# Decomposition Reactions of Hydroxyalkylphosphorus Compounds. II. Reaction of Benzylbis(α-hydroxybenzyl)phosphine Oxide with Benzaldehyde Imines[1a]

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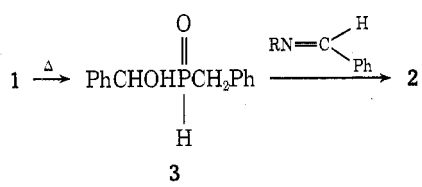
The reaction of benzylbis(α-hydroxybenzyl)phosphine oxide (1) with benzaldehyde imines produced the amino alcohols, $RNHCHPhP(=O)(CH_2Ph)CHOHPh$. If 2 mol of the imine are used then the diamine, $(RNHCHPh)_2P(=O)CH_2Ph$, resulted. For all of the benzaldehyde imines (RN=CHPh), even when R = *tert*-butyl, the reaction with 1 proceeded smoothly indicating that there was no steric hindrance. During decomposition, 1 must have lost benzaldehyde to form the secondary phosphine oxide $[PhCHOHP(=O)(H)CH_2Ph]$ since 1 itself could not react with the imines to form the amino alcohols. The role of the imine was confirmed when the *p*-tolualdehyde imine of benzylamine ($PhCH_2N=CHC_6H_4$-*p*-$CH_3$) was treated with 1. Only the amino alcohol having the *p*-tolyl group was obtained. The decomposition, which appeared to be temperature dependent, required reflux conditions in benzene. The ambient temperature experiments gave a quantitative recovery of 1.

We have shown[2] that benzylbis(α-hydroxybenzyl)phosphine oxide (1) reacted with primary amines to form phosphorus amino alcohols [$RNHCHPhP(=O)(CH_2Ph)CHOHPh$, 2]. In a mechanism proposed for this reaction, 1 loses benzaldehyde to form a secondary phosphine oxide 3 which adds to the imine (formed from the free benzaldehyde and the amine) to produce 2. If this mechanism is operative, then 1, on decomposition through loss of benzaldehyde, should react with imines[3-6] to produce the amino alcohols.



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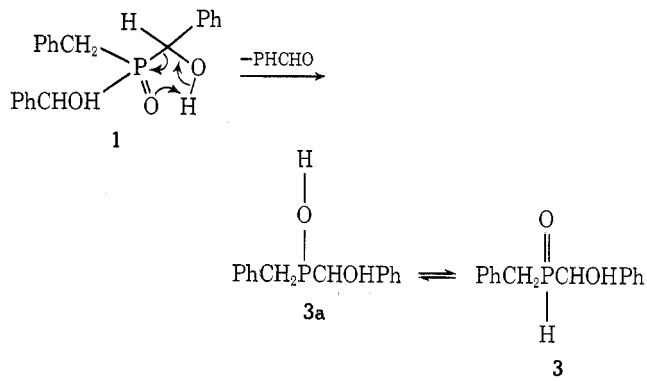
## Results and Discussion

Oxide 1 was treated with *N*-benzylidenebenzylamine (4) under several sets of conditions. Reaction occurred when the two were heated in refluxing benzene for 4 hr with or without catalysis by *p*-toluenesulfonic acid. The yield of 2 (R = benzyl) was higher without acid catalysis. In similar experiments at room temperature for extended times, recovery of 1 was quantitative. Subsequent reactions were conducted by heating equimolar amounts of 1 and the imine in benzene at reflux for 4 hr.

It is highly improbable that 1 combines with the imine, since tertiary phosphine oxides are notoriously poor phosphorus nucleophiles[7] and reaction, if it occurred, would involve oxygen attack on the carbon which would not yield the amino alcohol. These results indicate that decomposition, through loss of benzaldehyde, to form the secondary phosphine oxide 3 and subsequent addition of 3 to the imine is the operative mechanism. Possibly the imine base catalyzes the loss of benzaldehyde. However, imines are invariably weaker bases than the corresponding amines by as much as 5 p$K$ units.[8] Base catalysis by the imine is unnecessary. Miller et al.[9] and Abramov et al.[10] demonstrated that α-hydroxyalkylphosphine oxides decompose on heating in the absence of acid or base to yield the carbonyl compound. Abramov[10] proposed a cyclic transition state for the decomposition of 1-hydroxyalkyl-1-phosphonate esters which is a reasonable pathway for decomposition of 1 to 3. While spectroscopic evidence shows that the phosphoryl structure, $R_2P(O)H$, is highly preferred for compounds of the type $R_2POH$, kinetic studies have shown that extremely low concentrations of the trivalent form, $R_2POH$, are present in the nucleophilic reactions of these types of compounds.[11] Thus while 3 and similar compounds will be referred to as "secondary phosphine oxides", it is postulated that, under neutral or acidic conditions, the reactive species is the trivalent phosphorus hydroxyl tautomer, $R_2POH$.



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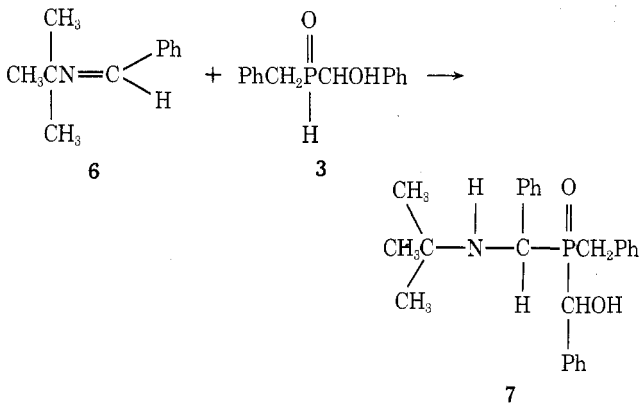
The imines of aromatic aldehydes are generally considered quite stable, being susceptible to hydrolysis only by aqueous mineral acids.[12] Thus it is highly improbable that decomposition of the imine to release the free amine is occurring under the conditions of reaction. Proof of this is afforded by the reaction of 1 with *N*-benzylidenemethylamine (5) in refluxing benzene. The reaction produced the amino alcohol (2, R = $CH_3$) in 73% yield with no evidence of evolution of methylamine. (The reaction of methylamine with 1 under refluxing benzene will not give the appropriate amino alcohol because of the low boiling point of the amine.) Prior preparation of the imine permits extension of the amino alcohol synthesis to low-boiling and gaseous amines. The reaction sequence was also successfully applied to cyclopropylamine.

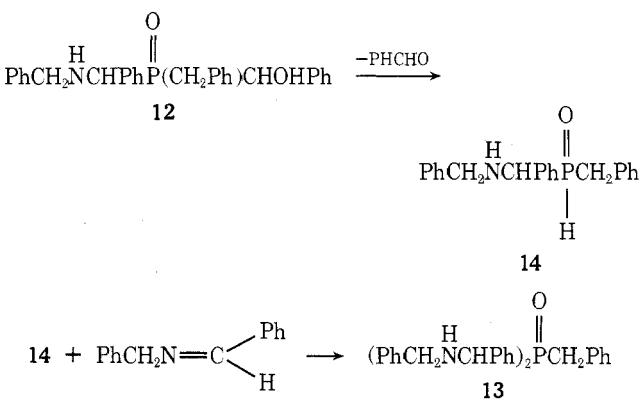
We found[2] that reaction of 1 with primary amines did not yield any of the amino alcohol when the carbon adjacent to the nitrogen was tertiary. It was of interest to determine if steric inhibition existed in the reaction of 1 with imines possessing similar substitution. The imine of *tert*-butylamine and benzaldehyde [*N*-benzylidene-1,1-dimethylethylamine (6)] was prepared with some difficulty as water was not evolved until a catalytic amount of *p*-toluenesulfonic acid was added. Even then the formation of the imine was slow, taking 2–3 hr to reach completion. The reaction of 1 with 6 proceeded readily and 76% of the amino

alcohol 7 was obtained. These results indicated no steric inhibition of attack by the secondary phosphine oxide on 6.

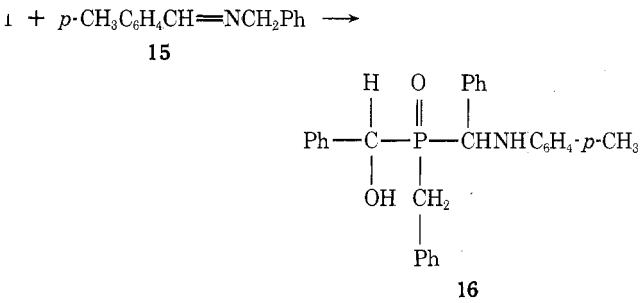


In the preparation of all the other imines used in this reaction sequence (see Table I) water evolution was rapid and complete in 2–15 min, with considerable heat evolution. Recovery of 1 from the reactions with *tert*-butyl- and *tert*-octylamine, as reported earlier,[2] was evidently due to steric difficulties in the formation of the imine. This difficulty was unexpected from reports in the literature.[5,13] Table I summarizes results from the reaction of 1 with several imines. Yields of product generally were higher from reactions of 1 with the imines than with the amine.[2] However, in both of the benzylamine examples, 12 and 13, yields were lower.

Oxide 1 reacted with 2 mol of *N*-benzylidenebenzylamine (4) to form the diamine 13. In this process 1 mol of benzaldehyde was lost from the amino alcohol 12 to form the secondary phosphine oxide 14, which adds to a second mole of the imine to form the diamine 13.



The role of the imine in the reaction was confirmed by the reaction of 1 with the *p*-tolualdehyde imine of benzylamine, 15. The only product isolated from this reaction was the amino alcohol 16, which has the *p*-tolyl group on the carbon $\alpha$ to phosphorus. The reaction of 1 with imines is



another demonstration[2,14] of decomposition of $\alpha$-hydroxyalkylphosphine oxides through loss of the carbonyl function.

**Table I**
**Products from the Reaction of 1 with Benzaldehyde Imines**

| R | Crude yield, %[a] | Recrystallizing solvent | Compd | Mp, °C |
|---|---|---|---|---|
| $CH_3$ | 73 | Methanol–acetone–ethyl acetate | 8 | 159–161 |
| $C_3H_5$ | 49 | Methanol–ether | 9 | 172–173 |
| $(CH_3)_3$ | 63 | Methanol–ethyl acetate–acetone | 7 | 160–161 |
| $CH_3CH_2CH_2CH_2$ | 46 | Acetone | 10 | 146–148 |
| Ph | 75 | Methanol–water | 11 | 168–169 |
| $PhCH_2$ | 61 | Acetone | 12 | 151–152 |
| $PhCH_2$ | 43[b] | Methanol–water | 13 | 145–147 |

[a] Based on the amino alcohol. [b] Based on the diamine since 2 mol of the imine were used.

## Experimental Section

Reagent grade chemicals and solvents were used without further purification. Other chemicals and solvents were purified as stated. Benzene was dried for 24 hr or more over Linde molecular sieve 4A before use.

The ir spectra were taken on a Perkin-Elmer 137 with NaCl optics. Solid samples were run as KBr pellets using about 1% of the sample. The NMR spectra were taken on a Varian A-60A or Jeolco MH-60-II. Elemental analyses were performed by Enviro Analytical Laboratory, Knoxville, Tenn., and Galbraith Laboratories, Inc., Knoxville, Tenn. All melting points are uncorrected.

Benzylbis($\sigma$-hydroxybenzyl)phosphine oxide (1) was prepared as described in the previous publication.[2]

**Imine Preparation.** All imines were prepared in essentially the same manner which consisted of mixing the neat liquid amine (where possible) and benzaldehyde together with rapid magnetic stirring. Heat evolution and water evolution were complete in a matter of minutes; the imine was taken up in $CH_2Cl_2$ or ether and the organic layer was separated and dried over $Na_2SO_4$. The solvent was removed in vacuo and the oily residue was vacuum distilled.

***N*-Benzylidenebenzylamine (4).** A mixture of 21.2 g (0.2 mol) of benzaldehyde and 21.43 g (0.2 mol) of benzylamine after reaction and work-up afforded 34.74 g (92% yield) of a colorless liquid, 4, bp 124° (0.5 mm), $n^{20}$D 1.6014 (lit.[15] bp 116–117° (0.1 mm), $n^{20}$D 1.6017). The ir spectrum of 4 showed a strong C=N absorption at 6.05 $\mu$.

**Benzyl($\alpha$-benzylaminobenzyl)($\alpha'$-hydroxybenzyl)phosphine Oxide (12).** Treatment of 1 with 4 was carried out under five sets of conditions: (1) 3.33 mmol of each were stirred together in 30 ml of ethanol at room temperature for 24 hr; (2) same as 1 except one or two crystals of TsOH were added; (3) same as 1 except 30 ml of benzene was used; (4) 3.33 mmol of each were stirred together at 80° in 150 ml of refluxing benzene for 4 hr; and (5) 3.33 mmol of 1 was heated in 150 ml of refluxing benzene for 2 hr with a crystal of TsOH, then 3.33 mmol of 4 was added and reflux was resumed for 2 hr. Methods 1, 2, and 3 led to 100% recovery of starting material. Method 4 yielded 61% of 12 and 5 gave 20% of 12. Method 4 was used for the rest of the reactions of 1 with imines. Recrystallization of the product twice from acetone yielded white platelets, mp 151–152°. The infrared spectrum was identical with that of the higher melting amino alcohol already identified.[2]

***N*-Benzylidenemethylamine (5).** A mixture of 0.1 mol of methylamine (50.75 g of a 5.7% solution in benzene) and 0.1 mol of benzaldehyde afforded after reaction and work-up 9.39 g (80% yield) of a colorless, white liquid, 5: bp 40° (1.5 mm), $n^{20}$D 1.5524 (lit.[16] $n^{20}$D 1.5519). The ir spectrum of 5 showed the C=N absorption at 6.05 $\mu$.

**Benzyl($\alpha$-hydroxybenzyl)($\alpha'$-methylaminobenzyl)phosphine Oxide (8).** A mixture of 3.52 g (10 mmol) of 1, 1.19 g (10 mmol) of 5, and 300 ml of dry benzene was refluxed for 4.5 hr. The benzene was removed in vacuo, the oily residue was dissolved in 200 ml of ether, and the solution was cooled in the freezer. The precipitate, which formed slowly, was collected over the next 3 months for a 73% yield. Recrystallization from methanol–acetone,

then methanol-acetone–ethyl acetate, yielded the analytical sample, **8:** mp 159–161°; ir (KBr) 2.95 (NH), 3.05, 3.13, and 3.24 (hydrogen bonded OH), 8.7 and 8.92 μ (P=O); an interpretable NMR spectrum of **8** could not be obtained owing to its poor solubility in the normal NMR solvents.

Anal. Calcd for $C_{22}H_{24}NO_2P$: C, 72.31; H, 6.62; N, 3.83; P, 8.48. Found: C, 72.40; H, 6.68; N, 3.72; P, 8.68.

***N*-Benzylidenecyclopropylamine (18).** A mixture of 70 mmol (4.0 g) of cyclopropylamine and 70 mmol (7.43 g) of benzaldehyde after reaction and work-up gave 6.86 g (68% yield) of a pale yellow liquid, **18,** bp 52–55° (1.5 mm), $n^{25}D$ 1.5728 (lit.[17] $n^{25}D$ 1.5728). The ir spectrum of **18** shows the C=N absorption at 6.09 μ.

**Benzyl(α-cyclopropylaminobenzyl)(α′-hydroxybenzyl)phosphine Oxide (9).** A mixture of 3.52 g (10 mmol) of **1,** 1.45 g (10 mmol) of **18,** and 300 ml of dry benzene was refluxed for 4.5 hr. The benzene was removed in vacuo and the oily residue was dissolved in 300 ml of ether. No solid had formed after several days; so the oil was triturated with a mixture of ether–petroleum ether on the steam bath until most of the solvent had been removed and some solid had formed. Ether (150 ml) was added and the mixture was returned to the freezer. The solid which precipitated (1.94 g, 49% yield) had mp 160–162°. Recrystallization from methanol–ether afforded the analytical sample, **9:** mp 172–173°; ir (KBr) 3.0 (NH), 3.22 (hydrogen-bonded OH), 8.72 and 8.88 μ (P=O); an interpretable NMR spectrum could not be obtained owing to the low solubility of **9** in normal NMR solvents. The ir spectrum of **9** was identical with that of the same derivative (**12**) previously prepared in a different manner.[2] However, the melting point and carbon analysis of **12** were consistently low so the elemental analysis of **9** is reported.

Anal. Calcd for $C_{24}H_{26}NO_2P$: C, 73.64; H, 6.70; N, 3.58; P, 7.91. Found: C, 73.51; H, 6.82; N, 3.65; P, 7.82.

***N*-Benzylidene-1,1-dimethylethylamine (6).** Imine **6** was prepared in a slightly different manner than were the other primary amines. Benzaldehyde (10.6 g, 0.1 mol) was mixed vigorously with *tert*-butylamine (7.3 g, 0.1 mol) at room temperature for 30 min with no evolution of water or heat. A crystal of TsOH added to the mixture caused the solution to warm and water evolution was noticeable within 30 min. After reaction has proceeded for 3 hr, ether was added and the organic layer was extracted once with 5% $Na_2CO_3$. The ether layer was dried over $Na_2SO_4$, the solvent was removed in vacuo, and the oily residue was vacuum distilled to yield 12.19 g (76% yield) of a clear liquid, **6,** bp 48–50° (1.5 mm), $n^{20}D$ 1.5210 (lit.[18] $n^{20}D$ 1.5211). The ir spectrum of **6** showed the C=N absorption at 6.08 μ.

**Benzyl(α-1,1-dimethylethylaminobenzyl)(α′-hydroxybenzyl)phosphine Oxide (7).** A mixture of 3.52 g (10 mmol) of **1,** 1.61 g (10 mmol) of **6,** and 300 ml of benzene was refluxed for 4 hr. The benzene was removed in vacuo and the oily residue was dissolved in 300 ml of ether. Within 2 weeks, 2.54 g (63% yield) of white solid was collected, mp 146–151°. Two recrystallizations from methanol–ethyl acetate–acetone yielded the analytical sample, **7:** mp 160–161°; ir (KBr) 2.97 (NH), 3.15 (hydrogen-bonded OH), 3.32 (aliphatic CH), 8.71 μ (P=O); NMR ($CDCl_3$) δ 0.98 (s, 9 H, $(CH_3)_3C$), 2.85 (m, 2 H, $PCH_2$), 4.34–4.62 (m, 1 H, PCHN), 5.21 (d, $J$ = 3 Hz, 0.6 H, PCHO), 5.57 (d, $J$ = 11 Hz, 0.4 H, PCHO), 6.67–7.67 (m, 15 H, aromatics). The NMR spectrum showed **7** to be an isomeric mixture.

Anal. Calcd for $C_{25}H_{30}NO_2P$: C, 73.69; H, 7.42; N, 3.44; P, 7.60. Found: C, 73.70; H, 7.33; N, 3.37; P, 7.75.

***N*-Benzylidenebutylamine (19).** A mixture of 0.1 mol (7.31 g) of *n*-butylamine and 0.1 mol (10.6 g) of benzaldehyde gave after reaction and work-up 13.29 g (83% yield) of a clear liquid, **19,** bp 67°, (0.6 mm), $n^{20}D$ 1.5249 (lit.[16] $n^{20}D$ 1.5252). The ir spectrum of **19** showed the C=N absorption at 6.05 μ.

**Benzyl(α-butylaminobenzyl)(α′-hydroxybenzyl)phosphine Oxide (10).** A mixture of 3.52 g (10 mmol) of **1,** 1.61 g (10 mmol) of **19,** and 300 ml of benzene was refluxed for 4 hr. The benzene was removed in vacuo, the oily residue was taken up in ether, and the flask was put in the freezer. After several days no solid had formed; so the ether was removed with the addition of petroleum ether. Solid slowly began to precipitate and 1.88 g (46% yield) was collected which had mp 120–145°. Recrystallization from acetone gave the analytical sample, **10:** mp 146–148°; ir (KBr) 3.0 (shoulder, NH), 3.06, 3.15, and 3.22 (hydrogen-bonded OH), 3.35 (aliphatic CH), 8.68 μ (P=O); NMR ($CDCl_3$) δ 0.6–1.7 [m, 7 H, $CH_3(CH_2)_2$], 3.95 (d, $J$ = 17.5 Hz, 0.5 H, PCHN), 4.06 (d, $J$ = 7.5 Hz, 0.5 H, PCHN), 5.0 (d, $J$ = 11 Hz, 0.5 H, PCHO), 5.13, (d, $J$ = 8 Hz, 0.5 H, PCHO), 6.67–7.67 (m, 15 H, aromatics); the assignments were made on the $D_2O$-exchanged spectrum. In the earlier publication only one pure isomer was obtained.[2] The NMR spectrum showed **10** to be an equal mixture of two isomers; thus the elemental analysis is reported.

Anal. Calcd for $C_{25}H_{30}NO_2P$: C, 73.69; H, 7.42; N, 3.44; P, 7.60. Found: C, 73.46; H, 7.28; N, 3.26; P, 7.83.

**Benzalaniline (17).** Imine **17** was prepared by the method of Bigelow and Eatough[19] using 0.1 mol (10.6 g) of benzaldehyde and 0.1 mol (9.3 g) of aniline. The solid which formed was collected (17.07 g, 94% yield) and had mp 48–50°. One recrystallization of the light-yellow solid afforded pure **17,** mp 50–51° (lit.[20] mp 51°). The ir of **17** showed a strong C=N absorption at 6.08 μ.

**Benzyl(α-anilinobenzyl)(α′-hydroxybenzyl)phosphine Oxide (11).** A mixture of 3.52 g (10 mmol) of **1,** 1.81 g (10 mmol) of **17,** and 300 ml of benzene was refluxed for 4.5 hr. The benzene was removed in vacuo and the oily residue was dissolved in 200 ml of ether. Over a period of 4 weeks 3.18 g (75%) of white solid was collected. Two recrystallizations from methanol–water afforded the analytical sample, **11:** mp 168–169°; ir (KBr) 2.95 (NH), 3.15 and 3.25 (hydrogen-bonded OH), 6.25 and 6.67 (intense C=C), 8.7 and 8.9 μ (P=O); NMR (DMSO-$d_6$) δ 2.7–3.6 (m, 2 H, $PCH_2$), 4.6–5.5 (m, 2 H, PCHN and PCHO), 6.1–7.8 (m, 20 H, aromatics); the assignments were made after $D_2O$ exchange. The ir of **11** prepared by the imine reaction was identical with that of the amino alcohol obtained in the amine reaction.[2]

**Benzylbis(α-benzylaminobenzyl)phosphine Oxide (13).** A mixture of 1.76 g (5 mmol) of **1,** 1.95 g (10 mmol) of **4,** and 200 ml of benzene was refluxed for 21 hr. The benzene was removed in vacuo and the resultant yellow oil was dissolved in 200 ml of ether. Within 2 weeks, 1.13 g (43% yield) of white solid was collected. Recrystallization twice from methanol–water afforded the analytical sample, **13:** mp 145–147°; ir (KBr) 3.02 (NH), 3.25 (aromatic CH), 3.49 (aliphatic CH), 8.59 and 8.67 μ (P=O); NMR ($CDCl_3$) δ 2.5–4.5 (m, 10 H, $PCH_2$, $NCH_2$, NH, PCHN), 6.9–7.6 (m, 25 H, aromatics), two protons were lost from the 2.5–4.5 region on $D_2O$ exchange. There are significant differences between **13** and the same product formed in the primary amine reaction. The complexity of the NMR spectrum of **13** indicated an isomeric mixture while the NMR spectrum of the same compound, prepared by the primary amine reaction, afforded the meso isomer.[2]

Anal. Calcd for $C_{35}H_{35}N_2OP$: C, 79.22; H, 6.65; N, 5.28; P, 5.84. Found: C, 78.85; H, 6.67; N, 5.13; P, 6.08.

***N*-(*p*-Methylbenzylidene)benzylamine (15).** A mixture of 21.43 g (0.2 mol) of benzylamine and 23.6 g (0.2 mol) of *p*-tolualdehyde after reaction and work-up afforded 32.9 g of pale yellow liquid (79.5% yield) which hardened to a white solid on cooling, **15,** mp 27° (lit.[21] mp 27°). The ir spectrum of **15** shows the C=N absorption at 6.04 μ.

**Benzyl(α-hydroxybenzyl)(α′-*p*-methylbenzylaminobenzyl)phosphine Oxide (16).** A mixture of 3.52 g (10 mmol) of **1,** 2.07 g (10 mmol) of **15,** and 300 ml of benzene was refluxed for 4.5 hr. The benzene was removed in vacuo and the oily residue was dissolved in 300 ml of ether. The ether was allowed to evaporate slowly at ambient temperature. The solid which was collected (1.57 g, 35% yield) was recrystallized twice from acetone to afford long white needles as the analytical sample, **16:** mp 151–152; ir (KBr) 2.97 (NH), 3.22 (hydrogen-bonded OH), 8.7 and 8.88 μ (P=O); NMR ($CDCl_3$) δ 2.43 (broad s, 3 H, $CH_3Ph$), 2.6–4.4 (m, 5 H, $PCH_2$, $NCH_2$, PCHN), 4.9–5.5 (m, 1 H, PCHO), 6.9–7.6 (m, 19 H, aromatics). These assignments were made on the $D_2O$-exchanged spectrum since the NH and OH protons were spread along the base line and interferred with accurate integration. The methine proton on the carbon bonded to both phosphorus and oxygen appeared as two distinct, though broadened, doublets indicating an isomeric mixture in a 60:40 ratio. The isomeric mixture is also evidenced by the broadened singlet for the tolyl methyl group.

Anal. Calcd for $C_{29}H_{30}NO_2P$: C, 76.49; H, 6.64; N, 3.08; P, 6.80. Found: C, 76.46; H, 6.40; N, 3.14; P, 6.82.

**Registry No.**—**1,** 36871-68-8; **4,** 780-25-6; **5,** 622-29-7; **6,** 6852-58-0; **7,** 55133-75-0; **8,** 55133-76-1; **9,** 54617-90-2; **10,** 54617-86-6; **11,** 54617-97-9; **12,** 54617-83-3; **13,** 55176-53-9; **15,** 24431-15-0; **16,** 55133-77-2; **17,** 538-51-2; **18,** 3187-77-7; **19,** 1077-18-5; benzaldehyde, 100-52-7; benzylamine, 100-46-9; methylamine, 74-89-5; cyclopropylamine, 765-30-0; *tert*-butylamine, 75-64-9; *n*-butylamine, 109-73-9; *p*-tolualdehyde, 104-87-0.

## References and Notes

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# Decomposition Reactions of Hydroxyalkylphosphorus Compounds. III. Reaction of Benzylbis(α-hydroxybenzyl)phosphine Oxide with Benzaldehyde and *p*-Tolualdehyde[1a]

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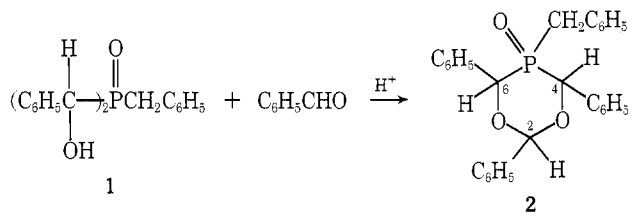
The reaction of benzylbis(α-hydroxybenzyl)phosphine oxide (1), a *dl*-diol, with benzaldehyde yielded both *dl* (**2a**) and meso (**2s**) cyclic acetals (5-benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane 5-oxides). The interconversion of **2a** and **2s** was found to occur with the equilibrium constant expressed as $K_{dl} = 3.8 \pm 0.4$. The mechanisms proposed for both of these reactions involve P–C bond cleavage between the oxygen-substituted carbon and phosphorus. The reaction of **1** with *p*-tolualdehyde afforded, as the only isolable product (15% yield), a meso cyclic acetal (**13**) which had *two p*-tolyl groups adjacent to phosphorus (5-benzyl-4,6-di-*p*-tolyl-2-phenyl-1,3,5-dioxaphosphorinane 5-oxide). The production of **13** required P–C bond cleavage twice and the loss of 2 mol of benzaldehyde from **1**.

Buckler has shown that the reaction of benzylbis(α-hydroxybenzyl)phosphine oxide (1) with benzaldehyde affords the cyclic acetal **2** as a mixture of isomers.[2] The isomers, when separated, had markedly different ir and NMR spectra and were identified from NMR spectra and symmetry considerations as one meso and one *dl* form.[3] Since the starting diol **1** was the *dl* form,[3] we studied the mechanism by which meso acetal was produced from *dl* diol.



1 2

## Results and Discussion

The expected mechanism for the formation of **2** is shown in Scheme I. Diol **1** plus benzaldehyde forms the intermediate hemiacetal **3**. It does not matter which carbon is involved, since in this step the absolute configuration at the carbon will be unchanged. This hemiacetal can be protonated at either of the two remaining hydroxyl groups. Elimination of water to form the carbonium ion and closure to the cyclic acetal **2** occurs readily. However, since the starting material **1** is the *dl* isomer and closure leads predominantly to the *dl* cyclic isomer, it follows that carbonium ion formation occurs predominantly at the carbon adjacent to the ether oxygen (**5**). This is as expected for carbonium ion stability, since the oxygen has free electron pairs capable of resonance stabilization of the carbonium ion while the phosphoryl group would destabilize the carbonium ion.

**Scheme I**
**Mechanism for the Formation of the Cyclic Acetal 2**