Preparation of *cis*- and *trans*-4-*tert*-Butyl-1-phenylphosphorinane and a Study of Reaction Stereochemistry of Its Derivatives

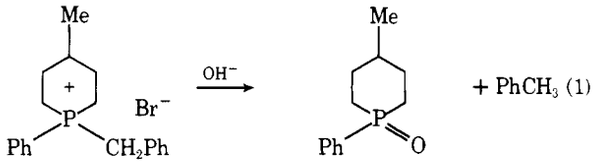
Kenneth L. Marsi,* James L. Jasperse, Francisco M. Llort, and David B. Kanne

California State University, Long Beach, Long Beach, California 90840

Received October 26, 1976

Syntheses of pure cis and trans isomers of 4-*tert*-butyl-1-phenylphosphorinane and its 1-oxides (**4**), 1-benzyl-4-*tert*-butyl-1-phenylphosphorinanium bromide (**3**), and 4-*tert*-butyl-1-methyl-1-phenylphosphorinanium bromide (**7**) in addition to 4-*tert*-butyl-1,1-diphenylphosphorinanium bromide (**10**) and an isomeric mixture of 4-*tert*-butyl-1-phenylphosphorinane 1-oxide (**8**) are reported. Evidence for configurational assignments is discussed. It was found that hydroxide cleavage of *cis*-**3** produced 66% *trans*-**4** and 34% *cis*-**4** while cleavage of *trans*-**3** yielded 21% *trans*-**4** and 79% *cis*-**4**. Hydroxide cleavage of *cis*-**7** gave 38% *trans*-**8** and 62% *cis*-**8** while *trans*-**7**, similarly treated, gave 25% *cis*-**8** and 75% *trans*-**8**. Treatment of **10** with aqueous sodium hydroxide yielded 60% *cis*-**4** and 40% *trans*-**4**. The pseudo-first-order kinetics of debenzylation of the isomers of **3** and **7** were determined. Mechanistic conclusions were drawn from stereochemical and kinetic information.

As part of a series of studies designed to assess the effect of ring size on reactivity of phosphorus[1] we previously determined that the overall debenzylation of *cis*- and *trans*-**1** by aqueous sodium hydroxide is not stereospecific.[2,3] Furthermore, the cis isomer (**1a**)[4] produces a *different* ratio of diastereomeric oxides (**2**) than does the trans isomer (**1b**). These results were explained by the operation of a dual mechanism[5] in which the balance between inversion and retention in eq 1 is obviously affected in some manner by the steric effect

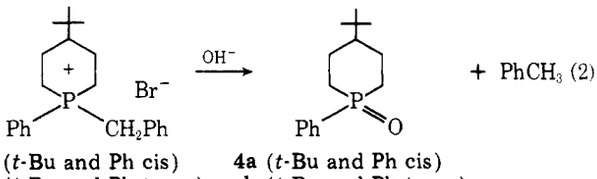


1a (Me and Ph cis) **2a** (Me and Ph cis)
b (Me and Ph trans) **b** (Me and Ph trans)

exerted by the ring methyl. In order to elucidate more fully the role of the substituent in regulating stereochemistry of this reaction, it was deemed necessary to prepare the cis and trans isomers of **3**. The *tert*-butyl group would be expected to ensure conformational homogeneity as well as provide a large steric bulk effect in position 4. Moreover, the *tert*-butyl protons offer a sensitive analytical probe for determining composition of mixtures by NMR. In addition, it was desired to gain synthetic access to the 4-*tert*-butylphosphorinane system for future conformational and configurational studies which we have planned.

Discussion of Results

Cleavage of *cis*- and *trans*-1-Benzyl-4-*tert*-butyl-1-phenylphosphorinanium Bromide. When cleavage data for **1** and **3** were compared it was found that, within experimental error, **1b** and **3b** gave identical results. However, for **1a** and **3a** the ratios of oxides produced were quite different.



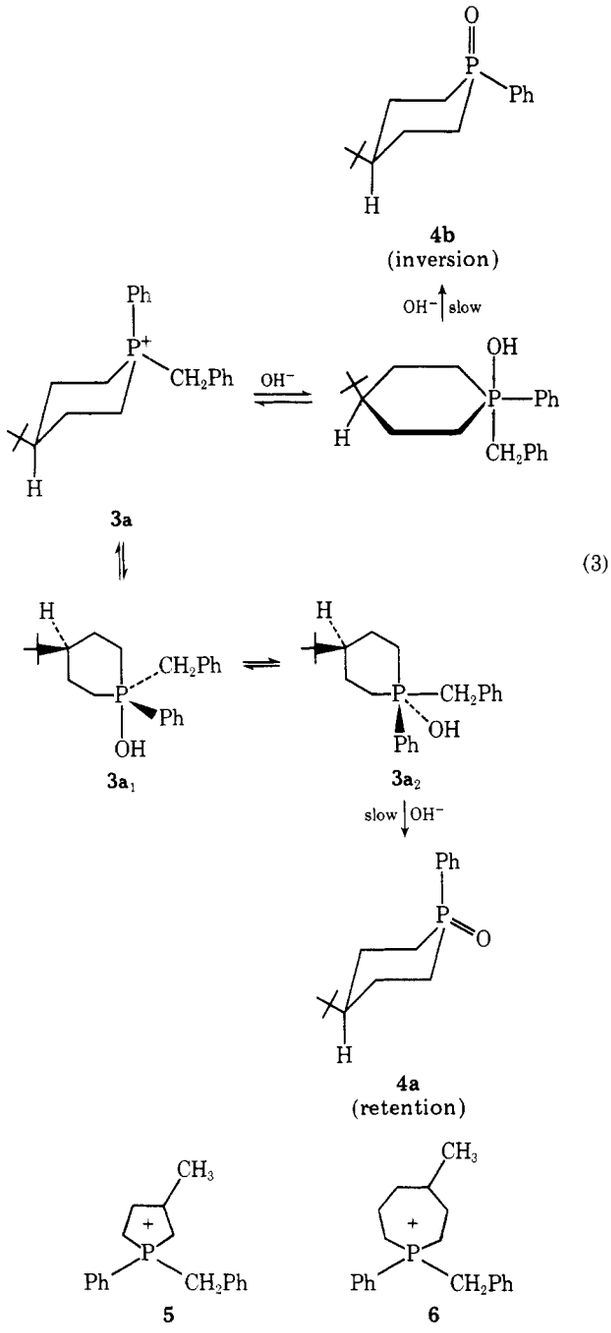
3a (*t*-Bu and Ph cis) **4a** (*t*-Bu and Ph cis)
b (*t*-Bu and Ph trans) **b** (*t*-Bu and Ph trans)

					retention/inversion
1a	$\xrightarrow{OH^-}$	**2a**	+	**2b**	
		48%		52%	0.92
3a	$\xrightarrow{OH^-}$	**4a**	+	**4b**	
		66%		34%	1.9
1b	$\xrightarrow{OH^-}$	**2a**	+	**2b**	
		22%		78%	3.6
3b	$\xrightarrow{OH^-}$	**4a**	+	**4b**	
		21%		79%	3.8

For both isomeric salts of **1** and **3** it has been established conclusively that isomerization does not occur prior to the cleavage process. The corresponding oxides are also stereochemically stable to base. When cleavage reactions of diastereomerically pure salts are interrupted, only stereochemically unchanged salts are recovered. It seems reasonable that whatever processes are occurring for the decomposition of **1b** and **3b**, the 4 substituents offer minimal effect on stereochemistry because a change from methyl to *tert*-butyl produces effectively no change in isomer ratio.

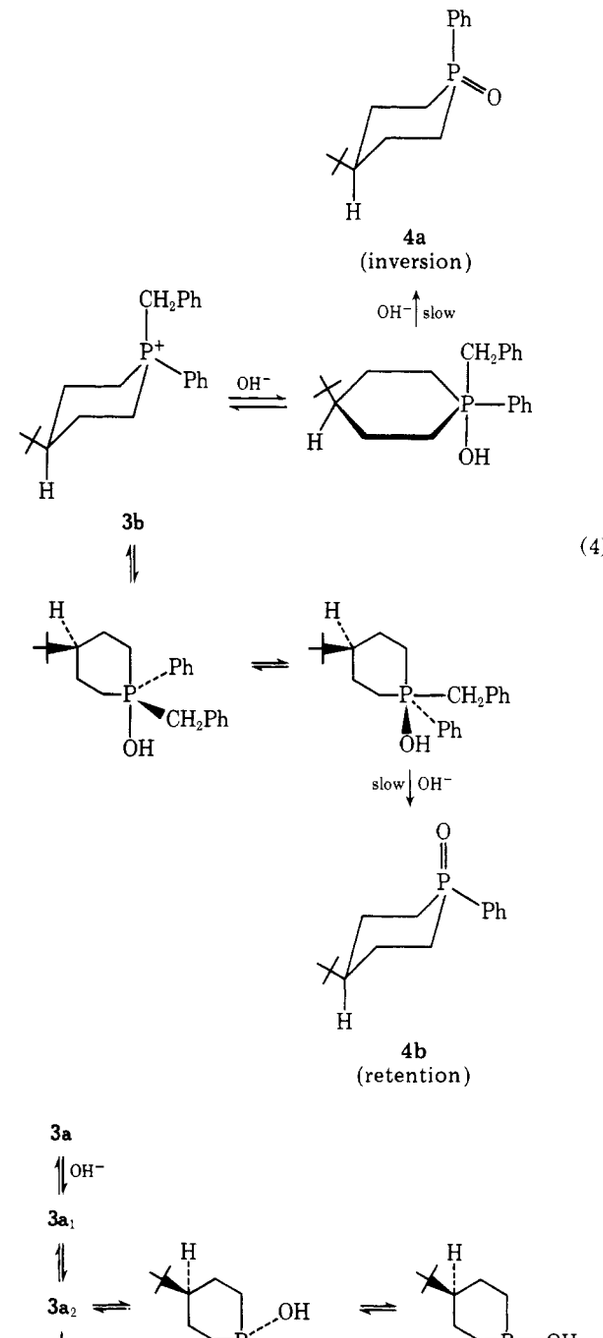
It is noteworthy that retention predominates in base cleavage of **3a** and **3b**. We interpret this as a resistance of the six-membered ring to involvement of the two C–P ring bonds in equatorial positions in the trigonal bipyramidal intermediate leading to inversion (**3a** → **4b** and **3b** → **4a** in eq 3 and 4). It is also seen that the cis isomers **1a** and **3a** produce more oxide of inverted configuration than **1b** and **3b**. We believe that the greater incidence of inversion in the former case is due to resemblance of the transition state to product oxides. In a separate experiment we have equilibrated **4a** and **4b** in aqueous acid and have obtained a thermodynamic mixture of oxides of **4b**/**4a** = 3/1. Therefore, the more stabilized transition state, from the standpoint of product stability, should lead to inversion for cleavage of **3a** and retention for cleavage of **3b**. However, for the inversion process transition state stability would be adversely affected by the ring strain effect just mentioned. Thus, inversion accompanying cleavage of **3a**, although greater than for **3b**, does not predominate. If these considerations are true, it might be expected that **3b** should react more rapidly with base than **3a**. As discussed subsequently, this was found to be so with **3b** reacting twice as rapidly as **3a**.

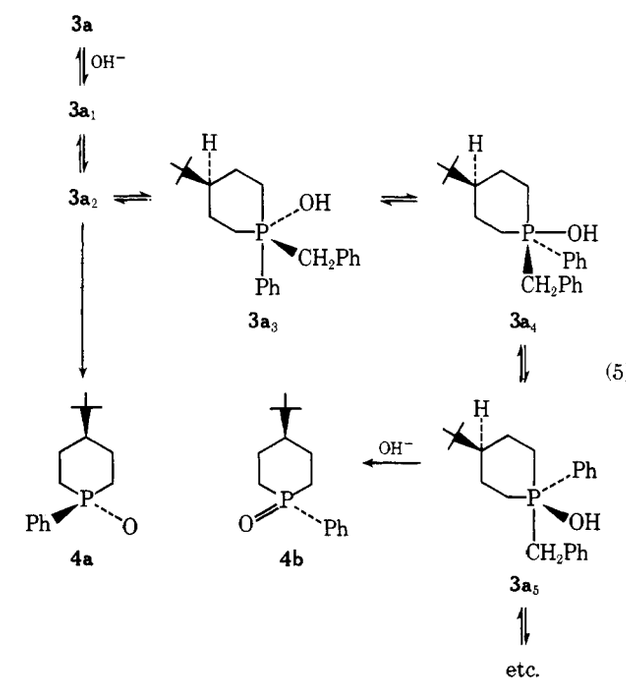
The possibility that some inversion of configuration seen for these reactions comes about through further isomerization of fluxional intermediates such as $\mathbf{3a}_1$ and $\mathbf{3a}_2$ (eq 5) can reasonably be dismissed. Any crossover occurring by eq 5 should result in isomerization of starting material. This is not observed for either isomer of **1** or **3**. Furthermore, cleavage of **5** under similar conditions occurs completely stereospecifically (retention)[6] as does cleavage of **6** (inversion).[5] Presumably the former takes place by a retention pathway and the latter by an inversion pathway, analogous to those shown in eq 3 and 4.



The mechanisms as discussed above assume the generally accepted apical introduction of nucleophile and apical loss of leaving group[7] and also assume expulsion of benzyl to be rate determining.[8]

The pseudo-first-order kinetics for the base cleavage of **3a** and **3b** were determined in aqueous ethanol. The solvent and conditions were initially chosen to conform to those used by Cremer et al.[8c] for studying rates of debenzylation of a variety of phosphorus heterocycles. In attempting to duplicate Cremer's kinetics for hydroxide-induced debenzylation of the unsubstituted phosphorinanium salt (eq 6), we have found that the process measured by Cremer at 25 °C is not conversion of **15** to its oxide, but some minor competing reaction (possibly reversible ylide formation). After several days at 25 °C we found no perceptible conversion of the salt to the oxide (eq 6). In fact, the spectrum of oxide, either in neutral solution or in base, shows no absorption at 307.5 nm, the wavelength used by Cremer. We have been able to duplicate the rate constant (5.64×10^{-4} L^2 mol^{-2} s^{-1} this work; 5.60×10^{-4} L^2 mol^{-2} s^{-1} Cremer et al.), but it *cannot* be associated with the appearance of the oxide.

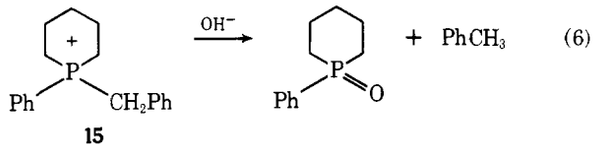




We therefore turned to pseudo-first-order conditions in 50% aqueous ethanol (1.28 N NaOH) at 80.0 °C to determine the reactivities of **3a, 3b,** and **15** which are listed in Table I.

Table I. Pseudo-First-Order Rate Constant for Debenzylation of 3a, 3b, and 15 at 80.0 °C

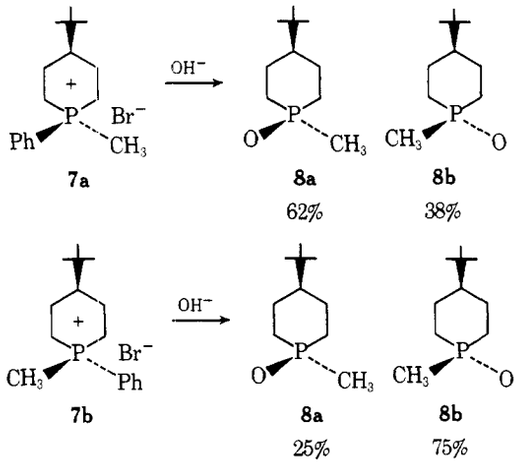
	λ, nm	k_1, s^{-1}	Rel rate
3a	273.5	2.81×10^{-3}	1.77
3b	273.5	5.54×10^{-3}	3.48
15	273.5	1.59×10^{-3}	1.00



15 (6)

It is surprising to see both *tert*-butyl salts showing greater reactivity than the unsubstituted salt. However, this may be rationalized on the basis that the transition state for either **3a** and **3b** in the rate-determining step leading to the oxides shows less crowding, due to the presence of the *tert*-butyl group, than does the initial salt; i.e., the ground-state energy of **3a** or **3b** is higher than for **15**.

Cleavage of *cis*- and *trans*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide. Hydroxide-induced displacement of phenyl from **7a** and **7b** is a much slower process (about 200 times slower) than that observed for either **3a** or **3b** because the leaving group is a poorer one. The results show both **7a** and **7b** to give predominantly *retention* of



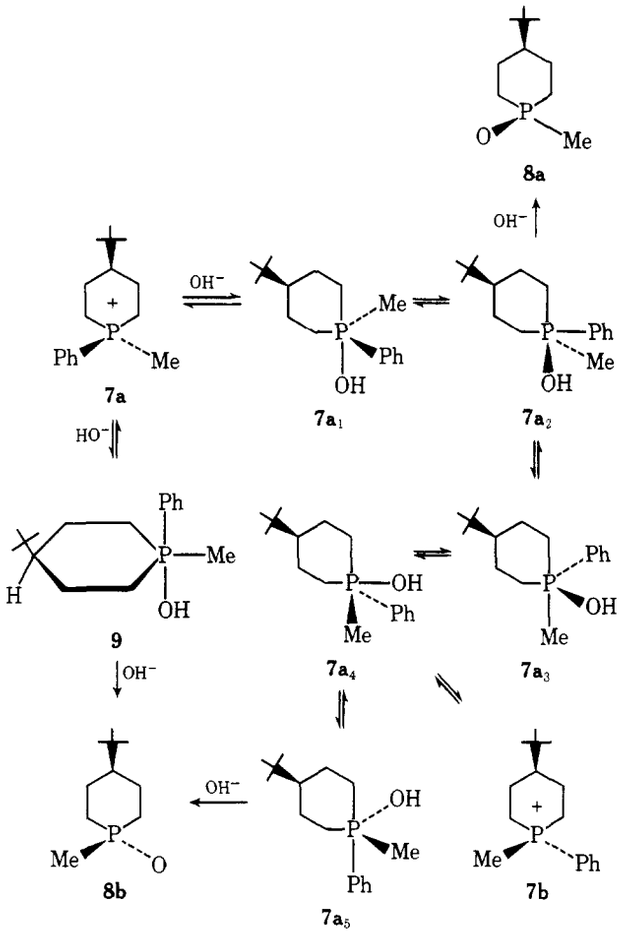
configuration. Some stereomutation of both pure phosphonium salts was observed in 1.00 N aqueous sodium hydroxide at reflux temperature for 24 h as shown in Table II. The relative rate of cleavage for **7b/7a** under these conditions is seen to be 4.5. Pseudo-first-order rate constants, determined at 75 °C in 1:1 EtOH–H_2O, also showed **7b** to be cleaved more rapidly than **7a**. The rate constants are 0.099 and 0.061 h^{-1} for the trans and cis isomers, respectively. The significance of these rate differences will be commented upon subsequently.

It will be noted from the information given in Table II that **7a** and **7b** are not in complete thermodynamic equilibrium under reaction conditions, but each shows *some* stereomutation. This leads us to believe that three processes are occurring simultaneously as illustrated in Scheme I for the isomer **7a**. In addition to stereospecific processes **7a** → **8b**, **7a** → **7a**$_1$ → **7a**$_2$ → **8a** and **7b** → **7a**$_4$ → **7a**$_5$ → **8b**, a third competing process involving limited stereomutation at phosphorus must occur in order to explain **7a** ⇌ **7b**. This is represented in Scheme I for **7a** → **8a** + **8b** via the appropriate phosphorane intermediates. The low degree of inversion, which parallels closely the degree of isomerization of **7a** ⇌ **7b** (see Table II), may occur largely through stereomutation. Since neither phenyl nor

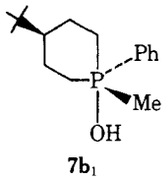
Table II. Isomerization of *cis*- and *trans*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7a and 7b)

	7a	7b
% completion of cleavage	13.3	60.0
% of recovered material isomerized	16.4	22.7
Product composition		
8a/8b	3.65	0.22
% inversion	21.5	18.3

Scheme I. Pathways Available for Displacement of Phenyl from *cis*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7a)

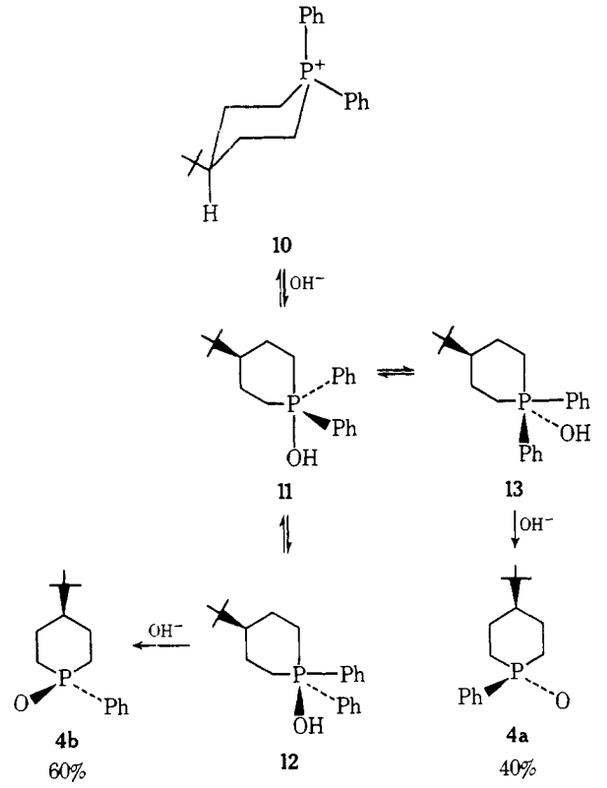


methyl is an especially good leaving group (low apicophilicity) there may be a limited tendency for inversion to occur via a phosphorane such as **9**. There would in effect be little relief of stereolectronic strain to balance ring strain introduced by diequatorial ring bonds. The more rapid decomposition of **7b** to product as compared to **7a** is probably associated with slower formation of **7a**$_1$ in a preequilibrium step. **7a**$_1$ exhibits sterically interacting *tert*-butyl and phenyl groups whereas **7b**$_1$, derived from **7b**, does not.



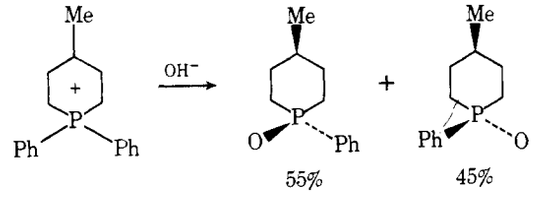
7b$_1$

Cleavage of 4-*tert*-Butyl-1,1-diphenylphosphorinanium Bromide. 4-*tert*-Butyl-1,1-diphenylphosphorinanium bromide (**10**), by analogy with the previously discussed findings for **7**, probably cleaves primarily via the intermediate **11**.



The product ratio is probably the result of product-resembling transition states which could tend to favor formation of the more thermodynamically stable product **4b.**

The same argument would hold for results previously reported for the methyl analogue.[1]

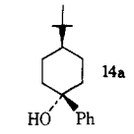
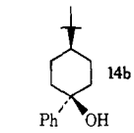


Syntheses. The key structure from which the 4-*tert*-butylphosphorinanes described in this paper are derived is **10.** This compound was obtained in good yield by cyclization of 1,5-dibromo-3-*tert*-butylpentane[9] with tetraphenyldiphosphine.[10] Base cleavage of **10** produced a mixture of *cis*- and *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxides (**4b** and **4a,** respectively) which were cleanly separated by preparative thin layer chromatography. The oxides were stereospecifically reduced by use of phenylsilane[11] to the corresponding *cis*- and *trans*-4-*tert*-butyl-1-phenylphosphorinanes which were quaternized either by methyl bromide to yield isomerically pure **7b** and **7a,** respectively, or with benzyl bromide to furnish **3b** and **3a,** respectively.

Stereochemical Assignments. Several independent facts support the stereochemical assignments given to the isomeric oxides **4a** and **4b.** A comparison of the NMR spectra of the oxides with those of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexanols (**14**) of known configuration[12] show significant similarities as listed in Table III. The shapes of the doublet for **4b** and **14b** correlate nicely.

Use has been made of R_f values in assigning disposition of polar groups in six-membered rings.[13] Diastereomers with axial polar substituents are quite generally observed to have higher R_f numbers than those with equatorial polar substituents. Assignment of structure is consistent with R_f values; **4a** and **4b** exhibit values of 0.17 and 0.57, respectively, when

Table III. A Comparison of NMR Spectra for Diastereomeric Oxides (4) and *cis*- and *trans*-4-*tert*-Butyl-1-phenylcyclohexanol (14)

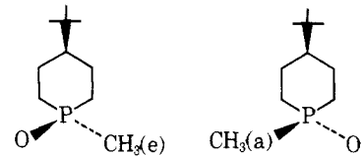
	δ, *tert*-butyl singlet, ppm	2,6 ring proton doublet
 14a	0.76	2.52
4a (mp 89–95 °C)	0.83	2.45
 14b	0.91	1.75
4b (mp 159.5–161 °C)	0.94	1.90

separated on silica gel with acetone. It might be noted that carbinol **14b** is eluted ahead of **14a** in column chromatographic (silica gel) separation.[12]

It has also been observed that for relatively simple phosphine oxides, those diastereomers containing alkyl or acyl groups in trans positions usually have higher melting points.[14] The melting points of **4a** and **4b** are respectively 88.5–95 and 159.5–161 °C, and thus in agreement with assignment of configuration. The melting range for **4a** is due to its extreme hygroscopicity.

Likewise, equilibration of either **4a** or **4b** with 6 N hydrochloric acid at 125 °C produces a mixture of 24.7% **4a** and 75.3% **4b.** Because of conformational considerations[15] **4b** would be predicted to be more thermodynamically stable than **4a.** Therefore, this finding is also in accordance with assignment of configuration.

Once the configurations of **4a** and **4b** have been established, those of the phosphines and phosphonium salts (derived from the phosphines) are also known since phenylsilane reduction of phosphine oxides[12] and quaternization of phosphines are known to take place with retention of configuration at phosphorus. However, the configurations of the diastereomeric 4-*tert*-butyl-1-methylphosphorinane 1-oxides (**8**) were uncertain because they were formed by nonstereospecific cleavage of salts **7a** and **7b.** Therefore, a mixture of oxides, **8,**



	8a	**8b**
δ_{CH_3}, ppm	1.46	1.51
J_{PCH_3}, Hz	13.2	12.7
$\delta_{t\text{-Bu}}$, ppm	0.90	0.90

composed of 28 and 72% of the two oxides of unknown configuration, was reduced with phenylsilane (retention).[11] The resulting phosphine mixture was quaternized with bromobenzene in the presence of nickel(II) bromide (retention)[16] to produce a mixture of **7a** and **7b** in the same ratio as starting oxides. Since the configurations of **7a** and **7b** are known (vide supra), and their NMR spectra determined, it was possible to assign configurations to the two oxides. This assignment is also consistent with the observation that the protons of an axial P–CH_3 exhibit smaller coupling with phosphorus than protons of an equatorial P–CH_3.[17] This phenomenon is also observed for **7a** and **7b** (J_{PCH_3} = 13.7 and 14.7 Hz, respectively).

Experimental Section

General. NMR spectra were determined with the use of a Perkin-Elmer R12-B spectrometer, and chemical shifts are reported in parts per million from Me_4Si as an internal standard. Analyses of mixtures of all *tert*-butylphosphorinane derivatives were by integration of *tert*-butyl proton signals except for mixtures of 4-*tert*-butyl-1-methylphosphorinane 1-oxides where integration of the P-CH_3 proton signal was employed. Composition of mixtures of phosphorinane oxides before and after distillation was essentially unchanged. In two cases hygroscopic oxides analyzed as fractional hydrates only because transfer operations by the analyst were not conducted in a drybox.

1,5-Dibromo-3-*tert*-butylpentane. This compound was synthesized by the method of Johnson from 4-*tert*-butylpyridine.[9] We have discovered that yields are improved significantly if the mixture of *N*-benzoyl-4-*tert*-butylpiperidine and bromine is allowed to remain at room temperature for a minimum of 2 days. We were unable to obtain satisfactory yields following the procedure of Sakurai.[18] A recent approach to the synthesis of this compound was published by Purdum and Berlin.[19]

4-*tert*-Butyl-1,1-diphenylphosphorinanium Bromide (10). Cyclization of 1,5-dibromo-3-*tert*-butylpentane with tetraphenyldiphosphine was accomplished by an adaptation[10b] of Markl's procedure:[10a] yield 43.4%; mp 316.5–318.5 °C dec; NMR (CF_3CO_2H) δ 0.95 (s, 9, *t*-Bu), 7.76 (m, 10, C_6H_5).

Anal. Calcd for $C_{21}H_{28}PBr$: C, 64.45; H, 7.21. Found: C, 64.18; H, 7.46.

***cis*- and *trans*-4-*tert*-Butyl-1-phenylphosphorinane 1-Oxide (4).** 4-*tert*-Butyl-1,1-diphenylphosphorinanium bromide (**10**, 6.00 g, 0.0153 mol) was refluxed with 75 ml of 1.00 N sodium hydroxide with magnetic stirring for 44 h. After cooling to room temperature 18 potassium hydroxide pellets were added and the resulting aqueous solution extracted with 6 × 50 mL of chloroform. The combined chloroform extracts were flash evaporated and the residue distilled to yield 3.19 g of the corresponding oxide (96.9%), bp 205° (0.15 mm) (Kugelrohr), mp 131–145 °C.

Anal. Calcd for $C_{15}H_{23}OP$: C, 71.68; H, 9.26. Found: C, 71.79; H, 9.51.

NMR integration of the separated *tert*-butyl signals showed the mixture to be composed of 40% **4a** and 60% **4b.**

Separation of *cis*- and *trans*-1-Phenyl-4-*tert*-butylphosphorinane 1-Oxide. Glass plates (8 × 8 × 0.25 in.) were coated to a thickness of 3 mm with silica gel G and heated overnight at 110 °C. An acetone solution of the mixture of isomers obtained above was then applied. The plate was placed in a chamber saturated with reagent grade acetone. The positions of the isomers were identified by development of the plate in an iodine chamber and the spots removed by scraping. The scrapings were extracted in a Soxhlet apparatus with methanol to yield a 90% total recovery of oxides by concentration and vacuum distillation of separate extracts, bp 180–200 °C (0.15 mm) (Kugelrohr).

***trans*-1-Phenyl-4-*tert*-butylphosphorinane 1-oxide (4a)** (very hygroscopic) showed the following properties: R_f 0.17; mp 88.5–95 °C; NMR ($CDCl_3$) δ 0.83 (s, 9, *t*-Bu), 7.58 (m, 5, C_6H_5) (isomerically pure).

Anal. Calcd for $C_{15}H_{23}OP \cdot \frac{1}{5}H_2O$: C, 70.94; H, 9.28. Found: C, 70.93; H, 9.05.

***cis*-4-*tert*-Butyl-1-phenylphosphorinane 1-oxide (4b)** gave R_f 0.57; mp 160–161 °C; NMR ($CDCl_3$) δ 0.96 (s, 9, *t*-Bu), 7.53 (m, 5, C_6H_5) (isomerically pure).

Anal. Calcd for $C_{15}H_{23}OP$: C, 71.97; H, 9.26. Found: C, 72.00; H, 9.41.

It is also possible to obtain the higher melting isomer (**4b**) in an isomerically pure state by fractional recrystallization of the cleavage mixture from carbon tetrachloride. The filtrates do not yield pure **4a.**

***trans*-4-*tert*-Butyl-1-phenylphosphorinane** was obtained in 100% yield by phenylsilane reduction of **4b** using the general procedure described elsewhere:[11] bp 110–120 °C (0.1 mm) (Kugelrohr); NMR ($CDCl_3$) δ 0.84 (s, 9, *t*-Bu), 7.04 (s, 5, C_6H_5).

***cis*-4-*tert*-Butyl-1-phenylphosphorinane** was obtained in 92% yield by phenylsilane reduction of **4a:**[11] bp 110–120 °C (0.1 mm) (Kugelrohr); NMR ($CDCl_3$) δ 0.72 (s, 9, *t*-Bu), 7.30 (s, 5, C_6H_5).

***trans*-1-Benzyl-4-*tert*-butyl-1-phenylphosphorinanium Bromide (3b).** The trans phosphine was quaternized with benzyl bromide in benzene[6c] to yield 95% of the bromide salt **3b:** mp 268–270 °C dec after recrystallization from ethanol–ethyl acetate; NMR ($CDCl_3$) δ 0.88 (s, 9, *t*-Bu), 4.50 (d, J_{PCH} = 14.7 Hz, 2, $CH_2C_6H_5$), 7.18 (s, 5, CC_6H_5), 7.77 (m, 5, PC_6H_5).

Anal. Calcd for $C_{22}H_{30}PBr$: C, 65.18; H, 7.46. Found: C, 65.20; H, 7.46.

***cis*-1-Benzyl-4-*tert*-butyl-1-phenylphosphorinanium Bromide (3a).** This compound was obtained as above in 87% yield from this cis phosphine: mp 224.5–226 °C dec (ethanol–ethyl acetate); NMR ($CDCl_3$) δ 0.74 (s, 9, *t*-Bu), 4.62 (d, J_{PCH_2} = 16 Hz, 2, $CH_2C_6H_5$), 7.17 (s, 5, CC_6H_5), 7.75 (m, 5, PC_6H_5).

Anal. Calcd for $C_{22}H_{30}PBr$: C, 65.18; H, 7.46. Found: C, 65.07; H, 7.51.

Base Cleavage of *cis*- and *trans*-1-Benzyl-4-*tert*-butylphosphorinanium Bromide. The pure diastereomers were cleaved under the same conditions as reported previously.[2b] Salt **3a** yielded a mixture of oxides consisting of 68% **4a** and 32% **4b,** while **3b** gave 23% **4a** and 77% **4b.** Whether or not the initial heterogeneous conditions for this reaction had an effect on the results was checked by performing the same reaction under homogeneous conditions by dissolving 0.15 g of salt in 16.4 mL of water and heating until the salt was dissolved. At that point 16.4 mL of 2 N sodium hydroxide was added and the solution refluxed for 9 h. The reaction mixture was worked up as previously described. **3a** yielded a mixture of oxides consisting of 34% **4b** and 66% **4a,** while **3b** yielded 21% **4a** and 79% **4b.** It was concluded that the difference in results between heterogeneous and homogeneous base cleavage were within experimental error.

Incomplete Base Cleavage of *cis*- and *trans*-1-Benzyl-4-*tert*-butyl-1-phenylphosphorinanium Bromide. Treatment of **3a** and **3b** under the above reaction conditions for 0.5 h and recovery of unreacted salt showed no epimerization of **3a** to **3b** or vice versa. For example, 0.15 g of **3a** after 0.5-h treatment was 51.4% cleaved, the balance of unreacted salt being unchanged configurationally. The product consisted of 32.1% **4b** and 67.9% **4a.**

***cis*- and *trans*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7).** Enough methyl bromide was dissolved in 10 mL of benzene to produce a 2 M solution. 4-*tert*-Butyl-1-phenylphosphine (1.21 g, 5.18 mmol) (either cis or trans) was added and the mixture permitted to stand for 1 day. Crystals were removed by filtration, washed with benzene, and vacuum desiccated, yield 91%.

***cis*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7b):** yield 91%; mp 234.5–237 °C dec (ethanol–ethyl acetate); NMR ($CDCl_3$) δ 0.83 (s, 9, *t*-Bu), 2.58 (d, J_{PCH_3} = 14.7 Hz, 3, PCH_3), 7.94 (m, 5, C_6H_5).

Anal. Calcd for $C_{16}H_{26}PBr$: C, 58.36; H, 7.96. Found: C, 58.61; H, 8.04.

***trans*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7a):** yield 84%; mp 178–179 °C dec (ethanol–ethyl acetate); NMR ($CDCl_3$) δ 0.91 (s, 9, *t*-Bu), 2.50 (d, J_{PCH_3} = 13.7 Hz, 3, PCH_3), 7.96 (m, 5, C_6H_5).

Anal. Calcd for $C_{16}H_{26}PBr$: C, 58.36; H, 7.96. Found: C, 58.56; H, 8.09.

Base cleavage of *cis*- and *trans*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7). The pure isomer (0.150 g, 0.455 mmol) was dissolved in 4.5 mL of 5.00 N sodium hydroxide and the mixture refluxed for 8 h. The reaction mixture was cooled and extracted with 2 × 10 mL of $CHCl_3$. The aqueous layer was saturated with 2 g of sodium chloride and extracted with 2 × 10 mL of $CHCl_3$. The extracts were combined and concentrated to 10 mL. This solution was centrifuged and the supernatant liquid evaporated to about 0.5 mL. Residual liquid was distilled: bp 155–175 °C (0.13 mm) (Kugelrohr); 80% yield. The trans salt (**7a**) gave a mixture of 25.1 and 74.9% while the cis salt (**7b**) yielded 38.1 and 41.9%.

Anal. Calcd for $C_{10}H_{21}OP \cdot \frac{1}{5}H_2O$: C, 62.60; H, 11.24. Found: C, 62.63; H, 11.14.

NMR of **8b:** δ 1.51 (d, J = 12.7 Hz, 3, PCH_3), 0.90 (s, 9, *t*-Bu). NMR of **8a:** δ 1.47 (d, J = 13.2 Hz, 3, PCH_3), 0.90 (s, 9, *t*-Bu).

Incomplete Base Cleavage of *cis*- and *trans*-4-*tert*-Butyl-1-methyl-1-phenylphosphorinanium Bromide (7). Each pure isomer was treated under conditions described immediately above, but for a period of 0.5 h with 1 N sodium hydroxide. The trans salt (**7b**) reacted to 60% completion. Recovered salt consisted of 22.7% **7a** and 77.3% **7b.** The product oxide was composed of 18.3% **8a** and 81.7% **8b.** The cis salt (**7a**) yielded 13.3% cleavage product consisting of 21.5% **8b** and 78.5% **8a** and showed 16.4% of the recovered salt to have been isomerized to **7b.** A slightly higher amount of inversion for both isomeric salts was observed for 5 N sodium hydroxide (vide supra).

Phenylation of a Mixture of *cis*- and *trans*-4-*tert*-Butyl-1-methylphosphorinane. The phosphine mixture obtained as described above (0.170 g, 0.903 mmol), 0.0987 g (0.452 mmol) of finely divided, well-dried nickel(II) bromide, and 0.19 ml of bromobenzene were heated together at 200 °C in a sealed ampule for 3 h.[16] The cooled reaction mixture was dissolved in hot water and the resulting mixture extracted with 4 × 10 mL of ether. The water layer was then extracted

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.

References and Notes

(1) For a brief review see K. L. Marsi, *J. Org. Chem.*, **40**, 1779 (1975).
(2) (a) K. L. Marsi and R. T. Clark, *J. Am. Chem. Soc.*, **92**, 3791 (1970); (b) K. L. Marsi, *J. Org. Chem.*, **40**, 1779 (1975).
(3) Y. Kashman and O. Awerbouch, *Tetrahedron*, **26**, 4213 (1970), have also reported nonstereospecific cleavage of benzyl from phosphonium phosphorus in two compounds derived from 8-phosphabicyclo[3.2.1.]octan-3-one in which the phosphorus atom is simultaneously present in both a five- and six-membered ring. Retention of configuration predominates in both cases.
(4) The cis and trans designations are in accordance with *Chemical Abstracts* usage by which, for example, the cis isomer has the senior groups (as defined by the sequence rule) on the same side of the reference plane of the ring. Cf. *Chem. Abstr.*, **76**, 85l (1972); *J. Chem. Inf. Comput. Sci.*, **15**, 67 (1975).
(5) K. L. Marsi, *J. Am. Chem. Soc.*, **93**, 6341 (1971).
(6) (a) K. L. Marsi, *Chem. Commun.*, 846 (1968); (b) *J. Am. Chem. Soc.*, **91**, 4724 (1969); (c) K. L. Marsi, F. B. Burns, and R. T. Clark, *J. Org. Chem.*, **37**, 238 (1972).
(7) K. Mislow, *Acc. Chem. Res.*, **3**, 321 (1970).
(8) (a) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. Vanderwerf, *J. Am. Chem. Soc.*, **86**, 2378 (1964); (b) G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **19**, 931 (1965); (c) S. E. Cremer, B. C. Trivedi, and F. L. Weitl, *J. Org. Chem.*, **36**, 3226 (1971).
(9) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 1109 (1965).
(10) (a) G. Markl, *Angew. Chem., Int. Ed. Engl.*, **7**, 620 (1963); G. Markl, *Angew. Chem.*, **75**, 859 (1963); (b) K. L. Marsi, D. M. Lynch, and G. D. Homer, *J. Heterocycl. Chem.*, **9**, 331 (1972).
(11) K. L. Marsi, *J. Org. Chem.*, **39**, 265 (1974).
(12) E. W. Garbisch, Jr. and D. B. Patterson, *J. Am. Chem. Soc.*, **85**, 3228 (1963). Because the spectra of these isomers were only partially reported in this reference, we have prepared and separated **14a** and **14b** and determined their NMR spectra; cf. also M. Mousseron, J. M. Bessiere, P. Geneste, J. M. Kamenka, and C. Marty, *Bull. Soc. Chim. Fr.*, 3803 (1968).
(13) R. Hirschmann, G. A. Bailey, R. Walker, and J. M. Chemerda, *J. Am. Chem. Soc.*, **81**, 2822 (1959).
(14) M. J. Gallagher and I. D. Jenkins, *Top. Stereochem.*, **3**, 6 (1968).
(15) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).
(16) L. Horner, G. Mumenthey, H. Moser, and P. Beck, *Chem. Ber.*, **99**, 2782 (1966). The stereochemistry of arylation of heterocyclic phosphines (retention) has been established; cf. A. Fitzgerald, G. D. Smith, C. N. Caughlan, K. L. Marsi, and F. B. Burns, *J. Org. Chem.*, **41**, 1155 (1976).
(17) L. D. Quin and J. H. Somers, *J. Org. Chem.*, **37**, 1217 (1972); S. I. Featherman, S. O. Lee, and L. D. Quin, *ibid.*, **39**, 2899 (1974).
(18) H. Sakurai and M. Murakami, *J. Am. Chem. Soc.*, **94**, 5080 (1972); H. Sakurai and M. Murakami, *Org. Prep. Proced. Int.*, **5**, 1 (1973).
(19) W. R. Purdum and K. D. Berlin, *Org. Prep. Proced. Int.*, **7**, 283 (1975).

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

James A. Marshall* and Morris E. Lewellyn

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received September 16, 1976

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-