Steric and Electronic Factors in 1,3-Dipolar Cycloadditions. The Stereochemical Course of the Addition of Dimethyl Aryl- and Alkyldiazomethylphosphonates to Norbornadiene

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The addition of 14 dimethyl aryl- and alkyldiazomethylphosphonates, $RC(N_2)P(O)(OCH_3)_2$, to norbornadiene has been studied and the stereochemistry of the resulting *exo*-Δ^1-pyrazolines determined by n.m.r. The *anti*/*syn* ratio of the cycloadducts is discussed in terms of steric and electronic factors. For alkyldiazomethylphosphonates steric factors are the dominant ones, while with aryldiazomethylphosphonates electronic factors seem to be of importance.

L'addition de 14 aryl- et alkyldiazomethylphosphonates, $RC(N_2)P(O)(OCH_3)_2$ au norbornadiène a été étudiée et la stéréochimie des Δ^1-pyrazolines-*exo* formées a été déterminée par r.m.n. Le rapport *anti*/*syn* des produits d'addition est discuté en termes de facteurs stériques et électroniques. Pour les alkyldiazomethylphosphonates, ce sont les facteurs stériques qui sont prédominants alors que pour les aryldiazomethylphosphonates les facteurs électroniques sont importants.

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1,3-dipolar cycloaddition reactions provide a general route to five-membered rings containing several heteroatoms (1). The most generally accepted mechanism is the one proposed by Huisgen (1), namely, that cycloaddition is a concerted "no-mechanism" reaction (2). Recently, Firestone (3) has proposed a two-step diradical mechanism. A clear assignment of the role of steric and electronic factors should give some insight into the mechanism of such reactions: steric factors should be more important in a concerted one-step than in a two-step reaction.

Although 1,3-dipolar cycloadditions with activated double bonds are well documented, there has been no systematic study of the reaction of dipoles with isolated double bonds whose reactivity stems from their strain. With dimethyl diazoalkylphosphonates, $RC(N_2)P(O)(OCH_3)_2$, the addition to an olefin such as norbornadiene results in the formation of two Δ^1-pyrazolines (Fig. 1) and the *anti* to *syn*[1] ratio should give some information about the influence of the R group. For R = CH_3 and C_6H_5 we found recently (4) that the distribution of adducts could not be explained by consideration of steric factors only and we therefore undertook the study of the addition of 14 dimethyl alkyl- and aryldiazomethylphosphonates to norbornadiene. The results are reported here.

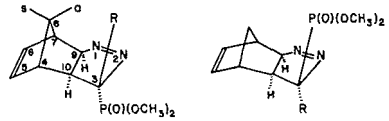


FIG. 1. *Anti* and *syn* pyrazolines.

Results

All the diazomethylphosphonates necessary for this study, except the *p*-nitrophenyl derivative **5**, were prepared by a general route devised by Seyferth and co-worker (5) from α-ketophosphonates whose tosylhydrazone derivatives decomposed in basic medium to yield the desired starting material. Because of the reactivity of trialkyl phosphite toward *p*-nitroaromatics (6), the Regitz "diazo transfer method" (7) was used to make compound **5**.[2] The synthesis and ^{13}C n.m.r. spectra of some of them (**1**–**5** and **7**) have appeared recently (8).

All cycloadditions were carried out under the same conditions, as described previously (4); a

[1]The words *anti* and *syn* refer to the relative position of the C_8 bridge and of the dimethylphosphono group.

[2]After our manuscript (ref. 8) had been submitted for publication, a paper by Regitz and co-workers (7*b*) described compounds **2** and **5**. The physical constants and the spectral data of their compounds agreed well with those of our compounds.

mixture of the diazophosphonate, norbornadiene in more than 40-fold excess, and methylene chloride was heated at 55–60°.[3] The addition reaction was fast (24 h for more than 90% completion) with components **1–6**, **9–11**, and **14**, and much slower for derivatives **7**, **8**, **12**, and **13**. See Experimental section for details.

The configurations of the pyrazolines were determined essentially by proton n.m.r. and the *anti*/*syn* ratio could be estimated directly on the n.m.r. spectrum of the crude by integrations of the signal due to the H_9 protons.[4] The n.m.r. spectra of some of the *aryl* pyrazolines (**14–23**, and **26**) have been described elsewhere (9). Of the four possible diastereomeric pyrazolines only the *exo* adducts were formed, a result quite common in addition to the bicyclo[2.2.1]heptene or -heptadiene systems (10). The *exo* attachment of the pyrazoline ring is proved by the existence of a 2.0 Hz long-range $H_{8s}CCCH_{10}$ coupling (11) and the absence of any H_{10},H_4 vicinal coupling. The configuration at C_3 is based essentially on the existence of a large (19–20 Hz) P,H_{10} coupling in the *anti* epimer and of a small (6–8 Hz) P,H_{10} coupling in the *syn* derivative. This is in accord with the known dihedral angular dependence of P—C—C—H coupling (12) in phosphonates; Dreiding models show that the pyrazoline ring is planar in this system and that the dihedral P,H angles are near 0° in the *anti* epimer (large $^3J_{PH}$ coupling) and near 120° in the *syn* epimer (small $^3J_{PH}$ coupling) (12).

Although this contrasting difference in P,H vicinal coupling allows unambiguous assignments to be made, it is not always sufficient because, in the case of the alkyl derivatives, the H_{10} signal lies under the absorptions of the alkyl protons. In those cases, the stereospecificity of P—C—N=N—C—H *homoallylic* couplings (9), 4–4.8 Hz in the *anti* configuration and 5.5–6.6 Hz in the *syn* configuration, allows unambiguous assignments to be made.

In the case of the *syn* benzyl derivative **39**, the signal for H_9 is shifted upfield (δ 3.40 p.p.m.) as compared with the usual 4.67–4.83 p.p.m. range for this absorption in *syn* derivatives. There is no doubt about the assigned configuration since the P,H_{10} coupling is 6.0 Hz (P,H_{10} = 18.0 Hz in the *anti* epimer). This unusual shielding effect probably corresponds to a preferred conformation of the phenyl ring; additional evidence for preferred conformation is the finding that vicinal *P*—C—CH_2(C_6H_5) couplings are different for the two benzylic hydrogens.

The mixture of epimeric pyrazolines was separated on a silica gel column chromatograph. In one instance, it was not possible to isolate pure *syn* derivative (compound **24**) and the amount of this epimer was estimated by n.m.r. of **24** with the starting diazo compound. The results of cycloaddition are summarized in Table 1.

Discussion

All the pyrazolines isolated possess the *exo* configuration. Radical (13) as well as electrophilic (10) additions to norbornene lead mostly, if not exclusively, to products resulting from *exo* attack. Additions to norbornadiene are more complex. Homolytic additions usually give mixtures of nortricyclene derivatives, as well as *exo*-norbornene derivatives (14). Some *endo* products have been reported for the addition of thiols to polyhalonorbornadienes (15). Addition of carbenes to norbornadiene leads to a fair amount of *endo* attack (16). In contrast to the number of products obtained with norbornadiene in radical, electrophilic, or carbenic

TABLE 1. Results of the cycloaddition reactions

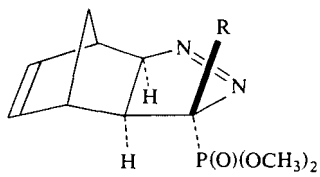
Diazo compound $RC(N_2)P(O)(OCH_3)_2$		Amount of pyrazolines (%)	
No.	R	*anti*[a]	*syn*
1	*p*-$CH_3OC_6H_4$	95	5
2	*p*-$CH_3C_6H_4$	90	10
3	*p*-BrC_6H_4	90	10
4	C_6H_5	95	5
5	*p*-$NO_2C_6H_4$	93	7
6	*p*-$CH_3OCOC_6H_4$	91	9
7	*o*-$CH_3OC_6H_4$	~100[b]	~0
8	α-Naphthyl	~100[b]	~0
9	β-Naphthyl	90	10
10	CH_3	75	25
11	C_2H_5	60	40
12	iso-C_3H_7	50	50
13	*tert*-C_4H_9	0	100[b]
14	$C_6H_5CH_2$	55	45

[a]% *anti* + % *syn* = 100; estimated accuracy ±2%;
[b]Estimated by n.m.r. and confirmed by chromatographic separation: no trace of the other epimer could be detected.

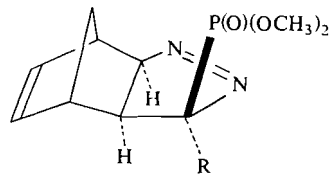
[3]The reaction was followed by n.m.r.: appearance of new P—OCH_3 peaks and of characteristic H_9 absorptions.

[4]The estimate was confirmed within ±2% by chromatographic separation of the mixture.

TABLE 2. Pyrazolines



anti



syn

Compound No.	R	Compound No.
15	*p*-$CH_3OC_6H_4$	**16**
17	*p*-$CH_3C_6H_4$	**18**
19	*p*-BrC_6H_4	**20**
21	C_6H_5	**22**
23	*p*-$NO_2C_6H_4$	**24**
25	*p*-$CH_3OCOC_6H_4$	**26**
27	*o*-$CH_3OC_6H_4$	—
28	α-Naphthyl	—
29	β-Naphthyl	**30**
31	CH_3	**32**
33	C_2H_5	**34**
35	iso-C_3H_7	**36**
—	*tert*-C_4H_9	**37**
38	$C_6H_5CH_2$	**39**

additions, only adducts resulting from *exo* attack have been reported in 1,3-dipolar cycloaddition reactions. Thus, although the exclusive formation of *exo*-Δ^1-pyrazolines is certainly striking, it is not unprecedented: additions of nitrilimines (17*a*), azides (17*b*), and diazoalkanes (18) to norbornadiene give mono- and bisadducts resulting from exclusive *exo* attack.

The results shown in Table 1 clearly reveal that steric factors are dominating, except in the case of the aromatic derivatives. This is particularly striking for the alkyldiazophosphonates **10–13**: as the size of the R group increases from methyl to *tert*-butyl, the amount of *syn*-pyrazoline increases from 25 to 100%. This is in accord with a concerted mechanism of addition. Incidentally, this would suggest that the dimethylphosphono group is almost as bulky as an isopropyl group.

It is more difficult to explain the results for the aromatic derivatives (**15–30**). A consideration of most of the 1,3-dipolar cycloadditions studied by Huisgen's group shows that kinetic control of the reaction is important (2). We have evidence that the reactions we are studying are also kinetically controlled: there was no change in the *anti*/*syn* ratio with time and the pyrazolines did not epimerize when submitted to the same conditions. Therefore, the *anti*/*syn* ratio of the products should reflect the differences in energy between the transition states leading to the *anti* and to the *syn* pyrazolines, respectively.

Steric factors alone could not explain the predominance of the *anti* derivatives. From the *A* values of the phenyl group (3.0 kcal/mol) (19) and of the $P(O)(OCH_3)_2$ group (2–3 kcal/mol),[5] there seems to be little difference in size between those two groups and one would expect a 1:1 *anti*/*syn* ratio rather than the ~9:1 ratio observed. Of course, these *A*-values should be considered as indicative only, since they refer to 1,3-diaxial interactions in the cyclohexane system. In fact, depending on its orientation, a phenyl group can be "smaller" than predicted from the *A*-value (20) and, indeed, there are examples in the literature where a phenyl–methyl nonbonded 1,3-diaxial interaction in a cyclohexyl derivative seems to be preferred to a corresponding methyl–methyl interaction (21). A possible explanation is therefore that the phenyl group, at least in the system studied here, is smaller than the dimethylphosphonate. This interpretation does not seem satisfactory to us

[5]J. L. Bravet and C. Benezra, unpublished results.

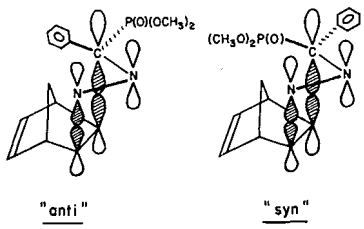


FIG. 2. Transition states leading to the *anti* and to the *syn* Δ^1-pyrazolines respectively.

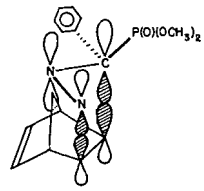


FIG. 3. Transition state leading to the *anti* Δ^1-pyrazoline with an "anti" arrangement of the phenyl *vs.* the nitrogen end of the dipole.

because of the results for the *o*-methoxyphenyl (**7**) and the α-naphthyl (**8**) derivatives: it is evident that the α-naphthyl group, at least, is bulkier than the phosphorus moiety and, still, only the *anti* derivative is obtained.

We rather favor a dominating effect of electronic factors in the aryl derivatives. Since we get mostly the *anti* derivatives, this means that the transition state leading to these products is stabilized, as compared with that for the *syn* ones (Fig. 2). This stabilization can be envisaged in three different ways.

In the transition state of 1,3-dipolar cycloadditions, the dipole is bent (2). Stabilization of the "anti" arrangement depicted in Fig. 2 can occur by favorable coulombic interaction between the phenyl ring and the nitrogen end of the dipole. Such an electrostatic effect can occur only when the phenyl and the nitrogen end of the dipole are *cis* to each other.

Stabilization can also occur from resonance: the steric hindrance of the C_8 bridge could cause the aromatic ring to be *coplanar* with the dipole in the "*anti*" arrangement, while in the "*syn*" alternative, the aromatic ring is a free rotor.

Finally, the dipole in an "*anti*" arrangement (with the aromatic ring *cis* to the nitrogen end of the dipole) could react *faster* than in the other conformation.[6] This difference is not unprecedented in the literature. For instance, the *cis* and *trans* forms of azomethine ylide dicarboxylic esters have a very different reactivity (22). In the particular case of the addition to norbornadiene, it is not possible to draw a clear-cut conclusion concerning this point; the arrangement depicted in Fig. 3 (with the phenyl "*trans*" to the nitrogen end of the dipole), which could also lead to the *anti* pyrazoline, seems to be precluded for steric reasons. It is of interest to note that there is no substituent effect: the difference between the *anti*/*syn* ratio found in the case of the *p*-methoxyphenyl derivative for instance and of the *p*-nitrophenyl is within experimental error (±2%).

Preliminary results for the addition of dimethyl aryldiazomethylphosphonates to 7-oxabenzonorbornadiene indicate that the effect of the —CH_2— bridge is not important: essentially the same *anti*/*syn* ratio is obtained. It seems therefore that polar effects predominate for aryldiazophosphonates. More work along those lines is in progress.

Experimental

Trimethyl phosphite was purchased from Aldrich Company and distilled before use. The benzoyl and naphthyl derivatives were prepared according to a published procedure (5). Silicic acid (Merck (0.05–0.20 mm)) was used for column chromatography. The i.r. spectra were recorded on a Beckman-20 i.r. Spectrometer either in chloroform solutions or as Nujol mulls. The n.m.r. spectra were run on a HA-100 Varian Spectrometer in deuteriochloroform solutions and chemical shifts are given in δ p.p.m. values with TMS as internal reference. Analyses were performed in Organic Microanalyses Laboratories (Dr. C. Daesslé) in Montreal. Norbornadiene was purchased from Aldrich Company and used as such.

Preparation of p-Carbomethoxybenzoyl Chloride

Since the preparation of *p*-carbomethoxybenzoyl chloride has not been described yet and since that of the monomethyl ester of terephthalic acid is described in a patent (23), we give here detailed procedures, starting from the commercially available dimethyl terephthalate (purchased from Baker).

$$p\text{-MeOOC—}C_6H_4\text{—COOMe} \xrightarrow[(2)\ SOCl_2]{(1)\ HO^-} p\text{-MeOOC—}C_6H_4\text{—COCl}$$

In a three-necked round-bottom flask equipped with a condenser, a dropping funnel, and a mechanical stirrer, was put dimethyl terephthalate (45 g) in 200 ml anhy-

[6]A referee suggested that determination of the frontier orbital energies and of the coefficients of the terminal atoms in the HOMO of the dipole could perhaps show that the *cis* form of the dipole (Fig. 2, transition state "*anti*") reacts faster than the *trans* form (Fig. 2, "*syn*"). This could indeed lead to conclusive results and those calculations will be undertaken and reported later.

TABLE 3. Ketophosphonates $RC(O)P(O)(OCH_3)_2$

R	RCOCl (g)	$P(OCH_3)_3$ (ml)	$RCOP(O)(OCH_3)_2$	Boiling point	Analysis (%) Calcd.	Analysis (%) Found	Infrared	Nuclear magnetic resonance
p-$CH_3OCOC_6H_4$[a]	27.1	19	23.55[b]	165–170° (0.015 Torr)	C 48.54 H 4.81 P 11.38	48.71 4.64 10.92	C=O 1660[c] P=O 1240 POC 1050	3.91 (d, 6H, $POCH_3$, J_{PH} = 11.2), 8.06, 8.15, 8.23, 8.32[d] (4H aromatic)
α-Naphthyl	18.7	12	23.8	Oil	C 58.87 H 4.94 P 11.68	58.78 5.01 11.65	C=O 1670 P=O ~1250 POC 1040	3.93 (d, 6H, $POCH_3$, J_{PH} = 10.8), 7.45–9.05 (m, 7H, H aromatic)
β-Naphthyl	18.8	12	23.8	Oil	C 58.87 H 4.94 P 11.68	59.11 4.97 11.31	C=O 1650[e] P=O 1240 POC 1050	3.94 (d, 6H, $POCH_3$, J_{PH} = 10.9), 7.28–8.20 (m, 7H, H aromatic)
C_2H_5[a]	31	12	29.70[b]	70° (0.05 Torr)	C 36.15 H 6.67 P 18.64	36.49 6.61 18.72	C=O 1700 P=O 1265 POC ~1040	1.11 (d of t, 3H, CH_3CH_2, J_{HH} = 7.25, $^4J_{PH}$ = 1.0), 2.86 (d of 9, 2H, CH_3CH_2—, $^3J_{PH}$ = 1.0), 3.88 (d, 6H, $POCH_3$, J_{PH} = 11.0)
$C_6H_5CH_2$	15.4	15	19.72[b]	125° (0.1 Torr)	C 52.40 H 5.72 P 13.51	52.27[f] 5.63 13.33	C=O 1675 P=O 1210 POC ~1030	3.76 (d, 2H, CH_2(CO), J_{PH} = 11), 3.81 (d, 6H, P—O—CH_3, J_{PH} = 11.2), 2 multiplets at ~7.3 and ~7.8 (5H, H aromatic)

[a]Both ketophosphonates purified by distillation under vacuum.
[b]After distillation.
[c]The $(CO)OCH_3$ absorption appeared at 1720 cm^{-1}.
[d]AA'BB' part of an AA'BB'X (X = P); positions of main absorptions given.
[e]There was another strong absorption at 1625 cm^{-1}.
[f]Analysis performed by Chemalytics Inc., Tempe, Arizona (Dr. A. M. Yates).

TABLE 4. Tosylhydrazones $RC(NNHTS)P(O)(OCH_3)_2$

R	$RCOP(O)(OCH_3)_2$ (g)	Hydrazone[a] (g)	Melting point	Analysis (%) Calcd.	Found
p-$CH_3OCOC_6H_4$	20	25.8	118–120°	C 49.09	49.05
				H 4.78	4.75
				N 6.36	6.08
				P 7.02	6.71
α-Naphthyl	18.5	26.7	127°	C 55.42	55.68
				H 4.88	4.98
				N 6.46	6.60
				P 7.14	7.00
β-Naphthyl	18.5	26.9	193–194°	C 55.42	55.27
				H 4.88	4.89
				N 6.46	6.50
				P 7.14	6.97
C_2H_5	20.7	34	155–160°	C 43.11	42.85
				H 5.72	5.59
				N 8.37	8.51
				P 9.26	9.50
$C_6H_5CH_2$	11.4	16.8	125–126°	C 51.52	51.10[b]
				H 5.33	5.44
				N 7.07	7.44
				P 7.81	7.46

[a]Purified by recrystallization in methanol.
[b]Analysis performed by Chemalytics Inc., Tempe, Arizona (Dr. A. M. Yates).

drous methanol. A solution of KOH (12.9 g) in methanol (250 ml) was added dropwise for 3.30 h while the temperature of the reaction mixture was maintained at 75° (or a little less). After cooling to room temperature, the precipitate was filtered and was further dissolved in water (1500 ml); only the monosalt was soluble and the unreacted diester was filtered off. The filtrate was acidified with a 10% HCl solution (pH 2) and a precipitate formed which was filtered and washed several times with water. The monoacid was dried (at a temperature less than 80°) and 28.5 g were obtained (m.p. 221°, lit. (24) m.p. 230°).

This acid was dissolved in 15 ml anhydrous benzene to which 1 drop of pyridine had been added. Then thionyl chloride (80 ml, from a freshly opened new bottle) was added and the mixture was refluxed for 5 h. Excess $SOCl_2$ and benzene were removed by distillation under vacuum (water pump); 50 ml anhydrous benzene were added and further distillation (water pump) removed the remaining $SOCl_2$. The monochloride (27.10 g) was purified by crystallization from cyclohexane, m.p. 52–53° (b.p. 90°, 0.015 Torr)., i.r. ($CHCl_3$): 1730 ($COOCH_3$), 1785 ($COCl$).

Anal. Calcd. for $C_9H_7ClO_3$ (mol. wt. 198.61): C, 54.43; H, 3.55; Cl, 17.85. Found: C, 54.49; H, 3.68; Cl, 18.02.

Preparation of the Ketophosphonates and of the Diazophosphonates

The ketophosphonates were prepared from the acyl chlorides, according to Seyferth's general procedure (5). It is very important for the preparation of the p-carbomethoxyphenyl and benzyl derivatives that the Arbuzov reaction be conducted in dilute solution to avoid polymerization. In a typical run, to an anhydrous, vigorously stirred benzene (200 ml) solution of phenylacetyl chloride (20 g) was added an anhydrous benzene (100 ml) solution of trimethyl phosphite (10 g) over 4 h with cooling in an ice-bath. After the addition was completed, the mixture was left under nitrogen, for 24 h at room temperature, then the benzene was distilled off and the phosphonate separated by distillation.

The diazophosphonates, except the p-nitrophenyl derivative (8), were prepared from the tosylhydrazone derivatives of the ketophosphonates, as described previously (4).

Tables 3–5 give the details (weight, analysis, etc.) for new compounds, as well as the spectral data.

Kinetic Studies of the Cycloaddition Reaction

All the runs were done at the same time by heating mixtures of 1 mmol of the diazophosphonate, 5 ml norbornadiene, and 0.5 ml of CH_2Cl_2 in the same bath, at a temperature of 55–60 °C. A sample was taken after 2, 5, 10, 24, and 50 h, evaporated to dryness (no more norbornadiene present), and the T-60 n.m.r. spectrum in $CDCl_3$ was taken. It was possible to estimate the amount of cycloadducts formed by integrating the signal due to H_9 which was well isolated from the others and by comparing it with the CH_3O signals. Since the CH_3O signals were quite different in the pyrazolines and in the diazo compounds, it was also possible to estimate the com-

TABLE 5. Diazomethylphosphonates $RC(N_2)P(O)(OCH_3)_2$

R	Hydrazone (g)	Diazo compound[a] (g)	Analysis (%) Calcd.	Analysis (%) Found	Infrared	Nuclear magnetic resonance
p-$CH_3OCOC_6H_4$ **6**	15.6	9.56 (orange crystal m.p. 48° dec. 140°)	C 46.48 H 4.61 N 9.86 P 10.90	46.81 4.62 9.71 10.89	C=N_2 2080[b] P=O 1240 POC 1040	3.82 (d, 6H, $POCH_3$, J_{PH} = 12.2), 3.90 (s, 3H, CH_3OCO), 8.05, 7.96, 7.19, 7.15[c] (AA′BB′, 4H, H aromatic)
α-Naphthyl **8**	13	4.4 (yellow oil)	C 56.53 H 4.74 N 10.13 P 11.21	56.30 4.95 10.27 10.93	C=N_2 2080 P=O ~1220 POC 1030	3.81 (d, 6H, $POCH_3$, J_{PH} = 10.5), 7.73 (complex m, fine structure 7H)
β-Naphthyl **9**	12	8.0 (orange crystal m.p. 40° dec. 137°)	C 56.53 H 4.74 N 10.13 P 11.21	56.40 4.85 9.85 10.98	C=N_2 2080 P=O ~1240 POC 1030	3.78 (d, 6H, $POCH_3$, J_{PH} = 12.0), 7.20–7.90 (m, 7H, fine structure)
C_2H_5 **11**	18	6.5 (yellow oil)	C 33.71 H 6.22 N 15.72 P 17.38	33.97 6.44 15.67 17.52	C=N_2 2080 P=O 1265 POC ~1040	1.17 (t, 3H, CH_3CH_2, J_{HH} = 7.5), 2.20 (d of q, 2H, CH_3CH_2, J_{PH} = 9.5), 3.75 (d, 6H, $POCH_3$, J_{PH} = 12.0)
$C_6H_5CH_2$ **14**	11.0	7.3 (yellow oil)	N 9.46 P 10.45	9.45 10.45	C=N_2 2030 P=O ~1290 POC ~1050	3.42 (d, 2H, $CH_2C_6H_5$, J_{PH} = 9.6), 3.67 (d, 6H, $POCH_3$, J_{PH} = 12.0), 7.27 (m, H aromatic)

[a]All the diazo compounds were purified by chromatography on a silica gel column.
[b]CO at 1715 cm^{-1}.
[c]AA′BB′ part of an AA′BB′X (X = P) spectrum, the positions of the 4 main peaks (2 of them are doubled by $^4J_{PH}$ coupling) are given.

TABLE 6. % completion of the cycloaddition reaction

Diazo compound No.	Reaction time (h) 1	2	5	10	24	50
1	n.m.[a]	20	40	55	90	90
2	n.m.	15	30	50	90	90
3	n.m.	25	30	55	90	95
4	n.m.	30	55	70	90	95
5	0	n.m.	50	65	75	95
7	0	0	0	8	11	60
10	—	75	83	100[b]	—	—
11	—	25	50	60	90	—
12	0	0	0	0	10	45

[a]Not measurable.
[b]No more trace of the starting material.

TABLE 7. Cycloaddition conditions; cycloadducts

$RC(N_2)P(O)(OCH_3)_2$		Products isolated		Pyrazoline				
						Analysis %		
R	Reaction time (h)	Compound	Weight (g)	Compound	Melting point	Calcd.	Found	Infrared[a]
p-$CH_3OC_6H_4$	24	Diazo **1**	0.210	*anti* **15**	129–130°	C 59.48 H 6.16	59.86 6.34	P═O ~1240
		syn **16**	0.180			N 8.16 P 8.89	8.29 8.85	P—OC ~1050
1		*anti* **15**	1.97	*syn* **16**	Oil	C 59.48 H 6.16	59.17 6.50	P═O ~1250
						N 8.16 P 8.89	8.50 9.10	P—OC ~1050
p-$CH_3C_6H_4$	24	Diazo **2**	0.260	*anti* **17**	108–109°	C 61.44 H 6.36	61.57 6.50	P═O ~1230
		syn **18**	0.300			N 8.42 P 9.31	8.64 9.10	P—OC ~1040
2		Mixture	0.210	*syn* **18**	Oil	C 61.44 H 6.36	61.57 6.42	P═O ~1240
		anti **17**	2.98			N 8.42 P 9.31	8.64 9.50	P—OC ~1050
p-BrC_6H_4	24	Diazo **3**	0.100	*anti* **19**	147–148°	C 48.36 H 4.56	48.06 4.86	P═O ~1230
		syn **20**	0.340			N 7.05 P 7.80	7.15 8.05	P—OC ~1040
3		*anti* **19**	3.100	*syn* **20**	Oil	C 48.36 H 4.56	48.26 4.80	P═O ~1220
						N 7.05 P 7.80	6.91 7.50	P—OC ~1050

TABLE 7 (*Continued*)

$RC(N_2)P(O)(OCH_3)_2$		Products isolated		Pyrazoline				
						Analysis %		
R	Reaction time (h)	Compound	Weight (g)	Compound	Melting point	Calcd.	Found	Infrared[a]
C_6H_5[b]	24	Diazo **4**	0.2	*syn* **22**	Oil	C 60.37 H 6.02	60.56 6.04	P=O ~1240
4		*syn* **22**	0.1			N 8.80 P 9.73	8.72 9.35	P—OC ~1050
		anti **21**	1.9					
p-$NO_2C_6H_4$	24	Diazo **5**	0.280	*anti* **23**	124°	C 52.90 H 4.99	53.19 5.05	P=O ~1240
5		*syn* **24**[c]	0.230			N 11.56 P 8.52	11.81 8.77	P—OC ~1100
		anti **23**	0.980					
p-$CH_3OCOC_6H_4$	24	Diazo **6**	0.150	*anti* **25**	149°	C 57.46 H 5.63 N 7.44 P 8.23	57.74 6.03 7.61 8.37	P=O ~1240 P—OC ~1050 CO 1725
		syn **26**	0.332					
6		*anti* **25**	3.290	*syn* **26**	145°	C 57.46 H 5.63 N 7.44 P 8.23	57.20 5.59 7.73 8.31	P=O ~1240 P—OC ~1050 CO 1725
o-$CH_3OC_6H_4$	54	Diazo **7**	0.780	*anti* **27**	94–95°	C 59.48 H 6.16 N 8.16 P 8.89	59.22 6.20 8.28 9.09	P=O ~1270 P—OC ~1050
7		*anti* **27**	3.570					
α-Naphthyl	168	Diazo **8**	0.120	*anti* **28**	136–138°	C 65.21 H 5.74 N 7.60 P 8.40	65.48 5.71 8.01 8.74	P=O ~1230 P—OC 1050
8		*anti* **28**	3.130					
β-Naphthyl	24	Diazo **9**	0.110	*anti* **29**	128°	C 65.21 H 5.74 N 7.60 P 8.40	65.31 5.76 7.86 8.23	N=N 1550 P=O ~1230 P—OC ~1050
		syn **30**	0.250					
9		*anti* **29**	1.970	*syn* **30**	Oil	C 65.21 H 5.74 N 7.60 P 8.40	65.47 5.53 7.78 8.59	P=O ~1230 P—OC ~1050

TABLE 7 (*Concluded*)

$RC(N_2)P(O)(OCH_3)_2$ R	Reaction time (h)	Products isolated: Compound	Products isolated: Weight (g)	Pyrazoline: Compound	Pyrazoline: Melting point	Pyrazoline: Analysis % Calcd.	Pyrazoline: Analysis % Found	Pyrazoline: Infrared[a]
C_2H_5	27	No diazo left		*anti*[e] **33**	Oil	C 53.33 H 7.05 N 10.36 P 11.46	53.25 7.16 10.18 11.43	P=O ~1230 P—OC ~1040
		Mixture **33** + **34**	1.990					
11		*syn* **34**	2.79					
				syn[e] **34**	Oil	—		P=O 1230 P—OC 1040
iso-C_3H_7	216	Diazo **12**	0.320	*anti*[e] **35**	Oil	C 54.92 H 7.44 N 9.85 P 10.98	54.57 7.14 9.64 11.10	P=O ~1230 P—OC ~1050
		Mixture **35**+**36**[d]	1.390					
12		*syn* **36**	1.360					
				syn[e] **36**	Oil	—		P=O ~1230 P—OC ~1040
tert-C_4H_9	26 days	Diazo **13**	1.900	*syn* **37**	Oil	C 56.36 H 7.77	55.98 8.12	P=O ~1230
		syn **37**	1.040			P 10.38	10.12	P—OC ~1040
13		Unidentified	0.440					
$C_6H_5CH_2$	24	Diazo **14**	0.44	*anti* **38**	82–83°	C 61.47 H 6.37 N 8.43 P 9.32	61.22 6.45 8.55 9.33	P=O ~1220 P—OC ~1040
		syn **39**	1.00					
14		*anti* **38**	1.55					
				syn **39**	128–129°	C 61.47 H 6.37 N 8.43 P 9.32	61.10 6.57 8.46 9.54	P=O ~1230 P—OC ~1040

[a]Cm^{-1}.
[b]The *anti* derivative **20** has been described (4).
[c]The *syn* pyrazoline was identified in a mixture with the diazo compound, by n.m.r.
[d]Pure samples of *anti* **33** and **35** respectively could be obtained by further chromatography.
[e]Analyzed as a 1:1 mixture of *syn* + *anti*.

TABLE 8. Nuclear magnetic resonance spectra of the pyrazolines (chemical shifts in δ p.p.m.)

R	8	4	10	7	P—OCH_3	9	5,6	Others
p-$CH_3OCOC_6H_4$	C 0.69	2.42	2.80	3.54	3.70	5.19	6.20	3.93
	Δδ 0.64							(CH_3OCO)
anti **25**	δ_s 1.01							7.85, 7.93
	δ_a 0.37							8.09, 8.17[a]
p-$CH_3OCOC_6H_4$	C 1.49	3.36	2.32	3.65	3.83	4.79	6.25[b]	8.04, 7.95
	Δδ 0.26	or		or	3.51			7.59, 7.50
syn **26**	δ_s 1.49	3.65		3.36				(4H aromatic,
	δ_a 1.23							AA′BB′)
α-Naphthyl	C 0.65	2.24	3.16	3.55	3.29	5.25	6.21	7.39–7.61
	Δδ 0.57				3.68			(m, 7H aromatic)
anti **28**	δ_s 0.94							
	δ_a 0.36							
β-Naphthyl	C 0.71	2.46	2.87	3.56	3.73	5.19	6.18	7.37–8.31
	Δδ 0.50				3.47			(m, 7H aromatic)
anti **29**	δ_s 0.96							
	δ_a 0.46							
β-Naphthyl	C 1.38	3.42	2.45	3.66	3.84	4.78	6.25[b]	7.32–7.90
	Δδ 0.20	or		or	3.46			(m, 7H aromatic)
syn **30**	δ_s 1.48	3.66		3.42				
	δ_a 1.28							
C_2H_5	—	2.71	—	3.52	3.78	5.25	6.21	
anti **33**					3.71			
C_2H_5	C 1.28	3.05	~2	3.55	3.90	4.69	6.23[b]	0.69
	Δδ 0.21	or		or	3.87			(t, CH_3)
syn **34**	δ_s 1.39	3.55		3.05				
	δ_a 1.18							
iso-C_3H_7		2.75	2.34	3.50	3.63	4.98	6.16	1.63, 1.29,
anti **35**					3.67			(2d, 6H, nonequivalent
								$CHMe_2$)
iso-C_3H_7		3.09	1.87	3.56	3.87	4.67	6.21[b]	0.56, 1.22
syn **36**		or		or	3.80			(2d, 6H, nonequivalent
		3.56		3.09				$CHMe_2$)
tert-C_4H_9	C 1.23	3.05	1.94	3.55	3.82	4.72	6.24[b]	1.03 (s, $(CH_3)_3C$)
	Δδ 0.17	or		or				
syn **37**	δ_A 1.32	3.55		3.05				
	δ_B 1.15							

TABLE 8 (*Concluded*)

R		8	4	10	7	P—OCH_3	9	5,6	Others
$C_6H_5CH_2$	C	1.03	2.84	2.47	3.57	3.45	5.05	6.21	3 (m, 2H, CH_2Ph),
	$\Delta\delta$	0.31				3.34			7.20–7.60
anti **38**	δ_A	1.34							(m, H aromatic)
	δ_B	0.72							
$C_6H_5CH_2$	C	1.10	2.99	1.90	3.28	3.94	3.40	6.08[b]	3.29 (ABX m, 2H, CH_2Ph,
	$\Delta\delta$	0.34	or		or	3.92			$\delta_A = 3.58$, $\delta_B = 3.04$,
syn **39**	δ_s	1.27	3.28		2.99				$J_{AB} = 14.0$, $J_{PA} = 6.2$,
	δ_a	1.01							$J_{PB} = 8.1$)

[a]AA′BB′ part of an AA′BB′X spectrum (X = ^{31}P). The main absorptions are given.
[b]Center of an eight-line multiplier.

TABLE 9. Nuclear magnetic resonance spectra of pyrazolines (coupling constants[a] in Hz)

R	H_{8a},H_{8s}	H_9,H_{10}	H_{8s},H_9	H_{8s},H_{10}	H_5,H_6	P,H_{10}	P,H_9	P—OCH_3	Others[b]
p-$CH_3OCOC_6H_4$ *anti* **25**	10.0	6.5	1.0	1.5	4.8[c]	19.5	4.0	10.0[d]	P,H aromatic = 2.25
p-$CH_3OCOC_6H_4$ *syn* **26**	9.2	6.0	—	—	6.0	6.0	6.0	10.5	P,H aromatic = 2.25 5,4 = 6,7 = 3.2
α-Naphthyl *anti* **28**	10.0	6.4	1.0	1.6	4.5[c]	19.2	4.0	10.8	—
β-Naphthyl *anti* **29**	10.0	6.0[d]	—	—	4.5[c]	20.0	4.4	10.8	—
β-Naphthyl *syn* **30**	9.2	6.0		—	5.6	6.0		10.8	5,4 = 6,7 = 3.2
C_2H_5 *anti* **33**	9.2	6.8	1.0	—	—	—	4.8	11.2	
C_2H_5 *syn* **34**	8.0	6.6	1.0	—	6.0	—	6.6	10.2	CH_3CH_2 = 7.2 5,4 = 6,7 = 3.2
iso-C_3H_7 *anti* **35**	—	6.2	1.2	1.6	—	20.0		11.0[d]	$CH(CH_3)_2$ = 6.4
iso-C_3H_7 *syn* **36**	—	6.5	1.0	1.5	5.7	6.5	6.5	10.8	$CH(CH_3)_2$ = 5.2 5,4 = 6,7 = 3.2
tert-C_4H_9 *syn* **37**	10.0	6.4	1.0	—	—	6.4	6.4	10.0	
$C_6H_5CH_2$ *anti* **38**	9.0	6.0	—	1.5	—	18.0	—	10.2	
$C_6H_5CH_2$ *syn* **39**	10.0	6.0	—	1.5	6.0	6.0	—	10.6	*p*-CCH_2Ph: 6.2 and 8.1 5,4 = 6,7 = 3.0

[a] ± 0.2 Hz.
[b] All the H_9 resonances show, in addition, a small coupling (1.0 Hz) with one of the bridgehead (the upfield one in the *anti* derivatives).
[c] $W_{1/2}$.
[d] ± 0.5 Hz.

pletion of the reaction in this way. The % completion given here can be estimated to be accurate within ±5%. For the *tert*-butyl derivative **13**, there was no noticeable reaction after 50 h. No kinetic studies were done on **6**, **8**, **9**, and **14** (Table 6).

General Procedures for the Cycloaddition Reactions

A mixture of norbornadiene (40 ml), diazophosphonate (3 g), and CH_2Cl_2 (3 ml) was warmed at a bath temperature never exceeding 55–60°. The proportions were changed slightly for the *p*-methylphenyldiazo derivative **2** (norbornadiene, 50 ml, diazo compound, 3.42 g, and CH_2Cl_2, 5 ml) and for the *p*-nitrophenyldiazo derivative **5** (norbornadiene, 35 ml, diazo compound, 2 g, CH_2Cl_2, 2 ml). The reaction time varied from 24 h to 26 days (see Table 7). The addition with the phenyl **4** and the methyl **10** derivatives have been described (4). The reaction time was 24 h for both reactions.

General Procedure for the Isolation of the Cycloadducts

The reaction mixture was poured as such on a 180 g silica gel column chromatograph. Excess diazo compound was eluted with ether while the pyrazolines came out with MeOH–ether mixtures. In the case of the aryl derivatives, the *syn* epimer was eluted first (5% MeOH in ether) and then the *anti* (10% MeOH in ether). Separation was much more difficult with alkyl derivatives. The addition of the methyl derivative **10** has already been described (4). For all the alkyl derivatives, the excess diazo compound was eluted with pure ether. In the case of the ethyl **11** and the isopropyl **12** derivatives, the *anti* epimer was eluted before the *syn*; the eluent in both cases was a 20% solution of MeOH in ether. As to the *tert*-butyl diazo compound **13**, only one pyrazoline (*syn*) could be detected and was isolated with MeOH–ether (20:80).

Nuclear Magnetic Resonance Spectra of the Pyrazolines (Tables 8 and 9)

Those spectra are typical of a *syn* or an *anti* configuration. For all isomers, H_8 appears as an AB quartet, the center (C) of which is given; H_{8s} (*syn* to the 5,6 double bond) is assigned the low-field signals because of long-range couplings with H_9 and H_{10} protons; otherwise (*e.g.* compound **36**) the assignment (*s* or *a*) is not specified (δ_A and δ_B are given). P—OCH_3 gives two doublets (unequivalent OCH_3's).

In the *anti* isomers, the bridgehead protons (H_4 and H_7) are broad singlets > 1.0 p.p.m. apart; H_{10} gives rise to a d or d of d signal (eight lines in all) by coupling with H_9, H_{8s}, and P; H_9 appears as a d of d (coupling with P, H_{10}; fine resolution shows each signal as a t, due to coupling with H_{8s} and either H_4 or H_7); H_5 and H_6 each give a narrow multiplet; $w_{\frac{1}{2}}$ is given.

In the *syn* isomers the bridgehead protons are broad s 0.3–0.5 p.p.m. apart, and no assignment is made; H_{10} gives rise to a t signal (in fact it is a d of d by coupling with H_9 and P; the fine structure reveals further long-range coupling with H_{8s}); H_9 appears as a t (in fact d of d, by coupling with P and H_{10}; also small couplings with H_{8s} and either H_4 or H_7 are visible); H_5 and H_6 give an eight-line multiplet (AB part of an ABXY spectrum by coupling with H_4 and H_7) the center of which is given in Table 8.

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