Preparation and Rearrangement of Bridgehead Phosphorus Ylides and Their Derivatives in the Homocubane Ring System

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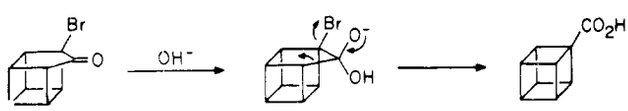
Experiments are described in which carbanions are generated at the bridgheads adjacent to phosphorus in phosphonium salt **2** and in phosphine oxide **1**. These experiments were undertaken to find ways to make the intermediates in a proposed scheme (Scheme III) for the synthesis of derivatives of cubane. When attempts are made to prepare the conjugate base of **2** using sodium hexamethyldisilylamide in tetrahydrofuran (THF), the ylide apparently rearranges rapidly to a *syn*-tricyclooctadienyldiphenylphosphine (**5**), a novel example of the electrocyclic process summarized as eq 5. The conversion constitutes a preparation of the tricyclooctadienyl ring system. On oxidation with hydrogen peroxide, **5** gives its phosphine oxide (**21**), but at −2 °C this equilibrates with an isomer (**22**). At 138 °C these isomers rearrange to give **7**. Similarly at 74.5 °C, **5** isomerizes to cyclooctatetraenyldiphenylphosphine (**6**), but shows no evidence of giving an isomer analogous to **22**. Unlike the carbanion **3** derived from **2**, lithiated phosphine oxide **1** is stable in solution at ambient temperature. This lithium derivative can be made from **1** and phenyllithium in THF at room temperature, while at −78 °C the same reagents give **8**. D_2O, CH_3I, and $(C_6H_5S)_2$ react with the lithiated material to introduce substituents adjacent to phosphorus. The thiophenyl substituent can be oxidized to the sulfone (**16**), and this with sodium hexamethyldisilylamide gives **18**. With phenyllithium **16** gives the analogue **20**. These last rearrangements are novel, and since **1** does not undergo them, they reflect the leaving ability of sulfone anions.

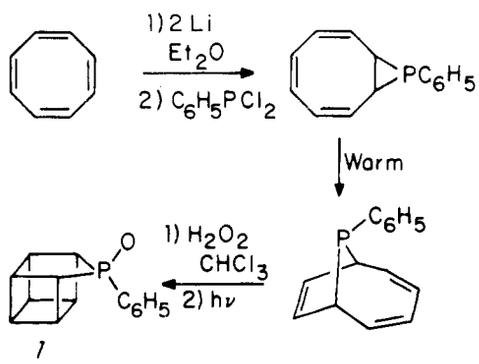
The cubic hydrocarbon C_8H_8, known as cubane, was first synthesized by Eaton and Cole in 1964.[1] Shortly afterwards a related synthesis was reported by Barborek, Watts, and Pettit,[2] and additional ways to arrive at intermediate molecules on the original routes were found by Chin, Cuts, and Masamune[3] and by Eaton and Cole.[4] These syntheses, and all of those developed since for derivatives of cubane,[5] employ as a key step the Favorskii rearrangement[6] of an α-bromohomocubanone (Scheme I), and despite difficulties experienced in some laboratories,[5f,c] although not in others,[5f,h] and despite the length of the synthesis, the original route of Eaton and Cole[1] remains the most effective. Alternative syntheses have not been reported and seem to have been sought only rarely.[7]

The availability of phenylphosphahomocubane oxide from the cyclooctatetraenyl dianion (Scheme II)[8-10] suggested that another route to cubane might be found if a phosphorus analogue of the Favorskii rearrangement could be discovered (Scheme III), and the research described here was toward this goal. A sulfur analogue of such arrangements, the Ramberg–Bäcklund rearrangement,[11] has been applied effectively in many syntheses, but because it proceeds by way of an episulfone and fails when the intermediate three-membered ring is highly strained, path B in Scheme III is unlikely. Path A,

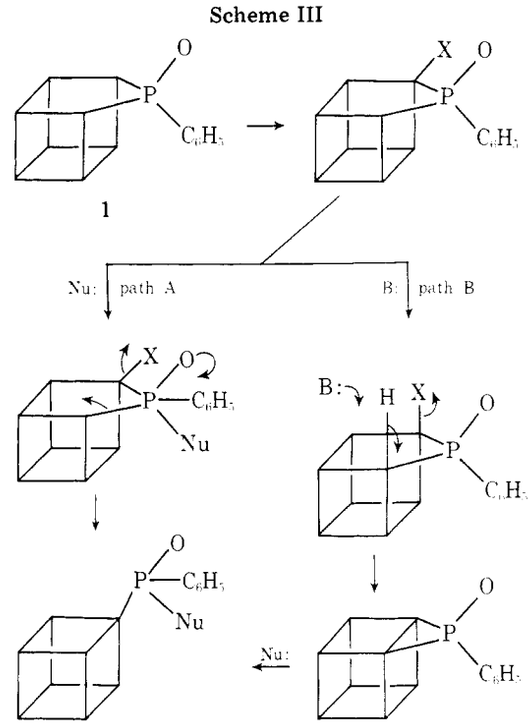
Scheme I



Scheme II



Scheme III



however, seems possible, for although the ring contraction is unprecedented, a number of examples are known of alkaline hydrolyses of α-halo- and α-unsaturated phosphonium salts in which nucleophiles attach to phosphorus and a carbon atom migrates to the α position.[12,13]

The experiments described below show how substituents can be introduced into molecule **1** on the ring carbon next to the phosphorus atom and how derivatives of **1** when combined with bases rearrange.

Results

A. Reactions of Diphenylphosphoniahomocubane Bromide (2). Brominating the ylide **3** derived from the phosphonium salt **2** (Scheme IV) seems a possible way to introduce a halogen at the ring carbon next to phosphorus in the phosphahomocubane ring system, and it seems to be a good way considering the ease with which the salt **2** can be prepared.[10,14] However, although simple phosphonium salts upon

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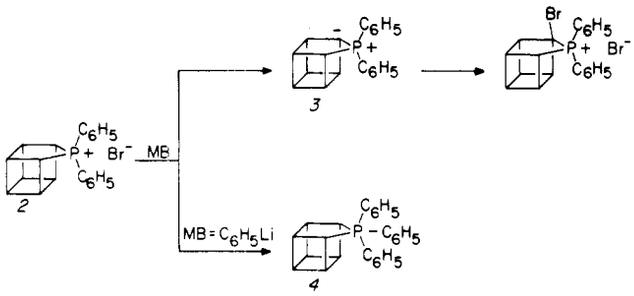
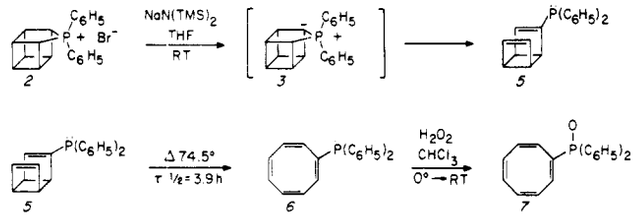
Scheme IV



Scheme V



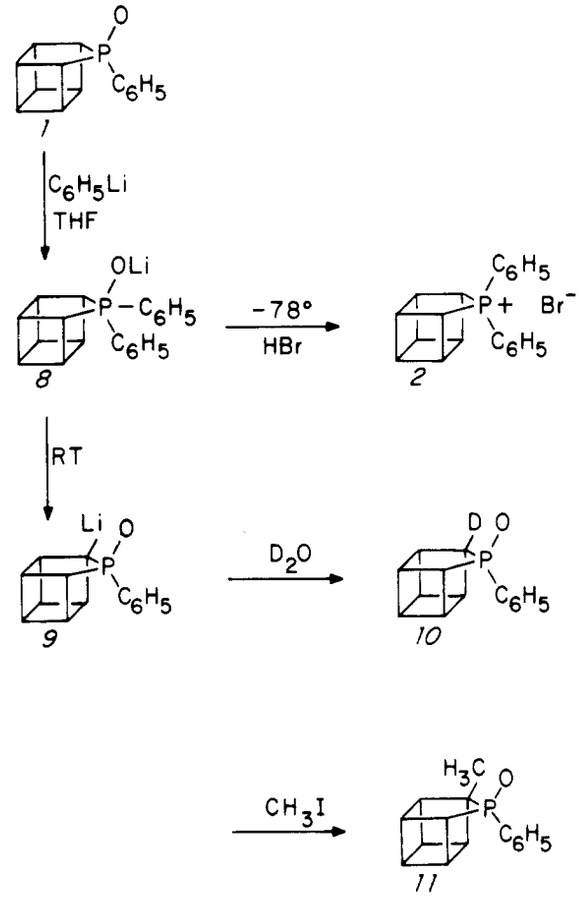
reaction with phenyllithium are generally transformed into their ylide derivatives, the phosphonium salt **2** with this reagent gives the triphenylphosphorane **4** instead.[10,14] Thus, a reagent had to be used that would abstract a proton rather than react irreversibly with the phosphorus, and because of its effectiveness in enolizing ketones,[15] sodium hexamethyldisilylamide, $NaN[Si(CH_3)_3]_2$, was tried.

Surprisingly, when the salt **2** was combined with this reagent in tetrahydrofuran (THF) at room temperature, instead of giving the ylide **3** it gave in good yield (38–74%) the novel *syn*-tricyclooctadienyldiphenylphosphine **5** (Scheme V). As the phosphine probably arises by the expected ylide **3** fragmenting, attempts were made to suppress the fragmentation by lowering the reaction temperature, but these experiments failed, for at 0 °C the formation of the ylide was suppressed also and only the starting salt **2** was obtained when the reaction mixture was quenched with deuterium bromide. When in place of sodium hexamethyldisilylamide two other bases were used that are also noted for their ability to abstract protons rather than bring about other reactions, the results were similar. Lithium 2,2,6,6-tetramethylpiperidide[16] after 3 h at ambient temperature gave a 48% yield of **5** and 26% recovered **2**, and lithium diisopropylamide[17] at either ambient temperature or 0 °C gave **5** completely and at −20 °C only starting salt **2**. Other bases tried[18] brought about either no reaction or partially hydrolyzed salt **2** to the phosphine oxide **1**.

The tricyclooctadienyldiphenylphosphine structure **5** was assigned to the product of the reactions above on the basis of its proton nuclear magnetic resonance (^1H NMR) spectrum (described in the Experimental Section and also in part in this section, below) and because heating converts it into a material identified by its spectra as cyclooctatetraenyldiphenylphosphine (**6**). The half-life for the thermal conversion of **5** to **6** in benzene at 74.5 °C (the kinetics are first order) is 3.9 h, much like that for the conversion of the parent *syn*-tricyclooctadiene to cyclooctatetraene.[19] Phosphine **6** upon oxidation in chloroform with 30% H_2O_2 gives its phosphine oxide (**7**), but the analogous oxidation of **5** is more interesting, and this reaction and other aspects of the chemistry of **5** are discussed further below.

B. Reactions of *P*-Phenylphosphahomocubane Oxide (1). It seems likely that for the conjugate base of phosphine oxide **1** to fragment should be more difficult than for the phosphonium salt **2**, and indeed when **1** is combined in THF with phenyllithium at ambient temperature and the reaction mixture is quenched 20 min later with deuterium bromide in

Scheme VI



deuterated water the phosphine oxide is recovered, but containing one deuterium atom (Scheme VI). Thus, the lithiated phosphine oxide **9**, unlike the ylide **3**, is stable in THF at ambient temperature, but that it forms at all in this reaction is remarkable for when the reaction of phosphine oxide **1** in THF with phenyllithium is conducted at −78 °C and quenched with HBr it gives instead the diphenylphosphonium salt **2**.[10,14] This must mean that at room temperature the oxyphosphorane **8** extrudes phenyllithium and that phenyllithium reacts with **1** quickly at phosphorus but gradually and irreversibly at the α hydrogen. The reaction of triphenylphosphine oxide with methyllithium to yield lithiomethyldiphenylphosphine oxide provides a precedent,[20] although the stabilization of **8** relative to **1** and phenyllithium that should be consequent on the constraints of the ring system[10] might have prevented **8** from following this course.

Further evidence that **9** is formed from **1** and phenyllithium at room temperature is provided by the observation that quenching the reaction mixture with methyl iodide introduces a methyl group into **1** on the carbon next to the phosphorus.

However, procedures effective for other lithiated phosphine oxides could not be found that could be used to convert **9** into an α-halophosphine oxide, although many examples of lithiated phosphine oxides reacting with electrophiles other than halogens, such as aldehydes, ketones, and carbon dioxide, have been published.[21–23] Accordingly, various ways were studied to combine solutions of **9** with bromine by adding the former to the latter or the latter to the former, but all such experiments gave intractable products. Experiments were done with other halogenating agents, including iodine, iodobenzene, phenyliodine dichloride, 1,2-dibromoethane, *N*-bromosuccinimide, *N*-chlorosuccinimide, and 2,2,5-trimethyl-5-bromo-1,3-dioxane-4,6-dione, some of which convert lithiated sulfones to their α-halosulfone derivatives,[24] but they

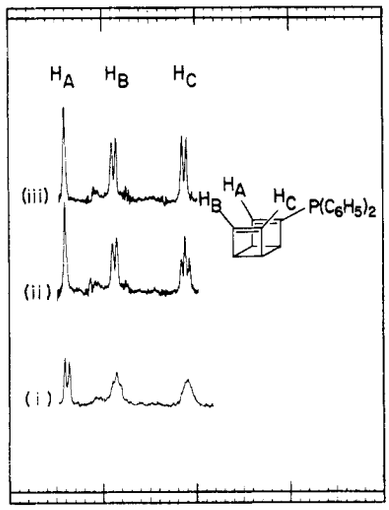
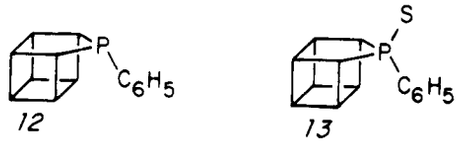


Figure 1. 100 MHz ^1H NMR spectrum of **5** in $CDCl_3$. Only the vinyl proton resonances are displayed: (i) undecoupled; (ii) hydrogens on saturated carbons decoupled; (iii) both hydrogens on saturated carbons and ^{31}P decoupled.

either yielded recovered **1** after aqueous workup or gave intractable materials. No α-halophosphine oxide could be found. Experiments were tried in which in place of the phosphine oxide **1** the corresponding phosphine sulfide **13,** prepared from

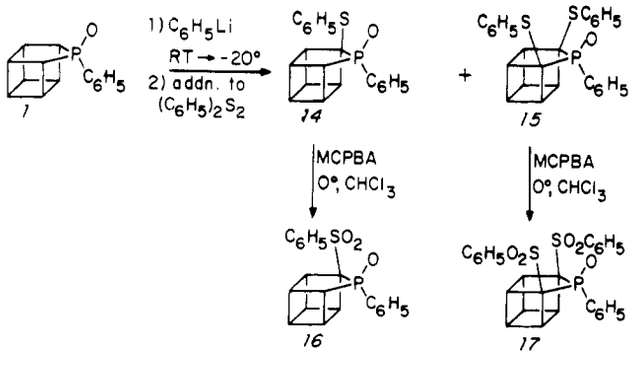


12[9,10] and elemental sulfur, was used, but reaction with phenyllithium in THF followed by bromine at −78 °C also gave only tars. Experiments were tried with phosphine **12** itself plus *N*-chlorosuccinimide or sulfuryl chloride, on the basis of analogy to procedures known to chlorinate sulfides,[25] but these gave mainly phosphine oxide **1,** the product of reaction at phosphorus and not at the α carbon.

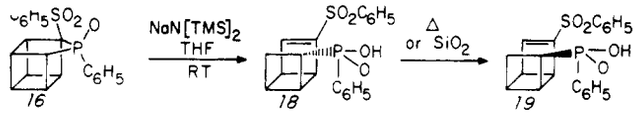
Accordingly, the possibility was considered of introducing into the ring system a leaving group other than a halogen, and as summarized in Scheme VII this could be accomplished by attaching a sulfide group and then oxidizing it. Thus, adding a cold solution of **9** in THF to a solution of diphenyl disulfide in THF at 0 °C gave in up to 68% yield the sulfide **14** together with up to 5% of the disulfide **15;** *m*-chloroperbenzoic acid oxidizes these to their sulfone derivatives (**16** and **17**). Experiments using trifluoromethyl disulfide[26] in place of diphenyl disulfide were also tried, but failed.

Attempts were then made to carry through with sulfone **16** the transformation to a substituted cubane envisioned in Scheme III. However, with sodium hexamethyldisilylamide

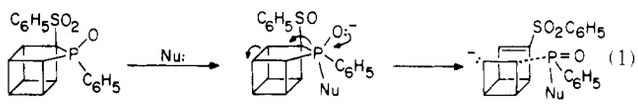
Scheme VII



in THF at ambient temperature, **16** gave a product that still contained the sulfone group and exhibited a single olefin proton resonance. On the basis of this and other spectroscopic data it was assigned structure **19.** When the reaction mixture



was worked up so as to avoid overheating or excessive contact with silica gel, the product isolated was not **19** but a similar material, seemingly **18.** [The two are distinguished by their different mobilities on thin-layer chromatography and by their different olefin proton nuclear magnetic resonance frequencies (δ 6.04 for **18** and δ 5.86 for **19** in CD_3CN).] The formation of these phosphinic acids must reflect the facility with which oxyphosphoranes extrude sulfone anions and the facility with which carbanions cleave adjacent carbon–carbon bonds to relieve ring strain (eq 1). What the nucleophile is that



(1)

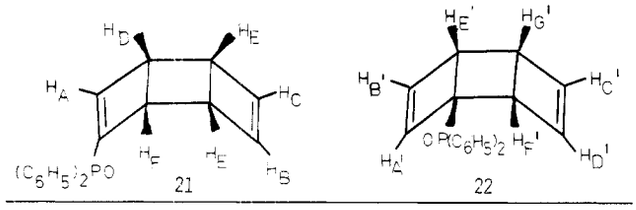
initiates this transformation is, however, uncertain, for although the sulfone **16** had been dried at 56 °C and 0.1 mm pressure for 24–48 h or at 100 °C and 0.1 mm pressure for 24 h, adventitious water might still have been present to form hydroxide anions.

Other nucleophiles bring about similar transformations. Thus, phenyllithium in THF at −78 °C followed by HBr, which might convert **16** to its diphenylphosphonium salt if the oxyphosphorane were stable at −78 °C, instead gives (in 32% yield) the diphenylphosphine oxide **20,** the analogue of **18** or **19** in which the OH on phosphorus is replaced by phenyl. The structure was assigned the phosphine oxide on the basis of its spectra, but whether the stereoisomer characterized was the analogue of **18** or **19** was not analyzed.

C. Chemistry of 5. The preparation of **5** was discussed above, but other aspects of its chemistry are considered here. A portion of the proton nuclear magnetic resonance spectrum, which was used as part of the evidence to assign its structure, is displayed in Figure 1. The figure shows that irradiation at the resonance frequencies of the protons on the saturated carbons simplifies the resonances of the protons on olefinic carbons to a singlet, a doublet, and a triplet. (The coupling constants are 2 Hz.) Further decoupling at the phosphorus resonance frequency collapses the triplet to a 2-Hz doublet. Accordingly, we assign the pair of doublets to H_B and H_C (2 Hz is the magnitude of the proton–proton coupling in other cyclobutenes),[27] but this means that while H_A is not coupled to the phosphorus, either H_B or H_C is.[28]

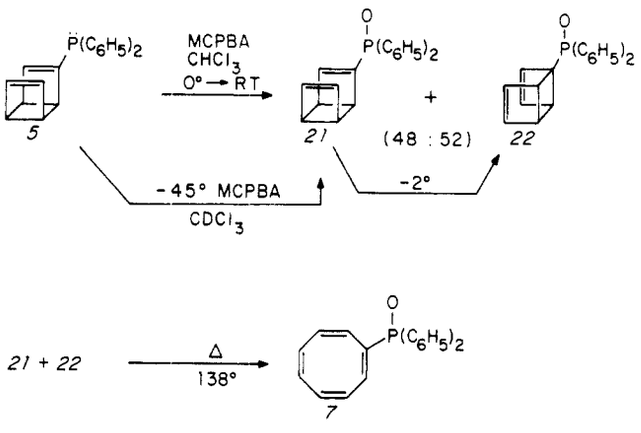
Combining phosphine **5** in chloroform with 30% aqueous hydrogen peroxide at 0 °C oxidizes it to the phosphine oxide, but the ^1H NMR spectrum (Figure 2) of the product, a white crystalline material, mp 109–109.5 °C, homogeneous according to the thin-layer chromatography, is unusually complex. With the help of proton decoupling, the shift reagent tris(dipivaloylmethanato)europium(III), and a 100 MHz ^1H NMR spectrometer, this spectrum could be analyzed (the chemical shifts and coupling constants are collected in Table I) as that of a 48:52 mixture of **21** and **22,** molecules related by a Cope rearrangement (Scheme VIII).[29] Thus, presumably the oxidation initially gives **21,** but this must transform easily into **22.** This last hypothesis is demonstrable for the Cope rearrangement should be suppressed at temperatures that are sufficiently low, and in fact when the oxidation is effected at −45 °C in $CDCl_3$ with *m*-chloroperbenzoic acid, only phosphine oxide **21** is produced. But when the solution of this

Table I. Chemical Shifts (in $CDCl_3$) and Coupling Constants (Absolute Values) for 21 and 22



proton	chemical shift, δ	coupling constant, Hz	proton	chemical shift, δ	coupling constant, Hz
H_A	6.77	$J_{PA} = 3.0$	$H_{A'}$, $H_{B'}$	6.13–5.96	$J_{PA'} = 4$–6
H_C	5.91	$J_{AD} = 2.0$	$H_{C'}$, H_D		$J_{PE'} = 11.0$
H_B	5.30	$J_{BC} = 3.0$	$H_{E'}$	3.64	$J_{PF'} = 5.0$
H_D	3.46	$J_{BE} = 2.0$	$H_{F'}$	3.48	$J_{A'B'} = 2.0$
H_E	3.21	$J_{CE} = 2.0$	$H_{G'}$	3.27	$J_{B'E'} = 2.0$
					$J_{C'D'} = 2.0$
					$J_{C'G'} = 2.0$
					$J_{D'F'} = 2.0$
					$J_{E'G'} = 3.0$
					$J_{F'G'} = 8.0$

Scheme VIII



phosphine oxide is then warmed to −2 °C for 14 min, the transformation takes place to give the characteristic mixture (presumably an equilibrium mixture) of **21** and **22**. When this is heated further in tetrachloroethylene, the rate of interconversion does not increase enough to cause the ^1H NMR spectra to coalesce, but the spectra are slowly replaced by that of cyclooctatetraenyldiphenylphosphine oxide (**7**). This last isomerization is analogous to the thermal conversion of **5** into **6** (see above), except that no Cope rearrangement product is observed by ^1H NMR during that reaction.

The photochemistry of **5, 21,** and **22** was also explored to see whether ring closures to derivatives of phosphahomocubane would take place. However, instead of rings closing, rings already present opened. Thus, the mixture of oxides **21** and **22** in CD_2Cl_2 when irradiated for 1.0 h with ultraviolet filtered through Vycor ($\lambda > 254$ mm) gave cyclooctatetraenyldiphenylphosphine oxide (**7**), and when irradiated for 18.3 h in the presence of Michler's ketone it gave, according to ^1H NMR analysis, a mixture of 66 parts of **7** and 34 parts of starting materials. Phosphine **5** behaved similarly; upon irradiation for 5 h in CD_2Cl_2 with light of 254 nm in wavelength, it gave a mixture of 72 parts of **6** and 28 parts of **5**.

Discussion

The intermediate **3** that must form when strong bases transform **2** into **5** is a rare example of a bridgehead phosphorus ylide, and accordingly it is not known how typical its behavior is. However, the ylide **23,** the only other example known,[10,30] does not fragment so easily (eq 2), and the fragmentation observed for **2** is reminiscent of that which homocubylcarbinyl anions undergo (eq 3)[31] presumably to relieve the ring strain. It is therefore plausible that **3** gives **24** (eq 4), and even more so that **24** gives **5** as phosphines are eliminated by carbanions generated on carbons adjacent to carbon–phosphonium bonds.[32] However, to the extent that **24** violates Bredt's rule, its formation is likely to be avoided, and the transformation in eq 4 would then be concerted. Thus, the reaction would be an example of a novel electrocyclic process, summarized in its essential form in eq 5.[33]

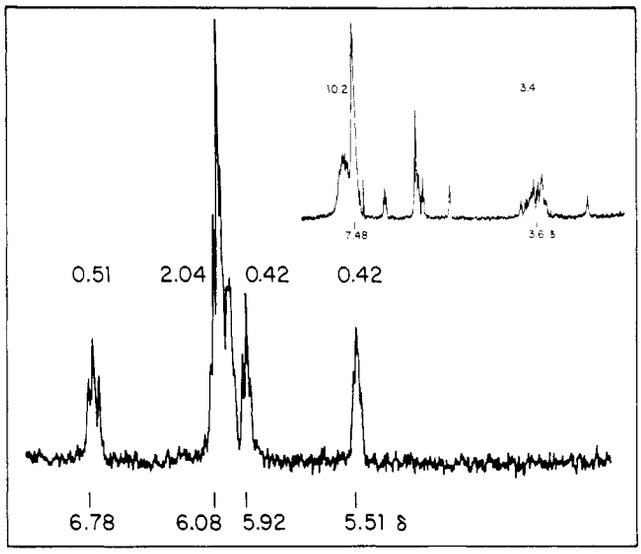
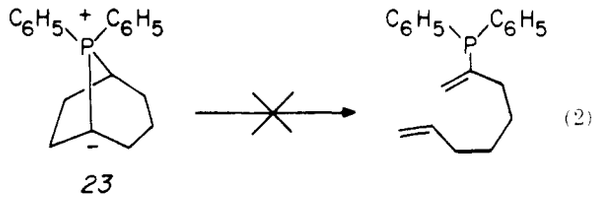


Figure 2. ^1H NMR spectrum (100 MHz) of a mixture of **21** and **22** in $CDCl_3$. Chemical shifts are displayed below and intensities above the resonances. The full spectrum is shown in the insert.



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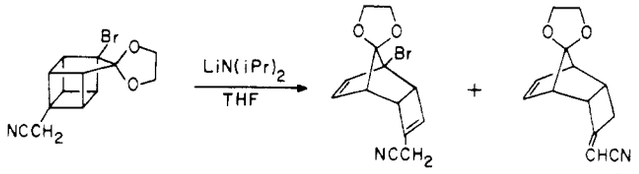

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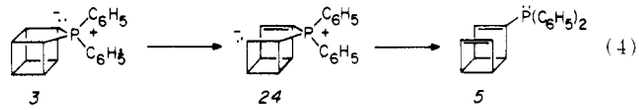

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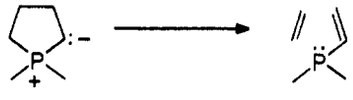


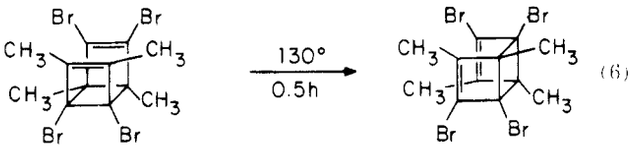
(5)

It is interesting that the phosphine oxide analogue of **3,** molecule **9,** does not undergo the analogous fragmentation, presumably because the phosphine oxide does not provide as good as leaving group as the phosphonium salt.

There is also an interesting contrast between the behavior of the intermediate oxyphosphoranes in eq 1 and the parent oxyphosphorane (**8**). The fragmentation in eq 1 undoubtedly reflects the stability of the sulfone anion and the drive to relieve ring strain, exemplified by eq 3.[34] However, the parent (**8**), which also could fragment to relieve ring strain, does not, and this must mean that this relief provides insufficient drive

for the ring carbon–phosphorus bond to cleave. Thus, **8**, as is usual,[35] eliminates phenyllithium rather than alkyllithium, but when the sulfone substituent is present the basicity of the carbanion is decreased,[36] facilitating elimination of the latter. It must be the formation of the ring carbanion that causes the carbon–carbon bond to cleave as summarized in eq 1.

The facility of the Cope rearrangement in converting **21** into **22** (the reaction takes place in minutes at −2 °C) contrasts with the greater difficulty of an analogous transformation (eq 6),[37] which does not take place during recrystallization from



(6)

acetone but does on heating to 135 °C. That phosphine **5** does not seem to undergo the reaction possibly means that it is more stable than its Cope rearrangement product, just as bullvalenes with substituents on their double bonds are almost always more stable than their Cope rearrangement products.[38] Thus, the phosphine oxide **21** might have a driving force for rearrangement that the phosphine **5** does not, and this might be an electronic force driving electronegative substituents to bond with orbitals having little s character.

Experimental Section

Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined with Varian A-60A, T60, or HA-100 spectrometers [tetramethylsilane (Me_4Si) as an internal standard]; infrared (IR) spectra with Perkin-Elmer 137, 727B, and 621 spectrophotometers (calibrated using polystyrene film); ultraviolet (UV) spectra with Cary Model 15 or 17 spectrophotometers; and mass spectra with a Jeol JMS-07 electron impact spectrometer. The mass spectral data listed are the intensities as a percentage of the base peak of the peaks due to the parent ions and of those fragment ions whose abundance is greater than a stated fraction of the base peak. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y. Melting points, determined on a Thomas-Hoover melting point apparatus, are uncorrected.

Just prior to its use, tetrahydrofuran (THF) was dried over potassium hydroxide pellets and distilled from $LiAlH_4$ into Linde type 5A molecular sieves. Phenyllithium was obtained from Alfa Inorganics, Beverly, Mass., as a 2.2–2.3 N solution in 70:30 benzene–ether. Dry solvents and reagents sensitive to air or moisture were transferred by syringe.

***P,P*-Diphenyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dien-3-ylphosphine (5).** To a flame-dried, three-neck, N_2-flushed, 50-mL round-bottom flask equipped with a serum inlet, N_2 inlet, stopper, and magnetic stirrer was added 660 mg (1.78 mmol) of *P,P*-diphenylphosphoniahomocubane bromide[10] and 15 mL of dry THF. A solution of 291 mg of sodium hexamethyldisilylamide (1.59 mmol, 1.15 equiv) in dry THF was added by syringe to the slurry and stirred at ambient temperature. The slurry turned a salmon color after 15 min and was allowed to stir for 2.0 h before it was quenched with 3 mL of 24% HBr. Ether (100 mL) was added, and the organic solution was washed successively with 30 mL of 10% HCl, H_2O, and brine and dried over $MgSO_4$. Filtration and removal of solvent gave 330 mg of a yellow oil, which was chromatographed on a 2 × 50 cm column of 35 g of SiO_2 eluting with CH_2Cl_2. A yellow, foul-smelling oil was isolated (217 mg, 69%) and identified as *P,P*-diphenyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dien-3-ylphosphine: ^{1}H NMR (CCl_4) δ 7.38 (m, 10.27 H), 6.24 (d, J = 2.0 Hz, 0.75 H), 5.96 (t, J = 2.0 Hz, 1.04 H), 5.62 (m, 0.81 H), 3.14 (m, 3.96 H); IR ($CHCl_3$) 3074 (w), 3058 (m), 3021 (s), 3008 (m), 1964 (w), 1888 (w), 1812 (w), 1770 (w), 1660 (w), 1584 (w), 1540 (w), 1478 (s), 1442 (s), 1298 (m), 1274 (m), 1244 (m), 1162 (w), 1146 (w), 1094 (w), 1070 (w), 1026 (w), 1000 (w), 954 (w), 914 (w), 838 (w), 820 (m), 692 (s), 662 (m) cm^{-1}; mass spectrum (75 V, peaks ≥ 10%), *m/e* 289 (M$^+$ + 1, 10), 288 (M$^+$, 46), 287 (63), 281 (24), 211 (24), 210 (41), 209 (21), 207 (18), 185 (19), 183 (100), 179 (37), 178 (67), 167 (10), 165 (16), 152 (16), 147 (23), 133 (28), 115 (16), 109 (10), 108 (52), 107 (46), 104 (10), 103 (78), 102 (23), 78 (18), 77 (60), 73 (50), 63 (11), 51 (45), 50 (15), 39 (19); UV (95% EtOH) λ_{max} 251 nm (ε 7830).

A second product eluted from the column was a yellow oil (13 mg), later identified as the equilibrium mixture of phosphine oxides **21** and **22** (3%).

Cyclooctatetraenyldiphenylphosphine (6). To a flame-dried, N_2-flushed, 100-mL round-bottom flask equipped with a condenser and a N_2 inlet was added a solution of 285 mg of *P,P*-diphenyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dien-3-ylphosphine (0.99 mmol) in 50 mL of dry benzene. Simultaneously a ^{1}H NMR tube containing 28 mg of the phosphine (0.10 mmol), 1 drop of Me_4Si, 1 drop of CH_2Cl_2 as an internal standard, and benzene-d_6 (total volume = 0.5 mL) was sealed at 0.05 mm pressure. Both the flask and the tube were placed in an insulated oil bath maintained at 74.5 ± 0.2 °C, and the reaction was monitored by observing in the ^{1}H NMR spectrum the disappearance of the resonances of protons on saturated carbons. After 20.0 h the ^{1}H NMR sample was completely isomerized, but heating was continued for an additional 18 h. The samples were combined and the solvents evaporated at 157 °C (0.07 mm), giving 312 mg of bright yellow, viscous, foul-smelling oil (99%). The kinetic data showed the isomerization to be first order, with k = 0.41 h^{-1} ($\tau_{1/2}$ = 3.9 h): ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 10.06 H), 5.82 (s, 7.00 H); IR ($CHCl_3$) 3140 (w), 3083 (m), 3059 (m), 3006 (s), 2973 (m), 2928 (w), 2852 (w), 1954 (w), 1885 (w), 1813 (w), 1750 (w), 1621 (w), 1600 (w), 1585 (w), 1480 (s), 1431 (s), 1365 (w), 1301 (w), 1130 (m), 1091 (m), 1070 (w), 1051 (w), 1022 (w), 995 (w), 865 (w), 630 (m) cm^{-1}; mass spectrum (75 V, peaks ≥ 10%), *m/e* 289 (M$^+$ + 1, 10), 288 (M$^+$, 51), 287 (29), 211 (25), 210 (46), 209 (13), 185 (15), 184 (12), 183 (72), 179 (32), 178 (56), 167 (10), 165 (15), 152 (15), 133 (28), 115 (14), 109 (10), 108 (46), 107 (45), 104 (11), 103 (100), 102 (32), 91 (13), 81 (10), 78 (22), 77 (92), 76 (11), 63 (15), 57 (16), 55 (14), 52 (11), 51 (66), 50 (19), 43 (14), 41 (14), 39 (28), 28 (19), 27 (17); UV (95% EtOH) λ_{max} 253 sh nm (ε 12 500).

Cyclooctatetraenyldiphenylphosphine Oxide (7). To a solution of 300 mg of cyclooctatetraenyldiphenylphosphine (1.04 mmol) in 25 mL of $CHCl_3$ at 0 °C contained in a three-neck, 100-mL round-bottom flask equipped with an addition funnel, condenser, stopper, and magnetic stirrer was added 10 mL of 30% H_2O_2 in drops from the addition funnel during 0.5 h. The temperature was then raised to ambient for 0.5 h. Water (30 mL) and $CHCl_3$ (50 mL) were added, the layers were separated, and the organic layer was washed successively with 30 mL of 1 N $NaHSO_3$, H_2O, and brine and dried over $MgSO_4$. Filtration and removal of solvent gave 321 mg of yellow solid, mp 141.5–143.5 °C, which was recrystallized from cyclohexane (Norit, hot filtration) and dried overnight in an Abderhalden apparatus (78 °C, 0.02 mm) to give 267 mg (84%) of a light yellow solid: mp 142.5–144.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (m, 10.29 H), 6.63 (d, 0.84 H, J_{PH} = 20 Hz), 5.92 (s, 5.74 H); IR (KBr) 3052 (w), 3010 (w), 2966 (w), 2928 (w), 1630 (w), 1616 (w), 1590 (w), 1480 (w), 1440 (m), 1370 (m), 1320 (m), 1277 (w), 1260 (w), 1200 (m), 1177 (s), 1113 (s), 1100 (s), 1070 (w), 1058 (w), 998 (w), 931 (w), 887 (m), 811 (m), 780 (w), 762 (m), 750 (m), 738 (s), 720 (s), 699 (s), 676 (m), 662 (m), 636 (m), 553 (s), 540 (s), 492 (w), 448 (w) cm^{-1}; mass spectrum (20 V, peaks ≥ 10% intensity), *m/e* 305 (M$^+$ + 1, 18), 304 (M$^+$, 83), 303 (37), 202 (33), 201 (100), 183 (18), 179 (22), 178 (15), 155 (14), 125 (10), 103 (17), 102 (47), 77 (29), 47 (11); UV (95% EtOH) λ_{max} 273 nm (ε 12 100), 266 (14 400), 257 (15 200).

Oxidation of *P,P*-Diphenyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dien-3-ylphosphine. A. Preparation of 21 and 22. To a solution of *P,P*-diphenyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dien-3-ylphosphine (275 mg, 0.95 mmol) in 25 mL of $CHCl_3$ at 0 °C contained in a three-neck, 100-mL round-bottom flask equipped with an addition funnel, condenser, stopper, and magnetic stirrer was added 10 mL of 30% H_2O_2 in drops during 15 min. The mixture was stirred for 0.5 h at 0 °C and 0.5 h at ambient temperature. Water (20 mL) and chloroform (50 mL) were added, and after successive washing with 30 mL of saturated $NaHSO_3$, H_2O, and brine and drying over $MgSO_4$ the solvents were removed and the residue was triturated with ether–petroleum ether, giving 290 mg of a white solid, mp 108–109 °C. Recrystallization from ether–pentane gave 133 mg of white powder, mp 109–109.5 °C (46% yield). The intensities of the vinyl proton resonances in the ^{1}H NMR spectrum (Figure 2) show the ratio of the isomeric phosphine oxides **21** and **22** to be 48:52: ^{1}H NMR ($CDCl_3$) δ 2.40 (m, 9.97 H), 3.23 (t, J = 3 Hz, 0.47 H), 3.98 (m, 2.48 H), 4.68 (m, 0.41 H), 6.60 (m, 3.42 H); IR (KBr) 3090 (w), 3050 (w), 3028 (w), 2980 (w), 2922 (w), 2850 (w), 1652 (w), 1480 (w), 1440 (m), 1285 (m), 1260 (w), 1178 (s), 1110 (m), 1099 (w), 1070 (w), 995 (w), 982 (w), 948 (w), 920 (w), 882 (w), 804 (s), 745 (m), 718 (s), 700 (s), 587 (s), 541 (s), 502 (w) cm^{-1}; mass spectrum (75 V, peaks > 10% intensity), *m/e* 305 (M$^+$ + 1, 11), 304 (M$^+$, 42), 303 (21) 227 (10), 202 (37), 201 (100), 185 (11), 183 (25), 179 (20), 178 (15), 155 (16), 154 (10), 152 (14), 149 (23), 103 (19), 102 (50), 91 (10), 78 (25), 77, (66), 76 (11), 57 (13), 55 (11), 52 (11), 51 (36), 50 (11), 47 (26), 43 (11), 41 (16), 39 (11), 28 (16); UV (95% EtOH) λ_{max} 272 nm (ε 941), 265 (1290), 258 (1190), 222 (16 800).

B. Oxidation at Low Temperature and Thermal Rearrangements of the Oxide. A sample of the phosphine (23 mg, 0.08 mmol)

in 0.5 mL of $CDCl_3$ in a ^1H NMR sample tube was cooled to −78 °C, a cold solution of 20 mg of 85% *m*-chloroperbenzoic acid in 0.5 mL of $CDCl_3$ was added, and the mixture was shaken until the solution was homogeneous (~5 s). The ^1H NMR spectrum was then measured at −45 °C. The three olefinic multiplets of phosphine **5** disappeared and were replaced by the three olefinic multiplets of phosphine oxide **21**. Less than 5% of the isomeric phosphine oxide **22** was detected.

The sample was then removed from the spectrometer and stored at −78 °C while the temperature of the spectrometer's probe was raised to −2 °C. The sample was then warmed slightly from −78 °C and reinserted into the spectrometer, and the olefinic region was scanned every 2 min until the equilibrium mixture of **21** and **22** was observed (ca. 14–18 min).

When a mixture of **21** and **22** in tetrachloroethylene was heated to 138 °C, their spectra were slowly replaced by that of **7**.

Photolyses of Oxides 21 and 22. A. An evacuated, sealed quartz ^1H NMR tube containing 16 mg of the mixture of oxides **21** and **22** in 0.5 mL of CD_2Cl_2 (1.06×10^{-1} M) was irradiated with a Hanovia medium pressure Hg lamp through a quartz water jacket and Vycor filter ($\lambda > 254$ nm). After 1.0 h, the aliphatic protons clusterd about δ 3.3 had disappeared and a broad singlet at δ 5.86 attributed to cyclooctatetraenyldiphenylphosphine oxide was observed. According to analytical thin-layer chromatography, the photolysis product and an authentic sample were identical.

B. An evacuated, sealed Pyrex ^1H NMR tube containing a 0.5 mL CD_2Cl_2 solution of oxides **21** and **22** (1.0×10^{-1} M) and 1.9 mg of Michler's ketone (1.4×10^{-2} M) was irradiated with a medium pressure Hg Hanovia lamp through a Pyrex water jacket and uranium glass filter ($\lambda > 330$ nm). After 18.3 h the product, according to ^1H NMR analysis, was a mixture of 66% of cyclooctatetraenyldiphenylphosphine oxide and 34% of starting material.

Photolysis of *P*,*P*-Diphenyl-*syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dien-3-ylphosphine (5). A quartz ^1H NMR tube containing 28 mg of the phosphine (0.097 mmol) in 1 mL of CD_2Cl_2 (degassed and sealed at 10^{-5} mmHg) was photolyzed at 254 mm with an Ultraviolet Products, Inc., lamp (Model PCOXI). After 5.5 min, a singlet attributable to cyclooctatetraenyldiphenylphosphine began to emerge at δ 5.80 at the expense of the proton signals of the starting material. (After 5.5 min, the ratio of product to starting material was 6:94.) The photolysis was continued and monitored after 15, 45, 75, 180, and 300 min, and after 5 h the mixture consisted of 72 parts of cyclooctatetraenyldiphenylphosphine and 28 parts of starting material.

***P*-Phenyl-α-deuteriophosphahomocubane Oxide (10).** To a flame-dried, N_2-flushed, three-neck, 50-mL round-bottom flask equipped with a magnetic stirrer, N_2 inlet, stopper, and serum inlet was added 252 mg of *P*-phenylphosphahomocubane oxide[10] (1.11 mmol) and 15 mL of dry THF. The solution was treated with 0.6 mL of a 2.3 M phenyllithium solution (1.37 mmol, 1.24 equiv) and stirred for 20 min before quenching with 1.5 mL of DBr in D_2O. The organic material in 30 mL of $CHCl_3$ was extracted successively with 30 mL of water and brine and dried over $MgSO_4$. Filtration and removal of solvent gave 263 mg of a light yellow solid. Chromatography on a 2 × 40 cm SiO_2 column eluting with 5% CH_3OH–CH_2Cl_2 gave 214 mg of a white solid (85% yield), and after recrystallization from 7:2 benzene–cyclohexane and sublimation at 150 °C (0.1 mm) 36 mg was obtained. The product differs from the starting material in that the intensity of the ^1H NMR signal at δ 3.5 has decreased to 4.89 H (relative to 12 H total). The 75 eV mass spectrum showed a base peak at *m/e* 105 and peaks at *m/e* 228 (17%) and 229 (15%). The 25 eV mass spectrum of the undeuterated material showed a base peak at *m/e* 104 and peaks at *m/e* 227 (31%) and 228 (8%):[10] ^1H NMR ($CDCl_3$) δ 7.65 (m, 5.16 H), 4.00 (m, 1.95 H), 3.50 (m, 4.89 H); IR ($CHCl_3$) 2990 (s), 2470 (w), 1599 (w), 1490 (w), 1440 (m), 1240 (s), 1210 (s), 1170 (s), 1120 (s), 1070 (m), 1030 (m), 880 (w), 850 (w), 690 (m), 660 (m) cm^{-1}; mass spectrum (75 V, peaks > 20% intensity), *m/e* (relative intensity) 229 (M^+, 15), 228 (17), 149 (98), 106 (44), 105 (100), 104 (69), 97 (28), 85 (21), 83 (26), 81 (20), 79 (39), 78 (35), 77 (27), 71 (36), 69 (27), 57 (62), 56 (26), 55 (42), 51 (30), 50 (21), 47 (20), 44 (62), 43 (65), 41 (57), 39 (32), 36 (35), 32 (54), 29 (37), 28 (99), 27 (38), 26 (27).

***P*-Phenyl-α-methylphosphahomocubane Oxide (11).** To a three-neck, flame-dried, N_2-flushed, 50-mL round-bottom flask equipped with a serum inlet, N_2 inlet, stopper, and magnetic stirrer was added a 15-mL solution of 229 mg of *P*-phenylphosphahomocubane oxide (1.00 mmol) in dry THF. A solution of 0.6 mL of 1.8 M phenyllithium (1.08 mmol) in 70:30 benzene–ether was added by syringe, and the reddish brown solution was stirred for 10 min at ambient temperature. Excess methyl iodide (2.0 mL, 32 mmol) was then syringed into the mixture, and the resulting amber colored solution was allowed to stir for 0.5 h at ambient temperature. Chloroform (100 mL) was added, and the organic layer was washed successively with 3 × 30 mL of H_2O and 30 mL of brine and dried over $MgSO_4$. Filtration and removal of solvent gave 231 mg of a yellow oil. Chromatography on a 2 × 50 cm SiO_2 column (35 g) eluting with 2% CH_3OH–CH_2Cl_2 yielded 136 mg (56.1%) of a yellow oil, and after evaporative distillation (120 °C, 0.1 mm) 97 mg of colorless oil was obtained. Trituration with ether gave 91 mg of white crystals, mp 82–83.3 °C (38% yield), identified as *P*-phenyl-α-methylphosphahomocubane oxide: ^1H NMR ($CDCl_3$) δ 7.56 (m, 5.19 H), 3.94 (m, 1.62 H), 3.55 (m, 4.90 H), 3.14 (m, 0.93 H), 1.58 (d, J = 13.5 Hz,[39] 2.45 H); IR ($CHCl_3$ solution) 3081 (w), 3060 (w), 2987 (s), 2925 (m), 2877 (w), 2467 (w), 1960 (w), 1900 (w), 1815 (w), 1700 (w), 1590 (w), 1483 (w), 1450 (m), 1438 (s), 1375 (w), 1238 (s), 1215 (s), 1162 (s), 1150 (s), 1118 (s), 1105 (s), 1008 (w), 992 (w), 940 (w), 882 (w), 835 (w), 688 (m), 648 (m) cm^{-1}; mass spectrum (75 V, peaks > 10% intensity), *m/e* 242 (M^+, 5), 241 (16), 118 (100), 117 (64), 115 (12), 102 (19), 92 (14), 91 (22), 78 (11), 77 (16), 51 (13), 47 (10); UV (95% EtOH) λ_{max} 272 nm (ϵ 592), 264 (726), 258 (619).

Reaction of *P*-Phenylphosphahomocubane Oxide with Penyllithium and Diphenyl Disulfide. Preparation of 14 and 15. A 200-mL three-neck, round-bottom flask equipped with a serum inlet, N_2 inlet, stopper, and magnetic stirrer was alternately flame-dried under vacuum and flushed with N_2 three times. A solution of 1.528 g (6.71 mmol) of *P*-phenylphosphahomocubane oxide in 100 mL of dry tetrahydrofuran was added and cooled to 0 °C, and a solution of 4.3 mL of 1.7 M phenyllithium (7.31 mmol) in 70:30 benzene–ether was then added. The solution (now brown) was stirred for 5 min at 0 °C and then cooled to −20 °C to prevent decomposition of the anion.

To a second flame-dried three-neck, 500-mL round-bottom flask equipped with a N_2 inlet, addition funnel, serum inlet, and magnetic stirrer was added a solution of 2.244 g of diphenyl disulfide (10.31 mmol) in 50 mL of dry THF. After this solution had been cooled to 0 °C, the phosphine oxide anion was added at a moderate rate from a dropping funnel into which 20-mL aliquots were periodically added. The total time for the addition was 1.0 h. The brown reaction mixture was stirred for 1.0 h at 0 °C and 1.0 h at ambient temperature and then was quenched with 20 mL of H_2O. Chloroform (300 mL) was added, the layers separated, and the organic layer after washing with H_2O (2 × 100 mL) and brine (50 mL) was dried over $MgSO_4$. Removing the solvent left 3.602 g of crude brown oil, which when chromatographed on a 2.5 × 70 cm SiO_2 column eluting with 2% methanol–methylene chloride (v/v) gave two distinct products. The first band isolated from the column contained 136 mg of a mixture of compounds A and B. Product A was obtained in other runs as a light yellow oil that yielded white crystals upon trituration with acetone and melted at 210–211 °C after recrystallization from benzene. Its yield ranged between 1 and 4.9%. It was identified as *P*-phenyl-α,α′-bis(benzenesulfenyl)-phosphahomocubane oxide on the basis of the following spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.30 (m, 15.26 H), 3.70 (m, 1.82 H), 3.47 (m, 3.87 H); IR (KBr) 3056 (w), 3012 (w), 2997 (w), 2926 (w), 2852 (w), 1652 (w), 1578 (m), 1479 (s), 1437 (s), 1432 (s), 1235 (w), 1190 (s, P=O str), 1180 (s), 1132 (w), 1100 (m), 1082 (w), 1062 (w), 1039 (w), 1019 (m), 995 (w), 922 (w), 741 (s), 705 (m), 690 (s), 557 (s), 525 (s) cm^{-1}; mass spectrum (75 V, peaks > 10% intensity), *m/e* (relative intensity) 444 (14), 336 (23), 335 (100), 225 (17), 211 (65), 210 (16), 178 (17), 78 (71), 77 (26), 52 (15), 51 (15); UV (95% EtOH) λ_{max} 261 nm (ϵ 6950).

The second, slower moving product, B, was obtained as a light yellow oil that yielded 1.535 g of white crystals after trituration with acetone (67.8%). The crystals were used in the next step, oxidation, without further purification. In experiments conducted at various temperatures, yields ranged between 32 and 68%. The highest yield was obtained in the procedure above, which prevented decomposition of the phosphine oxide anion and suppressed bissulfenylation. When diphenyl disulfide was added to the lithiated phosphine oxide, rather than the other way around, the yield was much lower.

The solid, mp 155.5–157.0 °C, after recrystallization from benzene, was identified as *P*-phenyl-α-benzenesulfenylphosphahomocubane oxide on the basis of the following spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.46–7.18 (m, 10.27 H), 3.86 (m, 1.90 H), 3.50 (m, 4.76 H); IR (KBr) 3058 (w), 2985 (m), 2940 (w), 2000 (w), 1919 (w), 1852 (w), 1754 (w), 1650 (w), 1610 (w), 1488 (m), 1445 (m), 1337 (w), 1325 (w), 1241 (s), 1233 (m), 1215 (m), 1188 (s), 1164 (m), 1121 (s), 1076 (w), 1031 (w), 1004 (w), 968 (w), 956 (w), 928 (m), 916 (w), 886 (w), 863 (w), 853 (w), 791 (w), 757 (s), 747 (s), 741 (s), 713 (s), 694 (s) cm^{-1}; mass spectrum (75 V, peaks > 10% intensity), *m/e* (relative intensity) 337 (10, $M^+ + 1$,), 336 (36, M^+), 227 (16), 213 (19), 212 (100), 211 (23), 179 (13), 178 (10), 149 (10), 135 (11), 134 (12), 126 (13), 110 (10), 104 (10), 103 (71), 102 (11), 78 (45), 77 (26), 52 (10), 51 (16), 28 (16); UV (95% EtOH) λ_{max} 258 mm (ϵ 3960).

An analytical sample was prepared by recrystallizing twice from 1:1 benzene–cyclohexane and once from benzene, subliming at 124

°C (0.04 mm), and drying in an Abderhalden apparatus at 55 °C (0.01 mm) for 48 h. Anal. Calcd for $C_{20}H_{17}OPS$: C, 71.40; H, 5.10; P, 9.21; S, 9.53. Found: C, 71.49; H, 5.12; P, 8.93; S, 9.51.

***P*-Phenyl-α-benzenesulfonylphosphahomocubane Oxide (16).** To a 500-mL three-neck, round-bottom flask fitted with an addition funnel, condenser, stopper, and magnetic stirrer was added 2.352 g (7.0 mmol) of *P*-phenyl-α-benzenesulfenylphosphahomocubane oxide in 200 mL of $CHCl_3$. The solution was cooled to 0 °C, and a solution of 85% *m*-chloroperbenzoic acid (5.210 g, 25.7 mmol, 3.69 equiv) in 100 mL of $CHCl_3$ was added in drops from the addition funnel during 1.0 h. The reaction mixture was stirred for1.0 h at 0 °C and at ambient temperature for 3.0 h. Washing successively with 1 N NaOH (3 × 60 mL), H_2O (35 mL), and brine (50 mL), drying over $MgSO_4$, and removing the solvent gave 2.923 g of white solid, which after recrystallization from benzene and drying in an Abderhalden apparatus (overnight, 55 °C, 0.1 mm) produced 1.699 g (67% yield) of white powder: mp 214–216 °C; ^1H NMR ($CDCl_3$) δ 7.62 (m, 10.21 H), 4.20 (m, 3.12 H), 3.57 (m, 3.66 H); IR (KBr) 3084 (w), 3050 (w), 3022 (w), 2990 (m), 2924 (w), 2850 (w), 1660 (w), 1590 (m), 1584 (m), 1482 (m), 1450 (s), 1436 (s), 1306 (s), 1288 (s), 1236 (s), 1210 (s), 1190 (s), 1149 (s), 1110 (s), 1081 (s), 1017 (s), 970 (m), 916 (s), 764 (s), 750 (s), 740 (s), 720 (s), 710 (s), 692 (s), 610 (s), 552 (s), 540 (s), 505 (s), 488 (s), 460 (m) cm^{-1}; 368 (M^+, 2), 243 (38), 227 (11), 179 (20), 149 (10), 125 (12), 119 (30), 104 (16), 103 (100), 102 (14), 78 (10), 77 (27), 28 (10); UV (95% EtOH) λ_{max} 273 nm (ε 2014), 266 (7020), 259 (2039).

***P*-Phenyl-α,α′-bis(benzenesulfonyl)phosphahomocubane Oxide (17).** To a 100-mL three-neck, round-bottom flask equipped with a condenser, stopper, and addition funnel was added a solution of 87 mg of *P*-phenyl-α,α′-bis(benzenesulfenyl)phosphahomocubane oxide (0.196 mmol) in 20 mL of $CHCl_3$. The solution was cooled to 0 °C, whereupon a solution of 270 mg of 85% *m*-chloroperbenzoic acid (1.34 mmol, 6.82 equiv) in 15 mL of $CHCl_3$ was added in drops from the addition funnel during 0.5 h. The reaction mixture was stirred for 0.5 h at 0 °C and then at ambient temperature for 3.0 h. Chloroform (50 mL) was added, and the solution was washed successively with 30 mL of 1 N $NaHSO_3$, H_2O, and brine and dried over $MgSO_4$. Removing the solvent gave 128 mg of a white solid, which after recrystallization from methanol produced 57 mg (57% yield) of a white powder: mp 300–301 °C; ^1H NMR (Me_2SO-d_6) δ 7.60 (m, 15.20 H), 4.30 (m, 3.42 H), 3.61 (m, 2.40 H); IR (KBr) 3084 (w), 3064 (w), 3028 (w), 3002 (w), 2920 (w), 2841 (w), 1665 (w), 1580 (w), 1475 (w), 1440 (s), 1435 (s), 1310 (s), 1302 (s), 1238 (w), 1210 (s), 1180 (s), 1144 (s), 1130 (m), 1108 (m), 1082 (s), 1060 (w), 1035 (w), 1018 (w), 996 (w), 978 (w), 950 (w), 934 (w), 921 (m), 872 (w), 792 (w), 762 (m), 748 (s), 715 (s), 682 (m), 618 (s), 608 (s), 565 (m), 550 (s), 510 (s), 362 (w) cm^{-1}; mass spectrum (75 V, peaks > 10% intensity), *m/e* (relative intensity) 508 (M^+, 1) 383 (14), 367 (27), 253 (39), 242 (15), 179 (14), 178 (19), 165 (11), 164 (20), 149 (11), 147 (16), 146 (20), 126 (10), 125 (100), 119 (10), 118 (14), 109 (10), 103 (10), 102 (42), 97 (21), 95 (14), 79 (10), 78 (16), 77 (50), 76 (11), 55 (10), 51 (15), 41 (16), 28 (16); UV (95% EtOH) λ_{max} 273 nm (ε 1871), 267 (2339), 262 (1671).

8-Benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]oct-7-en-3-yl-*exo*-phenylphosphinic Acid (19). To a flame-dried, N_2-flushed, three-neck, 50-mL round-bottom flask equipped with a serum inlet, N_2 inlet, stopper, and magnetic stirrer was added 202 mg of *P*-phenyl-α-benzenesulfonylphosphahomocubane oxide (0.55 mmol) and 15 mL of dry THF. To this slurry was syringed a 10-mL solution of 126 mg of sodium hexamethyldisilylamide (0.69 mmol) in THF. After 5 min the mixture was a yellow slurry and after 25 min a clear orange solution. The solution was allowed to stir for 1.0 h before it was quenched with 10 mL of saturated aqueous ammonium chloride. Sufficient water was added to dissolve the amine salt, the solution was extracted with 100 mL of $CHCl_3$, and the organic solution was washed successively with H_2O (2 × 30 mL) and brine and dried over $MgSO_4$. The solvent was removed while the flask was warmed, and 175 mg of a white solid was obtained that was almost homogeneous [one major spot, according to thin-layer chromatographic analysis (R_f 0.20, 5% CH_3OH–CH_2Cl_2, SiO_2), with traces of two minor components]. Recrystallization from hot benzene gave 85 mg of a white solid, R_f 0.20, mp 93–94 °C (40% yield), identified as the *exo*-phosphinic acid: ^1H NMR (100 MHz, CD_3CN) δ 7.95 (m, 1.81 H), 7.76 (m, 8.11 H), 5.84 (s, 0.98 H), 3.93 (m, 1.01 H), 3.72 (m, 6.04 H), 2.89 (m, 1.01 H); IR (KBr) 3609 (s), 3446 (s), 3343 (s), 3246 (s), 3063 (m), 3015 (m), 2990 (s), 2964 (m), 2873 (w), 1904 (w), 1830 (w), 1601 (m), 1483 (m), 1450 (m), 1440 (m), 1312 (m), 1282 (s), 1265 (s), 1223 (m), 1166 (s), 1140 (s), 1114 (s), 1085 (s), 1038 (m), 1022 (w), 995 (w), 970 (w), 908 (s), 838 (w), 776 (w), 750 (s), 688 (s), 582 (s), 535 (s), 512 (w), 437 (w) cm^{-1}; mass spectrum (30 V, peaks > 10% intensity), *m/e* 386 (M^+ < 1%), 244 (53), 227 (30), 167 (18), 166 (24), 150 (21), 149 (13), 141 (48), 140 (100, $C_6H_5PO_2$), 125 (23), 124 (13), 104 (32), 103 (61), 102 (12), 95 (12), 78 (71), 77 (59), 64 (16), 46 (14), 28 (11); UV (95% EtOH) λ_{max} 273 nm (ε 965), 264 (1102), 258 (1011), 252 (459).

8-Benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]oct-7-en-3-yl-*endo*-phenylphosphinic Acid (18). To a flame-dried, N_2-flushed, three-neck, 50-mL round-bottom flask equipped with a serum inlet, N_2 inlet, stopper, and magnetic stirrer was added a slurry of 204 mg of *P*-phenyl-α-benzenesulfonylphosphahomocubane oxide (0.55 mmol) in 15 mL of dry THF. A 5 mL THF solution of 112 mg of sodium hexamethyldisilylamide (0.61 mmol, 1.1 equiv) was syringed into the mixture to give an orange-colored slurry. After 25 min, a clear orange solution resulted, which was allowed to stir for an additional 0.5 h before being quenched with 5 mL of saturated aqueous NH_4Cl. Methylene chloride (75 mL) was added, and the mixture was washed successively with H_2O (3 × 20 mL) and brine (30 mL) and dried over $MgSO_4$. Filtration and removal of solvent (bath temperature between 30 and 40 °C to prevent thermal epimerization) gave a light yellow solid. Chromatography on a 2 × 50 cm column of 35 g of SiO_2 eluting rapidly with 5% CH_3OH–CH_2Cl_2 gave 82 mg (39% yield) of a white solid, mp 71–77 °C, identified as 8-benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]oct-7-en-3-yl-*endo*-phenylphosphinic acid on the basis of its R_f value (0.40 in 5% CH_3OH–CH_2Cl_2 on SiO_2) and its vinyl proton chemical shift in the ^1H NMR spectrum (δ 6.04 compared with δ 5.86 for the *exo*-phosphinic acid.) Some (15 mg, 7%) 3-*exo*-phosphinic acid was also obtained. The yields of *endo*-phosphinic acid in several runs varied, after chromatography, from 17 to 48%, while the 3-*exo*-phosphinic acid was obtained in yields ranging from 6 to 14%. The total yields of both epimers ranged between 26 and 57%. A suitable recrystallization solvent system for the *endo*-phosphinic acid could not be found. In one experiment 123 mg of *endo*-phosphinic acid when rapidly recrystallized from hot benzene gave 38 mg of a mixture of 88.5% *endo*- and 11.5% *exo*-phosphinic acids (analysis by ^1H NMR). The endo acid is more soluble than the exo isomer in $CHCl_3$ and CH_3CN: ^1H NMR (100 MHz, CD_3CN) δ 7.92 (m, 2.00 H), 7.54 (m, 8.37 H), 6.04 (s, 0.82 H), 5.86 (s, 0.18 H, from *exo*-phosphinic acid), 3.87 (m, 1.00 H), 3.57 (m, 1.09 H), 3.22 (m, 4.55 H), 2.89 (m, 1.00 H).

Epimerization of 8-Benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]-oct-7-en-3-yl-*endo*-phenylphosphinic Acid (18). Into a flame-dried, N_2-flushed, 50-mL round-bottom flask equipped with a condenser, N_2 inlet, and magnetic stirrer was placed 65 mg of 8-benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]oct-7-en-3-yl-*endo*-phenylphosphinic acid (0.168 mmol) in 30 mL of dry benzene. The mixture was refluxed, and the disappearance of the *endo*-phosphinic acid TLC spot at R_f 0.40 (5% CH_3OH–CH_2Cl_2, SiO_2) was monitored hourly. Epimerization was complete after 5.0 h. Removing the solvent and recrystallization from benzene gave 22 mg of a white powder, mp 92–93 °C (34%), identified as 8-benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]oct-7-en-3-yl-*exo*-phenylphosphinic acid (19).

8-Benzenesulfonyl-*syn*-tricyclo[4.2.0.0^{2,5}]oct-7-en-3-yldi phenylphosphine Oxide (20). To a flame-dried, N_2-flushed, three-neck round-bottom flask equipped with a serum inlet, N_2 inlet, stopper, and magnetic stirrer and containing a slurry of 203 mg of *P*-phenyl-α-benzenesulfonylphosphahomocubane oxide (0.55 mmol) in 10 mL of THF at −78 °C was added 0.40 mL of 1.7 M phenyllithium in 70:30 benzene–ether (0.68 mmol, 1.23 equiv) in drops from a syringe. A yellow slurry resulted, which was allowed to stir for 5.5 h at −78 °C, and then adding 2 mL of 24% HBr at −78 °C gave a clear green solution. Chloroform (100 mL) was added, and the organic solution was washed successively with H_2O (30 mL) and brine and dried over $MgSO_4$. Removing the solvent gave 296 mg of a light yellow solid. Preparative TLC on four SiO_2 plates (20 × 20 cm, 1000 μm) eluting twice with 5% methanol–methylene chloride gave 151 mg of a fluffy white solid (61% yield), which when recrystallized from 3:1 benzene–cyclohexane (v/v) produced 79 mg (32% yield) of a white powder: mp 206–207.5 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 8.00 (m, 2.24 H), 7.50 (m, 12.98 H), 5.95 (s, 0.94 H), 3.64 (m, 4.96 H), 3.40 (m, 1.77 H); IR (KBr) 3094 (m), 3060 (m), 3030 (m), 2982 (s), 2940 (s), 2864 (w), 1980 (w), 1918 (w), 1828 (w), 1783 (w), 1683 (w), 1612 (w), 1598 (w), 1478 (m), 1446 (s), 1438 (s), 1316 (s), 1286 (s), 1266 (s), 1250 (s), 1220 (m), 1186 (s), 1140 (s), 1110 (s), 1084 (s), 1070 (m), 1032 (m), 1018 (s), 990 (m), 966 (s), 948 (w), 932 (w), 850 (w), 834 (s), 774 (m), 754 (s), 740 (s), 714 (s), 700 (s), 620 (w), 590 (s), 550 (s), 460 (w), 435 (w) cm^{-1}; mass spectrum (30 V, peaks > 10% intensity), *m/e* (relative intensity) 446 (M^+, 1), 306 (11), 305 (48), 228 (27), 227 (26), 203 (11), 202 (66), 201 (82), 183 (10), 155 (17), 125 (28), 104 (22), 103 (15), 78 (100), 77 (61), 52 (32), 51 (33), 50 (21), 39 (16), 28 (17); UV λ_{max} (95% EtOH) 553 nm (ε = 707), 273 (1305), 265 (1577), 258 (1142).

***P*-Phenylphosphahomocubane Sulfide (13).** To a 100-mL three-neck, flame-dried, N_2-flushed round-bottom flask equipped with a condenser with a N_2 inlet, two stoppers, and magnetic stirrer was added a solution of 481 mg (2.26 mmol) of phenylphosphahomocubane[10] in 40 mL of dry benzene. One stopper was replaced by a Gooch tube attached to a 50-mL Erlenmeyer flask containing 1.753

g (6.59 mmol) of S_8 under N_2. The sulfur was added at ambient temperature over 20 min. Clouding was noted. The reaction mixture was stirred for 1.0 h at room temperature and refluxed for 3.0 h. Methylene chloride (75 mL) was added, and after filtration, washing with H_2O (30 mL) and brine, and drying over $MgSO_4$, removal of solvent gave 1.952 g of yellow solid. Trituration with CH_2Cl_2 and two filtrations removed 874 mg of sulfur. Chromatography on 38 g of SiO_2 (2 × 50 cm column) eluting with 20% ether–hexane and sublimation (130 °C, 0.05 mm) gave 265 mg of phenylphosphahomocubane sulfide (48% yield): mp 162–162.5°C; ^1H NMR ($CDCl_3$) δ 7.61 (m, 4.97 H), 3.82 (m, 9.01 H); IR (KBr) 3050 (w), 3018 (w), 2998 (m), 2970 (w), 1665 (w), 1588 (w), 1470 (w), 1430 (s), 1383 (w), 1312 (w), 1248 (s), 1235 (s), 1185 (w), 1150 (w), 1110 (s), 1095 (s), 1062 (m), 1020 (w), 990 (s), 955 (m), 928 (s), 872 (w), 848 (m), 790 (w), 750 (s), 720 (s), 695 (s), 655 (s), 510 (s), 472 (m) cm^{-1}; mass spectrum (75 V, peaks > 10% intensity), *m/e* (relative intensity) 244 (M^+, 24), 211 (13), 179 (12), 140 (11), 134 (13), 133 (21), 108 (15), 107 (20), 105 (10), 104 (100), 103 (37), 78 (38), 77 (30), 63 (25), 51 (32), 50 (12), 44 (12), 39 (18), 32 (27), 28 (81); UV (95% EtOH) λ_{max} 253 nm (ϵ 3310).

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Supplementary Material Available: Decoupled spectra (7 pages). Ordering information is given on any current masthead page.

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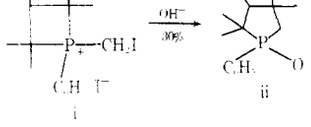

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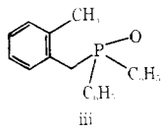

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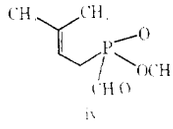

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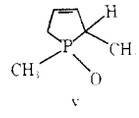

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