with 6 × 10 mL of chloroform and an NMR spectrum ($CDCl_3$) obtained on the crystalline residue after evaporation of the solvent. The spectrum of the product corresponded to that of a mixture of **7a** and **7b** and showed the same ratio of salts (28% **7a**:72% **7b**) as the corresponding oxides from which they were derived (25% **8a**:75% **8b**) by phenylsilane reduction and phenylation.

Kinetic Procedure for Cleavage of 7a and 7b. Rate measurements were taken on a Cary 14 spectrophotometer and followed the disappearance of the salt at 2725 Å. To 2.50 mL of a 0.01 M solution of the salt in 1:1 (v:v) ethanol–water in each of 12 ampules was added 2.50 mL of 0.2 M sodium hydroxide in 1:1 (v:v) ethanol–water at 0 °C. Benzene (0.01 mL) was added to each ampule and the ampules sealed, shaken, and placed in a water bath at 75.0 ± 0.5 °C. At given time intervals the ampules were removed, cooled in ice, centrifuged to separate benzene, and opened and the contents decanted into a cuvette (leaving droplets of benzene in the ampule) and the solution scanned. A least-squares first-order plot was generated by the Finalal computer program. Molar extention coefficients at 2725 Å for **7a** and **7b** were 9.28×10^2 and 9.34×10^2, respectively.

Kinetic Procedure for Base Cleavage of 1-Benzyl-1-phenylphosphorinanium Bromide (15) and *cis*- and *trans*-1-Benzyl-4-*tert*-butyl-1-phenylphosphorinanium Bromide (3). The rate measurements were made at 273.5 nm using a Beckman Model DU ultraviolet spectrophotometer equipped with a thermostated cell compartment. A carbonate-free mixture of ethanol–water (1:1 by volume at 25 °C) was prepared and sodium hydroxide pellets were added under an inert atmosphere in making up a 1.28 N solution. Phosphonium salt was added under an inert atmosphere to this solution until a concentration of 9×10^{-4} M was obtained. The mixture was shaken and then inserted in the thermostated cell compartment. A 10-cm cell was used to follow the disappearance of unsubstituted salt at 307.5 nm. For **3a** and **3b** a 1-cm cell was employed. In order to determine wavelengths that would provide suitable absorption differences a comparison of the ultraviolet spectra of the salts and oxides was made. All the kinetic runs were followed for at least 4 half-lives, and A_∞ was measured after 10 half-lives. The rate constants were determined first graphically and then by computer.

Acknowledgments. The authors wish to thank Robert Freerks for the preparation of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexanol and the National Science Foundation for support of this work under Grant GP 38756X.

Registry No.—**3a**, 61332-79-4; **3b**, 61332-80-7; **4a**, 61332-81-8; **4b**, 61332-82-9; **7a**, 61332-83-0; **7b**, 61332-84-1; **8a**, 61332-71-6; **8b**, 61332-85-2; **10**, 61332-86-3; 1,5-dibromo-3-*tert*-butylpentene, 758-75-8; tetraphenyldiphosphine, 1101-41-3; benzyl bromide, 100-39-0; methyl bromide, 74-83-9; *trans*-4-*tert*-butyl-1-phenylphosphorinane, 61332-72-7; *cis*-4-*tert*-butyl-1-phenylphosphorinane, 61332-73-8.

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Reduction–Elimination of Cyclic Phosphate Derivatives as a Route to Alkenes

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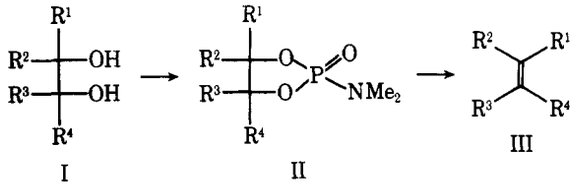
The conversion of 1,2-diols to alkenes has been effected through reduction of the cyclic ethyl phosphate or *N,N*-dimethylamidophosphate derivatives with lithium in ammonia or titanium metal in THF. Accordingly, *cis*-1,2-dimethylcyclodecane-1,2-diol was converted to a 9:1 mixture of *cis*- and *trans*-1,2-dimethylcyclodecene in 81% yield through its dimethylamidophosphate derivative whereas the ethyl phosphate derivative afforded a 6.7:1 mixture of these products in 57% yield. *trans*-1,2-Dimethylcyclodecane-1,2-diol gave a 6:1 mixture of *trans*- and *cis*-1,2-dimethylcyclodecene in 24% yield via the amidophosphate and a 4.3:1 mixture of these isomers in 55% yield via the ethyl phosphate. The analogous cyclododecanediols were converted to the 1,2-dimethylcyclododecenes in 53–86% yield with syn-elimination preferences of 9:1–13.3:1. The 2,3-decanediols afforded the 2-decenes in 75% yield. The erythro diol gave 1.4:1 (phosphate) and 1.9:1 (amidophosphate) mixtures of *cis*- and *trans*-2-decenes. The threo isomer afforded a 6.7:1 mixture of trans and cis isomers from both cyclic phosphate derivatives.

We recently described a stereoselective method for the conversion of vicinal diols to alkenes via reduction–elimination of cyclic phosphoric amide derivatives with dissolving metals (I → II → III).[1] We have now completed studies which further delineate the scope and stereochemistry of the sequence and show that, in some cases, cyclic phosphoric esters offer ad-

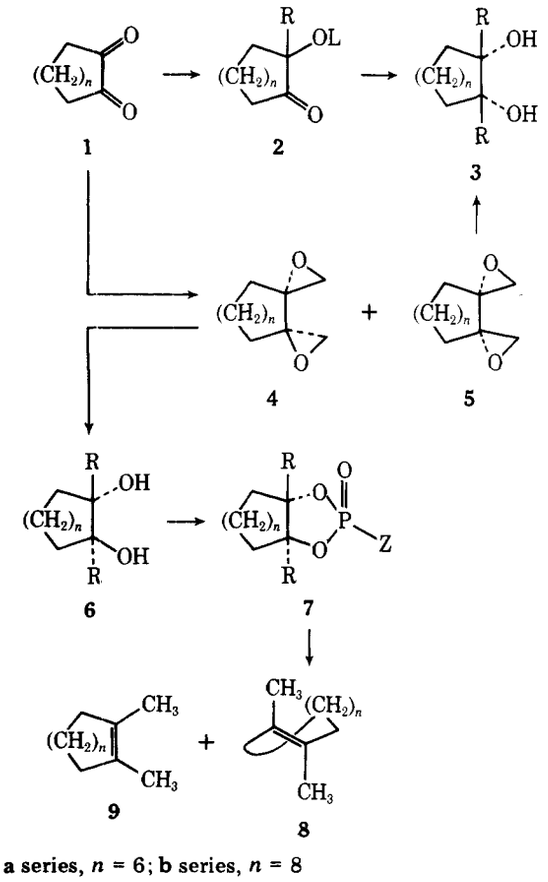
vantages over amides. We have also examined alternative reducing agents.



I II III

Our initial impetus for studying vicinal glycol eliminations arose from a need for 1,2-disubstituted *trans*-cyclodecenes and cyclododecenes as synthetic intermediates. Sharpless and Flood found that vicinal glycols could be directly deoxygenated with potassium hexachlorotungstate.[2] The reaction proceeds by syn elimination but isomerization of the starting glycol gives rise to stereochemically impure olefins. We hoped to find alternative methods of greater stereoselectivity which would be applicable to *ditertiary* glycols. For the systems of interest to us, the phosphoric amide reduction–elimination reaction (II → III)[1] gave slightly better results than the hexachlorotungstate deoxygenation.[2] In either event, since both schemes involve preferential syn elimination and since we wished to prepare trans cycloalkenes, our main problem was to find an efficient route to *trans*-1,2-dialkylcycloalkane-1,2-diols. The addition of organometallic reagents to 1,2-cyclodecanedione (**1a**) and 1,2-cyclododecanedione (**1b**) affords only the cis glycols **3a** and **3b** under a variety of reaction conditions.[2,3] We examined Grignard reagents and organolithium reagents in ether, hexane, and hexamethylphosphoric amide as solvents at temperatures ranging from −80 to 30 °C and found no indication of trans products. Presumably, the intermediate mono adducts **2** (L = MgX or Li) exist in a chelated form which favors approach leading to the cis isomer **3**.[4]

Chart I[a]



[a] **a** series, n = 6; **b** series, n = 8

In support of this hypothesis we found that derivatives of the intermediate mono adduct in which chelation could not occur, such as the trimethylsilyl ether **2** (L = $SiMe_3$), gave mixtures of trans and cis glycols **3** and **6**. Thus keto ether **2b** (L = $SiMe_3$, R = 4-pentenyl) upon treatment with 4-pentenyllithium in ether–hexane followed by removal of the silyl group in methanolic potassium carbonate afforded a 3:2 mixture of the trans and cis glycols in 22% yield. Unfortunately, the reaction proceeded with significant recovery of starting ketol **2b** (L = H, R = 4-pentenyl) and attempts to improve the yield were to no avail. The use of *tert*-butyldimethylsilyl[5] and allyl protecting groups proved even less satisfactory. Evidently, enolzation seriously interferes with addition in these cases.

A more satisfactory route to the trans diols **6** evolved from our discovery that dimethylsulfonium methylide[6] adds to diones **1a** and **1b** to yield mainly the trans diepoxides **4**. Dione **1a** gave a 7:3 ratio of trans and cis diepoxides **4a** and **5a** in over 70% yield while dione **1b** afforded a 5:3 ratio of trans and cis isomers **4b** and **5b** in comparable yield. These stereoisomers could be readily separated by chromatography. Reduction of each with lithium aluminum hydride afforded the known *trans*- and *cis*-cyclodecanediols (**4a, 5a**) and cyclododecanediols (**4b, 5b**) in high yield, thereby confirming the stereochemical assignments.[2,3] Preliminary experiments with the cyclododecane *trans*-diepoxide **4b** indicated that organolithium reagents smoothly attack the epoxides to give *trans*-1,2-dialkyl-1,2-cyclododecanediols. For example, the bisbutenyl diol **6b** (R = 3-butenyl) was obtained as a crystalline solid in 75–80% yield upon treatment of epoxide **4b** with allyllithium.

The next phase of our studies involved conversion of the trans diols **6** to the cyclic phosphoramides **7** (Z = dimethylamino) and subsequent reduction–elimination along the lines previously reported for the cis diols **3**.[1] To that end, treatment of *trans*-1,2-dimethyl-1,2-cyclodecanediol **6a** (R = CH_3) with methyllithium followed by *N,N*-dimethylamidophosphorodichloridate[7] in ether–tetrahydrofuran–hexamethylphosphoramide afforded the cyclic phosphoramide **7a** (R = CH_3; Z = dimethylamino). This reaction was significantly slower than the analogous conversion of the cis glycol **3a** (R = CH_3) and mixtures of products containing appreciable hydroxylic material were isolated in only moderate yield even after prolonged reaction time. Treatment of these crude mixtures with lithium in ammonia afforded *trans*- and *cis*-1,2-dimethycyclodecene **8a** (R = CH_3) and **9a** (R = CH_3) in an 86:14 ratio.

trans-1,2-Dimethyl-1,2-cyclododecanediol **6b** (R = CH_3) also reacted less efficiently than its cis counterpart **3b** (R = CH_3) with *N,N*-dimethylamidophosphorodichloridate. The resulting crude cyclic phosphoramide **7b** (R = CH_3, Z = dimethylamino) gave a 92:8 mixture of *trans*- and *cis*-1,2-dimethylcyclododecenes **8b** (R = CH_3) and **9b** (R = CH_3) upon reduction with lithium in ammonia. The butenyl homologue of diol **6b** (R = 3-butenyl) gave only a trace of cyclic phosphoramide **7b** (R = 3-butenyl, Z = dimethylamino) even after prolonged reaction time. The main products consisted of polyenes and acidic materials.

In view of the problems encountered in forming the cyclic phosphoramides **7** (Z = dimethylamino) we decided to examine the cyclic phosphates (Z = OEt). This decision was prompted by Ireland's finding that tertiary alcohols react more readily with diethyl phosphorochloridate than with the bis(dimethylamino) analogue.[8] The ditertiary diols **6a** and **6b** appear to follow a similar trend in their reaction with ethyl phosphorodichloridate to give the cyclic phosphates **7a** and **7b** (R = CH_3; Z = OEt). In both cases reaction times were shorter and the products contained fewer impurities. Reduction with lithium in ammonia afforded an 81:19 mixture of *trans*- and *cis*-1,2-dimethylcyclodecenes **8a** (R = CH_3) and

Table I. Net Conversion of Diols to Olefins via Reduction–Elimination of Cyclic Phosphate Derivatives Using Lithium/Ammonia

Registry no.	Diol	Reagent	Products	Yield, %[a]	Syn/anti
56491-42-0	**3a** (R = CH_3)	Cl_2PONMe_2	**9a** (90%), **8a** (10%)	81	9.0
	3a (R = CH_3)	Cl_2PO_2Et	**9a** (87%), **8a** (13%)	57	6.7
61376-38-3	**6a** (R = CH_3)	Cl_2PONMe_2	**9a** (14%), **8a** (86%)	24	6.1
	6a (R = CH_3)	Cl_2PO_2Et	**9a** (19%), **8a** (81%)	55	4.3
56499-08-2	**3b** (R = CH_3)	Cl_2PONMe_2	**9b** (90%), **8b** (10%)	86	9.0
	3b (R = CH_3)	Cl_2PO_2Et	**9b** (93%), **8b** (7%)	76	13.3
61376-39-4	**6b** (R = CH_3)	Cl_2PONMe_2	**9b** (8%), **8b** (92%)	53	11.5
	6b (R = CH_3)	Cl_2PO_2Et	**9b** (8%), **8b** (92%)	66	11.5
	n-C_7H_{15}CH(OH) | CH_3CH(OH)		n-C_7H_{15}CH=CHCH_3		
19721-82-5	Erythro (**10**)	Cl_2PONMe_2	Cis (66%), trans (34%)	40,[a] 76[b]	1.9
	Erythro (**10**)	Cl_2PO_2Et	Cis (58%), trans (42%)	23[b]	1.4
19721-81-4	Threo (**11**)	Cl_2PONMe_2	Cis (13%), trans (87%)	42,[a] 76[b]	6.7
	Threo (**11**)	Cl_2PO_2Et	Cis (13%), trans (87%)	25[b]	6.7

[a] Isolated yield based on diol. [b] Yield based on analysis by gas chromatography.

Table II. Reduction–Elimination of the Phosphoramide Derived from Diol 3b (R = CH_3)

Reagent	Yield, %[b]	Syn/anti
Li, NH_3[a]	98	9.0
Na–naphthalene[a]	73	24
Na–xylene[a]	61	>99
$TiCl_4$–Mg(Hg)	77	7.3
$TiCl_3$–K	92	7.3
Zn–HOAc	0[c]	
Al(Hg)	0[c]	
$Cr(ClO_4)_2$–$(CH_2NH_2)_2$	0[c]	

[a] See ref 1. [b] Isolated yield. [c] Recovered starting material.

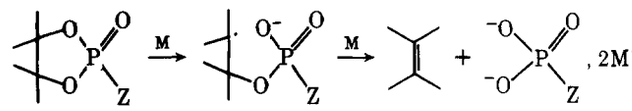
9a (R = CH_3) and a 92:8 mixture of *trans*- and *cis*-1,2-dimethylcyclododecenes **8b** (R = CH_3) and **9b** (R = CH_3).

Table I summarizes conversions of vicinal diols to alkenes via reduction–elimination of cyclic phosphoric acid amide or ester derivatives. With cyclic ditertiary trans diols **6a** and **6b** (R = CH_3) the ester derivative gives a higher overall yield than the amide with comparable stereoselectivity. The corresponding cis diols **3a** and **3b** (R = CH_3) are most efficiently converted to olefins through their cyclic phosphoramides. Both disecondary vicinal acyclic diols, *erythro*- and *threo*-2,3-decanediol,[9] behave like the cyclic cis diols. These trends suggest that the phosphoramides are more efficiently reduced than the phosphoric esters, a fact noted by Ireland[8] in his work on alcohol phosphate and phosphoramidate hydrogenolysis, but in some cases the phosphoric esters are more readily formed.

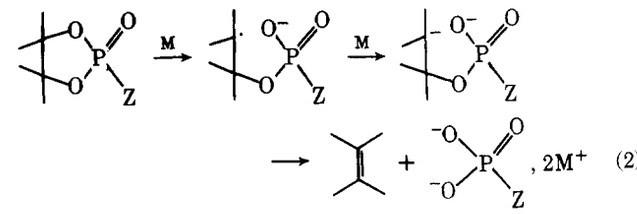
We conducted a brief survey of other reducing agents which might convert cyclic phosphate derivatives to alkenes. For these studies, summarized in Table II, we used the crystalline *N,N*-dimethyl phosphoramidate derived from *cis*-1,2-dimethylcyclododecane-1,2-diol (**3b**).[1] The titanium reagents of Corey[10] and McMurry[11] effected the reduction–elimination about as efficiently as alkali metal reagents whereas less active reducing agents such as zinc,[12] aluminum amalgam,[13] and chromous perchlorate[14] were ineffective.

In conclusion, the two-step conversion of diols to olefins via cyclic phosphates or phosphoramidates can be effected with reasonable efficiency and with a relatively high degree of stereoselectivity. The method of Sharpless and Flood[2] using potassium hexachlorotungstate accomplishes the same overall conversion in one step in comparable yield. In some cases (the *trans*-1,2-cyclodecanediol **6a**, for example) we have found that the two-step method proceeds more stereoselectively. Clearly, the preference for one or the other method will depend upon diol structure and availability of reagents.

As for mechanism, our findings suggest a two-step process for the reduction–elimination. Two possibilities are shown below. In each case rotation about the carbon–carbon bond



(1)



(2)

of the intermediate radical anion (or dianion) leads to the product of net anti elimination. Thus the syn–anti ratio will depend upon the relative timing of the first and second bond breaking steps and, possibly, the relative transition state stability for phoshate expulsion in a carbanion-type elimination reaction.

Experimental Section[15]

***cis*-1,2-Dimethylcyclodecane-1,2-diol (3a,R = Me). A. From 1,2-Cyclodecanedione (1a).** To a solution of 3.73 g of 1,2-cyclodecanedione (**1a**)[16] in 100 mL of ether at 0 °C was added 80 mL of 2.2 M ethereal methyllithium. The mixture was stirred at room temperature for 23 h, cooled to 0 °C, and 80 mL of water was carefully added. The product, isolated by extraction with ethyl acetate, showed appreciable carbonyl absorption in its infrared spectrum so the above described methyllithium addition was repeated. The product thus obtained was distilled at 115 °C (0.02 mm) to give 3.75 g of crystalline diol **3a** (R = Me), mp 44–45 °C. Recrystallization from hexane afforded material of mp 55–56 °C; IR (KBr) 3300, 2840, 1430, 1350, 1075 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.17 (CH_3), 1.47 (m, CH_2), 2.86 ppm (OH).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.85; H, 12.15.

B. From Diepoxide 5a. A solution of 0.58 g of diepoxide **5a** in 30 mL of ether was stirred with 0.27 g of lithium aluminum hydride at room temperature for 2 h. The mixture was treated successively with 0.3 mL of water, 0.3 mL of 15% aqueous sodium hydroxide, and 0.9 mL of water and stirring was continued to granulate the resulting inorganic salts. Filtration and removal of the solvent afforded 0.62 g of diol **3a** (R = Me).

Additional confirmation of the cis stereochemistry was secured by the method of Flood[2] which involves heating the diol with dimeth-

ylformamide dimethyl acetal to obtain the cyclic formamide acetal derivative. The substance obtained from diol **3a** (R = Me) showed two equal peaks for the acetal proton in its NMR spectrum reflecting the cis, trans isomer population at this center relative to the cyclodecane substituents.

***cis*-1,2-Dimethylcyclododecane-1,2-diol (3b, R = Me). A. From 1,2-Cyclododecanedione (1b).** To a solution of 5 g of 1,2-cyclododecanedione (**1b**)[17] in 150 mL of ether at −78 °C was added 35 mL of 2.1 M ethereal methyllithium. The mixture was stirred overnight and cooled to 0 °C, and water was carefully added. Extraction with ethyl acetate afforded 6 g of crude material which was recrystallized from hexane to give 4.2 g (72%) of diol **3b** (R = Me): mp 94–95 °C (lit.[2] mp 92–95 °C); IR (KBr) 3400, 2950, 2870, 1480, 1450, 1380, 1110, 1100 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.15 (CH_3), 1.38 (m, CH_2), 2.25 ppm (OH).

B. From Diepoxide 5b. A solution of 1.52 g of diepoxide **5b** in 80 mL of ether was reduced as described above for epoxide **5a** to give 1.43 g of diol **3b** (R = Me).

***cis*- and *trans*-Dimethylenecyclodecane Bisepoxide (4a, 5a).**[18] A solution of dimsylsodium was prepared from 5.2 g of 57% sodium hydride in mineral oil (which was freed of the oil by three successive washings with hexane) and 50 mL of dimethyl sulfoxide.[6] Tetrahydrofuran (50 mL) was added, the solution was cooled to −10 °C, and 25 g of trimethylsulfonium iodide in 120 mL of Me_2SO was added, followed by 5.1 g of 1,2-cyclodecanedione (**1a**)[16] in 5 mL of THF. The mixture was stirred overnight, water was added, and the product was isolated by ether extraction to give 3.9 g of oil. Separation of the cis and trans diepoxides **5a** and **4a** was achieved by chromatography on silica gel. Final purification was effected by high-pressure liquid chromatography on Porasil using 5% ethyl acetate in hexane as the eluent. In this way 1.6 g of the trans diepoxide **4a** and 0.7 g of the cis isomer **5a** were obtained.

4a: bp 70 °C (0.1 mm); IR (film) 3060, 3000, 2940, 2880, 1480, 1425, 910 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.58 (m, CH_2), 2.73 ppm (ABq, $-CH_2O-$).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.2; H, 10.6.

5a: bp 70 °C (0.1 mm); IR (film) 3060, 2940, 2880, 1480, 1425 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.60 (m, CH_2), 2.72 ppm (ABq, $-CH_2O-$).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.2; H, 10.6.

***cis*- and *trans*-1,2-Dimethylenecyclododecane Bisepoxide (4b, 5b).**[18] The procedure described above for **4a** and **5a** was followed using 10.2 g of dione **1b**[17] and 42.6 g of trimethylsulfonium iodide. The crude product (11.1 g) was chromatographed on silica gel to give 5.6 g of trans isomer **4b** and 3.6 g of cis isomer **5b**.

4b: bp 85 °C (0.1 mm); IR (film) 3060, 2950, 2770, 1470, 995, 915 cm^{-1}; δ_{Me_4Si} (CCl_4) 1.40 (m, CH_2), 2.53 ppm (ABq, $-CH_2O-$).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.30; H, 10.84.

5b: mp 65.5–66.5 °C (hexane); IR (KBr) 3070, 3000, 2950, 2870, 1470, 970, 900 cm^{-1}; δ_{Me_4Si} (CCl_4) 1.38 (m, CH_2), 2.48 ppm (ABq, $-CH_2O-$).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.02; H, 10.96.

***trans*-1,2-Dimethylcyclodecane-1,2-diol (6a, R = Me).** The procedure described for the reduction of diepoxide **5a** to diol **3a** (R = Me) was employed using 1.4 g of diepoxide **4a** and 0.64 g of lithium aluminum hydride. The product thus obtained (1.47 g) was recrystallized from hexane to give 1.0 g of trans diol **6a** (R = Me): mp 84–85.5 °C; IR (KBr) 3440, 2990, 2940, 2850, 1480, 1370, 1340, 1100, 1080, 1060, 930 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.23 (CH_3), 1.8–1.1 (m, CH_2), 2.48 ppm (OH).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.9; H, 12.0.

The cyclic formamide acetal prepared by the method of Flood[2] showed a single peak for the acetal proton in its NMR spectrum.

***trans*-1,2-Dimethylcyclododecane-1,2-diol (6b, R = Me).** The procedure described for the reduction of diepoxide **5a** was followed using 0.5 g of diepoxide **4b** and 0.23 g of lithium aluminum hydride. The product thus obtained (0.53 g), an oil, was identical with an authentic sample:[2,3] IR (film) 3450, 3000, 2950, 2870, 1470, 1370, 1100 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.23 (CH_3), 1.37 (m, CH_2), 2.00 ppm (OH).

***trans*-1,2-Bis(3-butenyl)cyclododecane-1,2-diol (6b, R = 3-Butenyl).** A 400-mL portion of a solution of allyllithium, prepared from 25.2 g of tetraallyltin in 550 mL of ether and 150 mL of 2.3 M phenyllithium in ether–benzene according to the procedure of Seyferth and Weiner,[19] was added to 10.3 g of diepoxide **4b** in 100 mL of ether. The mixture was stirred at room temperature overnight, then it was cooled to 0 °C and water was added. Extraction with ether afforded 30 g of oily solid which was recrystallized from hexane to give 11.9 g (84%) of diol **6b** (R = 3-butenyl): mp 112–113 °C; IR (KBr) 3460, 2950, 2870, 1640, 900 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 1.2–2.3 (m, CH_2, OH), 4.8–5.2 (m, $CH{=}CH_2$), 5.5–6.2 ppm (m, $CH{=}CH_2$).

Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76. Found: C, 77.83; H, 11.82.

General Procedure for the Preparation of Cyclic *N,N*-Dimethylphosphoramidates. A solution of 1 mmol of diol in 10 mL of THF was cooled to 0 °C and 1.1 mL of 2.1 M ethereal *n*-butyllithium was added with stirring. After a few minutes 5 mL of hexamethylphosphoramide (HMPA) was added followed by 0.4 g (2.5 mmol) of *N,N*-dimethylamidophosphorodichloridate[7] in 5 mL of THF. The solution was stirred overnight (or longer with less reactive diols), water was added, and the cyclic phosphoramidate was isolated by ether extraction. The cyclic phosphoramidates derived from diols **3a** (R = Me), **6a** (R = Me), **6b** (R = Me), **10,** and **11** were oils and were used without purification. The phosphoramidate, mp 131–138 °C, derived from diol **3b** (R = Me), has been described previously.[1]

General Procedure for the Preparation of Cyclic Ethyl Phosphates. The procedure described above for the phosphoramidates was followed using ethyl phosphorodichloridate[20] save for the quantity of HMPA which was 0.5 mL. The phosphates prepared from diols **3a** (R = Me), **3b** (R = Me), **6a** (R = Me), **6b** (R = Me), **10,** and **11** were oils and were used without purification.

General Procedure for the Reduction–Elimination of Cyclic Phosphoramidates and Phosphates Using Lithium in Ammonia. A solution of ca. 1 mmol of the crude phosphoramidate or phosphate in 2–3 mL of ether was added to a solution of 40 mg (5.7 g-atoms) of lithium wire in 50 mL of liquid ammonia with stirring. After 15–30 min solid ammonium chloride was added to discharge the blue color, the ammonia was allowed to evaporate, and the product was isolated by ether extraction. The results of these reductions are summarized in Table I.

Analyses of Olefin Mixtures. The 1,2-dimethylcyclodecenes (**8a, 9a**) could not be separated by gas or liquid chromatography so the ratios were estimated from the intensity of the vinylic CH_3 signals in their NMR spectra.

An enriched sample (87%) of the *Z* isomer **9a** showed the following properties: IR (film) 3010, 2940, 2870, 1475, 1380 cm^{-1}; δ_{Me_4Si} (CCl_4) 1.37 (m, CH_2), 1.57 (87%) and 1.80 (13%) (vinylic CH_3 of *Z* and *E* isomers **9a** and **8a,** respectively), 2.23 ppm (allyl CH_2). These properties compared favorably with those of an authentic sample.[3,21]

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.6; H, 13.65.

An enriched sample (81%) of the *E* isomer **8a** showed the following properties: IR (film) 2940, 2870, 1460, 1375 cm^{-1}; δ_{Me_4Si} (CCl_4) 1.1–1.7 (m, CH_2), 1.57 (19%) and 1.80 (81%) (vinylic CH_3 of *Z* and *E* isomers **9a** and **8a**), 2.1–2.9 ppm (m, allylic CH_2).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.5; H, 13.55.

The 1,2-dimethylcyclododecenes (**8b, 9b**) were analyzed and separated by gas chromatography on silver nitrate impregnated Carbowax 20M. The pure isomers were compared with authentic samples using IR, NMR, and GLC.[2,3]

The 2-decenes were analyzed by gas chromatography on silver nitrate impregnated 1,4-butanediol. The pure isomers were compared with authentic samples using IR, NMR, and GLC.[22] Dodecane was used as the internal standard for estimation of yields by gas chromatography (see Table I).

Reduction Elimination of the Cyclic Phosphoramidate Derived from *cis*-1,2-Dimethylcyclododecane-1,2-diol (3b, R = Me). A. Using Titanium Tetrachloride–Magnesium Amalgam. The procedure of Corey[10] was used to prepare the reagent from 0.044 g of mercuric chloride, 0.144 g of magnesium, and 0.33 mL of titanium tetrachloride. To this reagent in 5 mL of THF at room temperature was added a solution of 100 mg of phosphoramidate[1] in 5 mL of THF. The mixture was heated at reflux for 3.5 h, it was then cooled to 0 °C, and 0.5 mL of saturated aqueous potassium carbonate was added. After stirring for 0.25 h the mixture was filtered through Celite and extracted with ether to give 55 mg of an oil which was further purified by chromatography on silica gel. The resulting 47 mg (77%) of material was found to be an 88:12 mixture of (*Z*)- and (*E*)-1,2-dimethycyclododecene (**9b and 8b**) by gas chromatographic analysis and spectra comparison with authentic samples.[2,3]

B. Using Potassium–Titanium Trichloride. The procedure of McMurry was employed for the reduction of titanium trichloride.[11] To a suspension of 0.29 g of titanium trichloride in 10 mL of THF was added 0.24 g of potassium slices. The mixture was stirred at reflux for 0.5 h, 100 mg of phosphoramidate in 2–3 mL of THF was added, and reflux was maintained overnight. The mixture was cooled to 0 °C, ethanol was added, and the whole was filtered through Celite. Removal of solvent and chromatography on silica gel gave 56 mg (92%)

of an 88:12 mixture of (*Z*)- and (*E*)-1,2-dimethylcyclododecenes (**9b** and **8b**).

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Registry No.—**1a,** 96-01-5; **1b,** 3008-41-1; **4a,** 61349-14-2; **4b,** 61349-15-3; **5a,** 61376-40-7; **5b,** 61376-41-8; **6b** (R = 3-butenyl), 61349-16-4; **7a** (R = Me; Z = NMe_2), 61376-42-9; **7a** (R = Me; Z = OEt), 61349-17-5; **7b** (R = Me; Z = NMe_2), 61376-43-0; **7b** (R = Me; Z = OEt), 61349-18-6; **7b** (R = 3-butenyl; Z = NMe_2), 61349-19-7; **8a,** 61349-20-0; **9a,** 14113-67-8.

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The Structure in Solution of the Halogen Adducts of Phosphines and Arsines

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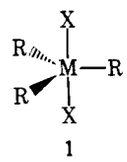
1-Methylphosphorinane (**4**) and 1-methylarsenane (**6**) form 1:1 and 1:2 adducts with Br_2 and I_2, but only 1:1 adducts with Cl_2, as determined by conductometric titrations and by isolation. The 1-phenyl compounds (**5, 7**) exhibit the same behavior. These materials can have either a trigonal bipyramidal structure with As or P between the two halogen atoms, or a simple molecular complex structure with As or P at the end of the halogens. We have been able to distinguish these structural types by the conductance of the adducts in solution and by the *R* value analysis (vicinal coupling constants) of deuterated derivatives. The 1:1 arsine adducts with Cl_2 and Br_2 are nonconducting trigonal bipyramids. All the 1:1 phosphine adducts, the 1:1 adducts of the arsines with I_2, and all the 1:2 adducts of both the phosphines and the arsines are highly conducting molecular complexes with presumably little distortion in the shape of the ring.

The halogen complexes of trivalent phosphines and arsines have been of interest not only because of their structural complexities but also because of their use in synthesis, as in the Wiley reaction for the preparation of alkyl halides[2a] and in the cleavage of the C–O bond of acids, acid anhydrides, esters, and lactones to form a C–Br bond under very mild conditions.[2b] A number of different structural methods have been applied to these compounds,[3] but hard structural data are particularly lacking in the solution phase. Previous work[3] has demonstrated that both 1:1 and 1:2 adducts are possible (eq 1). For the 1:1 adducts, there are at least two general

$$R_3M \xrightarrow{X_2} R_3MX_2 \xrightarrow{X_2} R_3MX_4 \qquad (1)$$

structural classes possible. The central atom M can be located between the two halogen atoms X, so that M is pentacoordinate and the overall structure is a trigonal bipyramid (TB) (**1**). Alternatively, the atom M can be at the end of the two halogens, in a simple molecular complex (MC), which can exist in hydrogen-bond-like (**2**) or ionic (**3**) forms. The problem,



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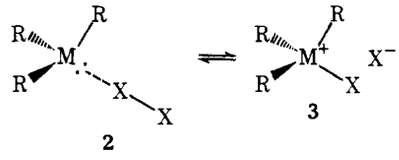

2 **3**

therefore, is to determine which structure (**1–3**) exists in solution for each of the adducts of trivalent phosphorus or arsenic with chlorine, bromine, or iodine. We hope to extend the results to antimony and fluorine by induction.