{H-H} \approx {}^3J_{P-H}$ = 7.0, CH_3-CH_2-O-).
6e	3210m (N-H), 1386m and 1655m ($(CH_3)_3$C), 1242s (P=O), 1165m, (Et-O-(P)), 1033s(P-O-(C))	δ = 1.05(s, 9H, $(CH_3)_3$C), δ = 1.32(t, 6H, J_{H-H} = 7.0, CH_3-CH_2-O) δ = 2.56-3.89(m, 3H, CH_2-CH-Cl) δ = 4.08(qt, 4H, $^3J_{P-H} \approx J_{H-H}$ = 7.0, CH_3-CH_2-O-).
8a	3130m (N-H), 1735s(C=O), 1233s (P=O), 1176m (Et-O-(P)), 1025s (P-O-(C)).	δ = 1.35(t, 9H, J_{H-H} = 7.0, CH_3-CH_2-O), 18 partially overlapping lines: δ = 3.18-4.68(12 lines of ABX system, CH_2-CH-Cl), δ = 4.11(qt, $J_{H-H} \approx {}^3J_{P-H}$ = 7.0, CH_3-CH_2-O-P), δ = 4.26(q, J_{H-H} = 7.0, CH_3-CH_2-O-C).
8b	3180m (N-H), 1740s (C=O), 1235s (P=O), 1165m (Et-O-(P)), 1033s (P-O-(C)).	δ = 1.32(t, 6H, J_{H-H} = 7.0, CH_3-CH_2-O-P), δ = 1.78 (s,3H,CH_3-C-Cl), δ = 3.41(d, 2H, $^3J_{P-H}$ = 9.0,CH_2-N-P), δ = 3.8 (s,3H, CH_3-O), δ = 4.06 (qt, 4H, $J_{H-H} \approx {}^3J_{P-H}$ = 7.0, CH_3-CH_2-O-P)
8c	3165m (N-H), 1741s(C=O), 1225s(P=O), 1160m(Et-O-(P)), 1030s (P-O-(C))	δ = 1.31(br.t., 9H, J_{H-H} = 7.0, CH_3-CH_2-O-P and CH_3-CH), δ = 3.7-4.6(m, overlapping with s(δ = 3.77, CH_3-O-) and qt(δ = 4.02, $J_{H-H} \approx {}^3J_{P-H}$ = 7.0, CH_3-CH_2-O-P)).

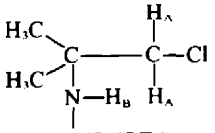
[a] Only characteristic absorption bands are included.

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

deuteration of the amide protons (H_B) which usually give broad signals overlapping with those of the CH_2–O–P groupings and make the complete analysis of the essential part of the spectra difficult or virtually impossible. It is demonstrated below how careful analysis of the multiplicity of relevant methylene signals was used for definite structure establishments. This is exemplified for DCPA-isobutylene adduct and DCPA-methyl methacrylate adduct. In the first case one can consider the structure of anti-Markovnikov adduct **6b** or its regioisomer **6b'**.



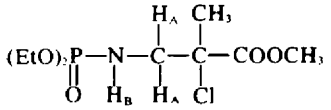
6b



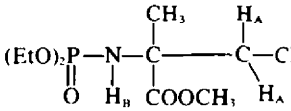
6b'

The NMR evidence is in accord only with the structure **6b**. In the NMR spectrum of DCPA-isobutylene adduct the methylene H_A protons appear as a broadened doublet centered at 3.11 ppm. This signal, assigned to the magnetically equivalent H_A protons, is split by P atom ($^3J_{PH}$ = 8.6 Hz). If the Cl atom and amido moiety were reversed (formula **6b'**) such a pattern would not be obtained and H_A protons would display a singlet with no further splitting by P atom. The remainder of the NMR shows a triplet at 1.33 ppm (6 H), a sharp singlet at 1.60 ppm (6 H), and a symmetrical quintet centered at 4.09 ppm with $J_{HH} = {}^3J_{PH}$ = 7.0 Hz, all the signals being however of no diagnostic value with respect to possible differentiation between **6b** and **6b'**.

Two isomeric structures **8b** and **8b'** could be proposed for DCPA-methyl methacrylate adduct, only the former being however consistent with the NMR spectrum of the reaction product.



8b

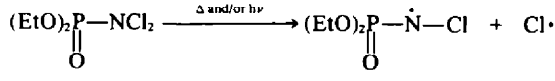


8b'

Detailed examination of this spectrum revealed the presence of characteristic doublet centered at 3.41 ppm assigned to H_A methylene protons. The observed splitting pattern is consistent with magnetic equivalency of H_A protons, the signal being resolved ($^3J_{PH}$ = 9.0 Hz) owing to long-range interaction with P atom. The NMR spectrum of possible regioisomer **8b'** would show an AB splitting pattern for magnetically nonequivalent H_A protons or a singlet, if these protons were magnetically equivalent. An upfield triplet centered at 1.32 ppm (6 H), an upfield singlet at 1.78 ppm (3 H), a downfield singlet at 3.80 ppm (3 H), and a downfield quintet centered at 4.06 ppm (4 H) belong to the remaining protons. These signals are, however, of no use for unambiguous structure elucidation.

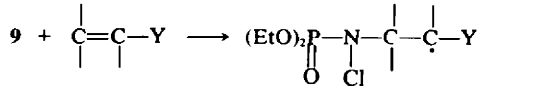
Mechanism of addition of DCPA to α-olefins and α,β-unsaturated esters. All reactions of DCPA with α-olefins and α,β-unsaturated esters exhibit several characteristic features of free-radical chain processes: (i) they afford anti-Markovnikov adducts exclusively; (ii) thermal or photolytical initiation is required; (iii) the reaction rates are evidently increased by UV irradiation and markedly diminished in the presence of typical free-radical scavengers like hydroquinone; (iv) allylic chlorination was observed with unsaturated compounds containing α-H atoms. All the above mentioned observations are fully consistent with the thermally or photolytically initiated free-radical chain reaction pathway depicted in Scheme 1.

Initiation:



1 (DCPA) **9**

Propagation:



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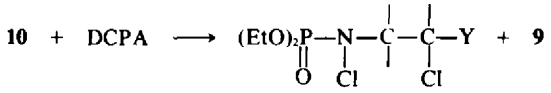
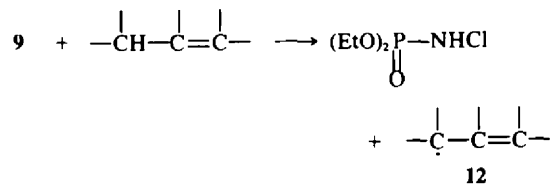


11

Y = alkyl or COOR (R = Me, Et)

Side reactions (allylic chlorination):



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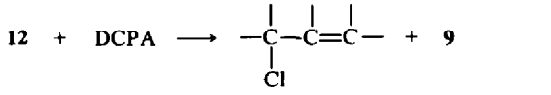

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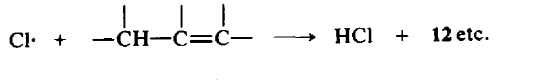
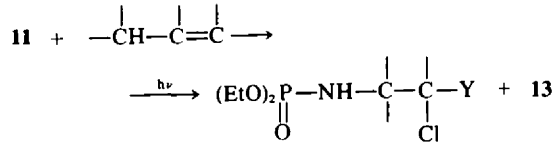




Scheme 1.

The propagation step to form adduct **11** is probably much faster than the vinyl polymerization propagation step because no polymerization was found to take place during addition. The concurrent allylic chlorination can be presumably initiated by amido radicals **9**, Cl atoms or N-chloro adducts **11**, the homolytic N–Cl bond rupture being primarily involved in the latter case. The complete selectivity for anti-Markovnikov addition observed for α-olefins and α,β-unsaturated esters is evidently the consequence of enhanced stability of the radical adduct 10 due to its additional stabilization by alkyl or carboalkoxyl substituent Y.

Table 3. β-Chloroamine and α-chloro-β-aminoacid ester hydrochlorides[a]

Compound No	Yield %	M.p. °C	Characteristic IR absorption maxima /kBr/ cm^{-1} [b]	NMR assignments /D_2O/ (δ in ppm from DSS, J in Hz)
14a	69.5	183 [c]	-	δ = 1.68 (s, 6H, CH_3), δ = 3.3 (s, 2H, CH_2), δ = 4.62 (s, NH_3^+)
14b	68	150-1	2850 s and 1587m (NH_3^+)	-
14c	67	157-8	2853 s and 1580m (NH_3^+)	-
14d	81.5	197-8	-	δ = 0.98(s, 9H, CH_3), ABX system (12 lines, 3H, δ_A = 2.53, δ_B = 2.18, δ_X = 3.05, J_{AX} = 2.3, J_{BX} = 12.3, J_{AB} = 14.1, $C\underline{H}_2$-$C\underline{H}$-Cl) δ = 4.64 (s, NH_3^+)
14e	82.0	121-2[d]	-	δ = 1.32(t,3H, J_{H-H} = 7.0, $C\underline{H}_3$-CH_2O), $C\underline{H}_3$-CH_2O), δ = 4.34(q, 2H, J_{H-H} = 7.0, CH_3-$C\underline{H}_2O$), ABX system/12 lines, 3H, δ_A = 3.75, δ_B = 3.59, δ_X = 4.98, J_{AX} = 3.75, J_{BX} = 8.25, J_{AB} = 14.4, $C\underline{H}_2$-$C\underline{H}$-Cl), δ = 4.64(s, NH_3^+)
14f	53	155-6	2860s and 1573 (NH_3^+), 1732s(C=O)	δ = 1.85(s,3H, $C\underline{H}_3$-C-Cl), AB system(4 lines, 2H, δ_A =3.70, δ_B = 3.48, J_{AB} = 14.0, $C\underline{H}_2$-C-Cl), δ = 3.87(s, 3H, $C\underline{H}_3$-O), δ = 4.6(s, NH_3^+)

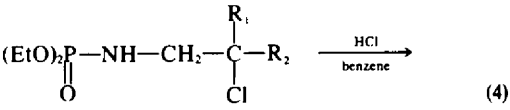
[a] The elemental analyses (C,H,N,P) of all compounds were in good accordance with the calculated values.

[b] Only some characteristic bands are included.

[c] Lit.[8] gives m.p. 183°.

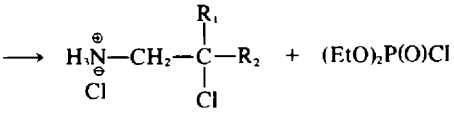
[d] Lit.[9] gives m.p. 120-121°.

Degradation of DCPA addition products. According to our expectations the majority of DCPA adducts (**6b–e**, **8a–b**) could be easily transformed into the corresponding β-chloroamine hydrochlorides **14** by means of gaseous hydrogen chloride in benzene (eqn 4). Degradation involving the P–N bond cleavage was readily accomplished by saturating the solution of the corresponding phosphoroamidate with hydrogen chloride and leaving it for 12 hr at room temperature. Methyl crotonate-DCPA adduct **8c** was not degraded under these conditions.



(4)

6(8)



14

14a: $R_1 = R_2 = CH_3$
14b: $R_1 = H$, $R_2 = n\text{—}C_4H_9$
14c: $R_1 = H$, $R_2 = n\text{—}C_6H_{13}$
14d: $R_1 = H$, $R_2 = t\text{—}C_4H_9$
14e: $R_1 = H$, $R_2 = COOC_2H_5$
14f: $R_1 = CH_3$, $R_2 = COOCH_3$

β-Chloroamine hydrochlorides **14** were formed in good yields (50–70%) and could be easily isolated in pure form. Their yields, melting points and spectral data are summarized in Table 3.

EXPERIMENTAL

Solvents and reagents were purified by conventional methods. All solns were dried over $MgSO_4$ and evaporated under reduced press. M.ps (taken in capillaries) are uncorrected. NMR spectra were measured at 60 MHz with a Jeol JNM-C-60 HL spectrometer in CCl_4 or D_2O solns using TMS or DSS as internal standard respectively. IR spectra were recorded using Infracord 137 (Perkin–Elmer) or UR-10 (C. Zeiss) spectrophotometers. Measurements were made on samples of analytical purity. TLC was performed on standard glass plates covered with 0.25 mm of Kieselgel G (E. Merck). Solvent system benzene–acetone–$CHCl_3$ (20:10:3) was employed. Chromatograms were developed by spraying them with 5% $AgNO_3$ aq followed by 2% ethanolic bromothymol blue soln.

Diethyl N,N-dichlorophosphoroamidate (DCPA, 1) was prepared as described previously[7] by chlorination of diethyl phosphoroamidate in an aqueous buffered soln.

Diethyl N(β-chloroethyl) phosphoroamidate **6a**. A mixture of diethyl phosphorochloridate (34.5 g, 0.2 mole) and triethylamine (40.4 g, 0.4 mole) was added dropwise with stirring at 0° to the suspension of β-chloroethylamine hydrochloride (23.2 g, 0.2 mole) in $CHCl_3$ (200 ml). Stirring was then continued at 0° for 1 hr. Triethylamine hydrochloride was filtered off and washed with benzene. The filtrate was evaporated and the residue distilled *in vacuo* to give **6a** as an oil, b.p. 93–94° (0.05 mm) bath temp. 140–145° (n_D^{20} 1.4468, yield ~35 g (81%); IR (film): 3162 cm^{-1} (NH), 1223 cm^{-1} (P=O), 1176 cm^{-1} [Et–O–(P)] and 1029 cm^{-1} [P–O–(C)]; (Found: C, 33.5; H, 7.0; P, 14.2; N, 7.05. $C_6H_{15}ClNO_3P$ requires: C, 33.4; H, 7.1; P, 14.4; N, 6.5%).

Addition of DCPA **1** *to α-olefins and α,β-unsaturated esters*

General procedure. A soln of an appropriate α-olefin or α,β-unsaturated ester (0.05 mole) and DCPA (11.1 g, 0.05 mole) in benzene (25 ml) was placed in a quartz flask and refluxed gently for 3–5 hr until fading or disappearance of a greenish-yellow colouration of the mixture. The flask was continuously irradiated by a UV lamp. In the case of isobutylene a slow stream of gaseous olefin was bubbled into the refluxing soln of DCPA (0.05 mole) in benzene (25 ml) for 4 hr. The mixture was then cooled to 0–5° and 20% $NaHSO_3$ aq (50 ml) was added dropwise at this temp. The organic layer was separated and the aqueous phase was extracted with ether (2 × 20 ml). Combined organic layers were then washed with 20% NaCl aq (2 × 20 ml), dried, and evaporated. The residual crude adducts were purified by high-vacuum distillation. Their yields and physical properties are given in Table 1.

Attempted addition of DCPA **1** *to ethylene.* Ethylene was bubbled into the refluxing soln of DCPA (11.1 g, 0.05 mole) in benzene (25 ml) placed in a quartz flask and irradiated by an UV lamp. The reaction was carried out for 8 hr. After standard work-up of the reaction mixture (see exp. described above) and removal of solvent an oil was obtained. TLC of this material revealed the presence of diethyl phosphoroamidate ($R_f = 0.19$) contaminated with minor amounts of the adduct **6a**-diethyl N-(β-chloroethyl) phosphoroamidate ($R_f = 0.36$).

Degradation of DCPA adducts by means of hydrogen chloride. Dry, gaseous HCl was bubbled into the soln of the appropriate DCPA adduct (**6b–e**, **8a–c**, 0.02 mole) in benzene (20 ml). The reaction was carried out at room temp for 2 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 (10–30 ml) was added to the residue. The crystalline ppt was filtered off, washed with ether and crystallized from a suitable solvent. Table 3 lists the yields, m.ps and spectral characteristics of β-chloroamine hydrochlorides 14 thus obtained.

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