weighting scheme $w = [\sigma^2(F_o) + 0.25(pF_o)^2]^{-1}$ ($p = 0.01$). The error in an observation of unit weights $S = 3.8$. Scattering factors were taken from standard tables.[37] All calculations were performed on a PDP-11/34 minicomputer with an Enraf-Nonius SDP program package and local programs. The final positional and isotropic temperature factors of the non-hydrogen atoms are given in the supplementary material.

Acknowledgment. We thank Professor Roland K. Robins for gifts of cAMP and cUMP. This research was supported by Grant CA 11045 (to W.G.B.) from the National Cancer Institute of the Public Health Service. Thanks are also extended to Professor W. J. Stee in whose laboratory J. Beres became aquainted with the use of the Appel reaction to prepare protected 3',5'-cyclic phosphoramidates.

(37) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1962; Vol. III.

Registry No. 1 (*R* isomer), 94903-45-4; 1 (*S* isomer), 94903-46-5; **1a**, 51642-68-3; 2 (*R* isomer), 71960-54-8; 2 (*S* isomer), 71960-53-7; **2a**, 59618-81-4; 3 (*R* isomer), 94903-47-6; 3 (*S* isomer), 94903-48-7; 4 (*R* isomer), 94844-12-9; 4 (*S* isomer), 94844-13-0; **4a**, 94844-11-8; 5 (*R* isomer), 94844-14-1; 5 (*S* isomer), 94844-15-2; 6 (*R* isomer), 94844-17-4; 6 (*S* isomer), 94844-18-5; 7 (*R* isomer), 94844-19-6; 7 (*S* isomer), 94844-20-9; **7a**, 20212-92-4; 8 (*R* isomer), 94844-23-2; 8 (*S* isomer), 94844-24-3; **8a**, 94844-22-1; 9 (*R* isomer), 94844-27-6; 9 (*S* isomer), 94844-28-7; **9a**, 94844-26-5; Ph_3P, 603-35-0; CCl_4, 56-23-5; dAMP·$2NH_3$, 94844-09-4; cdAMP·NH_3, 94844-10-7; benzylamine, 100-46-9; aniline, 62-53-3; piperidine, 110-89-4; 2'-deoxyadenosine, 958-09-8; uridine 3',5'-cyclic phosphate tributyl ammonium salt, 94844-16-3.

Supplementary Material Available: Listings of fractional atomic coordinates of hydrogen and non-hydrogen atoms, bond lengths, bond angles, torsion angles, weighted least-squares planes and lines, and general temperature factor expressions for the title compound **9**, and analytical data for compounds **1-9** (9 pages). Ordering information is given on any current masthead page.

Synthesis of Heterocyclic Compounds Containing Phosphorus Residues by Cycloaddition of 1,3-Dipoles to Cyclobutenylphosphorus Compounds

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Received September 27, 1984

The cycloaddition reactions of 1-cyclobutenylphosphorus compounds with 1,3-dipoles such as diazomethane, nitrile oxides, and a nitrone regiospecifically gave Δ^1-pyrazolin-3-yl-, Δ^2-isoxazolin-5-yl-, and isoxazolidin-4-ylphosphorus compounds, respectively. The reactivity of 1-cycloalkenylphosphonium salts toward diazomethane was investigated.

1,3-Dipolar cycloadditions of 1,3-dipoles such as diazoalkanes,[1] nitrones,[2] and nitrile imines[3] to vinylphosphonates and related phosphoryl compounds as well as a variety of olefins have been well studied so far. Similar cycloadditions of diazoalkanes,[4] an azide anion,[5] and nitrile ylides[6] to vinyl- and alkenylphosphonium salts and use of the resulting cycloadducts in syntheses of heterocyclic compounds such as pyrazoles, triazoles, and pyrroles as useful intermediate reagents have been reported. However, the reaction of 1,3-dipoles with their homologues, cycloalkenylphosphonium salts, has not been studied to date. On the other hand, we have recently reported the general synthesis[7] and some synthetic applications[8] of cycloalkenylphosphonium salts. In connection with our continuing interest in the utilization of 1-cycloalkenylphosphonium salts, we have examined herein the cycloaddition reactions of 1,3-dipoles with 1-cyclobutenylphosphorus compounds, which provide strained bicycloheterocyclic compounds retaining the phosphorus moiety. Furthermore, the influence of ring sizes of 1-cycloalkenylphosphonium salts on the cycloaddition reaction with diazomethane was investigated.

Results and Discussion

Reaction with Diazomethane. The reaction of 1-cyclobutenyltriphenylphosphonium perchlorate (**1a**) with diazomethane occurred even under mild conditions (0 °C, 5 h) to give only a Δ^1-pyrazolin-3-ylphosphonium salt **3a** in 80% yield. The similar reaction using 1-cyclobutenyldiphenylphosphine oxide (**2**) produced the corresponding Δ^1-pyrazolinylphosphine oxide **4** in 72% yield although rather prolonged reaction time (10 h) was necessitated. On the other hand, similar treatment of **1a** with diphenyldiazomethane led to none of the cycloadduct. In order to investigate the influence of ring sizes of 1-cyclo-

(1) See, for examples: (a) Gareev, R. D.; Loginova, G. M.; Pudovik, A. N. *Zh. Obshch. Khim.* **1979**, *49*, 493; *Chem. Abstr.* **1979**, *91*, 4894*w*. (b) Gareev, R. D.; Pudovik, A. N. *Zh. Obshch. Khim.* **1979**, *49*, 728; *Chem. Abstr.* **1979**, *91*, 56196*q*. (c) Gareev, R. D.; Pudovik, A. N. *Zh. Obshch. Khim.* **1982**, *52*, 2637; *Chem. Abstr.* **1983**, *98*, 143529*p*.

(2) See, for an example: Arbuzov, B. A.; Lisin, A. F.; Dianova, E. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1980**, 715; *Chem. Abstr.* **1980**, 93, 186452*x*.

(3) Platonov, A. Yu.; Trostyanskaya, I. G.; Kazankova, M. A.; Chistokletov, V. N. *Zh. Obshch. Khim.* **1982**, *52*, 268; *Chem. Abstr.* **1982**, 96, 181361*u*.

(4) (a) Schweizer, E. E.; Kim, C. S. *J. Org. Chem.* **1971**, *36*, 4033. (b) Schweizer, E. E.; Kim, C. S. *J. Org. Chem.* **1971**, *36*, 4041. (c) Schweizer, E. E.; Labaw, C. S. *J. Org. Chem.* **1973**, *38*, 3069.

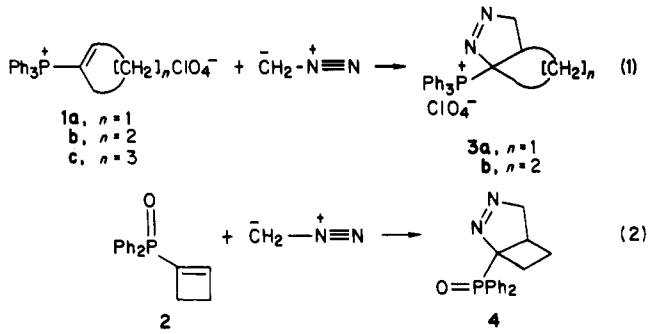
(5) (a) Zbiral, E.; Rasberger, M.; Hengstberger, H., *Justus Liebigs Ann. Chem.* **1969**, *725*, 22. (b) Rasberger, M.; Zbiral, E. *Monatsh. Chem.* **1969**, *100*, 64.

(6) Gakis, N.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta.* **1974**, *57*, 1403.

(7) Saleh, G.; Minami, T.; Ohshiro, Y.; Agawa, T. *Chem. Ber.* **1979**, *112*, 355.

(8) (a) Minami, T.; Sako, H.; Ikehira, T.; Hanamoto, T.; Hirao, I. *J. Org. Chem.* **1983**, *48*, 2569. (b) Minami, T.; Taniguchi, Y.; Hirao, I. *J. Chem. Soc., Chem. Commun.* **1984**, 1046.

0022-3263/85/1950-1278$01.50/0

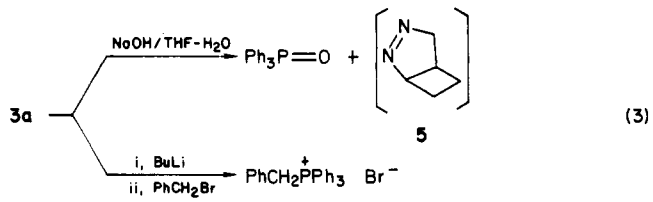


alkenylphosphonium salts on the cycloaddition reaction, treatment of the 1-cyclopentenylphosphonium salt **1b** with diazomethane under similar conditions (0 °C, 6 h) led to the expected 1,3-dipolar cycloadduct **3b** in rather low yield (48%), while the 1-cyclohexenylphosphonium salt **1c** afforded no cycloadduct.

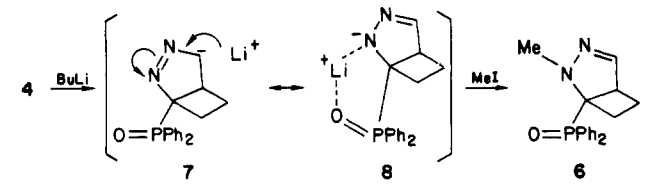
These results indicate that the reactivity of 1-cycloalkenylphosphonium salts toward diazomethane increased with decreasing ring sizes of the salts, that is, **1a** > **1b** > **1c**. Accordingly, the differences in the reactivities among the salts could be reasonably accounted for by their strain energies.

Alkaline hydrolysis of the Δ^1-pyrazolinylphosphonium salt **3a** in aqueous THF containing NaOH gave triphenylphosphine oxide in quantitative yield, but none of expected product derived from the Δ^1-pyrazoline moiety, cyclobuta-Δ^1-pyrazoline derivative, or its decomposition product was isolated in a pure form.

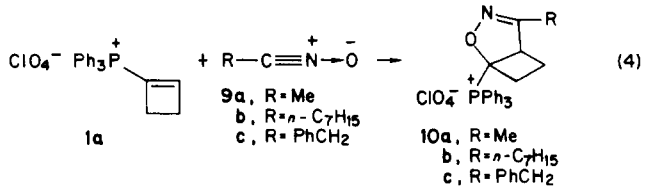
On the other hand, treatment of **3a** with butyllithium at −75 °C, followed by the addition of benzyl bromide, led to only benzyltriphenylphosphonium bromide in 60% yield as an isolable product.



In contrast, similar treatment of **4** with butyllithium and subsequent methylation with methyl iodide exclusively led to the N-methylated compound, (2,3-diazabicyclo[3.2.0]-hept-3-en-1-yl)diphenylphosphine oxide (**6**), in 75% yield.



Reaction with Nitrile Oxides. It is of interest to investigate whether the cycloaddition reactions of nitrile oxides with **1a** and **2** can be either regiospecific or nonregiospecific, since the low regiospecificity in the reactions with olefins such as α,β-unsaturated ketones[9] and esters,[10] styrenes,[11] and indenes[12] have been reported.[13] The reaction of **1a** with methanenitrile oxide (**9a**), generated in situ from nitroethane and phenyl isocyanate in the presence of triethylamine, produced a bicyclic Δ^2-isoxazolinylphosphonium salt **10a** as a sole product in 47% yield.

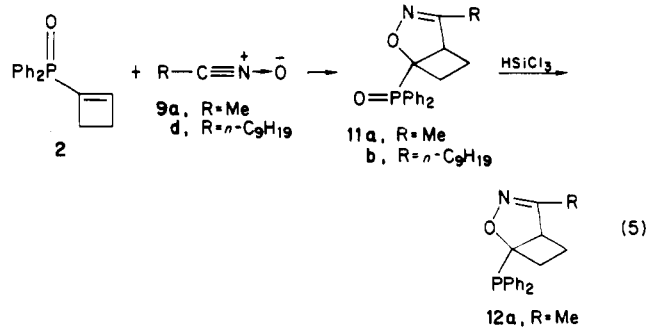


Structural assignment of **10a** was clearly made by its ^1H and ^{13}C NMR spectra (see Experimental Section and Table I). Similar treatment with heptane- (**9b**) and phenylmethanenitrile oxides (**9c**) led to the corresponding cycloadducts **10b** and **10c** in 54% and 44% yields, respectively.

The reaction of **2** with **9a** and nonanenitrile oxide (**9d**) under the similar conditions gave the expected bicyclic Δ^2-isoxazolinylphosphine oxides **11a,b** in comparable yields (43–57% yields).

Since cyclobutenylphosphorus compounds, **1** and **2**, are electron-deficient dipolarophiles, the cycloadditions of nitrile oxides to the phosphorus compounds would be expected to produce 4-substituted Δ^2-isoxazolinylphosphorus compounds along with the 5-substituted isomers.[15] However, the above results show that, regardless of the substituents on the nitrile oxides, the cycloaddition reactions of cyclobutenylphosphorus compounds with nitrile oxides regiospecifically proceed to afford 5-substituted adducts **10** and **11**. Similar cycloaddition behavior has been recently reported in the case using related dipolarophiles such as vinylsilanes bearing electron-withdrawing groups.[14]

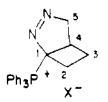
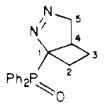
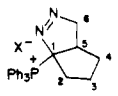
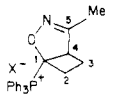
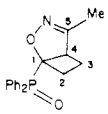
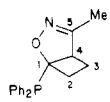
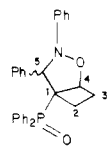
Thus, the regiospecific formation of 5-substituted isoxazolines suggests that the cycloaddition of nitrile oxides to cyclobutenylphosphorus compounds is controlled by LUMO (nitrile oxides) − HOMO(the phosphosphorus compounds).[15] Furthermore, in an attempt to obtain a new type of functionalized phosphine, reduction of the phosphine oxide **11a** with trichlorosilane successfully afforded the hoped-for bicyclic Δ^2-isoxazolinylphosphine **12a** in essentially quantitative yield.



Reaction with a Nitrone. It is well-known that nitrones react with mono- and 1,1-disubstituted alkenes to form regioselectively 5-substituted isoxazolidines.[13,16] We have also investigated the cycloaddition behavior of 1-

(9) Bianchi, G.; de Micheli, C.; Gandolfi, R.; Grünanger, P.; Vita Finzi, P.; Vanja de Pava, O. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1148.
(10) See, for examples: (a) Huisgen, R.; Christl, M. *Chem. Ber.* **1973**, *106*, 3291. (b) Christl, M.; Huisgen, R. *Chem. Ber.* **1973**, *106*, 3345. (c) Huisgen, R.; Christl, M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 456.
(11) Bast, K.; Christl, M.; Huisgen, R.; Mack, W.; Sustmann, R. *Chem. Ber.* **1973**, *106*, 3258.
(12) (a) Bianchi, G.; Gandolfi, R.; Grünanger, Perotti, A. *J. Chem. Soc. C* **1967**, 1598. (b) Bailo, G.; Caramella, P.; Cellerino, G.; Gamba-Invernizzi, A.; Grünanger, P. *Gazz. Chim. Ital.* **1973**, *103*, 47.
(13) For a review, see: Bianchi, G.; de Micheli, C.; Gandolfi, R. "The Chemistry of Double-Bonded Functional Groups"; Patai, S., Ed.; Wiley: London, 1977; Part 1, 435.
(14) Padwa, A.; MacDonald, J. G. *J. Org. Chem.* **1983**, *48*, 3189.
(15) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.
(16) For a review, see: Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; p 861.

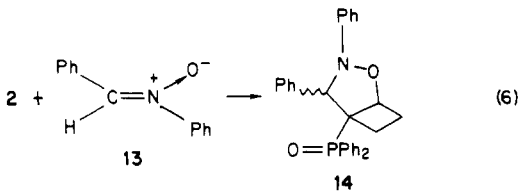
Table I.[a] ^{13}C NMR Data

compd	^{13}C chem shifts, ppm (^{31}P–^{13}C coupling const)						
	1	2	3	4	5	6	Me
 3a	93.05 (53.30)	31.89	25.13 (12.89)	33.78	88.13		
 4	98.34 (74.78)	27.78	24.52 (12.03)	30.69	84.48		
 3b	101.65 (59.31)	36.98	23.15 (8.60)	34.79 (7.74)	39.87 (6.02)	88.53	
 10a	83.44 (56.74)	33.35 (6.02)	23.49 (10.32)	58.18	161.09 (6.02)		10.52
 11a	84.41 (83.38)	30.35 (5.16)	22.69 (8.59)	55.61	159.49 (5.15)		10.74
 12a	86.96 (26.65)	33.89 (13.75)	21.66 (3.44)	56.90 (11.17)	158.69 (4.30)		11.26
 14	59.87 (71.35)	18.75	26.72 (12.89)	78.22 (2.55)	70.96 (7.74)		

[a] Chemical shifts for $CDCl_3$ solutions relative to Me_4Si.

cyclobutenylphosphorus compounds with a representative nitrone, *C,N*-diphenylnitrone (**13**).

In contrast to simple alkenes, treatment of **2** with **13** in refluxing benzene for 2 h regiospecifically produced an unexpected regioisomer, 4-(diphenylphosphinyl)isoxazolidine[18] **14** in 81% yield, while similar treatment of **1a** in



(6)

methylene chloride under reflux for 6 h led to none of the cycloadduct. The structure of **14** was assigned on the basis of spectral data. In contrast to the results using nitrile oxides as 1,3-dipoles, the formation of the cycloadduct **14**, with reversed regiochemistry, suggests that the cycloaddition of the nitrone **13** to the electron-deficient dipolarophile **2** is controlled by HOMO (the nitrone **13**) – LUMO (the phosphine oxide **2**).[15,17]

This result is in accordance with the cycloaddition reactions of nitrones with dipolarophiles such as nitroethylene[17] and a vinyl sulfoxide[19] to give 4-substituted isoxazolidines. Although a satisfactory explanation for such differences in regioselectivities between cycloadditions of the nitrile oxides and the nitrone to the phosphorus compounds could be given by maximal frontier orbital overlapping between HOMO (or LUMO) (1,3-dipoles) and LUMO (or HOMO) (the phosphorus compounds),[20] above results, though rather uncertain, may be readily rationalized by that, on the basis of the extended Hückel (EH) frontier orbital energies for the corresponding unsubstituted 1,3-dipoles,[21] the energy level of the HOMO of the nitrone **13** would be higher than that of the HOMO of the nitrile oxides.

In summary, we have found that cyclobutenylphosphorus compounds undergo ready 1,3-dipolar cycloaddition reactions with a variety of 1,3-dipoles to give regiospecific cycloadducts. Synthetic application of the cycloadducts is now under investigation.

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-FX-60 operating at 60 and 15.04 MHz with Me_4Si as an internal standard. IR spectra were recorded with a Shimazu

(17) Sims, J.; Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 5798.
(18) Although the absolute configuration at C-3 in **14** was not determined, ^1H and ^{13}C NMR data for **14** suggest that the cycloadduct **14** is a single stereoisomer **14**.
(19) Koizumi, T.; Hirai, H.; Yoshii, E. *J. Org. Chem.* **1982**, *47*, 4005.
(20) (a) Sustmann, R. *Tetrahedron Lett.* **1971**, 2717. (b) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 838.
(21) Houk, K. N.; Sims, J.; Duk, R. E., Jr.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287.

IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected.

(*cis*-2,3-Diazabicyclo[3.2.0]hept-2-en-1-yl)triphenylphosphonium Perchlorate (3a). To a solution of the phosphonium salt **1a** (1.41 g, 3.40 mmol) in 30 mL of methylene chloride was added a freshly distilled ethereal solution of diazomethane[22] (ca. 7.0 mmol) at 0 °C. After the mixture was allowed to stand for 5 h at this temperature, ether (30 mL) was added to the reaction mixture to give pure **3a** (1.24 g, 2.71 mmol, 80%) as white solids: mp 156–157 °C; IR (KBr) 1535, 1090 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.00–3.75 (m, 5 H, CH and CH_2), 4.60–5.00 (m, 2 H, CH_2N), 7.35–8.15 (m, 15 H, phenyl H).

Anal. Calcd for $C_{23}H_{22}N_2ClO_4P$: C, 60.47; H, 4.85; N, 6.13. Found: C, 60.23; H, 4.88; N, 6.10.

(*cis*-2,3-Diazabicyclo[3.3.0]oct-2-en-1-yl)triphenylphosphonium Perchlorate (3b). This compound was similarly prepared in 0.45 g (0.96 mmol, 48%) yield from the reaction of 1-cyclopentenyltriphenylphosphonium perchlorate (**1b**) (0.83 g, 1.93 mmol) with diazomethane at 0 °C for 6 h. The compound **3b** had mp 182–183 °C; IR (KBr) 1555, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48–3.60 (m, 7 H, CH and CH_2), 4.40–4.84 (m, 2 H, CH_2N), 7.60–8.00 (m, 15 H, phenyl H).

Anal. Calcd for $C_{24}H_{24}N_2ClO_4P$: C, 61.21; H, 5.14; N, 5.95. Found: C, 61.35; H, 5.35; N, 5.78.

(*cis*-2,3-Diazabicyclo[3.2.0]hept-2-en-1-yl)diphenylphosphine Oxide (4). This compound was similarly prepared in 0.21 g (0.709 mmol, 72%) yield from the reaction of **2** (0.25 g, 0.98 mmol) with diazomethane at 0 °C for 10 h. The compound **4** had mp 128–129 °C; IR (KBr) 1530 and 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–3.50 (m, 4 H, CH_2), 3.50–4.80 (m, 5 H, CH and CH_2N) 7.30-8.45 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{17}H_{17}N_2OP$ 296.113, found, 296.113.

Anal. Calcd for $C_{17}H_{17}N_2OP$: C, 68.90; H, 5.78; N, 9.45. Found: C, 68.66; H, 6.02; N, 9.22.

Alkaline Hydrolysis of 3a. A solution of **3a** (0.30 g, 0.656 mmol) in THF/H_2O (1/1, 20 mL) containing sodium hydroxide (0.56 g, 14 mmol) was stirred at room temperature for 12 h. After evaporation of the solvent in vacuo, the residue was neutralized and extracted with $CHCl_3$. After the usual workup, triphenylphosphine oxide was obtained in 0.18 g (0.647 mmol, 98%) yield together with a mixture of oily products (0.03 g) showing several spots on TLC analysis whose purification was not attempted.

Reaction of 3a with Benzyl Bromide in the Presence of Butyllithium. To a solution of **3a** (0.456 g, 1 mmol) in 10 mL of dry THF was added butyllithium (1.1 mmol) at −75 °C, and the solution was stirred at this temperature for 0.5 h. After benzyl bromide (0.21 g, 1.23 mmol) was added to the solution, the reaction mixture was stirred at room temperature for 3 h. Filtration of the resulting precipitate afforded benzyltriphenylphosphonium bromide in 0.26 g (0.6 mmol, 60%) yield. After the usual workup, the filtrate gave a mixture of oily products (0.23 g) showing several spots on TLC analysis whose purification was not attempted.

Reaction of 4 with Methyl Iodide in the Presence of Butyllithium. The reaction was carried out as described above using **4** (0.09 g, 0.303 mmol), butyllithium (0.303 mmol), and methyl iodide (0.1 mL). After the usual workup, the residue was chromatographed on preparative TLC with ethyl acetate as eluent to give a 0.07 g (0.226 mmol, 74%) yield of white solid whose structure was assigned as **(*cis*-2-methyl-2,3-diazabicyclo-[3.2.0]hept-3-en-1-yl)diphenylphosphine oxide (6)** (mp 95.5–97.0 °C) on the basis of its spectral properties: IR (KBr) 1660, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–2.44 (m, 2 H, CH_2), 2.50–3.00 (m, 2 H, CH_2), 3.13 (s, 3 H, NCH_3), 4.48–4.88 (dt, J = 4.98, 9.82 Hz, CH), 5.60–5.88 (br d, J = 9.82 Hz, CH=N), 7.20–7.90 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{18}H_{19}N_2OP$ 310.123, found 310.122.

Cycloaddition Reactions of Cyclobutenylphosphorus Compounds, 1a and 2, with Nitrile Oxides. General Procedure. To a solution of a cyclobutenylphosphorus compound (1 mmol) and phenyl isocyanate (0.36 g, 3 mmol) in dry CH_2Cl_2 (5 mL) was added nitroalkane (1.5 mmol) and triethylamine (20 drops). The mixture was allowed to stir at room temperature for 1 h and at reflux temperature for 1 h. After removal of the resulting precipitate by filtration, the filtrate was concentrated. The residue was chromatographed on preparative TLC with ether as eluent to give a cycloadduct.

(*cis*-4-Methyl-2-oxa-3-azabicyclo[3.2.0]hept-3-en-1-yl)triphenylphosphonium perchlorate (10a) was prepared by the procedure described above with **1a** (0.41 g, 1 mmol) and nitroethane (0.12 g, 1.5 mmol) in 0.22 g (0.467 mmol, 46.7%) yield: mp 184–185 °C; IR (KBr) 1440, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (s, 3 H, CH_3), 2.10–3.30 (m, 4 H, CH_2), 4.20–4.80 (m, 1 H, CH), 7.40–8.10 (m, 15 H, phenyl H).

Anal. Calcd for $C_{24}H_{23}NClO_5P$: C, 61.09; H, 4.91; N, 2.96. Found: C, 60.94; H, 5.00; N, 2.90.

(*cis*-4-Heptyl-2-oxa-3-azabicyclo[3.2.0]hept-3-en-1-yl)triphenylphosphonium perchlorate (10b) was prepared as described above using **1a** (0.415 g, 1 mmol) and 1-nitrooctane (0.239 g, 1.5 mmol) in 0.295 g (0.54 mmol, 54%) yield: mp 155.5–157 °C; IR (KBr) 1440, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75–3.20 (m, 19 H, CH_3 and CH_2), 4.20–4.90 (m, 1 H, CH), 7.50–8.00 (m, 15 H, phenyl H).

Anal. Calcd for $C_{30}H_{35}NClO_5P$: C, 64.80; H, 6.34; N, 2.52. Found: C, 64.83; H, 6.31; N, 2.65.

(*cis*-4-Benzyl-2-oxa-3-azabicyclo[3.2.0]hept-3-en-yl)triphenylphosphonium perchlorate (10c) was prepared as described above using **1a** (1 mmol) and 2-phenyl-1-nitroethane (0.226 g, 1.5 mmol) in 0.24 g (0.44 mmol, 44%) yield: mp 146.5–148 °C; IR (KBr) 1440, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90–3.20 (m, 4 H, CH_2), 3.77 (s, 2 H, CH_2Ph), 4.20–4.80 (m, 1 H, CH), 7.23 (s, 5 H, phenyl H), 7.50–8.00 (m, 15 H, phenyl H).

Anal. Calcd for $C_{30}H_{27}NClO_5P$: C, 65.75; H, 4.97; N, 2.55. Found: C, 65.80; H, 5.18; N, 2.72.

(*cis*-4-Methyl-2-oxa-3-azabicyclo[3.2.0]hept-3-en-1-yl)diphenylphosphine oxide (11a) was prepared by the procedure described above with **2** (0.1 g, 0.39 mmol), phenyl isocyanate (0.12 g, 1.1 mmol), and nitroethane (0.045 g, 0.6 mmol) in dry benzene (5 mL) in a 0.07 g (0.225 mmol, 57.7%) yield: sticky oil; IR (neat) 1440, 1180, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (s, 3 H, Me), 2.00–3.10 (m, 4 H, CH_2), 3.60–4.20 (m, 1 H, CH), 7.30–8.10 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{18}H_{18}NO_2P$ 311.107, found 311.107.

(*cis*-4-Nonyl-2-oxa-3-azabicyclo[3.2.0]hept-3-en-1-yl)diphenylphosphine oxide (11b) was prepared by the procedure described above with **2** (0.125 g, 0.49 mmol) and 1-nitrodecane (0.14 g, 0.75 mmol) in a 0.09 g (0.21 mmol, 43%) yield: oil; IR (KBr) 1440, 1190, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60–1.60 (m, 17 H, CH_3 and CH_2), 1.80–3.20 (m, 6 H, CH_2), 3.70–4.20 (m, 1 H, CH), 7.30–8.10 (m, 10 H, phenyl H); MS, m/z 423 (M^+).

Anal. Calcd for $C_{26}H_{34}NO_2P$: C, 73.73; H, 8.09; N, 3.31. Found: C, 73.33; H, 8.39; N, 3.38.

Reduction of 11a. A solution of **11a** (0.07 g, 0.22 mmol) and trichlorosilane (0.3 mL, 2.97 mmol) in dry benzene (10 mL) was heated at 110 °C for 15 h in a sealed tube. After removal of solvent and excess trichlorosilane, the residue was dissolved in benzene. The benzene solution was washed with aqueous sodium hydroxide solution (25%). After removal of the resulting insoluble silicate by filtration, the organic layer was dried on sodium sulfate and concentrated in vacuo to give a crude phosphine. The crude phosphine was chromatographed on preparative TLC with $CHCl_3$ as eluent to afford a 0.06 g (0.203 mmol, 90%) yield of pure **(*cis*-4-methyl-2-oxa-3-azabicyclo[3.2.0]hept-3-en-1-yl)diphenylphosphine (12a)**: oil; IR (neat) 1430, 745, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (s, 3 H, CH_3), 2.00–3.00 (m, 4 H, CH_2), 3.20–3.80 (m, 1 H, CH), 7.10–7.76 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{18}H_{18}NOP$ 295.113, found 295.109.

(*cis*-3,4-Diphenyl-2-oxa-3-azabicyclo[3.2.0]hept-5-yl)diphenylphosphine Oxide (14). A solution of **2** (0.055 g, 0.22 mmol) and *C,N*-diphenylnitrone (0.052 g, 0.26 mmol) in dry benzene (5 mL) was heated at reflux for 2 h. After removal of the solvent, the residue was chromatographed on preparative TLC with ether as eluent to give a 0.08 g (0.177 mmol, 81%) yield of **14**: mp 146–147 °C: IR (KBr) 1595, 1490, 1440, 1180, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–2.80 (m, 4 H, CH_2), 4.84 (d, J = 13.18 Hz, 1 H, NC*H*Ph), 5.00–5.40 (m, 1 H, OCH), 6.80–7.90 (m, 20 H, phenyl H); HRMS, m/z calcd for $C_{29}H_{26}NO_2P$ 451.170, found 451.173.

(22) de Boer, Th. J.; Backer, H. J. "Organic Synthesis"; Wiley: New York, 1963; Collect. Vol. 4, p 250.