reaction mixtures containing chlorosilane products were filtered under N_2 and then distilled rather than being subjected to a hydrolysis step. The dibromide **7** was not prepared from the corresponding piperidine, but by the method of Anteunis starting from 3,3-dimethylglutaric acid.[14]

Preparation of *N*-Benzoyl-3-methylpiperidine. Sodium hydroxide pellets (52.5 g, 1.3 mol) and 400 mL of distilled water were placed in a three-necked round-bottomed flask equipped with mechanical stirrer, nitrogen inlet system, and an addition funnel. The solution was maintained at room temperature throughout the subsequent exothermic reaction by using an ice cold water bath. 3-Methylpiperidine (99.2 g, 1.0 mol) was poured into the sodium hydroxide solution and stirring commenced. From an addition funnel benzoyl chloride (140 g, 1.0 mol) was added slowly (ca. 2 h) to the solution. The reaction mixture became yellow in color and at the end of the addition was transferred to a separatory funnel and the top, yellow oily, layer was collected. Water was removed by simple distillation, and the product was collected by reduced pressure distillation, giving a colorless heavy oily liquid (190 g, 94%), bp 203-205 °C/(10 mm).

Preparation of 1,5-Dibromo-2-methylpentane. *N*-Benzoyl-3-methylpiperidine (42.6 g, 0.21 mol) was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, thermometer, addition funnel, and nitrogen inlet system, and phosphorus tribromide (56.8 g, 0.21 mol) was added from an addition funnel over ca. 2 h. An ice-water bath was used to maintain the reaction temperature between 24 and 34 °C. Liquid bromine (10.4 mL, 0.21 mol) was placed in another addition funnel and added slowly to the reaction mixture over 4 h. The reaction mixture became a very thick dark brown oily liquid. It was heated very gently for 2 h to remove fumes of Br_2 and then distilled at 112-130 °C/5 mm to collect a mixture of oxyphosphorus tribromide, phenyl cyanide, and the dibromide product. A black residue remained in the flask. The distillate was slowly poured into an Erlenmeyer flask which contained 250 g of crushed ice to decompose the oxyphosphorus tribromide. The resulting liquid was extracted with 2 × 200 mL of ligroine and the combined ligroine layers were extracted very carefully with 10 × 15 mL of concentrated sulfuric acid in order to convert phenyl cyanide to benzoic acid. The ligroine layer was neutralized by washing with 2 × 100 mL of dilute sodium hydroxide solution, then washed with 2 × 100 mL of distilled water, and finally dried over anhydrous calcium chloride. The ligroine was removed by simple distillation, and the product, 1,5-dibromo-2-methylpentane, was collected by reduced pressure fractional distillation to give a colorless liquid (31.5 g, 61.5%), bp 113-114 °C (15 mmHg).

Preparation of 1,3-Dimethyl-1-silacyclohexane. Magnesium turnings (2.3 g, 0.1 mol) and 100 mL of anhydrous ether were placed in a three-necked round-bottomed flask equipped with a mechanical stirrer, addition funnel, reflux condenser, and nitrogen inlet system. The Mg was activated with 1.0 mL of 1,2-dibromoethane for 2 h. 1,5-Dibromo-2-methylpentane (10.0 g, 0.04 mol) and 250 mL of anhydrous ether were placed in an addition funnel and added slowly to the activated Mg. After finishing the addition, the reaction mixture was refluxed for 8 h, and then cooled to room temperature. Methyldichlorosilane (4.6 mL, 0.04 mol) in 100 mL of anhydrous ether was added at a very slow rate to the di-Grignard solution, followed by reflux of the reaction mixture for 14 h. After cooling, saturated ammonium chloride was added while cooling externally with ice water. After two layers had clearly formed, an additional 50 mL of distilled water was added. The ether layer was collected, washed with 2 × 100 mL of distilled water, and dried over anhydrous magnesium sulfate. The ether was removed by fractional distillation and the product distilled under reduced pressure through a short path distillation head to give a 50:50 mixture of two isomers (2.8 g, 53%), bp 55-56 °C (71 mmHg) as a colorless liquid.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Utilization of a 1-Cyclobutenylphosphine Oxide as a 2-Phosphinyl-1,3-butadiene Synthon. Synthesis of Functionalized 1-Phosphinylcyclohexenes

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Received December 3, 1985

The Diels-Alder reactions of 2-(diphenylphosphinyl)-1,3-butadiene, generated in situ from (1-cyclobutenyl)diphenylphosphine oxide, with various unsymmetrical dienophiles such as ethyl acrylate, benzalacetone, benzalacetophenone, crotonaldehyde, ethyl methacrylate, and 1,3-butadiene gave functionalized (1-cyclohexenyl)diphenylphosphine oxides in 28-86% yields. The effect of boron trifluoride etherate and aluminum trichloride on the regiochemistry was examined. The 1-cyclobutenylphosphine oxide and a 1-cyclobutenylphosphonium salt have also been demonstrated to be good dienophiles in the Diels-Alder reactions with cyclopentadiene.

Although development of various kinds of functionalized dienes and their synthetic applications to the Diels-Alder reaction have been well-studied,[1] those of dienes having the phosphorus residues have, to our knowledge, been reported to a small degree.[2,3] On the other hand, functionalized 1-cyclohexenylphosphorus compounds are expected to be versatile reagents for introduction of cyclohexane structural units into complex organic molecules, but their syntheses have not been reported until our recent study[3] and the related studies.[4-6] Recently we reported a general synthesis[7] and some synthetic applications[3,8,9] of

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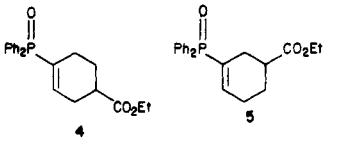
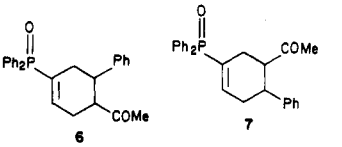
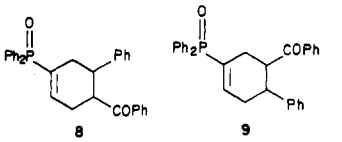
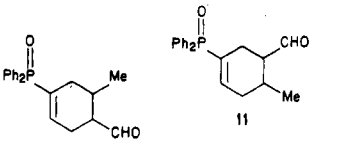
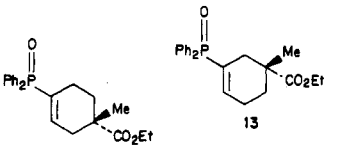
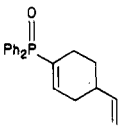
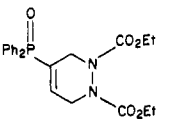
Table I. Reactions of 2-(Diphenylphosphinyl)-1,3-butadiene[a] (2)

entry	dienophile	conditns[b]	adducts	ratio[c]	yields (%)
1	ethyl acrylate	(a) neat, 150 °C, 3 h (b) neat, BF_3·OEt_2, 150 °C, 3 h (c) neat, $AlCl_3$, 150 °C, 3 h	 4 5	2.2:1 2.1:1 2.9:1	86 81 78
2	benzalacetone	(a) neat, 150 °C, 3 h (b) neat, BF_3·OEt_2, 150 °C, 6 h (c) neat, $AlCl_3$, 150 °C, 6 h	 6 7	1:2.1 1:1.3 1:0.8	38 30 30
3	benzalacetophenone	neat, 150 °C, 6 h	 8 9	1.5:1	33
4	crotonaldehyde	neat, 150 °C, 6 h	 10 11	1.3:1	55
5	ethyl methacrylate	neat, 150 °C, 3 h	 12 13	4:1	84
6	butadiene[d]	PhH, 170 °C, 1 h	 15		28
7	diethyl azodicarboxylate	PhH, 150 °C, 3 h	 19		82

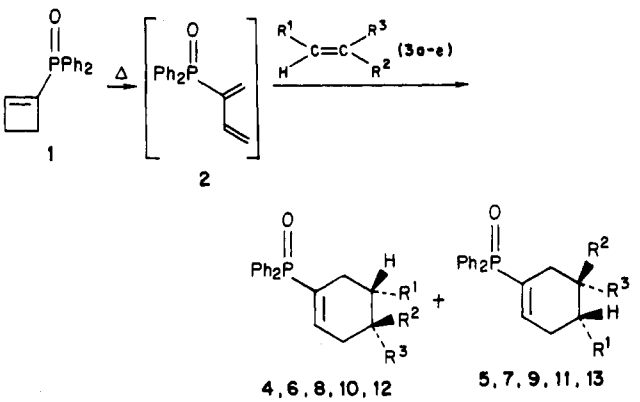
[a] Generated in-situ by thermolysis of (1-cyclobutenyl)diphenylphosphine oxide (1) in the reaction system. [b] All reactions were carried out in a sealed tube. [c] Determined by comparison of the intensity of C-2 resonances of two isomers in the ^{13}C NMR spectrum of the mixture. [d] Generated in situ by thermolysis of sulfolene (14) in the reaction system.

various ring size 1-cycloalkenylphosphorus compounds. We are now able to report the successful utilization of 1-cyclobutenylphosphine oxide **1** as a 2-(diphenylphosphinyl)-1,3-butadiene synthon in Diels–Alder reactions with dienophiles and dienes.

Results and Discussion

Synthesis of Functionalized (1-Cyclohexenyl)diphenylphosphine Oxides. Treatment of (1-cyclobutenyl)diphenylphosphine oxide (**1**) with excess amounts of ethyl acrylate (**3a**) at 150 °C for 3 h in a sealed tube produced a 2.2:1 mixture of (4-(ethoxycarbonyl)-1-cyclohexenyl)- and (5-(ethoxycarbonyl)-1-cyclohexenyl)diphenylphosphine oxides **4** and **5** in 86% yield. Although the ^1H NMR spectrum of the mixture of the adducts **4** and **5** did not play an important role in determining their structures, its proton-decoupled ^{13}C NMR spectrum showed characteristic singlet peaks at δ 38.17 and at δ 23.94, which were assigned as the C-4 carbons of **4** and **5**,

Scheme I



3a, 4, 5, R^1=H; R^2=CO_2Et; R^3=H
3b, 6, 7, R^1=Ph; R^2=COMe; R^3=H
3c, 8, 9, R^1=Ph; R^2=COPh; R^3=H
3d, 10, 11, R^1=Me; R^2=CHO; R^3=H
3e, 12, 13, R^1=H; R^2=CO_2Et; R^3=Me

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respectively, since the C-4 carbon of (1-cyclohexenyl)diphenylphosphine oxide exhibited a singlet peak at δ 21.4 in the ^{13}C NMR spectrum.[8] The assignments of other carbons of the cyclohexenyl ring in **4** and **5** rest upon the couplings between respective carbons and phosphorus and their chemical shifts (Table II). Thus, the structures of **4** and **5** were reasonably assigned as the structures **4** and **5**. The ratio of the regioisomers **4** and **5** was determined by comparison of the intensity of C-2 resonances in the ^{13}C NMR spectrum of the mixture. The reaction at 125 °C gave a mixture of **4** and **5** in low yield (ca. 30% yield) together with unreacted **1**, while the reaction at 100 °C afforded none of adduct. Accordingly, the following Diels–Alder reactions were carried out at 150 °C.

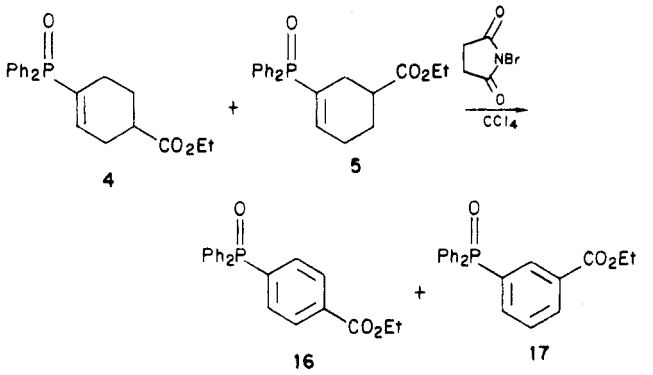
Treatment of **1** with benzalacetone (**3b**), benzalacetophenone (**3c**), and crotonaldehyde (**3d**) led to mixtures of the following regioisomeric Diels–Alder adducts: **6** and **7** (1:2.1), **8** and **9** (1.5:1), and **10** and **11** (1.3:1) in 38%, 33%, and 55% yields, respectively. The structural assignments of the adducts were similarly made. Although the diphenylphosphinyl group in the 2-position of 2-(diphenylphosphinyl)-1,3-butadiene (**2**), generated in situ via thermolysis of **1**, could be expected to be a regiochemical control group, the above results suggest that the diphenylphosphinyl group has little influence on the regiochemistry of the Diels–Alder addition of the diene **2** to the olefins **3a–d**.

With a view of improving regioselectivity in functionalized 1-cyclohexenylphosphine oxides, we have examined the effect of Lewis acids in these Diels–Alder reactions. The reaction of **1** and **3a** and **3b** in the presence of the boron trifluoride etherate (BF_3·OEt_2) showed no improvement in the regioisomeric ratio or yields (see Table I). On the other hand, using aluminum trichloride ($AlCl_3$) as a Lewis acid caused a significant change in the ratios of **4:5**, and of **6:7** (2.9:1, 78% and 1:0.8, 30%, respectively). These results indicate that, in the Lewis acid catalyzed Diels–Alder reactions, $AlCl_3$ exerts greater effect on regiochemistry than does BF_3·OEt_2. Although the degree of change was small, the direction of change of regioselectivity in the adduct with olefin **3a** relative to olefin **3b** is of importance.

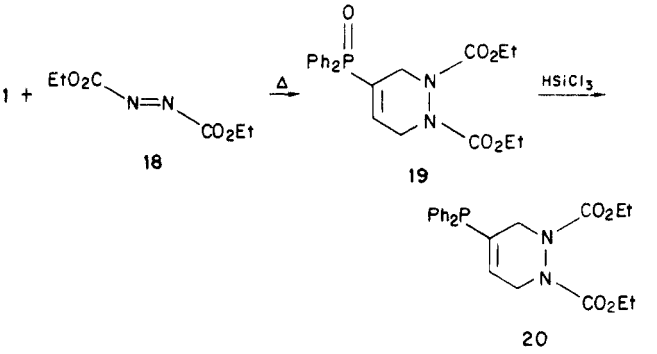
The Diels–Alder addition of **2** to a 1,1-disubstituted olefin, ethyl methacrylate (**3e**), gave a 4:1 mixture of (4-(ethoxycarbonyl)-4-methyl-1-cyclohexenyl)- and (5-(ethoxycarbonyl)-5-methyl-1-cyclohexenyl)diphenylphosphine oxides **12** and **13** in 84% yield. Thus, 1-substituted and 1,1-disubstituted dienophiles (**3a** and **3e**, entry 1 and 5 in Table I) gave cycloadducts in good yields, in which 4-substituted and 4,4-disubstituted 1-cyclohexenylphosphine oxides predominated. In contrast, 1,2-disubstituted dienophiles (**3b–d**, entry 2–4) gave cycloadducts in rather poor yields, since the reactions produced a dimeric product of **2** whose structure could not be assigned. It is interesting to note that whereas the major regioisomer from benzalacetone (**3b**) was the 5-acylated compound **7**, benzalacetophenone (**3c**) produced the 4-acylated product **8** as the major component of the isomeric mixture.

With 1,3-butadiene generated by the pyrolysis of sulfolene (**14**), **2** still acts as the diene component but also undergoes self trapping. Thus, when a mixture of **1** and **14** were heated in benzene at 170 °C for 1 h, a single regioisomer, (4-ethenyl-1-cyclohexenyl)diphenylphosphine oxide (**15**) albeit in low yield (28% yield), was produced together with the dimerization product (40%) of the diene **2**.

Treatment of the mixutre of **4** and **5** with *N*-bromosuccinimide in carbon tetrachloride led to a mixture of aromatization products **16** and **17** in the same ratio as that of the starting mixture. This provides additional structure proof for the regiochemistry of adducts **4** and **5**.



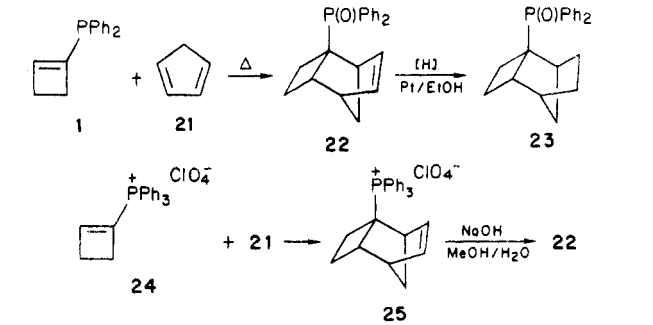
The thermal reaction of **1** with diethyl azodicarboxylate (**18**) (benzene, 150 °C, 3 h) produced the expected cycloadduct, 1,2-bis(ethoxycarbonyl)-1,2,3,6-tetrahydro-4-(diphenylphosphinyl)pyridazine (**19**) in 83% yield. Reduction



of the adduct **19** with trichlorosilane gave the corresponding phosphine **20** in rather low yield (32%). The low yield in the reduction may be due to the ease of hydrolysis of **20** during workup.

In contrast to the above results, the Diels–Alder reaction of the diene **2** with electron-rich dienophiles such as ethyl vinyl ether and benzylideneisopropylamine under the similar conditions produced either none or a very poor yield of cycloadduct but mainly led to the dimerization product of **2**.

Adducts of 1 and a 1-Cyclobutenylphosphonium Salt with Cyclopentadiene. Since the reaction of 1-cyclobutenylphosphorus compounds with 1,3-dipoles has successfully given cycloadducts,[3] the cyclobutenylphosphine oxide (**1**) could also be expected to act as a good



dienophile in addition to a diene precursor. Hence, we allowed **1** to react with cyclopentadiene (**21**) at 150 °C for 3 h and obtained exclusively the desired cycloadduct (tricyclo[4.2.1.$0^{2,5}$]non-7-en-2-yl)diphenylphosphine oxide (**22**) in 90% yield. Furthermore, catalytic hydrogenation of **22** in ethanol over platinum catalyst produced (tricy-

clo[4.2.1.$0^{2,5}$]nonan-2-yl)diphenylphosphine oxide (**23**) in good yield. Treatment of a 1-cyclobutenylphosphonium salt **24** with **21** similarly led to the corresponding Diels–Alder adduct **25** in 74% yield. Since both reactions exclusively gave single isomers **22** and **25**, respectively, their structures were tentatively assigned as the endo adducts on the basis of secondary orbital interactions, although the exo structures can not be eliminated. Hydrolysis of the adduct **25** in aqueous methanol containing excess sodium hydroxide at reflux for 10 days gave the phosphine oxide **22** in only 13% yield together with recovered **25**. In contrast to most alkyltriphenylphosphonium salts,[10] this has suggested that nucleophilic attack of hydroxide ion at phosphorus in **25** is strongly hindered by the tricyclononen substituent. The reaction of **1** with furan under the similar conditions gave no Diels–Alder adduct, but only the dimer of **2** was obtained.

In summary, we have found that (1-cyclobutenyl)diphenylphosphine oxide is a versatile 2-(diphenylphosphinyl)-1,3-butadiene synthon for the synthesis of functionalized cyclohexenylphosphorus compounds but in certain cases can also function as good dienophilic reagent for introduction of the cyclobutane moiety.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were obtained in a $CDCl_3$ solution 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 IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer.

General Procedure for the Synthesis of (1-Cyclohexenyl)diphenylphosphine Oxides 4–13 from 1 and Dienophiles 3a–e. A mixture of **1** (0.25 g, 1 mmol), **3** (2–5 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (BHT stabilizer, 50 mg) was heated at 150 °C without or with Lewis acid catalysis (1.2 mmol) under a nitrogen atmosphere in a glass tube. The reaction mixtures were chromatographed on preparative TLC to give pure Diels–Alder adducts. Isolation of each of regioisomers was unsuccessful. The yields and ^{13}C NMR data of the adducts are summarized in Table I and in Table II, respectively.

(4- and (5-(Ethoxycarbonyl)-1-cyclohexenyl)diphenylphosphine Oxides (4 and 5). A: yield 0.31 g (0.86 mmol, 86%); sticky oil; IR (neat) 1725, 1630, 1180 cm^{-1}; ^1H NMR δ 1.20 and 1.24 (2 t, J = 7.20 Hz, 3 H, CH_3), 2.00–2.60 (m, 7 H, CH_2 and CH), 4.10 and 4.15 (2 q, J = 7.20 Hz, 2 H, OCH_2), 6.36 (br d, J = 19.92 Hz, 1 H, olefinic H), 7.20–7.96 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{21}H_{23}O_3P$ 354.1385 (M^+), found 354.1409.

B. With BF_3·OEt_2. After similar treatment, the reaction mixture was dissolved in CH_2Cl_2 and washed with aqueous $NaHCO_3$ 3 times and with water, followed by drying over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on preparative TLC (ethylacetate) to give a mixture of **4** and **5** in 0.29 g (0.81 mmol, 81%) yield.

C. With $AlCl_3$: yield 0.28 g (0.78 mmol, 78%).

(4-Acetyl-5-phenyl-1-cyclohexenyl)- and (5-Acetyl-4-phenyl-1-cyclohexenyl)diphenylphosphine Oxides (6 and 7). A: yield 0.15 g (0.38 mmol, 38%); sticky oil; IR (neat) 1705, 1630, 1170 cm^{-1}; ^1H NMR δ 1.71 (s, 3 H, CH_3), 2.00–3.20 (br m, 6 H, CH_2 and CH), 6.35 (br d, J = 19.48 Hz, 1 H, olefinic H), 7.00–8.00 (m, 15 H, phenyl H); HRMS, m/z calcd for $C_{26}H_{19}O_2P$ 400.1590 (M^+), found 400.1574.

B. With BF_3·OEt_2: yield 0.12 g (0.30 mmol, 30%).

C. With $AlCl_3$: yield 0.12 g (0.30 mmol, 30%).

(4-Benzoyl-5-phenyl-1-cyclohexenyl)- and (5-benzoyl-4-phenyl-1-cyclohexenyl)diphenylphosphine oxides (8 and 9): yield 0.15 g (0.33 mmol, 33%); mp 103–105 °C; IR (KBr) 1670, 1635, 1170 cm^{-1}; ^1H NMR δ 2.16–3.60 (br m, 6 H, CH_2 and CH), 6.35 (br d, J = 20.65 Hz, 1 H, olefinic H), 7.0–8.0 (m, 20 H, phenyl H); HRMS, m/z calcd for $C_{31}H_{17}O_2P$ 462.1749 (M^+), found 462.1768.

(4-Formyl-5-methyl-1-cyclohexenyl)- and (5-formyl-4-methyl-1-cyclohexenyl)diphenylphosphine oxides (10 and 11): yield 0.18 g (0.55 mmol, 55%); sticky oil; IR (neat) 1720, 1625, 1170 cm^{-1}; ^1H NMR δ 0.85–1.15 (br, 3 H, CH_3), 1.75–3.25 (br m, 6 H, CH_2 and CH), 6.33 (br d, J = 17.03 Hz, 1 H, olefinic H), 7.25–8.00 (m, 10 H, phenyl H), 9.64 and 9.71 (2 d, J = 3.66 Hz, J = 5.12 Hz, 1 H, CHO); HRMS, m/z calcd for $C_{20}H_{21}O_2P$ 324.1255 (M^+), found 324.1278.

(4-(Ethoxycarbonyl)-4-methyl-1-cyclohexenyl)- and (5-(ethoxycarbonyl)-5-methyl-1-cyclohexenyl)diphenylphosphine oxides (12 and 13): yield 0.31 g (0.84 mmol, 84%); sticky oil; IR (neat) 1720, 1625, 1175 cm^{-1}; ^1H NMR δ 1.21 (t, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.50–3.10 (m, 6 H, CH_2), 3.90–4.32 (q, 2H, OCH_2), 6.34 (br d, J = 22.12 Hz, 1 H, olefinic H), 7.24–7.94 (m 10 H, phenyl H); HRMS, m/z calcd for $C_{22}H_{25}O_3P$ 368.1542 (M^+), found 368.1508.

Reaction of 1 with 14. A solution of **1** (0.50 g, 2 mmol) and **14** (0.50 g, 4.2 mmol) in benzene (3 mL) was heated at 170 °C for 1 h in a sealed tube. After usual workup, the residue was chromatographed on preparative TLC to give **15** (0.17 g, 0.55 mmol, 28%) and the dimer (0.20 g, 40%) of the diene **2**.

The compound **15** had the following properties: sticky oil; IR (neat) 1625, 1175 cm^{-1}; ^1H NMR δ 1.0–2.65 (m, 7 H, CH_2 and CH), 4.87 (br, 1 H, olefinic H), 5.10 (d, J = 3.66 Hz, 1 H, olefinic H), 5.50–5.95 (br, 1 H, olefinic H), 6.40 (br d, J = 20.3 Hz, 1 H, olefinic H), 7.20–8.0 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{20}H_{21}OP$ 308.1331 (M^+), found 308.1333.

The dimer had the following properties: sticky oil; IR (neat) 1625, 1175 cm^{-1}; ^1H NMR δ 1.10–3.20 (m, 6 H, CH_2), 5.0–5.75 (m, 3 H, olefinic H), 6.30 (br d, J = 20.69 Hz, 1 H, olefinic H), 7.10–8.15 (m, 20 H, phenyl H); HRMS, m/z calcd for $C_{32}H_{30}O_2P_2$ 508.1720 (M^+), found 508.1703.

Aromatization of 4 and 5. A solution of a mixture (0.09 g, 0.25 mmol) of **4** and **5**, *N*-bromosuccinimide (0.09 g, 0.5 mmol), and benzoyl peroxide (trace amounts) in CCl_4 (10 mL) was refluxed for 4 h. After the solution was cooled, the resulting precipitate was filtered. Upon concentration of the filtrate, the residue was chromatographed on preparative TLC with ethyl acetate as eluent to give 0.07 g (0.2 mmol, 80%) of a 2.2:1 mixture of **(4-(ethoxycarbonyl)- and (5-(ethoxycarbonyl)phenyl)diphenylphosphine oxides (16 and 17)** whose ratio was determined by HPLC analysis: IR (neat) 1720, 1185 cm^{-1}; ^1H NMR δ 1.34 and 1.38 (2 t, J = 7.18 Hz, 3 H, CH_3), 4.35 and 4.39 (2 q, J = 7.18 Hz, 2 H, OCH_2), 7.30–8.40 (m, 14 H, phenyl H); HRMS, m/z calcd for $C_{21}H_{19}O_3P$ 350.1079 (M^+), found 350.1071.

1,2-Bis(ethoxycarbonyl)-1,2,3,6-tetrahydro-4-(diphenylphosphinyl)pyridazine (19). The adduct **19** was similarly obtained from **1** (0.1 g, 0.39 mmol) and **18** (0.1 g, 0.57 mmol) in benzene (10 mL) as a sticky oil: yield 0.14 g (0.33 mmol, 83%); IR (neat) 1720, 1630, 1180 cm^{-1}; ^1H NMR δ 1.22 and 1.25 (2 t, J = 7.18 Hz, 6 H, CH_3), 3.60–4.90 (m, 4 H, CH_2), 4.18 and 4.20 (2 q, J = 7.18 Hz, 4 H, OCH_2), 6.45 (br d, J = 19.0 Hz, 1 H, olefinic H), 7.40–7.90 (m 10 H, phenyl H); HRMS, m/z calcd for $C_{22}H_{25}O_5N_2P$ 428.1499 (M^+), found 428.1467.

Reduction of 19. A solution of **19** (0.26 g, 0.61 mmol) and trichlorosilane (1 mL, 10 mmol) in dry benzene (10 mL) was heated at 100 °C for 10 h in a sealed tube. After the usual workup, the residue was chromatographed on preparative TLC (ether/hexane, 1:1) to give **20** (0.08 g, 0.19 mmol, 32%) as a sticky oil; IR (neat) 1710 cm^{-1}; ^1H NMR δ 1.20 and 1.23 (2 t, 6 H, CH_3), 3.40–4.80 (m, 4 H, CH_2), 4.16 and 4.19 (2 q, 4 H, OCH_2), 5.96 (br d, J = 11.57 Hz, 1 H, olefinic H), 7.20–7.60 (m 10 H, phenyl H); HRMS, m/z calcd for $C_{22}H_{25}O_4N_2P$ 412.1552 (M^+), found 412.1587.

Cycloaddition of 1 to Cyclopentadiene (21). A mixture of **1** (0.22 g, 0.87 mmol) and **21** (1 mL) was similarly heated at 150 °C for 3 h. After removal of excess **21** in vacuo, the residue was chromatographed on preparative TLC to give 0.25 g (0.78 mmol, 90%) yield of **22** as a sticky oil whose structure was assigned as **(tricyclo[4.2.1.$0^{2,5}$]non-7-en-2-yl)diphenylphosphine oxide** on the basis of its spectral properties: IR (neat) 1610, 1440, 1180 cm^{-1}; ^1H NMR δ 0.75–2.50 (m, 6 H, CH_2), 2.75–3.50 (m, 3 H, CH), 6.55 (s, 2 H, olefinic H), 7.30–7.95 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{21}H_{21}OP$ 320.1330 (M^+), found 320.1339.

Reduction of 22. The hydrogenation of **22** (0.18 g, 0.56 mmol) was accomplished in 8 h in ethanol over Pt (PtO_2, 10 mg) to afford **23** (0.15 g, 0.47 mmol, 83%) as a sticky oil: IR (neat) 1435, 1170

(10) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976; p 261.

cm^{-1}; ^{1}H NMR δ 1.10–3.30 (br m, 13 H, CH_2 and CH), 7.25–7.90 (m, 10 H, phenyl H); HRMS, m/z calcd for $C_{21}H_{23}OP$ 322.1486 (M^+), found 322.1473.

Cycloaddition of 24 to 21. A mixture of **24** (0.40 g, 0.96 mmol) and **21** (1.5 mL) in CH_2Cl_2 (3 mL) was similarly heated at 140 °C for 3 h. Addition of ether to the reaction mixture gave pure **(tricyclo[4.2.1.0^{2,5}]non-7-en-2-yl)triphenylphosphonium perchlorate (25)** (0.34 g, 0.71 mmol, 74%): mp 228–230 °C; IR (KBr) 1610, 1590, 1485, 1100 cm^{-1}; ^{1}H NMR δ 1.0–2.47 (br m, 6 H, CH_2), 2.80–3.60 (br m, 3 H, CH), 6.71 (br s, 2 H, olefinic H), 7.50–7.90 (m, 15 H, phenyl H).

Anal. Calcd for $C_{27}H_{26}O_4PCl$: C, 67.42; H, 5.45. Found: C, 67.27; H, 5.58.

Alkaline Hydrolysis of 25. A solution of **25** (1.40 g, 2.9 mmol) in methanol/H_2O (2:1, 60 mL) containing NaOH (1.40 g, 35 mmol) was heated at reflux for 10 days. After the usual workup, the residue was chromatographed on silica gel to give **22** in 0.12 g (0.38 mmol, 13%) yield together with recovered **25** (0.96 g, 2 mmol, 70%).

Registry No. **1**, 86046-76-6; **2**, 101630-34-6; **3a**, 140-88-5; **3b**, 1896-62-4; **3c**, 614-47-1; **3d**, 123-73-9; **3e**, 97-63-2; **4**, 101630-22-2; **5**, 101630-23-3; **6**, 101630-24-4; **7**, 101630-25-5; **8**, 101630-26-6; **9**, 101630-27-7; **10**, 101630-28-8; **11**, 101630-29-9; **12**, 101630-30-2; **13**, 101630-31-3; **14**, 77-79-2; **15**, 101630-32-4; **16**, 101630-35-7; **17**, 101630-36-8; **18**, 1972-28-7; **19**, 101630-33-5; **20**, 101630-37-9; **21**, 542-92-7; **22**, 101630-38-0; **23**, 101630-39-1; **24**, 86046-73-3; **25**, 101630-41-5.

Supplementary Material Available: ^{13}C NMR data for compounds **4–13, 15, 19, 20, 22, 23,** and **25** (Tables II, III) (2 pages). Ordering information is given on any current masthead page.

Metacyclophanes and Related Compounds. 18. Preparation of *anti*-5,14-Di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene and *anti*-5,15-Di-*tert*-butyl-8,18-dimethyl[2.4]metacyclophan-1-enes with Dichlorocarbene[1,2]

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Received May 10, 1985

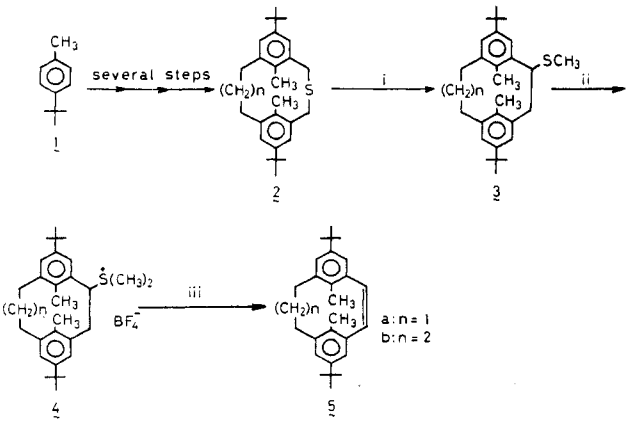
Preparations of *anti*-5,14-di-*tert*-butyl-8,17-dimethyl[2.3]metacyclophan-1-ene (**5a**) and *anti*-5,15-di-*tert*-butyl-8,18-dimethyl[2.4]metacyclophan-1-ene (**5b**) are described. Reaction of *anti*-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]metacyclophan-1-ene (**5c**) with dichlorocarbene in the presence of phase-transfer catalyst afforded heptafluvenophane (**6**) and cycloheptatrienophane (**7**) in 17% and 24% yield, respectively. It was also found that dichlorocarbene reacted with **6** to provide **7**. Reaction of **5a** with dichlorocarbene gave benzocycloheptatrienophane **12**. Reaction of **5b** with dichlorocarbene afforded only a mixture of isomers **14**. The electronic spectrum of **14** resembles that of **12**.

Although few [2.2]metacyclophan-1-enes[3,4] have been prepared, there is very little information about their chemical nature and reactivity.[4,5] In addition, the compounds of the [2.3]- and [2.4]metacyclophan-1-ene series are still unknown.

It is well recognized that dichlorocarbene reacts with various olefins to afford the corresponding dichlorocyclopropane derivatives.[6] Weyerstahl and Blüme have shown[7] that dichlorocarbene reacts with aromatic compounds like methylnaphthalenes and toluene in the presence of a phase-transfer catalyst to provide the corresponding cycloheptatriene in very poor yields. So far there is no report on the reaction of dichlorocarbene with dimethyl[2.*n*]-metacyclophan-1-enes, which possess both an olefinic bond as well as methylarene moities.

We now report the preparation of title compounds as well as the behavior of various dimethyl[2.*n*]metacyclophan-1-enes with dichlorocarbene in the presence or ab-

Scheme I[a]



[a] (i) *n*-BuLi, MeI; (ii) $(CH_3O)_2C^+HBF_4^-$; (iii) *t*-BuOK, THF.

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