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N,N-DIHALOPHOSPHORAMIDES—XV†

THE ADDITION OF DIETHYL N,N-DICHLOROPHOSPHOROAMIDATE (DCPA) TO CONJUGATED 1,3-DIENES

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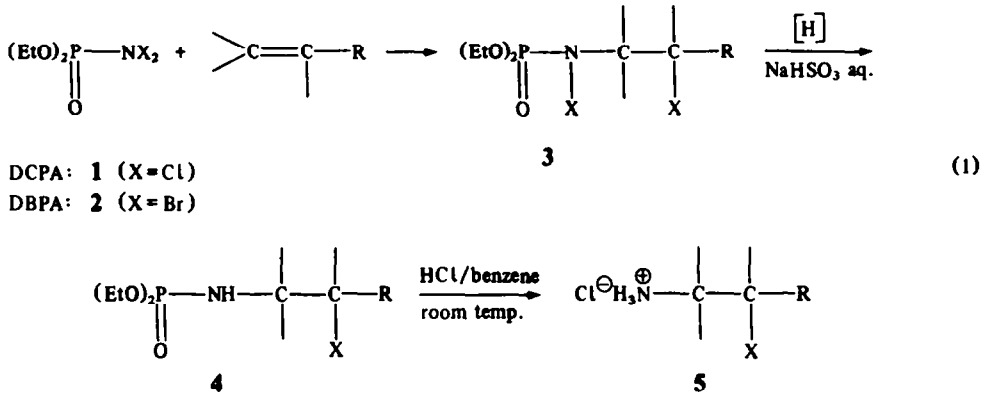
Abstract—The addition of DCPA to several conjugated 1,3-dienes has been studied. The reaction was found to proceed in dichloromethane and was spontaneously or photolytically initiated depending on the structure of the dienes. N-chloro adducts, formed upon addition, could be reduced "*in situ*" with sodium sulphite solution to give the corresponding diethyl N-(chloroalkenyl)posphoroamidates. Addition of DCPA to terminal double bond 1,3-dienes (butadiene, isoprene and 2,3-dimethyl-1,3-butadiene) leads regiospecifically to (*E*)-1,4-adducts. Similarly, 1,4-addition is also observed for 1,3-cyclohexadiene. Reaction of DCPA with nonterminal double bond 1,3-dienes (*trans*-piperylene, 4-methyl-1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene and 1,4-diphenyl-1,3-butadiene) usually affords a mixture of adducts. Spectral data and chemical transformations pertinent to the proof of structure of DCPA addition products are presented. A possible mechanism for the addition is discussed.

Some years ago we described a simple two-step aminohalogenation of olefins by means of free-radical anti-Markovnikov addition of diethyl N,N-dichlorophosphoroamidate (DCPA, **1**)[1] or N,N-dibromophosphoroamidate (DBPA, **2**)[2] to a double bond, followed by reduction and subsequent degradation of the corresponding N-halogeno adducts (**3**) with gaseous hydrogen chloride to the β-haloamine hydrochlorides (**5**) (Eq. 1). DCPA and DBPA seem to be reagents of choice for such functionalization of a double bond because the diethoxyphosphoryl group, in contrast to the acyl or sulphonyl moiety, can be readily removed from nitrogen under very mild anhydrous conditions.[3]



It is known that free-radical addition of thiols,[4a–c] sulphonyl chlorides[5] and some pseudo-halogens[6] to conjugated 1,3-dienes occurs in a regiospecific or highly regioselective manner affording 1,4-adducts as main or sole products. In the light of these and our preliminary findings[7] on regiospecific addition of DCPA (**1**) to some conjugated 1,3-dienes it seemed interesting to establish a correlation between the structure of the diene and the direction of addition (1,2- *vs* 1,4-addition).

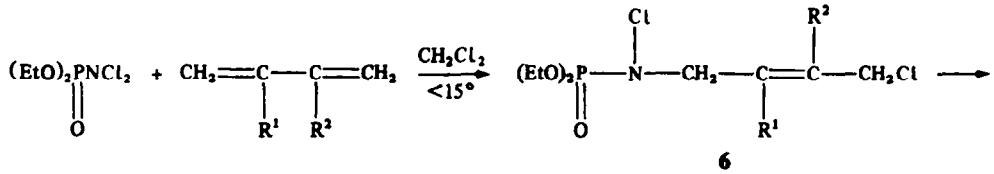
In the present paper we wish to report the results of the investigation on this subject.

Addition of DCPA (**1**) *to terminal double bond* 1,3-*dienes.* The addition of DCPA (**1**) to butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene has been examined. All reactions were carried out by dropwise addition of DCPA to a cooled (0–15°) solution of the diene in dichloromethane. After a short induction period the reaction was strongly exothermic and complete within 30 minutes. Progress of the addition could be easily followed by disappearance of the greenish-yellow DCPA colour. All reactions following the same general course outlined below (Eq. 2) were regiospecific and afforded diethyl N - chloro - N - (4 - chloroalkene - 2 - yl)phosphoroamidates (**6**).

Upon treatment with 10% aqueous sodium sulphite[8] at 0–10° the initially formed unstable N-chloro adducts (**6**) were reduced to (*E*)-diethyl N - (4 - chloroalkene - 2-yl)phosphoroamidates (**7a–c**). All crude compounds (**7a–c**) formed in high yields were analytically pure. Their physical constants, yields and elemental analysis are listed in Table 1.

The regioisomeric purity of the adducts (**7a–c**) was evident from ^{31}P-NMR spectra examination. Structure of the adducts, could be deduced from careful inspection of the ^{1}H-NMR spectra (Table 2).

† Part XIV: S. Zawadzki and A. Zwierzak, *Tetrahedron* **37**, 2675 (1981).



DCPA, 1

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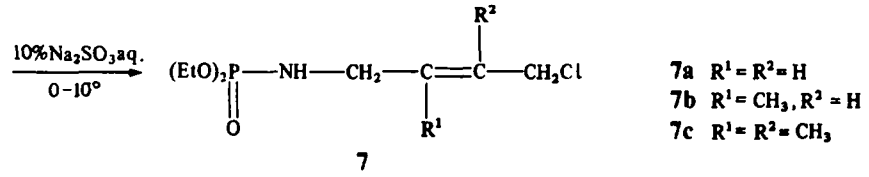

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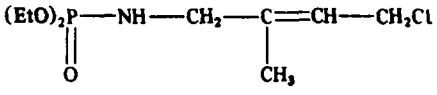
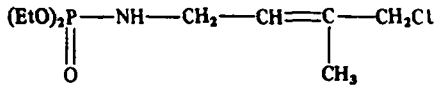
Multiplicity of the methylene protons adjacent to N atom and the protons next to Cl atom was of particular diagnostic value for definite structural assignments. All these data were fully consistent only with the structures of 1,4-*adducts*. This can be exemplified for DCPA-isoprene adduct for which one can consider four regioisomeric structures (**7b**, **8**–**10**) resulting from 1,2-*vs* 1,4-addition and 4,1- *vs* 4,3-addition. In the ^{1}H-NMR spectrum of DCPA-isoprene adduct, the signal of the methylene group next to nitrogen appears as a two hydrogen broad double doublet centered at 3.34 ppm. This pattern is consistent only with the structure **7b** resulting from 1,4-addition.



7b



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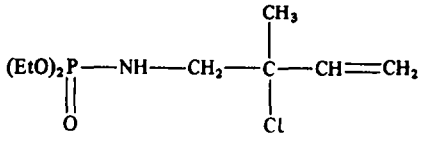

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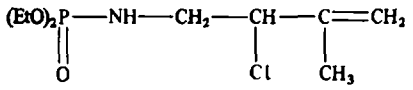

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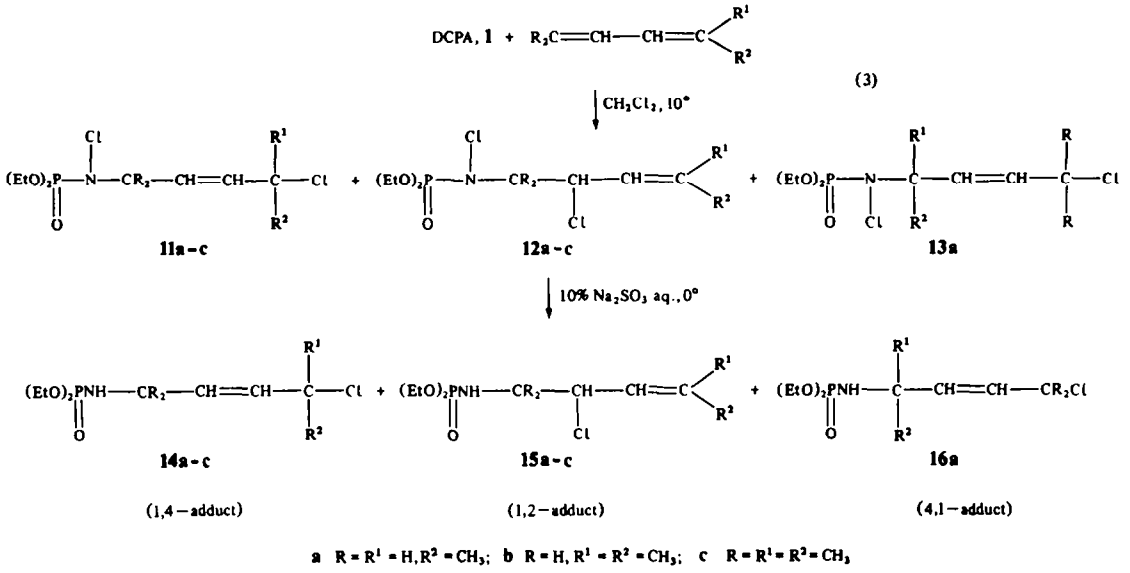
If the Cl atom and amidophosphoryl moiety were reversed (formula **8**, 4,1-adduct) such splitting would not be observed. The structures **9** (1,2-adduct) and **10** (4,3-adduct) were excluded on the basis of the lack of characteristic vinylic (—CH=CH_2) and methylene (=CH_2) signals at 5.0–6.0 ppm. (*E*)-Configuration of the double bond in the adducts (**7a–c**) was established by chemical transformations of well documented stereochemical course and subsequent X-ray analysis of the final pyrrolidine derivatives.[9]

Addition of DCPA to the nonterminal double bond of 1,3-dienes. DCPA (**1**) was found to react with *trans*-piperylene, 2,5-dimethyl-2,4-hexadiene and 4-methyl-1,3-pentadiene at a rate comparable to that of terminal double bond 1,3-dienes. All reactions were carried out under the conditions described previously and occurred after a short induction period. Addition of

Table 1. Diethyl N-(chloroalkenyl)phosphoroamidates (**7–19**)

Compound No.	Conditions (solvent temp)	Yield %	n_D^{20} or M.p. (°)	Analyses % Required C	H	N	P	Found C	H	N	P
7a	CH_2Cl_2, 15°	93	1.4697	39.8	7.1	5.8	12.8	39.8	7.6	5.9	12.5
7b	CH_2Cl_2 15°	87	1.4752	42.3	7.5	5.5	12.1	42.3	7.5	5.5	12.0
7c	CH_2Cl_2, 15°	89	1.4786	44.5	7.9	5.2	11.5	44.5	7.9	5.4	11.2
(14–16)a	CH_2Cl_2, 15°	78	1.4645	42.3	7.5	5.5	12.1	42.5	7.5	5.4	11.9
(14–15)c	CH_2Cl_2, 15°	90	1.4681	48.4	8.5	4.7	10.4	48.7	8.6	4.6	10.9
(14–15)b	CH_2Cl_2, 15°	54	1.4676	44.5	7.8	5.2	11.5	44.8	7.9	5.2	11.1
18a, b	CH_2Cl_2, hν, reflux	81	—	61.2	6.4	3.6	7.9	61.1	6.2	3.5	7.7
19	CH_2Cl_2, 0°	68	55–56 [n-hexane]	45.2	7.2	5.2	11.6	45.2	7.2	5.3	11.7

DCPA to the above dienes is not regiospecific and usually affords a mixture of products (Eq. 3). Initially elemental analysis data of the adducts are summarized in Table 1. The composition of the reaction mixture and



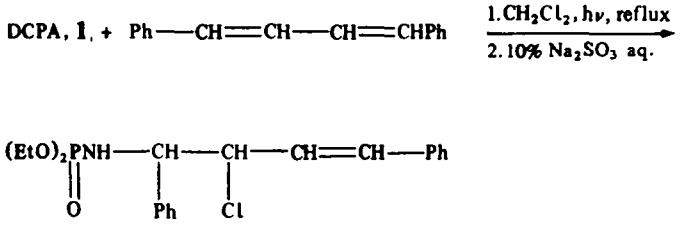
a $R = R^1 = H, R^2 = CH_3$; b $R = H, R^1 = R^2 = CH_3$; c $R = R^1 = R^2 = CH_3$

formed unstable N-chloro adducts (**11–13a–c**) can be easily reduced to the final products (**14–16a–c**) without allylic rearrangement.†

trans-*Piperylene*. The reaction of *trans*-piperylene with DCPA results in a 78% yield of the three isomeric adducts formed by 1,2-(27%), 1,4-(59%) and 4,1-(14%) addition to the conjugated system (Eq. 3), compounds **15a**, **14a** and **16a** respectively. Crude reaction mixture was analytically pure (Table 1). Composition of the mixture of adducts was established by ^{31}P-NMR and the structure of each isomer was deduced from detailed analysis of the ^{1}H-NMR spectrum of the crude mixture of products. These data were further supported by NMR double resonance technique. All attempts to separate the mixture into pure isomers by column chromatography failed.

4 - *Methyl* - 1,3 - *pentadiene and* 2,5 - *dimethyl* - 2,4 - *hexadiene*. 4 - Methyl - 1,3 - pentadiene reacted with DCPA to form a mixture of 1,2-adducts (**15b**, 65%) and 1,4-adducts (**14b**, 35%) in 54% overall yield. For the addition of DCPA to 2,5-dimethyl-2,4-hexadiene the ratio of 1,2-adduct (**15c**) to 1,4-adduct (**14c**) was reversed and the latter was found to be the main component of the mixture (80%) which was produced in 90% overall yield. Physical constants, yields and elemental analysis data of the adducts are summarized in Table 1. The composition of the reaction mixture and the structure of the adducts was established by careful analysis of the ^{31}P-NMR and ^{1}H-NMR spectra of the crude products (for details, see Table 2). The assignments were based on the well known chemical shifts of similar compounds formed by addition of methylsulphenyl chloride to 4-methyl-1,3-pentadiene[10] and thiols[4c] or diethyl dithiophosphoric acid[11] to 2,5-dimethyl-2,4-hexadiene.

1,4-*Diphenyl*-1,3-*butadiene*. Addition of DCPA to 1,4-diphenyl-1,3-butadiene takes a totally different course. It demands UV irradiation and elevated temperature for initiation and affords regiospecifically the 1,2-adduct **17** in 81% yield (Eq. 4). ^{31}P-NMR spectrum of the crude reaction mixture displayed two



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signals at 7.7 and 7.5 ppm. Integration of these signals allowed to establish the ratio of both diastereoisomers which was found to be 65:35 (*erythro*:*threo*-adduct).

Proof of structure and stereochemical assignments were arrived at by careful ^{1}H-NMR spectrum examination of the crude product, and its chemical transformation of known stereochemistry. Crude adduct (**17**, *erythro*:*threo* = 65:35) was cyclized in the presence of sodium hydride to give the mixture of *trans*- (**18a**) and *cis*-N-phosphorylated aziridines (**18b**) in almost the same ratio 66:34 (Eq. 5). Such transformations are known to proceed with inversion of configuration at the substituted C atom.[2,12] Structures **18a** and **18b** are evident from inspection of the ^{1}H-NMR spectrum of the crude mixture obtained on cyclization (Table 3).

Configurations of both N-phosphorylated aziridines

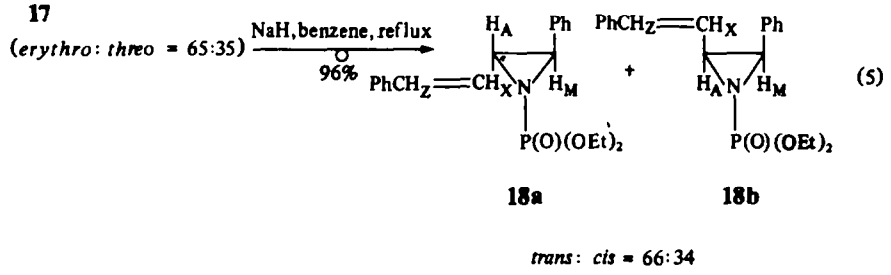
† To avoid solvolysis of the adducts (**11b, c–12b, c**) during the contact with Na_2SO_3 aq it was necessary to shorten the reduction time to 5 min in the case of 2,5-dimethyl-2,4-hexadiene and 4 - methyl - 1,3 - pentadiene - DCPA - adducts (**11b, c–12b, c**).

Table 2. ^{31}P-NMR and ^{1}H-NMR spectral assignments of diethyl N-(chloroalkenyl)phosphoroamidates (7–19)

Compd no.	Diene	Adduct	^{31}P-NMR (δ in ppm) (%)[a]	^{1}H-NMR assignments (δ in ppm from TMS, J in Hz)[b] R = $(CH_3CH_2O)_2P(O)NH$— structure: R—1–2–3–4–5	R							
					CH_3	CH_2	NH	1	2	3	4	5
7a	Butadiene	1,4	9.35	—CH_2—CH=CH—CH_2Cl	1.26t 6H J_{HH} = 7.0	3.96qt (4H)[d] $^{3}J_{PH} = J_{HH}$ = 7.0	4.94–5.25 m, 1H	3.27–3.55 m, 2H $^{3}J_{PH}$ = 11.2[c]		5.66–5.9 m, 2H	4.01d (2H)[d] $J_{3,4}$ = 5.6	
7b	Isoprene	1,4	9.5	—CH_2—$C(CH_3)$=CH—CH_2Cl	1.26t 6H J_{HH} = 7.1	3.94qt (4H)[d] $^{3}J_{PH} = J_{HH}$ = 7.1	4.93–5.44 m, 1H	3.34bdd 2H $^{3}J_{PH}$ = 11.2[e] J_{NHH} = 6.4	1.73bs, 3H	5.65bt, 1H J_{34} = 8.4	4.05d (2H)[d] J_{34} = 8.4	
7c	2,3-Dimethyl-1,3-butadiene	1,4	9.75	—CH_2—$C(CH_3)$=$C(CH_3)$—CH_2Cl	1.27t 6H J_{HH} = 7.2	3.93qt (4H)[d] $^{3}J_{PH} = J_{HH}$ = 7.2	4.94–5.26 m, 1H	3.38dd, 2H, $^{3}J_{PH}$ = 11.5[c] J_{NH-H} = 6.5		1.78bs, 6H	4.02s (2H)[d]	
14a	*trans*-Piperylene[e]	1,4	9.73 (59)	—CH_2—CH=CH—CH(Cl)—CH_3	1.17 and 1.18bdt	4.00bqt	5.2–5.44 m	3.41bdd $^{3}J_{PH}$ = 11.5[f] J_{12} = 4.5		5.4–5.77[g] m	4.32bqt $J_{3,4} = J_{45}$ = 6.5	1.41d J_{45} = 6.5
15a		1,2	9.13 (27)	—CH_2—CH(Cl)—CH=CH—CH_3	J_{HH} = 7.0	$^{3}J_{PH} = J_{NH}$ = 7.0		3.22bdt $^{3}J_{PH}$ = 11.0[f] J_{12} = 6.7 J_{NH-H} = 6.7[c]	4.4bq $J_{12} = J_{23}$ = 6.7	—[g]	—[g]	1.52d $J_{4,5}$ = 4.7
16a		4,1	8.56 (14)	—CH—(CH_3)—CH=CH—CH_2Cl				—[g]	—[g]	—[g]	—[g]	3.64bd $J_{4,5}$ = 5.5
15c	2,5-Dimethyl-2,4-hexadiene	1,2	6.55 (20)	—$C(CH_3)_2$—CH(Cl)—CH=$C(CH_3)_2$	1.26bt	4.00bqt	5.08–5.27	1.26s	4.78d J_{23} = 10.5	5.39bd J_{23} = 10.5	1.64 and 1.76bs	

14c		1,4	7.1 (80)	—C(CH$_3$)$_2$—CH=CH—C(CH$_3$)$_2$—Cl	J_{HH} = 7.3	$^3J_{PH}$ = J_{NH} = 7.3	m	1.26s	5.81bs		1.63s	
15b	4-Methyl-1,3-pentadiene	1,2	9.0 (65)	—CH$_2$—CH(Cl)—CH=C(CH$_3$)$_2$	1.27t	4.62bqt	4.87–5.18 m	3.07bdd $^3J_{PH}$ = 11.3 J_{12} = 6.7	4.67dt J_{12} = 6.7 J_{23} = 9.9	5.27bd J_{23} = 9.9	1.73bs	
14b		1,4	9.6 (35)	—CH$_2$—CH=CH—C(CH$_3$)$_2$Cl	J_{HH} = 7.4	$^3J_{PH}$ = J_{HH} = 7.4		3.3–3.63 m	5.63–5.95 m		1.67s	
17a	1,4-Diphenyl-1,3-butadiene[b]	1,2 *erythro*	7.7 (65)	—CH—CH(Cl)—CH=CH—Ph Ph[5]	1.05t and 1.26t J_{HH} = 7.0	3.96qt $^3J_{PH}$ = J_{HH} = 7.0	—[d]	4.55 (6 lines) J_{12} = 4.7, $^3J_{P1}$ = 9.8 J_{NH-1} = 10.3	4.88dd J_{12} = 4.7 J_{23} = 8.8	6.0 (4 lines) J_{23} = 8.8	6.61 (2 lines) J_{34} = 15.5	
17b		1,2 *threo*	7.5 (35)		1.00t and 1.22t J_{HH} = 7.1	3.7qt $^3J_{PH}$ = J_{HH} = 7.1		4.28 (5 lines) J_{12} = 8.8 $^3J_{P1}$ = 9.8	4.79dd J_{12} = 7.8, J_{23} = 7.8	6.35 (4 lines) J_{23} = 7.8,	6.63 (2 lines) J_{34} = 15.6	7.25–7.33 m
19	1,3-Cyclohexadiene	1,4	8.9	—CH—CH=CH—CH(Cl)—(CH$_2$)$_2$	1.29t 6H J_{HH} = 7.2	4.03qt 4H $^3J_{PH}$ = J_{HH} = 7.2	4.44–4.92 m, 1H	3.41–3.79 m, 1H	5.67–6.02 m, 2H		4.39–4.67 m, 1H	1.64–2.45 m, 4H

[a] Contents of the regioisomers are given in parentheses.
[b] Abbreviation used: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; qt, quintet; m, multiplet; b, broad.
[c] Calculated on deuteration of the amide proton.
[d] Overlapped with other signals.
[e] ^{1}H-NMR spectrum was recorded in C_6D_6 solution.
[f] Calculated on heterodecoupling of P nucleus.
[g] Overlapped for all regioisomers.
[h] ^{1}H-NMR spectrum was recorded in $CDCl_3$ solution.



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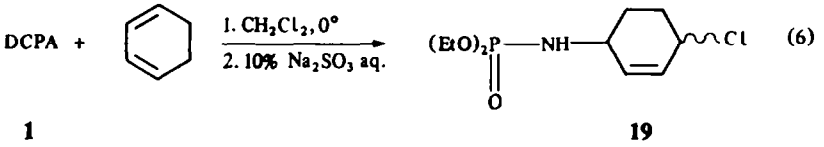
(**18a** and **18b**) were established on the basis of the well documented relationship between the values of coupling constants for aziridine protons ($J_{cis} > J_{trans} > J_{gem}$).[13,14] If vicinal coupling constant $J_{AM} = 6.2$ Hz is ascribed to *cis*-aziridine **18b**, the lower value of $J_{AM} = 2.8$ Hz seems to be consistent with the structure of the *trans*-isomer **18a**.

Additionally, cyclization of the pure *erythro*-isomer **17a** (isolated from the crude reaction mixture **17** by crystallization from acetone–hexane) afforded under the same conditions pure *trans* - N - (diethoxyphosphoryl) - 2 - phenyl - 3 - vinylphenylaziridine (**18a**) in 94% overall yield.

1,3-Cyclohexadiene. 1,3-Cyclohexadiene was chosen as a representative of *cis*-conjugated 1,3-dienes. DCPA was found to react with this unsaturate under the conditions described previously for terminal double bond 1,3-dienes, with the same induction period and subsequent exothermicity.

The reaction was regiospecific and afforded after the reduction of the initially formed N-chloro adduct by means of 10% sodium sulphite solution the crystalline 1,4-adduct (**19**) in 68% overall yield (Eq. 6). Crude **19**



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1 **19**

was analytically pure (Table 1). Regioisomeric purity of the adduct **19** was evident from its ^{31}P-NMR spectrum (one signal at 8.9 ppm). The structure was determined on the basis of careful analysis of the ^{1}H-NMR spectrum (Table 2). Chemical shift (4.39–4.67 ppm) observed for the chloromethine allylic proton next to methylene group was in good agreement with the value described in the literature (4.38–4.66 ppm) for the same moiety.[15] However without a detailed conformational analysis it is impossible to determine whether the reaction of DCPA with 1,3-cyclohexadiene can be classified as *syn* or *anti* 1,4-addition.

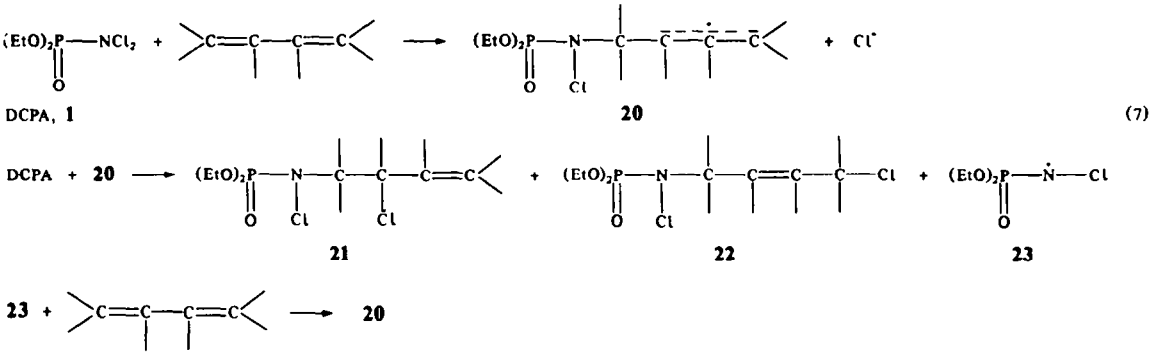
Mechanism of DCPA addition to conjugated 1,3-dienes. The observations and results obtained indicate that the addition of DCPA to 1,3-dienes has several characteristic features of a free-radical chain reaction: (i) an induction period is usually observed, followed by a rapid exothermic reaction; (ii) the reaction is evidently catalysed by light and speed up by UV irradiation. The presence of free-radical inhibitors, such as hydroquinone, markedly slows down the reaction rate, i.e. the addition of DCPA to isoprene in the presence of hydroquinone needs two hours in boiling dichloromethane for completion and affords 74% yield of 1,4-adduct; (iii) the high regioselectivity preferring 1,4-addition is a characteristic feature of free-radical reaction. Such course was previously observed for the addition of various reagents to conjugated 1,3-dienes.[4a,8,16–18]

Table 3. ^{31}P-NMR and ^{1}H-NMR spectral assignments of the mixture *trans*-(**18a**) and *cis*-N-(diethoxyphosphoryl)-2-phenyl-3-vinylphenylaziridine (**18b**)

Compound No.	^{31}P-NMR, (δ in ppm) (%)[b]	^{1}H-NMR assignments (δ in ppm from TMS, J in Hz)[a]				
		H_A	H_M	H_X	H_Z	Other protons
18a *trans*	11.3 (66)	3.16 (8 lines) $J_{AM} = 2.8$[c] $^3J_{PA} = 14.4$ $J_{AX} = 8.8$[c]	3.71 dd $J_{AM} = 2.8$[c] $^3J_{PM} = 15.85$	6.47 and 6.75 (4 lines) (2 lines) $J_{AX} = 8.8$ $J_{XZ} = 15.8$		1.26t ($J_{HH} = 7.0$, CH_3CH_2O—) 4.12 qt ($^3J_{PH} = J_{HH} = 7.0$, CH_3CH_2O—)[e]
18b *cis*	13.4 (34)	3.47 (8 lines) $J_{AM} = 6.2$[c] $J_{AX} = 8.15$[c] $^3J_{PA} = 15.8$	3.9d $J_{AM} = 6.2$[d]	5.66 and 6.75 (4 lines) (2 lines) $J_{AX} = 8.15$ $J_{XZ} = 15.9$		1.3t and 1.33t ($J_{HH} = 7.0$, CH_3CH_2O—) 7.03–7.33 m (aromat)[e]

[a] ^{1}H-NMR spectrum was recorded on a Bruker HX-72 Spectrometer in $CDCl_3$ solution.
[b] Contents of the isomers are given in parentheses.
[c] Calculated after P-heterodecoupling.
[d] Doublet after P-heterodecoupling. $^3J_{PM}$ is invisible.
[e] Overlapped for both diastereoisomers.

Mild conditions and lack of initiators required for the addition are characteristic of a spontaneously initiated free-radical chain reaction. Such phenomenon of spontaneous initiation was observed by Walling[19] and Poutsma[18,20] and also suggested by Daniher and Butler[8] for the reactions of N,N-dichlorocarbamates with dienes. The following steps illustrate the possible progress of DCPA addition to conjugated 1,3-dienes (Eq. 7). In the initiation step the molecules of DCPA and



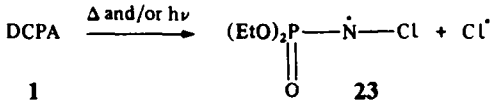
(7)

diene combine to give the allyl type radical **20** and a Cl atom. Propagation involves the reaction of radical **20** with another molecule of DCPA to give 1,2 N-chloro adduct **21** and 1,4 N-chloro adduct **22** together with amido radical **23** which reacts in turn with another molecule of diene to recover **20**. Main factors determining the preferred addition course are the stability of allyl type radical and of the formed alkene. Hence the abstraction of Cl atom from DCPA by the allyl type radical **20**, occurs exclusively or preferentially at the least substituted carbon atom to yield the more thermodynamically stable product.[4a,8] This is illustrated by the reactions of DCPA with terminal double bond 1,3-dienes, like butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene, which afford regiospecifically only 1,4-adducts.

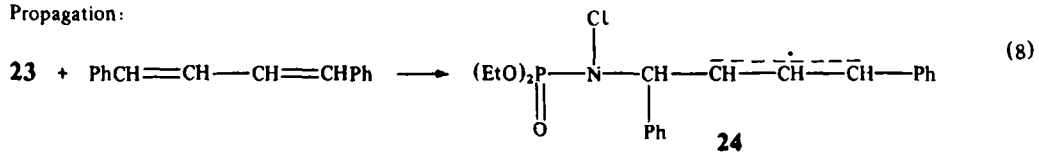
For nonterminal double bond 1,3-dienes, like piperylene, 4-methyl-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene, successive substitution of the terminal C atom with alkyl groups increase the amount of 1,2-adduct in the reaction mixture (27%, 65% and 20% respectively). These results can be interpreted in terms of electronic as well as steric interactions in the propagation step. Addition of DCPA to 1,4-diphenyl-1,3-butadiene is much slower than to the other dienes and needs UV irradiation and elevated temperature to take place. This observation is fully consistent with the thermally or photolytically initiated free-radical chain reaction pathway depicted below (Eq. 8).

In the initiation step homolytic splitting of DCPA molecule takes place. The amido radical **23** and diene combine to give the allyl type radical **24**, which in turn reacts with another molecule of DCPA giving N-chloro adduct **25** and the amido radical **23** again. The propagation step leading to (**25**) is probably much faster than vinyl polymerization propagation step because almost no polymerization was found to take place during the addition. The complete regioselectivity (1,2-addition) observed for 1,4-diphenylbutadiene is evidently a consequence of extended conjugation in the 1,2-adduct **25** which would be absent from the 1,4-adduct.

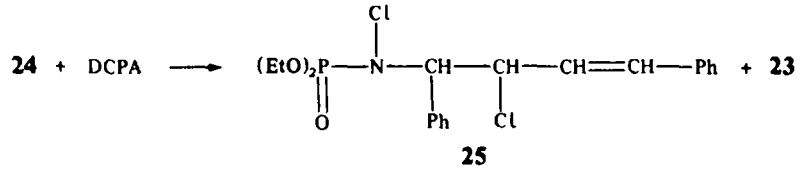
Initiation:



Propagation:



(8)



EXPERIMENTAL

Solvents and reagents were purified by conventional methods. All dienes 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. Mass spectra were recorded on a LKB

2091 spectrometer. ^{1}H-NMR spectra were measured at 80 MHz with a Telsa BS 487C or at 90 MHz with a Bruker HX-Series 72 (FT) spectrometer in CCl_4 soln unless otherwise stated using TMS as internal standard. ^{31}P-NMR spectra were recorded at 24.3 MHz with a Jeol JNM-C-60-HL spectrometer in CCl_4 solns using 85% H_3PO_4 as external reference. A Heteronuclear Spin Decoupler JNH-SD-HC was used for precise ^{31}P chemical shift determinations.

Measurements were made on samples of analytical purity. Column chromatography was performed on Silicagel (100–200 mesh). DCPA, **1** was prepared as described previously[21] by chlorination of diethyl phosphoroamidate in an aqueous buffered soln.

trans-1,4-Diphenyl-1,3-butadiene was synthesized in 48% yield according to Märkl and Merz[22] from cinnamaldehyde and benzyltriphenylphosphonium chloride in aq NaOH. M.p. 148–150° (EtOH) (lit.[22] m.p. 149–150°).

Addition of DCPA (**1**) *to conjugated dienes*

General procedure. DCPA (11.1 g, 0.05 m) was added dropwise with stirring to the soln of diene (0.05 m) in CH_2Cl_2 (20 ml) at 0°. After the addition of about one third of DCPA a spontaneous, strongly exothermic reaction started. The rest of the DCPA was added at such a rate as to maintain the mixture at the indicated temp (Table 1) (external cooling—dry ice–acetone bath). Stirring was then continued at this temp for additional 30 min. In the case of butadiene sat soln of this diene in dichloromethane was applied.[7]

The resulting colourless or pale-yellow soln was diluted with CH_2Cl_2 (50 ml), cooled to 0°, and 10% Na_2SO_3 aq (18.9 g, 0.15 m, 200 ml) was then added slowly at this temp. The organic layer was separated, washed with water (3 × 30 ml), dried, and evaporated. The residual crude adducts (**7–16** and **19**) were analytically pure when heated at 40°/0.1 mm for 1 hr to remove traces of solvent. Table 1 shows results and analyses.

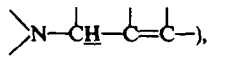
Addition of DCPA to 1,4-diphenyl-1,3-butadiene. A soln of 1,4-diphenyl-1,3-butadiene (1.92 g, 0.01 m) and DCPA (2.21 g, 0.01 m) in CH_2Cl_2 (30 ml) was placed in a quartz flask, refluxed gently and continuously irradiated by a UV lamp for 1 hr until fading of greenish–yellow colouration of the mixture. The product was worked up as described previously. Crude **17a, b** was passed through short silicagel column to remove traces of polymeric impurities.

erythro - *Diethyl* N - 4 - (3 - *chloro* - 1,4 - *diphenylbutene* - 1 - *yl*)*phosphoroamidate* (**17a**). Crude **17a, b** (3.2 g) was twice recrystallized from the mixture of acetone–hexane (1 : 3; 16 ml) to give 1.0 g of pure *erythro* isomer **17a**, m.p. 129–130°. (Found: C, 61.2; H, 6.3; N, 3.5; P, 7.8. $C_{20}H_{25}ClNO_3P$ Requires: C, 61.2; H, 6.4; N, 3.6; P, 7.9%.)

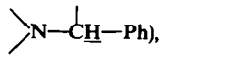
The IR spectrum (KBr) showed characteristic bands at: 3240 m (NH), 1455 m (CH_3, CH_2), 1055s, 1035s, 955s (POC), 970s (*trans*-CH=CH—), 745s, 695s (CH, aromat). The ^{31}P-NMR spectrum (CCl_4) displayed one signal at δ = 7.7 ppm (from H_3PO_4). The ^{1}H-NMR spectrum (CCl_4) showed signals at δ = 1.05t and 1.26t (6H, J_{HH} = 7.0 Hz, $\underline{CH_3}CH_2O$—), 3.96qt (5H, $^3J_{PH}$ = J_{HH} = 7.0 Hz, $CH_3\underline{CH_2}O$— and N$\underline{H}$—), 4.55 (6 lines) (1H, J_{HH} = 4.7 Hz, $^3J_{PH}$ = 9.8 Hz, J_{NH-H} = 10.3 Hz, >C$\underline{H}$—Ph), 4.88 dd (1H, J_{HH} = 4.7 Hz, J_{HH} = 8.8 Hz, >C$\underline{H}$—Cl), 6.0 and 6.61 (6 lines) (2H, J_{HH} = 8.8 Hz, J_{HH} = 15.55 Hz, —$\underline{CH}$=$\underline{CH}$—Ph), 7.25–7.33 m (10H, aromat).

trans - N - (*Diethoxyphosphoryl*) - 2 - *phenyl* - 3 - *vinylphenylaziridine* (**18a**). To a stirred soln of *erythro*-**17a** (0.7 g, 1.78 mM) in dry benzene (50 ml), NaH (0.048 g, 2.0 mM) was added at room temp. Stirring was continued for 30 min at this temp and then the mixture was refluxed for 1.5 hr. The resulting mixture was cooled to room temp, washed with water (3 × 15 ml), dried and evaporated to give 0.6 g (94%) of analytically pure **18a** as a thick yellow oil, n_D^{20} = 1.5745. MS: m/z = 357 (45%, M^+).

IR spectrum (film) showed characteristic absorption maxima at: 3020m (CH, aromat), 1260s, 1245s (P=O), 1055s, 1030s, 940s (POC), 745s, 690s (CH, aromat). The ^{31}P-NMR spectrum (CCl_4) displayed one signal at 11.38 ppm (from H_3PO_4). The ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ = 1.26t (6H, J_{HH} = 7.0 Hz, $\underline{CH_3}$—CH_2O—), 3.16 (8 lines) (1H, J_{HH}^{trans} = 2.8 Hz, J_{HH} = 8.8 Hz, $^3J_{PH}$ = 14.4 Hz,



), 3.71 dd (1H, J_{HH}^{trans} = 2.8 Hz, $^3J_{PH}$ = 15.85 Hz,



), 4.12 qt and 4.14 qt (4H, $^3J_{PH}$ = J_{HH} = 7.0 Hz, $CH_3C\underline{H_2}O$—), 6.47 and 6.75 (6 lines) (2H, J_{HH} = 8.8 Hz, J_{HH} = 15.8 Hz, —$\underline{CH}$=$\underline{CH}$—), 7.03–7.33 m (10H, aromat protons).

trans - *and* cis - N - (*Diethoxyphosphoryl*) - 2 - *phenyl* - 3 - *vinylphenylaziridines* (**18a, b**). The title compounds were prepared according to the procedure described for **18a**. Starting from the crude **17a, b** *erythro*/*threo* = 65 : 35, 1.2 g, 3.05 mM) the mixture of analytically pure *trans*- and *cis*-**18a, b** (1.05 g, 97%, t/c = 66 : 34) was obtained as a thick, yellow oil, n_D^{20} = 1.5768. MS: m/z = 357 (20%, M^+). (Found: C, 67.1; H, 6.9; N, 3.9. $C_{20}H_{24}NO_3P$. Requires: C, 67.1; H, 6.7; N, 3.9%.)

^{31}P-NMR and ^{1}H-NMR spectral data are reported in Table 3. The authors acknowledge financial support for this work by a grant MR-I. 12.1.3.1/2 from Polish Academy of Sciences.

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