not visible); ^{31}P NMR ($CDCl_3$) δ 32.72; MS, m/z (rel intensity) 407 (17), 375 (26), 315 (5), 288 (8), 229 (39), 202 (57), 201 (62), 183 (8), 157 (10), 133 (10), 113 (27), 101 (11), 93 (11), 77 (13), 51 (base peak); HRMS calcd for $C_{23}H_{22}NO_4P$ (M) 407.1286, found 407.1292.

Methyl β-(diphenylphosphinoyl)-*N*-phenylsuccinamate (15): white powder (ether); mp 193–195 °C; IR (KBr) 3255, 1738, 1680, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.57 (ddd, 1 H, ^2J = 16.8, ^3J = 3.4, $^3J_{H,P}$ = 11.2, H-2), 3.15 (ddd, 1 H, ^2J = 16.8, ^3J = 10.2, $^3J_{H,P}$ = 6.6, H-2), 3.59 (s, 3 H, OMe), 4.20 (ddd, 1 H, ^3J = 3.4 and 10.2, $^2J_{H,P}$ = 17.3, H-3), 6.99–7.08 (m, 1-H), 7.18–7.62 (m, 10 H), 7.73–7.90 (m, 4 H), 9.4 (br s, 1 H, *N*-H); ^{13}C NMR ($CDCl_3$) δ 31.12 (C-2), 45.2 (d, $^1J_{C,P}$ = 60, C-3), 52.2 (OMe), 120.1, 124.3, 128.6, 128.7, 128.9, 129.0, 131.4, 132.5, 132.6, 132.7 (each C–H), 128.9, 129.9, 130.9 (each q-C, Ph_2PO), 137.7 (q-C, *N*-Ph), 165.2 (q-C), 171.4 (q-C, d, $J_{C,P}$ = 15) (each C=O); ^{31}P NMR ($CDCl_3$) δ 34.89; MS, m/z (rel intensity) 407 (M, 9), 376 (6), 375 (12), 315 (32), 287 (12), 274 (18), 232 (12), 231 (21), 229 (11), 202 (58), 201 (68), 167 (22), 113 (27), 101 (14), 77 (28), 51 (base peak); HRMS calcd for $C_{23}H_{22}NO_4P$ (M) 407.1286, found 407.1295.

Diphenylphosphinoyl-Substituted Ylides. 2. 1,3-Dipolar Cycloaddition of α-(Diphenylphosphinoyl)glycine Ester Imines. Dipolar Cycloaddition as the Rate-Determining Step[1]

J. J. G. Steven van Es, Annemarie ten Wolde, and Arne van der Gen*

Department of Organic Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

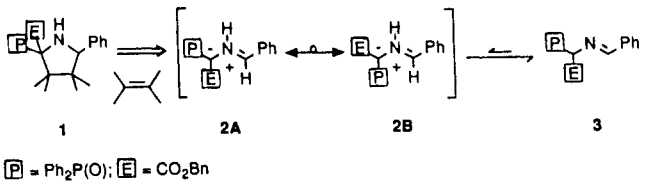
Received December 5, 1989

The thermal 1,3-dipolar cycloaddition of benzyl *N*-benzylidene-α-(diphenylphosphinoyl)glycinate (**3**) has been investigated as a general route to polyfunctionalized 2-(diphenylphosphinoyl)pyrrolidines. The Psyn and Panti dipoles **2A** and **2B**, generated via a formal [1,2]-H shift in chloroform or acetonitrile at reflux, were allowed to react with a variety of dipolarophiles to give the desired pyrrolidines, generally in good yields. When dipolar cycloaddition was the rate-determining step, a strong preference for reaction of the Psyn dipole **2A** was observed. With monoactivated dipolarophiles, the activating substituent is exclusively found at C-4 of the pyrrolidine ring, with a strong preference for Psyn 4-endo product formation. Only with cinnamonitrile was a nonregiospecific addition observed. With diactivated dipolarophiles, product distribution was markedly influenced by the substituent present at the β-carbon atom of the dipolarophile. This substituent could either enhance the selectivity for Psyn endo product formation, lead to preferential formation of the 4-exo adduct, or induce preferential addition to the Panti dipole **2B**. Structure eludication of the adducts with the aid of ^1H and ^{13}C NMR is discussed.

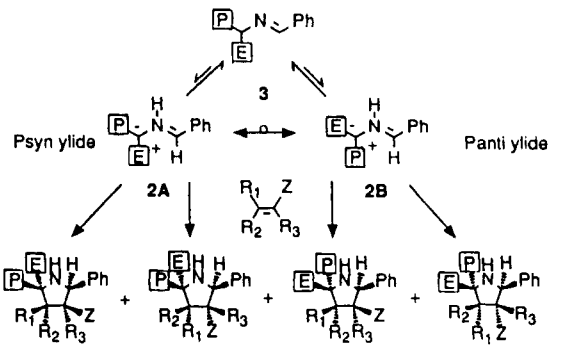
Introduction

The 1,3-dipolar cycloaddition of azomethine ylides,[2,3] stabilized by both a diphenylphosphinoyl and an ester group, has been investigated as a general route to polyfunctionalized 2-(diphenylphosphinoyl)pyrrolidines.[4] For the synthesis of N-unsubstituted pyrrolidines of type **1** (Scheme I), generation of the required ylides **2** via a formal [1,2]-H shift[2b,5] in α-(diphenylphosphinoyl)glycine ester imines such as **3** may be used.

Scheme I



Scheme II



In the preceding article,[1] the synthesis of the required starting materials was described. Also, the results of a study of the addition to the very reactive dipolarophile *N*-phenylmaleimide (i.e., with *dipole formation* as the rate-determining step) were reported. The Psyn Eanti **2A**

(1) Part 1: Van Es, J. J. G. S.; Jaarsveld, K.; Van der Gen, A. *J. Org. Chem.*, preceding paper in this issue.

(2) For recent reviews, see: (a) Lown, J. W. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 653–732. (b) Grigg, R. *Chem. Soc. Rev.* **1987**, *16*, 89. (c) Pearson, W. H. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1988; Vol. 1, Stereoselective Synthesis (Part A), pp 323–358. (d) Tsuge, O.; Kanemasa, S. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press, Inc.: San Diego, 1989; Vol. 45, pp 231–349.

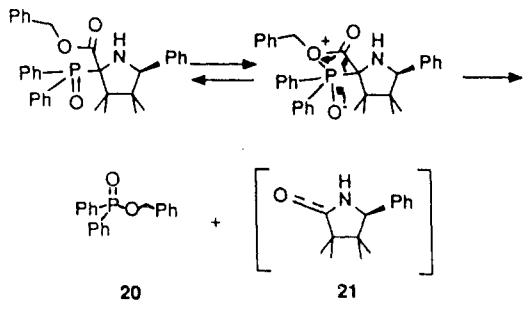
(3) Some leading references: (a) Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1987**, *35*, 593. (b) Ardill, H.; Grigg, R.; Sridharan, V.; Surendrakumar, S. *Tetrahedron* **1988**, *44*, 4953. (c) Joucla, M.; Mortier, J. *Bull. Soc. Chim. Fr.* **1988**, 579. (d) Padwa, A.; Gasdaska, J. R.; Haffmanns, G.; Rebello, H. *J. Org. Chem.* **1987**, *52*, 1027. (e) Chastanet, J.; Roussi, G. *Ibid.* **1988**, *53*, 3808. (f) Tsuge, O.; Kanemasa, S.; Ohe, M.; Takenaka, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4079. (g) Tsuge, O.; Kanemasa, S.; Sakamoto, K.; Takenaka, S. *Ibid.* **1988**, *61*, 2513. (h) Vedejs, E.; Grissom, J. W. *J. Org. Chem.* **1988**, *53*, 1876. (i) Yaozhong, J.; Shengde, W. *Synth. Commun.* **1987**, *17*, 33.

(4) For application of 2-(diphenylphosphinoyl)pyrrolidines as Horner–Wittig reagent: (a) Bakker, B. H.; Tjin A-Lim, D. S.; Van der Gen, A. *Tetrahedron Lett.* **1984**, *25*, 4259. (b) Zorgdrager, J.; Van der Gen, A. *Recl. Trav. Chim. Pays-Bas* In press.

(5) (a) Grigg, R.; Kemp, J.; Warnock, W. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2275 and references cited therein. (b) Tsuge, O.; Ueno, K.; Kanemasa, S.; Yorozu, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1809 and references cited therein. (c) Kairi, A. M.; Hamelin, J. *Tetrahedron Lett.* **1987**, *28*, 1397. (d) Joucla, M.; Fouchet, B.; Hamelin, J. *Tetrahedron* **1985**, *41*, 2707.

0022-3263/90/1955-4069$02.50/0

Scheme III



20 21

and Panti Esyn **2B** dipoles were formed simultaneously and trapped to give the Psyn Eanti endo and Panti Esyn endo adducts in excellent combined yields.

This paper describes results obtained with less reactive dipolarophiles, i.e., when *dipolar cycloaddition* is the rate-determining step. The scope of the thermal cycloaddition of benzyl *N*-benzylidene-α-(diphenylphosphinoyl)glycinate (**3**)[6] is outlined. The influence of the solvent will be evaluated. Attempts to catalyze the reaction will be briefly discussed. The structures of the cycloadducts obtained were determined by NMR spectroscopy.

Results of Dipolarophile Variation

General Remarks. Several dipolarophiles were tested in the thermal cycloaddition reaction (Scheme II) using the benzyl ester **3**. The results are presented in Table I. Reactions were monitored by drawing small aliquots from the reaction mixture and recording the ^{31}P NMR spectra. In all cases studied, the relative intensities of the peaks present in the ^{31}P NMR spectra corresponded nicely with the product composition as estimated from ^{1}H NMR spectra (which is usually more laborious, due to the complexity of the multiplets), as well as with the isolated yields (as long as products were stable to the conditions of isolation).

In Table I, two figures are recorded for the yield of each cycloadduct. The first one refers to the *relative* amount, in which the product was present in the crude reaction mixture. In two instances (entries 12 and 15) where the sum does not add up to 100%, one or more additional phosphorus-containing compounds were present in the crude reaction mixture that could not be isolated. In two other cases (entries 7 and 8) only the major products were isolated (see below).

The number between parentheses refers to the *isolated* amount of each pure product (for details see Experimental Section). Purification was routinely carried out by flash chromatography and crystallization. In one instance (entry 17) no complete separation could be accomplished. In another case (entry 3) product isomerization occurred. These yields have been included in the column listing the total amount of isolated cycloadducts.

In some cases, benzyl diphenylphosphinate (**20**) was present in the crude reaction mixture (entries 13 and 14),

Table I. Thermal Cycloaddition of Benzyl *N*-Benzylidene-α-(diphenylphosphinoyl)glycinate (3) to Various Activated Olefins in Chloroform or Acetonitrile at Reflux

entry	dipolarophile name	R_1	R_2	R_3	Z	conditions sol/refl	[ ] (M)	t (h)	3	no.	yield[a] (isolated[b]) (%) a	b	c	d	20	total[c]	selectivity Psyn	4-endo
1	dimethyl fumarate		CO_2Me		CO_2Me	$CHCl_3$	0.1	6		4	93 (87)[d]	4		3 (3)		90	97	93
2	dimethyl fumarate		CO_2Me		CO_2Me	CH_3CN	0.1	6		4	93 (90)[d]	4		3 (3)		93	97	93
3	dimethyl maleate[e]	CO_2Me			CO_2Me	$CHCl_3$	0.4	65		5	39 (8)[f]	34 (30)	27 (18)			73[f]	73	66
4	fumaronitrile		CN		CN	$CHCl_3$	0.1	6		6	93 (88)	2 (2)		5 (5)		95	95	93
5	fumaronitrile		CN		CN	CH_3CN	0.1	6		6	93 (88)	2 (2)		5 (5)		95	95	93
6	maleonitrile	CN			CN	$CHCl_3$	0.1	6		7	5 (–)	90 (86)	5 (4)		(4)	90	95	10
7	methyl (*Z*)-β-cyanoacrylate	CN			CO_2Me	$CHCl_3$	0.1	6		8		33 (25)				46		
		CO_2Me			CN					9			27 (21)					
8	methyl (*E*)-β-cyanoacrylate		CN		CO_2Me	$CHCl_3$	0.1	6		10	80 (60)					60		
9	ethyl acrylate				CO_2Et	$CHCl_3$	0.4	24		11	81 (81)	9 (7)	10 (8)			96	90	91
10	ethyl acrylate				CO_2Et	CH_3CN	0.4	24	17 (–)	11	70 (37)	6 (–)	7 (–)			37[g]	91	93
11	methyl methacrylate			Me	CO_2Me	$CHCl_3$	0.4	48		12	77 (59)	11 (5)	12 (8)		(2)	78	88	89
12	methyl crotonate		Me		CO_2Me	$CHCl_3$	0.4	72	33 (24)	13			25 (22)		11 (23)	22[h]		
13	methyl cinnamate		Ph		CO_2Me	$CHCl_3$	0.4	84	15 (5)	14	78 (71)				7 (17)	71	100	100
14	acrylonitrile				CN	$CHCl_3$	0.4	44		15	32 (28)	36 (30)	19 (17)		13 (8)	75	78	59
15	cinnamonitrile		Ph		CN	$CHCl_3$	0.4	120	15 (7)	16	26 (15)				11 (17)	30[i]		
			CN		Ph					17	31 (15)							
16	β-nitrostyrene		Ph		NO_2	$CHCl_3$	0.4	20	3 (–)	18	97 (70)					70	100	100
17	phenyl vinyl sulfone				SO_2Ph	$CHCl_3$	0.4	20		19	72 (3)	13 (–)	15 (5)			68[j]	85	87

[a] According to ^{31}P NMR. [b] Isolated yield of pure adduct. [c] Total amount of isolated adducts. [d] Product contains 5% of **4b**. [e] Addition of 0.25 equiv of extra dipolarophile after 48 h to effect complete conversion of the starting material. [f] Product isomerization of **5a** to **4a**. [g] After crystallization from ether. No product recovery when flash chromatography of the filtrate was attempted. [h] Two products (19% and 13%) were instable to all conditions of isolation. [i] One product (18%) could not be isolated. [j] 60% of a mixture of **19a** and **19c** isolated after flash chromatography. One product, presumably the Psyn exo adduct **19b**, was instable to all conditions of isolation.

(6) While other primary esters appear similar in scope, the *tert*-butyl ester gave dimerization as the prime reaction mode, yielding a mixture of diastereoisomeric imidazolidines (^{31}P NMR, four pairs of equally intense peaks, which amounted to 90% of the product), along with 10% of the Psyn endo adduct. Although this dimerization proved to be reversible and the resulting ylide could be trapped, the dimerization products still amounted to 70% after two more days of reflux.[7]

(7) Dimerization is also the dominant reaction path with aromatic imines of α-aminomalonates, cf. (a) Amornraksa, K.; Grigg, R. *Tetrahedron Lett.* **1980**, *21*, 2197. (b) Amornraksa, K.; Barr, D.; Donegan, G.; Grigg, R.; Piniti, R.; Visuvanthar, S. *Tetrahedron* **1989**, *45*, 4649.

or it was (also) formed during the isolation procedure (entries 6, 11, 12, and 15). This can be tentatively explained by assuming an interaction between the benzyloxy part of the ester and the phosphorus atom,[8] as depicted in Scheme III, resulting in loss of phosphinate **20**. The simultaneously formed ketene **21** would probably polymerize.

Effect of Solvent. In the cycloaddition of benzyl *N*-benzylidene-α-(diphenylphosphinoyl)glycinate (**3**) to *N*-phenylmaleimide (i.e., dipole formation as the rate-determining step), two dipoles, Psyn **2A** and Panti **2B**, were formed and trapped to give the Psyn endo and Panti endo adducts. The ratio to which they were formed was dependent on the polarity of the solvent.[1]

With the less reactive dipolarophiles studied here, dipole interconversion is expected to occur, as dipolar cycloaddition now becomes the rate-determining step. Thus, similar product ratios in polar and apolar solvents are to be expected. This was indeed observed in those cases studied (entries 1 vs 2, 4 vs 5, and 9 vs 10).

Diactivated Dipolarophiles. With dimethyl fumarate (entries 1 and 2) reaction was complete in 6 h and the products were isolated by flash chromatography. Two fractions were obtained: the first one consisted of the Psyn endo product **4a**, yield 87% (chloroform) or 90% (acetonitrile) (Table I). The second fraction afforded a second product, isolated in 3% yield, which proved to be the Panti exo compound **4d**. Closer inspection of the Psyn endo adduct **4a** revealed the presence of a small amount of a third product, probably the Psyn exo adduct **4b**, that could not be separated.

The reaction with dimethyl maleate (entry 3) was considerably slower and needed addition of extra dipolarophile (0.25 equiv) to reach completion. There is still a preference for formation of the Psyn and endo products, although less so than with the fumarate ester.

Upon isolation by column chromatography the main product, characterized as the Psyn endo adduct **5a**, underwent epimerization at C-3 to give **4a**, the major product of the cycloaddition to dimethyl fumarate. According to ^{31}P NMR, **4a** was not present in the crude reaction mixture. Thus, it can be concluded that the cycloaddition had occurred stereospecifically, consistent with the geometry of the double bond.

When treated with 1 equiv of DBU at room temperature, the Psyn endo product **5a** epimerized completely to **4a** within 30 min (TLC). The reason for this sensitivity to epimerization is probably relief of steric strain between the diphenylphosphinoyl substituent and the cis ester groups at C-3 and C-4. Remarkably, the Panti endo compound **5c** is stable to treatment with DBU, implying that a cis 2,3,4-triester configuration is more favorable.

With fumaronitrile as the dipolarophile (entries 4 and 5), reaction was complete within 6 h and high Psyn endo selectivities were again observed. The main product, isolated in 86% yield by being stirred in ether overnight, proved to be the Psyn 4-endo product **6a**. Some additional **6a** as well as the other two adducts **6b** and **6d** were isolated by flash chromatography.

Maleonitrile reacted as fast as fumaronitrile (cf. entry 6 vs 4). The main product was the Psyn exo adduct **7b**, which could be easily obtained in a pure state by being stirred in ether overnight. One of the minor products (5%), presumably the Psyn endo adduct **7a**, was unstable to all attempted conditions of isolation. Decomposition probably occurred via elimination of phosphinate **20**, which was not present in the original reaction mixture.

Two examples of asymmetrically substituted, diactivated dipolarophiles were investigated. When imine **3** was allowed to react with methyl *cis*-β-cyanoacrylate (entry 7), a complex mixture of eight regio- and diastereoisomers was formed. Still, the two major adducts could be isolated quite efficiently. They were shown to be the Psyn 3-cyano 4-carbomethoxy exo adduct **8b** (present in 33%, isolated yield 25%) and the regioisomeric Panti 3-carbomethoxy 4-cyano endo adduct **9c** (present in 27%, isolated yield 21%). Other products were present in small amounts (less than 10%) in the crude reaction mixture and no attempt was made in this case to purify these minor isomers.

With methyl *trans*-β-cyanoacrylate (entry 8), a clear preference for the Psyn 3-exo cyano 4-endo carbomethoxy product **10a** was observed. This adduct amounted to 80% of the crude reaction mixture and was isolated in 60% yield. No attempts were made to separate the other (minor) isomers.

Monoactivated Dipolarophiles. With ethyl acrylate as the dipolarophile (entry 9), the Psyn endo adduct **11a** again predominated. The major portion of this product (76%) could easily be isolated by merely being stirred in ether overnight. Flash chromatography afforded the remainder of **11a**, as well as the other two cycloadducts **11b** and **11c** in excellent combined yield. In this case, acetonitrile is less suitable as solvent, because of polymerization of the dipolarophile (entry 10).

Upon reaction with methyl methacrylate (entry 11), similar Psyn/anti and endo/exo ratios were observed. Flash chromatography afforded all three cycloadducts in a good combined yield.

With methyl crotonate (entry 12), this picture drastically changed: after 3 days, approximately one-third of the starting material was still present. Prolonged heating was not beneficial. Of the three products formed, two decomposed during flash chromatography or even when stirred in ether (partly via formation of phosphinate **20**). Their structure could not be deduced from the ^1H NMR spectrum of the crude reaction mixture. A third product eluted simultaneously with **20**, but could be separated by being stirred in ether. It was characterized as the Panti endo adduct **13c**.

Methyl cinnamate (entry 13) reacted slowly: after 3.5 days the conversion was 85%. A single product, identified as the Psyn endo adduct **14a**, was formed along with a small amount of phosphinate **20**. Pure **14a** was isolated in 71% yield. In view of the low reactivity of methyl crotonate and methyl cinnamate, the reaction with even less reactive ester-activated dipolarophiles such as methyl tiglate or ethyl 3,3-dimethylacrylate was not investigated.

When acrylonitrile was used as the dipolarophile (entry 14), the Psyn endo **15a** and Psyn exo **15b** products predominated. In contrast to what was observed in the case of ethyl acrylate (entry 9), there was only a marginal preference for endo product formation. By a combination of crystallization and flash chromatography, pure cycloadducts were obtained in a good combined yield.

With cinnamonitrile (entry 15), the expected drop in reactivity resulting from introduction of a β-phenyl substituent (cf. ethyl acrylate and methyl cinnamate) was observed. After 5 days the conversion was 85%. Four products were present, one of which (18%) was unstable to all conditions of isolation. The major product proved to be the Psyn 4-endo cyano adduct **16a**. The other product, isolated in 15% yield, proved to be the Psyn 3-exo cyano 4-endo phenyl compound **17a**. This was the only

(8) Similar interactions with a phosphorus substituent have been observed: (a) Meuwly, R.; Vasella, A. *Helv. Chim. Acta* **1986**, *69*, 25. (b) Kunz, H.; Schmidt, P. *Liebigs Ann. Chem.* **1982**, 1245.

Table II. ^{13}C NMR Shift Data ($CDCl_3$) and Carbon–Phosphorus Couplings[a]

compound					^{13}C NMR ($CDCl_3$)				
no.	R_1	R_2	R_3	Z	C-2 (^1J)	C-3 (s)	C-4 (^3J)	C-5 (^3J)	R_1, R_2, R_3, Z, CO_2Bn
4a		CO_2Me		CO_2Me	73.0 (76)	49.8	52.1 (9)	62.1 (10)	51.2, 51.3, 68.3, 169.8, 170.4, 170.4 (12)
5a	CO_2Me			CO_2Me	72.2 (65)	52.5	52.7 (7)	65.3 (10)	51.1, 51.8, 68.0, 169.2, 170.6, 170.6 (9)
6a		CN		CN	72.9 (70)	38.1	40.6 (7)	63.0 (9)	69.0, 115.0, 115.5, 168.5 (9)
10a		CN		CO_2Me	72.7 (72)	36.4	53.8 (7)	63.8 (9)	51.9, 68.6, 116.3, 169.0, 169.2 (7)
11a				CO_2Et	71.9 (79)	33.2	48.0 (10)	62.8 (12)	13.2, 60.1, 67.8, 170.6, 171.8 (9)
12a			Me	CO_2Me	71.6 (78)	41.6	54.5 (10)	72.8 (12)	24.7, 51.1, 67.9, 172.1 (9), 173.9
14a		Ph		CO_2Me	75.3 (75)	53.8	57.8 (9)	65.3 (9)	51.0, 67.3, 171.0, 171.2 (7)
15a				CN	69.7 (81)	35.1	37.0 (4)	65.7 (9)	68.5, 118.6, 171.9 (9)
16a		Ph		CN	75.5 (76)	55.1	49.7 (7)	65.1 (9)	67.6, 117.9, 170.7 (9)
17a		CN		Ph	72.3 (75)	38.6	53.9 (4)	63.9 (4)	68.7, 117.2, 170.4
18a		Ph		NO_2	74.4 (72)	56.2	97.5 (9)	67.8 (9)	67.7, 170.2 (7)
19a				SO_2Ph	70.9 (79)	32.3	69.5 (6)	62.2 (10)	68.3, 171.2 (10)
5b	CO_2Me			CO_2Me	73.8 (79)	54.9	51.5 (10)	62.7 (3)	51.6, 51.9, 67.7, 169.6, 170.4 (10), 171.0 (12)
6b		CN		CN	76.7 (73)	39.5	41.7	64.6 (4)	69.2, 115.4 (4), 115.8, 170.4 (12)
7b	CN			CN	76.2 (76)	41.3	38.7 (4)	64.6 (4)	69.4, 115.2, 115.3 (13), 168.8 (9)
8b	CN			CO_2Me	73.5 (76)	38.3	54.1	63.1 (4)	52.3, 69.1, 116.4 (10), 168.3, 169.5 (9)
11b				CO_2Et	70.4 (82)	35.0	51.7 (4)	65.3 (10)	13.9, 60.6, 68.1, 172.1, 172.5 (9)
12b			Me	CO_2Me	70.1 (79)	42.9	51.9 (7)	67.1 (12)	20.7, 52.1, 67.9, 170.1 (10), 176.1
15b				CN	74.5 (81)	39.7	35.0 (4)	62.0 (4)	68.9, 119.1 (10), 170.1 (9)
5c	CO_2Me			CO_2Me	74.1 (82)	52.2	52.8 (4)	64.6	51.3, 51.8, 68.2, 169.4 (9), 169.9 (3), 170.7
7c	CN			CN	72.7 (79)	41.1	39.2 (6)	64.7	69.6, 114.8 (4), 114.9, 168.4 (6)
9c	CO_2Me			CN	73.2 (82)	53.1	38.3 (6)	65.9	51.7, 68.9, 115.9 (3), 168.3 (4), 169.3
11c				CO_2Et	72.1 (82)	36.3	49.1	66.9	13.4, 60.1, 67.8, 171.7 (7), 172.4
12c			Me	CO_2Me	71.3 (82)	44.8	53.4	74.4	20.4, 51.1, 67.8, 171.9 (6), 174.4
13c		Me		CO_2Me	73.1 (81)	41.9	56.5 (10)	63.6 (10)	15.5, 51.1, 67.4, 171.1, 171.9 (10)
15c				CN	70.4 (79)	34.7	35.3 (9)	63.0 (12)	68.4, 118.3, 171.5 (7)
19c				SO_2Ph	70.8 (79)	32.4	65.2 (9)	62.4 (12)	68.2, 171.1 (5)
4d		CO_2Me		CO_2Me	73.1 (88)	55.7	54.6 (4)	66.3	52.0, 52.6, 170.3, 170.5, 172.0 (3)
6d		CN		CN	72.2 (84)	41.3	39.7 (4)	67.3	69.8, 115.0 (3), 115, 169.3

[a] All spectra were recorded at 50 MHz. Aromatic resonances are recorded in the Experimental Section. Where appropriate, absolute values for coupling constants are given. When no definite assignments could be made for the pyrrolidine ringcarbons (**6b**, **19a**, **19c**), carbon–hydrogen correlated NMR spectra were recorded.

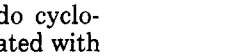
instance in which a *regioisomeric* adduct was found.

Nitro-activated olefins constitute an interesting class of dipolarophiles, because the nitro group in the product may be transformed into a host of other functionalities. Using β-nitrostyrene (entry 16), the reaction was complete within 24 h and a single product was formed. Stirring in ether afforded the pure Psyn endo adduct **18a** in 70% yield.

Phenyl vinyl sulfone also reacted smoothly (entry 17) and gave a result comparable with the one obtained with ethyl acrylate (entry 9). Product isolation proved to be more difficult, however. Stirring in ether overnight (even in the presence of triethylamine) caused disappearance of a minor product, presumably the Psyn exo adduct **19b**. The precipitate was a mixture of the two endo cycloadducts **19a** and **19c**, which could only be separated with difficulty by flash chromatography (silica, ether–triethylamine).[9] It should be borne in mind that for several foreseeable applications such a separation is not necessary.[1]

Attempted Catalysis of the Cycloaddition. The cycloaddition of imines of α-amino acid esters can be catalyzed by various metal salts (generally acetates), when cycloaddition is the rate-determining step. Exclusive formation of the ester syn endo adduct can be induced.[10] By addition of triethylamine the scope of this catalysis can be enhanced further.[11]

With benzyl ester **3** no enhancement in reaction rate occurred. With lithium acetate dihydrate and ethyl acrylate in refluxing THF, an increase in selectivity for the Psyn endo adduct **11a** was observed: 92% versus 81% in the uncatalyzed reaction (cf. Table I, entry 9). The product was isolated in 85% yield after being stirred in ether. Unfortunately, with less reactive dipolarophiles and with other metal salts, a competition between cycloaddition and removal of the ester group[12] to give *N*-benzylidene(aminomethyl)diphenylphosphine oxide (**22**)[1] was observed. With zinc acetate dihydrate even exclusive debenzyloxycarbonylation of **3** occurred to give **22** and benzyl alcohol.



22

Attempted catalysis with lithium bromide and triethylamine in THF at room temperature[11b] gave only decomposition with formation of benzyl alcohol, not benzyl bromide (according to ^1H NMR). Below approximately −50 °C the dipole, generated with 1 equiv of LDA, was stable, but showed no reaction with dipolarophiles. Increasing the reaction temperature led to decomposition of the starting material. No cycloaddition was observed.[13]

Identification of the Cycloadducts

Structure determination of the cycloadducts with the aid of NMR spectroscopy was greatly facilitated by con-

(9) Leaving out the triethylamine in the eluent resulted in a better separation of the cycloadducts, but a significant reduction in yield of Psyn endo compound **19a** and formation of the mixed anhydride of diphenylphosphinic and benzenesulfenic acid were observed.

(10) (a) Grigg, R.; Gunaratne, H. Q. N.; Sridharan, V. *Tetrahedron* **1987**, *43*, 5887. (b) Grigg, R.; Gunaratne, H. Q. N. *J. Chem. Soc., Chem. Commun.* **1982**, 384.

(11) (a) Barr, D. A.; Grigg, R.; Gunaratne, H. Q. N.; Kemp, J.; McMeekin, P.; Sridharan, V. *Tetrahedron* **1988**, *44*, 557. (b) Tsuge, O.; Kanemasa, S.; Yoshioka, M. *J. Org. Chem.* **1988**, *53*, 1384. (c) Kanemasa, S.; Yoshioka, M.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 869.

(12) Cf. Krapcho, A. P. *Synthesis* **1982**, 805, 893.

(13) This instability is in marked contrast with the stability of the anion of the corresponding phosphonate, which was synthesized at 0 °C. Cf. Ratcliffe, R. W.; Christensen, B. G. *Tetrahedron Lett.* **1973**, 4645. Elimination of the alkoxide was probably also the reason, that phenyl esters could not be prepared via alkoxycarbonylation of the imine **22** at low temperature (unpublished observations).

Table III. ^{1}H NMR Chemical Shifs and Multiplicities for the Obtained Cycloadducts[a]

compound					^{1}H NMR shift (multiplicity)						
no.	R_1	R_2	R_3	Z	H-3α	H-3β	H-4	H-5α	N-H	CO_2Bn	R_1, R_2, R_3, Z
							α				
4a		CO_2Me		CO_2Me		4.26 (dd)	3.82 (t)	4.74 (dd)	*f*	5.12, 5.12	3.04 (s, 3 H), 3.19 (s, 3 H)
5a	CO_2Me			CO_2Me	3.93 (d)		3.40 (dd)	4.82 (dd)	3.46 (br t)	5.01, 5.01	2.99 (s, 3 H), 3.38 (s, 3 H)
6a		CN		CN		3.99 (dd)	3.69 (dd)	4.76 (dd)	3.40 (dd)	5.02, 5.08	
10a		CN		CO_2Me		4.08 (t)	3.65 (t)	4.90 (d)	*f*	5.08, 5.09	3.10 (s, 3 H)
11a				CO_2Et[b]	2.80 (dd)	2.80 (dt)	3.23 ('q')	4.60 (d)	2.78 (d)	5.02, 5.10	0.70 (t, 3 H, J = 7.1), 3.46 (AA′ q, 2 H)
12a			Me	CO_2Me	2.52 (dt)	3.21 (dd)		3.97 (d)	3.20 (br)	5.07, 5.12	1.20 (s, 3 H), 2.89 (s, 3 H)
14a		Ph		CO_2Me		4.32 (dd)	3.70 (dd)	5.26 (dd)	3.79 (dd)	4.50, 4.67	2.82 (s, 3 H)
15a				CN[c]	2.84 (ddd)	3.11 (ddd)	2.58 (dt)	4.28 (d)		5.05, 5.16	
16a		Ph		CN		4.45 (dd)	3.60 (dd)	5.19 (dd)	3.61 (dd)	4.24, 4.61	
17a		CN		Ph		4.12 (dd)	3.89 (dd)	4.82 (dd)	3.24 (dd)	5.08, 5.16	
18a		Ph		NO_2		4.68 (dd)	5.55 (dd)	5.55 (t)	4.1 (br)	4.29, 4.56	
19a				SO_2Ph	3.14 (ddt)	2.92 (dt)	3.52 (ddd)	4.64 (dd)	3.25 (d)	5.09, 5.17	
							β				
5b	CO_2Me			CO_2Me		4.31 (dd)	3.57 (dd)	4.90 (ddd)	3.43 (br t)	4.64, 4.99	3.32 (s, 3 H), 3.47 (s, 3 H)
6b		CN		CN[d]	4.60 (d)		3.67 (dd)	4.51 (dd)		4.90, 5.19	
7b	CN			CN		4.37 (dd)	3.79 (dd)	4.76 (ddd)	3.40 ('t')	4.98, 5.11	
8b	CN			CO_2Me[c]		4.45 (dd)	3.42 (dd)	4.81 (dd)		4.97, 5.09	3.67 (s, 3 H)
11b				CO_2Et	2.85 (ddd)	2.97 (ddd)	2.59 (dt)	4.35 (dd)	3.1 (br)	5.12, 5.12	1.05 (t, 3 H, J = 7.1), 3.97 (AA′ q, 2 H)
12b			Me	CO_2Me	3.28 (dd)	2.39 (dd)		4.65 (d)	3.22 (br d)	5.06, 5.12	0.46 (s, 3 H), 3.57 (s, 3 H)
15b				CN[c]	2.37 (ddd)	1.90 (ddd)	4.16 (ddd)	4.62 (dd)		5.07, 5.07	
							α				
5c	CO_2Me			CO_2Me	4.25 (dd)		3.38 ('t')	3.85 (dd)	4.06 (dd)	4.80, 4.97	3.25 (s, 3 H), 3.30 (s, 3 H)
7c	CN			CN	4.22 (dd)		3.69 (dd)	3.91 (dd)	3.80 (dd)	5.11, 5.11	
9c	CO_2Me			CN	4.16 (dd)		3.37 ('t')	3.76 (dd)	4.07 (dd)	5.04, 5.15	3.30 (s, 3 H)
11c				CO_2Et[e]	2.99 (ddd)	3.01 (ddd)	2.83 ('q')	3.75 (dd)	3.77 (dd)	5.04, 5.12	0.74 (t, 3 H, J = 7.1), 3.57, 3.70 (AA′ q, 2 H)
12c			Me	CO_2Me	2.62 (dd)	3.20 (dd)		2.89 (d)	3.81 (dd)	5.04, 5.12	0.96 (s, 3 H), 3.15 (s, 3 H)
13c		Me		CO_2Me		3.32 (m)	3.06 (dd)	4.96 (ddd)	3.15 (br)	5.02, 5.10	1.04 (d, 3 H, J = 6.6), 3.03 (s, 3 H)
15c				CN[c]	2.69 (ddd)	3.14 (ddd)	3.32 (ddd)	4.28 (d)		5.03, 5.14	
19c				SO_2Ph[c]	2.84 (dt)	3.00 (dd)	3.91 ('q')	4.37 (d)		5.08, 5.12	
							β				
4d		CO_2Me		CO_2Me	4.20 (dd)		3.26 ('t')	3.06 ('t')	3.50 (dd)	4.79, 4.92	3.48 (s, 6 H)
6d		CN		CN	4.20 (dd)		3.08 ('t')	3.33 ('t')	3.55 (dd)	5.06, 5.15	

[a] All spectra were recorded at 300 MHz in $CDCl_3$, unless noted otherwise. The assignments "α" and "β" refer to protons trans, respectively, cis to the C-5 phenyl substituent. Aromatic resonances are reported in the Experimental Section. [b] Recorded in acetone-d_6. [c] Recorded in $CDCl_3$–$CD_3OD \approx 5:1$. [d] Recorded in CD_3OD. [e] Recorded at 400 MHz. [f] Not determinable.

sidering the ^{31}P–^1H and ^{31}P–^{13}C coupling constants. As will be illustrated below, the coupling to carbon allowed direct determination of the regiochemistry. Information concerning the conformational preference of the phosphinoyl substituent could also be obtained from the ^{13}C NMR spectra. Coupling to the vicinal proton(s) served to determine the relative configuration around the C-(2)–C(3) bond.

^{13}C NMR Spectroscopy. The ^{13}C NMR spectra of the cycloadducts share some characteristic features. With the exception of C-3, all ring carbon atoms show significant coupling to phosphorus (Table II). Coupling to C-2 was generally in the order to 70 to 85 Hz, while coupling to C-4 and C-5 was mostly in the range of 7 to 12 Hz. $^2J_{PCC}$ was 0 for all cycloadducts. Thus, by merely inspecting the multiplicity of the ring carbon resonances in the ^{13}C NMR spectrum of a cycloadduct, obtained with an asymmetrically substituted dipolarophile, the regiochemistry can immediately be assessed. This lack of coupling to C-3 has also been observed for 2-phosphonopyrrolidines[14] and comparable phosphine oxides.[15]

In some Panti adducts and nitrile-substituted Psyn adducts, smaller couplings of phosphorus to C-4 and/or C-5 were observed, probably arising from a more axial orientation of the phosphinoyl substituent, so that the corresponding dihedral angles come close to 90°.[14-16] Coupling to carbon substituents at C-3 only occurred when this substituent and the phosphorus substituent at C-2 occupied a trans quasi diaxial orientation.[17]

Little use appears to have been made of long-range phosphorus–carbon couplings for structure assignment or stereochemical analysis. In saturated ring systems, the possibility needs to be considered that a "W" pathway may lead to enhanced transmission.[16b] For a five-membered ring this implies an envelope conformation having both the phosphinoyl substituent and the substituent at C-4 or C-5 in quasi equatorial positions, located cis on the ring.

With the compounds studied thus far, $^4J_{P-C}$ were only observed when the phosphinoyl substituent and the substituent at C-4 were quasi axially disposed, trans relative to each other (compare **5c**, **7c**, and **9c**; cf. **15b**). The quasi

(14) For some 2-phosphonopyrrolidines, compare: Rabiller, C.; Dehnel, A.; Lavielle, G. *Can. J. Chem.* **1982**, *60*, 926. The coupling constants of phosphine oxides to both hydrogen and carbon will be significantly smaller, because of the smaller electronegativity of phosphine oxides, as compared to phosphonates.[16d]

(15) Van Es, J. J. G. S.; Van der Gen, A. Unpublished results.

(16) (a) For a general treatice on phosphorus–proton couplings; Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VHC: Weinheim, 1987; pp 365–390. (b) For a general treatice on phosphorus–carbon couplings: Quin, L. D. ref 16a, pp 391–424. Compare: (c) Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chestnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136. (d) Thiem, J.; Meyer, B.; Paulsen, H. *Chem. Ber.* **1978**, *111*, 3325. (e) Buchanan, G. W.; Morin, F. G. *Can. J. Chem.* **1980**, *58*, 530 and references cited therein. (f) Neeser, J.; Tronchet, J. M. J.; Charollais, E. J. *Ibid.* **1983**, *61*, 2112.

(17) $^1J_{P-C}$ was not decreased in these adducts, which is in contrast to what has been noted for axially disposed phosphonates.[14,16]

Table IV. Proton–Proton and Proton–Phosphorus Coupling Constants (in Hz)[a]

compound					$^2J_{H,H}$		$^3J_{H,H}$				$^3J_{H,P}$		
no.	R_1	R_2	R_3	Z	3α–3β	CO_2Bn	3α–4	3β–4	4–5α	5α–1	3α–P	3β–P	NH–P
							α	α	α		trans	cis	
4a		CO_2Me		CO_2Me		*h*		10.6	10.6	6.0		11.2	*h*
5a	CO_2Me			CO_2Me		12.0	8.3		10.9	10.0	0		7
6a		CN		CN		11.8		9.0	8.8	6.3		10.2	3.4
10a		CN		CO_2Me		11.8		10.6	10.5	*h*		10.6	*h*
11a				CO_2Et	12.9	12.1	8.5	10.1	10.4	1	0	10	9.1
12a			Me	CO_2Me[b]	13.3	12.0				5.1	1.5	15.8	*h*
14a		Ph		CO_2Me		11.7		9.6	10.1	8.1		13.9	7
15a				CN	14.1	12.0	9.9	8.9	9.9		12.4	15.2	
16a		Ph		CN		11.9		5.9	7.5	7.3		14.7	1.9
17a		CN		Ph		11.8		11.4	9.6	6.0		10.3	1.5
18a		Ph		NO_2		11.7		5.0	7.9	8		14.6	*h*
19a				SO_2Ph[c]	14.7	12.1	5.6	10.1	7.7	6.0	6.0	15.1	*h*
							β	β	β				
5b	CO_2Me			CO_2Me[d]		12.1		7.9	10.7	6.0		11.8	6
6b		CN		CN[e]		12.3	11.7		10.2		0		
7b	CN			CN[d]		11.6		6.8	10.6	5.8		9.9	5.0
8b	CN			CO_2Me[d]		11.8		8.0	10.1			11.1	
11b				CO_2Et	14.0	*h*	8.5	9.7	4.7	9.5	11.3	15.6	*h*
12b			Me	CO_2Me	13.9	12.2				4.5	4.7	16.7	*h*
15b				CN[f]	12.8	*h*	2.4	7.9	11		5.8	10.7	
							α	α	α		cis	trans	
5c	CO_2Me			CO_2Me		12.0	7.3		5.8	10.8	16.5		16.7
7c	CN			CN		*h*	7.0		5.8	9.6	12.8		14.2
9c	CO_2Me			CN		12.1	6.9		6.0	11.6	15.5		17.1
11c				CO_2Et	13.7	12.4	7	7.3	7.0	*h*	20.2	1.5	11.1
12c			Me	CO_2Me	14.6	12.3				11.4	19.6	5.9	15.7
13c		Me		CO_2Me[g]		12.1		11.2	10.6	6.1		6.6	*h*
15c				CN	13.9	12.0	4.9	9.0	7.2		15.4	4.9	
19c				SO_2Ph	13.7	12.1	9.4	8.0	9.1		13.1	0.9	
							β	β	β				
4d		CO_2Me		CO_2Me		12.4	11.0		10.7	10.7	16.3		18.8
6d		CN		CN		11.9	11.2		10.5	10.7	13.7		15.5

[a] Where appropriate, absolute values are given. The assignments "α" and "β" refer to protons located trans, respectively, cis to the C-5 phenyl group on the pyrrolidine ring. [b] $^4J_{1,3\alpha}$ = 1.5. [c] $^4J_{1,3\alpha}$ = 1.3. [d] $^4J_{H5,P}$ = 1.5. [e] $^4J_{H5,P}$ = 1.7. [f] $^4J_{H5,P}$ = 5.2. [g] $^4J_{H5,P}$ = 1.2. [h] Not determinable.

axial orientation of the phosphinoyl substituent was deduced from the strong reduction in or even lack of coupling to C-4 and C-5. The quasi axial disposition of the C-4 substituent was derived on the basis of extensive NOE-DIFF studies (more specifically, from the occurrence of NOE effects between H-3 and H-5, a 1,3 syn diaxial orientation of these protons and, consequently, a quasi axial orientation of the trans C-4 substituent may be derived).

^{1}H NMR Spectroscopy. In Tables III and IV the proton NMR data of the cycloadducts are collected. As may be concluded from Table IV, the magnitude of $^3J_{4,5}$ does not offer a direct clue to the relative position of the substituents at C(4) and C(5), both cis and trans couplings ranging from approximately 7 to 11 Hz. In those cases where the trans coupling is close to 11 Hz, the vicinal protons probably occupy quasi axial orientations.[18]

In all cycloadducts a phenyl group is present at C-5. When a cis ester group was present at C-4, it experienced a strong shielding effect (compare, e.g., **4a** with **4d**; **8a** and **8c** with **8b**, Table III).[19] Likewise, in the Psyn exo adduct to methyl methacrylate (**12b**), a strong shielding of the cis 4-Me was observed (δ 0.46).

Whenever possible, the conclusions based on chemical shifts were substantiated by NOE studies. Strong NOE effects were observed between H-4 (or 4-Me for the methacrylate adducts) and cis H-5. With the exception of the ethyl acrylate Psyn exo adduct **11b**, no NOE effects were observed between H-4 and trans H-5 for the exo compounds. As the ester group in **11b** is clearly non-shielded, the 4-ester and 5-phenyl will undoubtedly be trans relative to each other. The occurrence of NOE effects between H-4 and H-5 probably stems from a quasi diaxial orientation of the 4-(ethoxycarbonyl) and 5-phenyl groups.

When a cis phenyl group was present at C-3 (compounds **14a**, **16a**, and **18a**), the 2-benzyl ester group was strongly shielded. In some cases shielding was also observed when the 2-benzyl ester was cis with respect to a 3-carbomethoxy group, but these observations were less general (cf. **4d**, **5b** and **5c** vs **4a** and **9c**).[19]

A more direct method to determine the relative configuration around the C(2)–C(3) bond was inspection of the vicinal phosphorus coupling(s) to the C-3 hydrogen(s) (see Table IV). Generally, cis couplings were greater than 10 Hz, while trans couplings were in the order of 0–6 Hz. Comparable results have been found by Rabiller et al. for 2-phosphonopyrrolidines.[14] In some instances (**11b** and **15a**), trans couplings to phosphorus were quite large. This probably occurred when both the phosphine oxide (^{13}C NMR) and the trans hydrogen atom were quasi axially disposed.

The relative configuration around the C(3)–C(4) bond could be determined by examination of the vicinal coupling constant(s), in combination with NOE difference spectroscopy. When trans couplings were close to 11 Hz, these protons probably occupied quasi axial positions.[18] In several cases (e.g., **5a**, **5c**, **7c**, **9c**, **12c**, **15a**, and **19a**), NOE effects could also be observed between H-3 and H-5, indicating a 1,3-syn diaxial relationship.

(18) Cf. Benhaoua, H.; Piet, J. C.; Danion-Bougot, R.; Toupet, L.; Carrié, R. *Bull. Soc. Chim. Fr.* **1986**, 325 and references cited therein.

(19) Shielding was also observed for the relevant atoms in the ^{13}C NMR spectra, but the effects were less clear and less general.

Discussion

Compared to imines activated by a single ester or cyano group, benzyl *N*-benzylidene-α-(diphenylphosphinoyl)-glycinate (**3**) clearly shows increased reactivity. The reactions can be carried out at much lower temperature (refluxing chloroform instead of refluxing toluene or xylene) and cycloaddition was observed with a wider range of dipolarophiles.[5a,20] It is clear that the phosphinoyl substituent, although by itself not sufficiently capable of activating the thermal cycloaddition,[21] certainly aids in dipole generation from **3**.

In these cases, with dipolar cycloaddition as the rate-determining step, a clear preference for reaction of the Psyn dipole **2A** and formation of 4-endo-substituted products was observed (Table I). This Psyn selectivity was usually in the order of 90%. With dimethyl maleate (entry 3) and acrylonitrile (entry 14), a lower preference was observed. In the case of dimethyl maleate, it is probably the steric congestion in the transition state leading to the Psyn endo adduct **5a** that makes formation of the Psyn exo **5b** and Panti endo **5c** adducts relatively more attractive. Although the data for methyl crotonate are incomplete (entry 12), the yield of Panti endo compound **13c** indicates a change toward preferential reaction of the Panti dipole **2B**. Thus it appears that the Psyn/Panti selectivity is influenced by the nature of the substituent that ends up at C-3 of the pyrrolidine.

With all activating groups, except cyano, a preference for formation of 4-endo-substituted products was observed. Secondary orbital interactions have been invoked to explain the preference for endo orientation.[2,3] The presence of a β-phenyl substituent on the dipolarophile, as in methyl cinnamate (entry 13) and β-nitrostyrene (entry 16), seems to strengthen the preference for Psyn 4-endo adduct formation. Having the β-phenyl group at the same side of the incipient pyrrolidine ring as the benzyl ester allows for additional secondary orbital overlap.

Secondary orbital overlap may also occur between two ester groups.[5a] This can explain the strong preference for formation of the Psyn 4-endo adduct **4a** in the cycloaddition to dimethyl fumarate (entry 1), as compared to the reaction with ethyl acrylate (entry 9). The minor Panti 3-endo 4-exo adduct **4d** also accommodates ester/ester interactions. This can also help to explain, along with steric effects, the decrease in endo selectivity as well as Psyn preference in the reaction with dimethyl maleate (entry 3).

With acrylonitrile (entry 14), the endo selectivity was considerably lower. This indicates that secondary orbital interactions between a phenyl and a cyano substituent are less important. Similar decreases in endo selectivity have been observed by others.[5,11]

Remarkably, the addition to fumaronitrile (entry 4) again showed a strong preference for Psyn 4-endo product formation. It has been noted before that nitrile/ester interactions may be more favorable than nitrile/phenyl interactions in cycloaddition reactions.[5a] Apparently, in this case the transition state also profits from a favorable nitrile/ester interaction. The minor Panti 4-exo adduct **6d** also allows for preferential ester/nitrile interactions.

In the addition to maleonitrile (entry 6), the combined effects of preference for reaction of the Psyn dipole **2A** and the favorable ester/nitrile interaction lead to the preferential formation of the Psyn exo adduct **7b**. The importance of ester/nitrile interaction is further substantiated by the outcome of the reaction with methyl *cis*-β-cyanoacrylate, where the major product, having a 3-cyano 4-ester substitution pattern, was found to have the Psyn exo structure **8b**. This implies that ester/nitrile interactions are also more favorable than ester/phenyl interactions and even prevent the preferential reaction of the Panti dipole **2B** (which would have allowed both ester/nitrile and ester/phenyl interactions to occur).

The other isomer in this addition was the regioisomeric Panti endo 3-ester 4-cyano compound **9c**. This orientation combines ester/ester and nitrile/phenyl interactions. Although phenyl/nitrile interaction did not evoke a high endo/exo selectivity in the cycloaddition to acrylonitrile (entry 14), it may still have been a decisive factor in inducing preferential reaction of the Panti dipole **2B** in this case (entry 7).

These conclusions are fully confirmed by the results obtained with the *trans*-β-cyanoacrylate ester, where the major product, present in 80%, proved to be the Psyn 3-*exo*-cyano 4-*endo*-(methoxycarbonyl) adduct **10a**. Predominant formation of this cycloadduct may be explained by reaction of the Psyn dipole **2A** with combined favorable ester/nitrile and ester/phenyl interactions.

Although the results with cinnamonitrile were incomplete (entry 15), formation of the regioisomeric Psyn 3-*exo*-cyano 4-*endo*-phenyl adduct **17a** confirms these observations.

Experimental Section

All experiments were carried out in distilled and dry solvents under a nitrogen atmosphere. All dipolarophiles were obtained commercially unless noted otherwise. Phenyl vinyl sulfone was prepared according to the procedure of Paquette et al.[22] Maleonitrile was prepared from fumaronitrile via iodine-induced double-bond isomerization.[23] Methyl *cis*-β-cyanoacrylate was prepared in two steps from maleic anhydride.[24] Methyl *trans*-β-cyanoacrylate was prepared, along with the cis isomer, from methyl α-chloroacrylate.[24,25] Methyl and ethyl acrylate, methyl methacrylate, methyl crotonate, and acrylonitrile were purified immediately before use according to literature procedures. Other dipolarophiles were used as such. Salts employed in the catalysis experiments were obtained commercially. Reactions were monitored by drawing small aliquots from the reaction mixture, removing the solvent in vacuo, and recording both ^{1}H NMR and ^{31}P NMR spectra.

Flash chromatography was performed on Merck Kieselgel 60 (0.040–0.063 mm) under a nitrogen pressure. The eluent is specified for each experiment. All separations were carried out by using distilled solvents. Petroleum ether refers to the fraction boiling at 40–60 °C. TLC analyses were performed on Schleicher and Schuell F1500/LS 254 silica gel plates, using an UV lamp for detection.

The ^{1}H NMR spectra were recorded on a Brucker WM-300 (300 MHz) or on a JEOL NM FX-200 (200 MHz) spectrometer, using tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded on a JEOL NM FX-200 (50 MHz) spectrometer, using deuteriochloroform as internal standard. ^{31}P NMR spectra were recorded in deuteriochloroform on a JEOL NM FX-200 (80 MHz) spectrometer, using 85% aqueous phosphoric acid as external standard. {^{31}P}^{1}H spectra, carbon–hydrogen correlated NMR spectra, and NOEDIFF studies were recorded on a Brucker

(20) (a) Joucla, M.; Hamelin, J. *Tetrahedron Lett.* **1978**, 2885. (b) Grigg, R.; Kemp, J. *Ibid.* **1980**, *21*, 2461. (c) See also ref 11b, for thermal cycloaddition to methyl acrylate.

(21) Van Es, J. J. G. S.; Van der Gen, A. Unpublished results.

(22) Paquette, L. A.; Carr, R. V. C. In *Organic Synthesis*; Kende, A. S., Ed.; Wiley: New York, 1986; Vol. 64, pp 157–163.

(23) Ficken, G. E.; Linstead, R. P.; Stephen, E.; Whalley, M. *J. Chem. Soc.* **1958**, 3879.

(24) Sauers, C. K.; Cotter, R. J. *J. Org. Chem.* **1961**, *26*, 6.

(25) From methyl α-chloroacrylate: Crawford, J. W.; McLeish, N.; Wood, T. K. U.S. Pat. 2293967, 1942. Methyl α-chloroacrylate was prepared from commercially available methyl 2,3-dichloropropionate, according to Marvel, C. S.; Cowan, J. C. *J. Am. Chem. Soc.* **1939**, *61*, 3156.

WM-300 spectrometer. Mass spectra were obtained with an AEI MS 9/50 apparatus at an ionization voltage of 70 eV.[26] Infrared spectra were obtained with a Pye Unicam SP3-200 spectrophotometer. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Elemental analyses were performed by the University of East Anglia Microanalytical Laboratory.

Thermal Cycloaddition: General Procedure. Benzyl *N*-benzylidene-α-(diphenylphosphinoyl)glycinate (**3**)[1] (1.0 g, 2.2 mmol) and 1.15 equiv of the dipolarophile were refluxed under a nitrogen atmosphere under the conditions as specified in Table I. After evaporation of the solvent the products were isolated by crystallization from ether and/or flash chromatography.

Cycloaddition to Dimethyl Fumarate. Flash chromatography (1% methanol–ether) gave two fractions. The first one consisted of a mixture of Psyn 4-endo **4a** and probably Psyn 4-exo adduct **4b** (ratio 20:1), which were isolated in 1.15 g (87%) (reaction in chloroform) or 1.19 g (90%) (reaction in acetonitrile). These could not be further separated. The second fraction was the pure Panti 4-exo compound **4d** (0.040 g, 3%).

Psyn 3-Exo 4-Endo. (2α,3α,4β,5β)-(±)-3,4-Dimethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,3,4-pyrrolidinetricarboxylate (4a): oil; IR (KBr) 3360, 1735, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.20–7.53 (m, 16 H), 7.91–8.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.6, 127.7, 127.8, 128.0, 128.1, 128.3, 128.5, 129.0, 129.0, 131.6, 131.7, 131.8, 132.0, 132.1, 132.2, 132.6, 132.7 (each C–H), 128.8, 129.1, 130.8, 131.1 (each q-C, Ph_2PO), 134.0 (q-C, Bn), 139.5 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 26.78; MS, *m/z* (rel intensity) 396 (8), 395 (M – Ph_2POH, 9), 309 (11), 308 (7), 260 (7), 203 (82), 202 (70), 201 (75), 91 (base peak), 78 (21), 77 (41), 65 (82), 51 (33); HRMS calcd for $C_{22}H_{21}NO_6$ (M – Ph_2POH) 395.1368, found 395.1366.

Panti 3-Endo 4-Exo. (2α,3α,4β,5α)-(±)-3,4-Dimethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,3,4-pyrrolidinetricarboxylate (4d): white powder (ether); mp 130–131 °C; IR (KBr) 3390, 1740, 1178 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.13–7.65 (m, 16 H), 8.03–8.19 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.1, 127.2, 128.0, 128.0, 128.2, 128.4, 128.5, 128.8, 131.6, 131.8, 132.7, 132.3, 133.5, 133.6 (each C–H), 130.5, 130.9 (each q-C, Ph_2PO), 134.1 (q-C, Bn), 137.7 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 29.25; MS, *m/z* (rel intensity) 396 (5), 395 (M – Ph_2POH, 8), 260 (6), 203 (32), 202 (50), 201 (75), 125 (10), 124 (22), 91 (base peak), 78 (26), 77 (37), 65 (10), 51 (32); HRMS calcd for $C_{22}H_{21}NO_6$ (M – Ph_2POH) 395.1368, found 395.1353.

Cycloaddition to Dimethyl Maleate. After 48 h the conversion was 85% (^{31}P NMR), while ^1H NMR indicated that all dimethyl maleate had reacted. Addition of an extra 0.25 equiv of dipolarophile resulted in complete conversion of the starting material after 65 h.

Flash chromatography (ether) gave three fractions. The first fraction was the Psyn exo adduct **5b** (0.395 g, 30%). The second fraction consisted of the Psyn endo product **5a** and its epimerization product **4a** (0.40 g, 30%). The third fraction was the Panti endo product **5c**, containing a small amount of Psyn endo **5a**. The Panti endo product **5c** was obtained in a pure form by being stirred in ether overnight. Yield: 0.240 g (18%). The second fraction was again subjected to flash chromatography (15% petroleum ether–ether). First, a small amount of benzyl diphenylphosphinate (**20**) was obtained (0.014 g, 2%). Then 0.114 g (8%) of almost pure Psyn endo adduct **5a** was isolated. Next, a mixture of the Psyn endo adduct **5a** and the epimerization product **4a** was collected (0.223 g, 17%, in a ratio of 4:1).

Psyn Endo. (2α,3β,4β,5β)-(±)-3,4-Dimethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,3,4-pyrrolidinetricarboxylate (5a): white solid (ether–light petroleum ether); mp 70–72 °C; IR (KBr) 3325, 1724, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.18–7.55 (m, 16 H), 7.85–7.96 (m, 2 H), 8.10–8.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.8, 127.8, 127.9, 128.0, 128.2, 128.4, 128.9, 132.0, 132.2 (each C–H), 129.2, 130.1, 131.2 (each q-C, Ph_2PO), 134.2 (q-C, Bn), 137.6 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 28.20; MS, *m/z* (rel intensity) 396 (6), 395 (M – Ph_2POH, 4), 260 (4), 228 (10), 203 (84), 202 (65), 201 (base peak), 185 (15), 183 (14), 124 (34), 91 (46), 78 (37), 77 (49), 51 (46); HRMS calcd for $C_{22}H_{21}NO_6$ (M – Ph_2POH) 395.1368, found 395.1352.

Psyn Exo. (2α,3α,4α,5β)-(±)-3,4-Dimethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,3,4-pyrrolidinetricarboxylate (5b): white powder (ether); mp 134–135 °C; IR (KBr) 3325, 1724, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.03–7.08 (m, 2 H), 7.17–7.53 (m, 14 H), 7.85–8.07 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.5, 127.6, 127.9, 128.0, 128.2, 128.3, 128.4, 128.6, 131.7, 131.9, 132.3, 132.5 (each C–H), 128.6, 129.2, 130.6, 131.1 (each q-C, Ph_2PO), 133.9 (q-C, Bn), 140.2 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 32.38; MS, *m/z* (rel intensity) 396 (2), 395 (M – Ph_2POH, 4), 260 (6), 228 (10), 203 (44), 202 (69), 201 (base peak), 183 (18), 125 (10), 124 (31), 91 (95), 78 (30), 77 (49), 51 (54); HRMS calcd for $C_{22}H_{21}NO_6$ (M – Ph_2POH) 395.1368, found 395.1377.

Panti Endo. (2α,3α,4α,5α)-(±)-3,4-Dimethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,3,4-pyrrolidinetricarboxylate (5c): white solid (ether–light petroleum ether); mp 105–107 °C; IR (KBr) 3265, 1742, 1728, 1193 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.14–7.49 (m, 16 H), 8.04–8.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.4, 127.6, 127.8, 128.1, 128.3, 128.6, 131.9, 132.1, 132.3, 132.8, 132.9 (each C–H), 129.0, 129.2, 131.0, 131.1 (each q-C, Ph_2PO), 134.2 (q-C, Bn), 137.0 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 28.44; MS, *m/z* (rel intensity) 396 (5), 395 (M – Ph_2POH, 5), 260 (6), 228 (20), 203 (18), 202 (38), 201 (60), 124 (19), 91 (base peak), 78 (15), 77 (31), 51 (27); HRMS calcd for $C_{22}H_{21}NO_6$ (M – Ph_2POH), 395.1368, found 395.1383.

Cycloaddition to Fumaronitrile. Crystallization from ether gave 1.01 g (86%) of pure Psyn 4-endo product **6a**. Flash chromatography (ether) of the filtrate afforded two fractions. The first was pure Psyn exo product **6b** (0.026 g, 2%). The other fraction was a mixture of Psyn endo **6a** and Panti exo **6d** (0.089 g, 7.5%). Stirring in ether gave only crystallization of the Psyn endo compound **6a** (0.024 g, 2%). The filtrate afforded 0.064 g (5.5%) of more than 90% pure Panti exo product **6d**.

Psyn 3-Exo 4-Endo. (2α,3α,4β,5β)-(±)-Phenylmethyl 3,4-dicyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (6a): white powder (ether); mp 163–164 °C; IR (KBr) 3260, 2240, 1725, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.03–7.08 (m, 2 H), 7.17–7.53 (m, 14 H), 7.80–7.99 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.3, 128.6, 128.9, 129.1, 129.2, 132.0, 132.2, 132.4, 132.6, 132.9, 133.2 (each C–H), 133.3 (q-C, Bn), 136.8 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 31.31; MS, *m/z* (rel intensity) 302 (M – Ph_2POH – HCN, 1), 203 (19), 202 (61), 201 (base peak), 183 (13), 124 (32), 108 (40), 107 (19), 91 (87), 78 (40), 77 (75), 51 (49); HRMS calcd for $C_{19}H_{14}N_2O_2$ (M – Ph_2POH – HCN) 302.1055, found 302.1077.

Psyn 3-Endo 4-Exo. (2α,3β,4α,5β)-(±)-Phenylmethyl 3,4-dicyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (6b): oil; IR (KBr) 3320, 2230, 1724, 1178 cm^{-1}; ^1H NMR (CD_3OD) δ (Tables III and IV), 7.14–7.19 (m, 2 H), 7.30–7.60 (m, 14 H), 7.76–7.86 (m, 2 H), 7.95–8.06 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.0, 128.3, 128.5, 128.6, 128.7, 128.9, 129.0, 129.2, 132.0, 132.1, 132.4, 132.6 (each C–H), 127.7, 129.7, 130.6 (each q-C, Ph_2PO), 133.3 (q-C, Bn), 136.5 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 31.96; MS, *m/z* (rel intensity) 329 (M – Ph_2POH, 4), 302 (M – Ph_2POH – HCN, 3), 202 (18), 201 (26), 124 (10), 91 (base peak), 78 (10), 77 (24), 51 (18); HRMS calcd for $C_{20}H_{15}N_3O_2$ (M – Ph_2POH) 329.1165, found 329.1157; calcd for $C_{19}H_{14}N_2O_2$ (M – Ph_2POH – HCN) 302.1055, found 302.1052.

Panti 3-Endo 4-Exo. (2α,3α,4β,5α)-(±)-Phenylmethyl 3,4-dicyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (6d): oil; IR (KBr) 3270, 2240, 1723, 1178 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.09–7.66 (m, 16 H), 7.88–8.02 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.5, 126.5, 126.6, 127.3, 127.9, 128.2, 128.5, 128.6, 128.7, 128.8, 129.2, 129.3, 129.4, 129.6, 129.7, 131.4, 131.6, 132.0, 132.2, 132.4, 132.8, 133.0, 133.2 (each C–H), 127.0, 127.1 (each q-C, Ph_2PO), 133.2 (q-C, Bn), 134.5 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 28.92; MS, *m/z* (rel intensity) 329 (M – Ph_2POH, 2), 302 (M – Ph_2POH – HCN, 6), 202 (51), 201 (84),

(26) None of the cycloadducts showed a molecular ion peak in the EI spectrum (source temperature 150 °C; electron energy 70 eV) due to loss of diphenylphosphine oxide (Ph_2POH, loss of 202). Thus, HRMS was measured for the M – 202 peak. In some instances a CI spectrum (ionizing gas ammonia) was recorded, and in all cases the (M + 1) peak was prominent.

183 (11), 124 (24), 91 (base peak), 78 (31), 77 (57), 51 (50); HRMS calcd for $C_{20}H_{15}N_3O_2$ (M - Ph_2POH) 329.1165, found 329.1150; calcd for $C_{19}H_{14}N_2O_2$ (M - Ph_2POH - HCN) 302.1055, found 302.1050.

Cycloaddition to Maleonitrile. Stirring in ether overnight afforded 0.89 g (76%) of pure Psyn exo adduct **7b**. Flash chromatography (1% methanol–ether) of the filtrate afforded benzyl diphenylphosphinate (**20**) (0.026 g, 4%) as the first eluting product. Next, the remainder of Psyn exo adduct **7b** (0.119 g, 10%) was isolated. The third fraction consisted of pure Panti endo adduct **7c**, which was crystallized from ether (0.048 g, 4%). A third cycloadduct, presumably the Psyn endo compound **7a** (5% according to ^{31}P NMR), could not be isolated. Probably decomposition occurred via elimination of phosphinate **20**.

Psyn Exo. (2α,3α,4α,5β)-(±)-Phenylmethyl 3,4-dicyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (7b): white powder (ether); mp 162–164 °C dec; IR (KBr) 3360, 2250, 1726, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.11–7.16 (m, 2 H), 7.26–7.61 (m, 14 H), 7.67–7.89 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 118.1, 126.8, 128.1, 128.3, 128.3, 128.4, 128.5, 128.6, 128.7, 128.7, 129.0, 129.0, 131.4, 131.6, 131.8, 132.6 (each C–H), 127.6, 128.9, 129.5 (each q-C, Ph_2PO), 132.9 (q-C, Bn), 136.5 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 33.82; MS, *m/z* (rel intensity) 330 (0.6), 329 (M - Ph_2POH, 8), 238 (3), 202 (21), 201 (27), 184 (4), 124 (13), 113 (11), 92 (7), 91 (base peak), 78 (9), 77 (15), 65 (6), 51 (36); HRMS calcd for $C_{20}H_{15}N_3O_2$ (M - Ph_2POH) 329.1165, found 329.1162.

Panti Endo. (2α,3α,4α,5α)-(±)-Phenylmethyl 3,4-dicyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (7c): white powder (ether); mp 208–209 °C; IR (KBr) 3320, 2255, 1728, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.16–7.59 (m, 16 H), 7.86–8.01 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II) 126.8, 128.4, 128.5, 128.7, 128.8, 129.1, 129.2, 131.5, 131.7, 132.5, 132.7, 132.9 (each C–H), 127.2 (q-C, Ph_2PO), 133.3 (q-C, Bn), 134.7 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 30.39; MS, *m/z* (rel intensity) 330 (2), 329 (M - Ph_2POH, 11), 238 (3), 202 (12), 201 (17), 184 (4), 124 (6), 113 (3), 92 (8), 91 (base peak), 78 (6), 77 (8), 65 (5), 51 (10); HRMS calcd for $C_{20}H_{15}N_3O_2$ (M - Ph_2POH) 329.1165, found 329.1163.

Cycloaddition to Methyl *cis*-β-Cyanoacrylate. Stirring the crude product mixture in ca. 5% dichloromethane–ether (25 mL) overnight resulted in the exclusive precipitation of the Psyn exo 3-cyano 4-carbomethoxy adduct **8b** (0.315 g, 25%). With flash chromatography (1% methanol–ether) the other main product was separated. Stirring in ether overnight afforded 0.265 g (21%) of pure Panti endo 3-carbomethoxy 4-cyano adduct **9c**.

Psyn *exo*-3-Cyano 4-Carbomethoxy. (2α,3α,4α,5β)-(±)-4-Methyl 2-phenylmethyl 3-cyano-2-(diphenylphosphinoyl)-5-phenyl-2,4-pyrrolidinedicarboxylate (8b): white powder (ether); mp 155–156 °C; IR (KBr) 3330, 2245, 1738, 1725, 1188 cm^{-1}; ^1H NMR ($CDCl_3$–CD_3OD ≈ 5:1) δ (Tables III and IV), 7.14–7.58 (m, 16 H), 7.74–7.94 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 129.0, 131.7, 131.9, 132.1, 132.1, 132.3, 132.5 (each C-H), 129.9, 130.0 (each q-C, Ph_2PO), 133.4 (q-C, Bn), 139.2 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 32.46; MS, *m/z* (rel intensity) 363 (2), 362 (M - Ph_2POH, 11), 303 (7), 202 (20), 201 (27), 183 (3), 124 (9), 92 (7), 91 (base peak), 65 (6), 51 (10); HRMS calcd for $C_{21}H_{18}N_2O_4$ (M - Ph_2POH) 362.1266, found 362.1251.

Panti *endo*-3-Carbomethoxy 4-Cyano. (2α,3α,4α,5α)-(±)-3-Methyl 2-phenylmethyl 4-cyano-2-(diphenylphosphinoyl)-5-phenyl-2,3-pyrrolidinedicarboxylate (9c): white powder (ether); mp 161–162 °C; IR (KBr) 3285, 2253, 1738, 1722, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.11–7.15 (m, 2 H), 7.24–7.55 (m, 14 H), 7.95–8.07 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.1, 128.2, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 131.8, 132.0, 132.5, 132.8, 133.0 (each C–H), 127.5, 127.6, 129.4, 129.5 (each q-C, Ph_2PO), 134.0 (q-C, Bn), 135.3 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 29.13; MS, *m/z* (rel intensity) 363 (2), 362 (M - Ph_2POH, 14), 303 (7), 271 (3), 202 (6), 201 (11), 169 (2), 168 (2), 124 (6), 92 (8), 91 (base peak), 78 (4), 77 (7), 65 (5), 51 (13); HRMS calcd for $C_{21}H_{18}N_2O_4$ (M - Ph_2POH) 362.1266, found 362.1272.

Cycloaddition to Methyl *trans*-β-Cyanoacrylate. Flash chromatography (1:3 petroleum ether–ether), followed by stirring in ether overnight, afforded 0.75 g (60%) of pure Psyn 3-*exo*-cyano 4-*endo*-carbomethoxy adduct **10a**.

Psyn 3-*exo*-Cyano 4-*endo*-Carbomethoxy. (2α,3α,4β,5β)-(±)-4-Methyl 2-phenylmethyl 3-cyano-2-(diphenylphosphinoyl)-5-phenyl-2,4-pyrrolidinedicarboxylate (10a): white powder (ether); mp 157–158 °C; IR (KBr) 3260, 2240, 1738, 1725, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.16–7.65 (m, 18 H), 7.90–8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.8, 128.2, 128.4, 128.6, 128.8, 129.1, 131.9, 132.1, 132.7, 133.0, 133.2 (each C–H), 126.2, 130.0 (each q-C, Ph_2PO), 133.8 (q-C, Bn), 138.2 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 32.02; MS, *m/z* (rel intensity) 473 (3), 363 (1), 362 (M - Ph_2POH, 5), 345 (6), 303 (2), 219 (2), 202 (23), 183 (3), 113 (24), 108 (28), 107 (21), 101 (7), 95 (7), 92 (7), 91 (base peak), 80 (46), 79 (24), 78 (10), 77 (28), 65 (6), 52 (12), 51 (81); HRMS calcd for $C_{21}H_{18}N_2O_4$ 362.1266, found 362.1261.

Cycloaddition to Ethyl Acrylate. Stirring in ether overnight afforded 0.93 g (76%) of pure Psyn endo product **11a**. Flash chromatography (ether) of the filtrate gave two fractions. The first consisted of a mixture of Psyn endo **11a** and Psyn exo **11b** (0.150 g, 12%). The second fraction consisted of pure Panti endo adduct **11c** (0.100 g, 8%). The first fraction was again subjected to flash chromatography (15% petroleum ether–ether), and this gave 0.085 g (7%) of Psyn exo product **11b** as the first eluting product and next 0.061 g (5%) of Psyn endo product **11a**.

Psyn Endo. (2α,4β,5β)-(±)-4-Ethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,4-pyrrolidinedicarboxylate (11a): white powder (ether); mp 119–120 °C; IR (KBr) 3260, 1725, 1188 cm^{-1}; ^1H NMR (acetone-d_6) δ (Tables III and IV), 7.02–7.06 (m, 2 H), 7.16–7.58 (m, 14 H), 7.87–7.97 (m, 2 H), 8.07–8.17 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.3, 127.5, 127.7, 127.8, 127.9, 128.0, 128.0, 128.1, 128.2, 131.9, 131.9, 132.0, 132.2, 132.3, 132.4, 132.5 (each C–H), 128.4, 128.7, 130.4, 130.6 (each q-C, Ph_2PO), 134.6 (q-C, Bn), 139.1 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 31.60; MS, *m/z* (rel intensity) 352 (3), 351 (M - Ph_2POH, 5), 260 (4), 203 (7), 202 (14), 201 (21), 124 (7), 91 (base peak), 78 (8), 77 (25), 51 (11); HRMS calcd for $C_{21}H_{21}NO_4$ (M - Ph_2POH) 351.1470, found 351.1475.

Psyn Exo. (2α,4α,5β)-(±)-4-Ethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,4-pyrrolidinedicarboxylate (11b): white powder (ether); mp 131–132 °C; IR (KBr) 3315, 1732, 1715, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.19–7.60 (m, 16 H), 7.78–7.88 (m, 2 H), 8.11–8.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.9, 127.1, 127.2, 127.5, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 131.8, 132.0, 132.2, 132.8, 133.0 (each C–H), 130.3, 131.0 (each q-C, Ph_2PO), 134.8 (q-C, Bn), 140.4 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 30.75; MS, *m/z* (rel intensity) 352 (3), 351 (M - Ph_2POH, 2), 260 (2), 203 (40), 202 (67), 201 (base peak), 183 (12), 124 (26), 91 (56), 78 (33), 77 (53), 51 (59); HRMS calcd for $C_{21}H_{21}NO_4$ (M - Ph_2POH) 351.1470, found 351.1455.

Panti Endo. (2α,4α,5α)-(±)-4-Ethyl 2-phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-2,4-pyrrolidinedicarboxylate (11c): white solid (ether); mp 116–117 °C; IR (KBr) 3320, 1724, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.09–7.14 (m, 2 H), 7.17–7.52 (m, 12 H), 7.77–7.87 (m, 2 H), 8.08–8.18 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.3, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 131.8, 131.9, 132.0, 132.1, 133.0, 133.2 (each C–H), 128.9, 130.6, 130.9 (each q-C, Ph_2PO), 135.0 (q-C, Bn), 137.5 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 28.32; MS, *m/z* (rel intensity) 352 (9), 351 (M - Ph_2POH, 6), 271 (10), 260 (2), 233 (13), 232 (6), 231 (8), 216 (9), 203 (98), 202 (68), 201 (base peak), 185 (13), 183 (12), 125 (13), 124 (33), 91 (92), 78 (38), 77 (66), 65 (14), 51 (61); HRMS calcd for $C_{21}H_{21}NO_4$ (M - Ph_2POH) 351.1470, found 351.1472.

Cycloaddition to Methyl Methacrylate. Flash chromatography (1:3 petroleum ether–ether, and, after the Psyn endo adduct had been obtained, ether) gave as the first eluting product a small amount of benzyl diphenylphosphinate (**20**) (0.014 g, 2%). Then, the Psyn exo adduct **12b** was obtained (0.061 g, 5%). Next, a mixture of Psyn exo **12b** and endo **12a** was collected (0.072 g, 6%). Then, Psyn endo **12a** was obtained (0.720 g, 59%). The polarity of the eluent was raised and as the last product Panti endo adduct **12c** was collected (0.097 g, 8%).

Psyn Endo. (2α,4β,5β)-(±)-4-Methyl 2-phenylmethyl 2-(diphenylphosphinoyl)-4-methyl-5-phenyl-2,4-pyrrolidinedicarboxylate (12a): white powder (ether); mp 123 °C; IR (KBr) 3325, 1720, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV),

7.13–7.63 (m, 16 H), 7.90–8.00 (m, 2 H), 8.11–8.22 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.1, 127.7, 127.9, 128.2, 128.3, 128.7, 132.0, 132.2, 132.3, 132.5, 132.6, 132.8 (each C-H), 130.0, 130.8 (each q-C, Ph_2PO), 134.8 (q-C, Bn), 138.9 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 32.37; MS, m/z (rel intensity) 352 (9), 351 (M – Ph_2POH, 7), 260 (24), 202 (22), 201 (38), 124 (15), 91 (base peak), 78 (8), 77 (12); HRMS calcd for $C_{21}H_{21}NO_4$ (M – Ph_2POH) 351.1470, found 351.1446.

Psyn Exo. (2α,4α,5β)-(±)-4-Methyl 2-phenylmethyl 2-(diphenylphosphinoyl)-4-methyl-5-phenyl-2,4-pyrrolidinedicarboxylate (12b): white powder (ether); mp 129 °C; IR (KBr) 3320, 1720, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.16–7.56 (m, 16 H), 7.83–7.93 (m, 2 H), 8.06–8.16 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.3, 127.5, 127.8, 128.0, 128.2, 132.0, 132.2, 132.6, 132.7 (each C-H), 128.9, 129.7, 130.9 (each q-C, Ph_2PO), 134.7 (q-C, Bn), 138.4 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 32.20; MS, m/z (rel intensity) 352 (8), 351 (M – Ph_2POH, 12), 260 (24), 202 (22), 201 (29), 124 (9), 91 (base peak), 77 (13); HRMS calcd for $C_{21}H_{21}NO_4$ (M – Ph_2POH) 351.1470, found 351.1500.

Panti Endo. (2α,4α,5α)-(±)-4-Methyl 2-phenylmethyl 2-(diphenylphosphinoyl)-4-methyl-5-phenyl-2,4-pyrrolidinedicarboxylate (12c): white powder (ether); mp 161–162 °C; IR (KBr) 3320, 1720, 1192 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.93–6.98 (m, 2 H), 7.26–7.60 (m, 14 H), 8.08–8.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.2, 127.1, 128.0, 128.2, 128.3, 128.4, 132.0, 132.2, 132.3, 133.3, 133.5 (each C-H), 130.4, 130.4 (each q-C, Ph_2PO), 135.3 (q-C, Bn), 136.0 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 28.32; MS, m/z (rel intensity) 352 (15), 351 (M – Ph_2POH, 14), 260 (30), 202 (43), 201 (68), 124 (13), 91 (base peak), 78 (14), 77 (16), 51 (41); HRMS calcd for $C_{21}H_{21}NO_4$ (M – Ph_2POH) 351.1470, found 351.1435.

Cycloaddition to Methyl Crotonate. Flash chromatography (4% triethylamine–ether) gave a first fraction, largely consisting of starting material (yield approximately 24%). The second fraction was a mixture of Panti endo adduct **13c** and phosphinate **20** (0.448 g). These could be separated cleanly by being stirred in ether overnight. The precipitate was pure Panti endo adduct **13c** (0.271 g, 22%). The filtrate was almost pure benzyl diphenylphosphinate (**20**) (0.158 g, 23%). Two products, present in 19% and 13%, were instable to all conditions of isolation.

Panti Endo. (2α,3β,4α,5α)-(±)-4-Methyl 2-phenylmethyl 2-(diphenylphosphinoyl)-3-methyl-5-phenyl-2,4-pyrrolidinedicarboxylate (13c): white powder (ether); mp 167 °C; IR (KBr) 3240, 1742, 1714, 1192 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.88–6.93 (m, 2 H), 7.10–7.60 (m, 14 H), 7.84–8.02 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 128.7, 131.9, 132.1, 132.7, 132.9 (each C-H), 129.3, 131.3 (each q-C, Ph_2PO), 134.6 (q-C, Bn), 140.7 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 30.52; MS, m/z (rel intensity) 353 (5), 352 (8), 351 (M – Ph_2POH, 3), 260 (7), 202 (19), 201 (28), 183 (6), 163 (9), 151 (26), 133 (18), 124 (5), 113 (32), 95 (13), 91 (37), 78 (8), 77 (9), 51 (base peak); HRMS calcd for $C_{21}H_{21}NO_4$ (M – Ph_2POH) 351.1470, found 351.1453.

Cycloaddition to Methyl Cinnamate. Flash chromatography (0.5% methanol–ether) gave three fractions. The first product was Psyn endo adduct **14a** (0.967 g, 71%). The second fraction was benzyl diphenylphosphinate (**20**) (0.049 g, 7%). The last fraction was a remainder of the starting material **3** (0.052 g, 5%).

Psyn Endo. (2α,3α,4β,5β)-(±)-4-Methyl 2-phenylmethyl 2-(diphenylphosphinoyl)-3,5-diphenyl-2,4-pyrrolidinedicarboxylate (14a): white powder (ether); mp 134–135 °C; IR (KBr) 3350, 1735, 1690, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.63–6.73 (m, 4 H), 6.85–7.37 (m, 17 H), 7.57–7.74 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.8, 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.6, 128.7, 131.6, 131.8, 132.0, 133.0, 133.2 (each C-H), 127.0, 129.0, 130.4, 132.4 (each q-C, Ph_2PO), 133.5 (q-C, Bn), 136.6 (q-C, 3-Ph), 139.6 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 35.36; MS, m/z (rel intensity) 414 (3), 413 (M – Ph_2POH, 0.4), 322 (4), 203 (98), 202 (72), 201 (base peak), 183 (19), 162 (4), 155 (10), 131 (20), 125 (15), 119 (13), 91 (37), 78 (42), 77 (73), 69 (66), 51 (86); HRMS calcd for $C_{26}H_{23}NO_4$ (M – Ph_2POH) 413.1627, found 413.1628.

Cycloaddition to Acrylonitrile. The product was stirred in ether overnight. This gave a mixture of Psyn endo adduct **15a** and Psyn exo adduct **15b** (ratio 1:9) as a white solid. Pure Psyn exo adduct **15b** was obtained after flash chromatography (1:3 petroleum ether–ether); yield 0.232 g (21%). The remaining fractions were added to the filtrate of the crystallization, and this mixture was subjected to flash chromatography (10% petroleum ether–ether, and, after Psyn endo adduct **15a** had eluted, 2% methanol–ether). The first isolated product was the remainder of Psyn exo product **15b** (0.100 g, 9%). The second fraction consisted of Psyn endo product **15a** (0.314 g, 28%). Next, phosphinate **20** was obtained (0.054 g, 8%). The last fraction was Panti endo adduct **15c** (0.091 g, 8%).

Psyn Endo. (2α,4β,5β)-(±)-Phenylmethyl 4-cyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (15a): colorless prisms (CH_2Cl_2–hexane); mp 61–62 °C; IR (KBr) 3320, 2235, 1715, 1192 cm^{-1}; ^1H NMR ($CDCl_3$–$CD_3OD \approx 5$–1) δ (Tables III and IV), 7.18–7.59 (m, 16 H), 7.74–7.85 (m, 2 H), 8.03–8.14 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.7, 128.3, 128.5, 128.7, 131.7, 131.9, 132.3, 132.5, 132.7 (each C-H), 129.7, 130.4 (each q-C, Ph_2PO), 134.2 (q-C, Bn), 137.7 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 30.82; MS, m/z (rel intensity) 309 (2), 308 (3), 304 (M – Ph_2POH, 3), 203 (7), 202 (23), 201 (19), 198 (4), 124 (5), 91 (base peak), 78 (8), 77 (15), 51 (12); HRMS calcd for $C_{19}H_{16}N_2O_2$ (M – Ph_2POH) 304.1212, found 304.1218.

Psyn Exo. (2α,4α,5β)-(±)-Phenylmethyl 4-cyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (15b): white powder (ether); mp 166–167 °C; IR (KBr) 3245, 2230, 1730, 1192 cm^{-1}; ^1H NMR ($CDCl_3$–$CD_3OD \approx 5$–1) δ (Tables III and IV), 7.07–7.59 (m, 16 H), 7.78–8.00 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.8 127.6, 128.3, 128.4, 128.4, 128.5, 128.8, 131.6, 131.8, 132.4, 132.6, 132.8 (each C-H), 130.1, 130.3 (each q-C, Ph_2PO), 133.8 (q-C, Bn), 140.3 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 30.52; MS, m/z (rel intensity) 305 (3), 304 (M – Ph_2POH, 13), 202 (7), 201 (9), 91 (base peak), 78 (5), 77 (7), 65 (6), 51 (7); HRMS calcd for $C_{19}H_{16}N_2O_2$ (M – Ph_2POH) 304.1212, found 304.1204.

Panti Endo. (2α,4α,5α)-(±)-Phenylmethyl 4-cyano-2-(diphenylphosphinoyl)-5-phenyl-2-pyrrolidinecarboxylate (15c): white powder (ether); mp 136–137 °C; IR (KBr) 3345, 2235, 1717, 1188 cm^{-1}; ^1H NMR ($CDCl_3$–$CD_3OD \approx 5$–1) δ (Tables III and IV), 7.19–7.62 (m, 16 H), 7.82–7.92 (m, 2 H), 8.15–8.25 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.1, 128.2, 128.5, 128.7, 128.9, 130.3, 131.9, 132.0, 132.3, 132.5, 132.6 (each C-H), 126.9 (q-C, Ph_2PO), 134.4 (q-C, Bn), 137.1 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 30.38; MS, m/z (rel intensity) 309 (3), 308 (3), 304 (M – Ph_2POH, 1), 203 (8), 202 (30), 201 (21), 198 (3), 149 (13), 91 (base peak), 78 (11), 77 (23), 65 (9), 51 (10); HRMS calcd for $C_{19}H_{16}N_2O_2$ (M – Ph_2POH) 304.1212, found 304.1213.

Cycloaddition to Cinnamonitrile. Flash chromatography (ether) gave four fractions. The first product (0.190 g, 15%) proved to be regioisomeric Psyn 3-*exo*-cyano 4-*endo*-phenyl adduct **17a**. The second fraction consisted of Psyn 3-*exo*-phenyl 4-*endo*-cyano adduct **16a** (0.196 g, 15%). Next, benzyl diphenylphosphinate (**20**) was obtained (0.117 g, 17%). The last fraction was the remaining starting material **3** (0.069 g, 7%). One product (18%) was instable to all attempted conditions of isolation.

Psyn 3-*exo*-Phenyl 4-*endo*-Cyano. (2α,3α,4β,5β)-(±)-Phenylmethyl 4-cyano-2-(diphenylphosphinoyl)-3,5-diphenyl-2-pyrrolidinecarboxylate (16a): white powder (ether–light petroleum ether); mp 104–106 °C dec; IR (KBr) 3320, 2235, 1717, 1178 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.73–6.78 (m, 2 H), 7.00–7.05 (m, 2 H), 7.13–7.57 (m, 17 H), 7.68–7.78 (m, 2 H), 7.92–8.03 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 126.6, 127.3, 127.8, 128.1, 128.4, 128.4, 132.1, 132.3, 132.6, 132.8 (each C-H), 128.9, 129.8, 130.9 (each q-C, Ph_2PO), 133.4 (q-C, Bn), 136.7 (q-C, 3-Ph), 137.6 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 33.65; MS, m/z (rel intensity) 380 (M – Ph_2POH, 3), 345 (4), 203 (44), 202 (57), 201 (base peak), 183 (13), 125 (11), 124 (28), 91 (49), 78 (34), 77 (52), 69 (68), 51 (56); HRMS calcd for $C_{25}H_{20}N_2O_2$ (M – Ph_2POH) 380.1525, found 380.1527.

Psyn 3-*exo*-Cyano 4-*endo*-Phenyl. (2α,3α,4β,5β)-(±)-Phenylmethyl 3-cyano-2-(diphenylphosphinoyl)-4,5-diphenyl-2-pyrrolidinecarboxylate (17a): white powder (ether); mp 147–148 °C; IR (KBr) 3340, 2210, 1725, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.67–6.72 (m, 2 H), 6.89–7.00 (m, 7 H), 7.19–7.58 (m, 12 H), 7.86–8.05 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.0, 127.2, 127.5, 127.6, 127.9, 128.3, 128.5, 128.6, 128.7, 128.9, 129.1, 131.9, 132.1, 132.4, 132.5, 132.5, 132.7 (each C-H), 129.6, 129.8 (each q-C, Ph_2PO), 132.9 (q-C, Bn), 135.2 (q-C, 4-Ph), 139.5 (q-C, 5-Ph); ^{31}P NMR ($CDCl_3$) δ 31.51; MS, m/z (rel

intensity) 380 (M – Ph_2POH, 3), 346 (22), 345 (base peak), 344 (15), 289 (9), 268 (7), 202 (24), 201 (47), 129 (32), 115 (11), 108 (21), 107 (15), 102 (9), 91 (97), 89 (22), 79 (27), 78 (15), 77 (52); HRMS calcd for $C_{25}H_{20}N_2O_2$ (M – Ph_2POH) 380.1525, found 380.1543.

Cycloaddition to β-Nitrostyrene. Stirring in ether overnight afforded Psyn endo product **18a**. Yield: 0.927 g (70%).

Psyn Endo. (2α,3α,4β,5β)-(±)-Phenylmethyl 2-(diphenylphosphinoyl)-4-nitro-3,5-diphenyl-2-pyrrolidinecarboxylate (18a): white powder (ether); mp 152–154 °C dec; IR (KBr) 3260, 1721, 1552, 1370, 1192 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.63 (d, 2 H, J = 6.6), 6.74 (d, J = 6.7, 2 H), 7.05–7.60 (m, 17 H), 7.70–7.91 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.1, 127.8, 128.1, 128.2, 128.4, 128.5, 128.7, 128.9, 132.0, 132.2, 133.0, 133.2 (each C-H), 135.2, 135.6 (each q-C, 3-Ph and 5-Ph); ^{31}P NMR ($CDCl_3$) δ 35.16; MS, m/z (rel intensity) 354 (1), 353 (M – Ph_2POH – HNO_2, 2), 246 (8), 245 (14), 219 (34), 218 (21), 217 (32), 216 (10), 202 (12), 201 (24), 199 (11), 191 (10), 189 (11), 91 (base peak), 78 (12), 77 (18), 51 (13); HRMS calcd for $C_{24}H_{19}NO_2$ (M – Ph_2POH – HNO_2) 353.1416, found 353.1407.

Cycloaddition to Phenyl Vinyl Sulfone. Stirring in ether afforded a mixture of Psyn endo adduct **19a** and Panti endo adduct **19c** in 70% yield as a white solid. Flash chromatography (4% triethylamine–ether)[9] gave only a marginal separation: 0.042 g (3%) of pure Psyn endo adduct **19a** and 0.072 g (5%) of pure Panti endo adduct **19c** were obtained. The remaining fractions were mixtures (0.75 g, 55%). A third product present in 13% (which was probably Psyn exo adduct **19b**) was instable to all conditions of isolation.

Psyn Endo. (2α,4β,5β)-(±)-Phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-4-(phenylsulfonyl)-2-pyrrolidinecarboxylate (19a): white solid (ether); mp 120–122 °C; IR (KBr) 3350, 1712, 1306, 1188, 1146 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.06–7.53 (m, 21 H), 7.70–7.90 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.3, 127.7, 128.1, 128.3, 128.6, 128.9, 131.8, 132.0, 132.1, 132.3, 132.6, 132.7, 133.6 (each C-H), 129.5, 130.4 (each q-C, Ph_2PO), 134.6 (q-C, Bn), 137.5, 139.9 (each q-C, Ph); ^{31}P NMR ($CDCl_3$) δ 31.19; MS not possible. Anal. Calcd for $C_{36}H_{32}NO_5PS$: C, 69.55; H, 5.19; N, 2.25; S, 5.16. Found: C, 69.19; H, 5.27; N, 2.23; S, 5.21.

Panti Endo. (2α,4α,5α)-(±)-Phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-4-(phenylsulfonyl)-2-pyrrolidinecarboxylate (19c): white solid (ether); mp 137–139 °C; IR (KBr) 3320, 1708, 1305, 1195, 1142 cm^{-1}; ^1H NMR ($CDCl_3$–CD_3OD ≈ 5–1) δ (Tables III and IV), 7.11–7.65 (m, 21 H), 7.85–7.95 (m, 2 H), 8.13–8.23 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.6, 128.0, 128.2, 128.4, 128.6, 128.7, 129.4, 132.0, 132.2, 132.5, 132.6, 132.9 (each C-H), 134.6 (q-C, Bn), 136.0, 138.7 (each q-C, Ph); ^{31}P NMR ($CDCl_3$) δ 30.92; MS not possible. Anal. Calcd for $C_{36}H_{32}NO_5PS$: C, 69.55; H, 5.19; N, 2.25; S, 5.16. Found: C, 68.69; H, 5.12; N, 2.21; S, 5.25.

Benzyl diphenylphosphinate (20): oil; ^1H NMR ($CDCl_3$) δ 5.06 (d, 2 H, $J_{H,P}$ = 6.6, CH_2), 7.30–7.55 (m, 11 H), 7.78–7.89 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 66.2 (d, $J_{C,P}$ = 6, CH_2), 127.7, 128.2, 128.3, 128.6, 131.5, 131.7, 132.1 (each C-H), 129.8 (q-C, Ph_2PO), 132.5 (q-C, $J_{C,P}$ = 7, Bn); ^{31}P NMR ($CDCl_3$) δ 32.93.

Catalysis of the Cycloaddition. Benzyl *N*-benzylidene-α-(diphenylphosphinoyl)glycinate (**3**) (2.27 g, 5.0 mmol) and lithium acetate dihydrate (0.51 g, 5.0 mmol) were heated to reflux in 12.5 mL of dry THF. Ethyl acrylate (0.58 g, 1.16 equiv) was added and heating was continued for 24 h. The product mixture was cooled to room temperature, dichloromethane (50 mL) and water (50 mL) were added, and the layers were separated. The water was extracted twice with dichloromethane (50 mL each time). The combined organic layers were washed with saturated brine, dried over magnesium sulfate, and filtered and the solvents were evaporated. Stirring in ether overnight afforded 2.16 g (85%) of Psyn endo adduct **11a** as a white solid.

Photooxygenation of 1-Alkyl-2,3-diarylcyclopropanes via Photoinduced Electron Transfer: Stereoselective Formation of 4-Alkyl-3,5-diaryl-1,2-dioxolanes and Their Conversion to 1,3-Diols

Nobuyuki Ichinose, Kazuhiko Mizuno,* Toshiyuki Tamai,† and Yoshio Otsuji*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Received October 1, 1987

The 9,10-dicyanoanthracene-sensitized photooxygenation of 1-alkyl-2,3-diarylcyclopropanes in CH_3CN afforded *c*-4-alkyl-*r*-3,*t*-5-diaryl-1,2-dioxolanes in excellent yields with high stereoselectivity, which upon hydrogenolysis on Pd–charcoal gave quantitatively the corresponding 1,2-*threo*-2,3-*erythro*-2-alkyl-1,3-diaryl-1,3-diols. The mechanistic feature of this photoreaction is described.

The photooxygenation of small-ring compounds via photoinduced electron transfer has received considerable attention in recent years from mechanistic and synthetic viewpoints.[1-6] Cyclic peroxides such as 1,2-dioxolanes[5] and 1,2,4-trioxolanes[2] were prepared by utilizing this photoreaction from cyclopropanes and oxiranes, respectively. Feldman has suggested that 1,2-dioxolanes may be utilized as useful intermediates for the stereocontrolled synthesis of 1,3-diols.[7] However, the stereochemical feature of these photooxygenations has not yet been clarified. Previously, we have reported that the photooxygenation of 1,2-diarylcyclopropanes via photoinduced electron transfer gives *cis*- and *trans*-3,5-diaryl-1,2-dioxolanes. But, the stereo-

† Present address: Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536, Japan.

(1) Futamure, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 1* **1984**, 15. Miyashi, T.; Takahashi, Y.; Yokogawa, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1987**, 175.

(2) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *Ibid.* **1983**, *105*, 5149. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Rahman, A. F. M.; Oliver, J. F. *Ibid.* **1984**, *106*, 6087. Schaap, A. P.; Siddiqui, S.; Balakrishnan, P.; Lopez, L.; Gagnon, S. D. *Isr. J. Chem.* **1983**, *23*, 415. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229.

(3) (a) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493. (b) Shim, S. C.; Song, J. S. *J. Org. Chem.* **1986**, *51*, 2817.