Proton Magnetic Resonance Spectra and Stereochemical Assignments in 5-Benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane 5-Oxides

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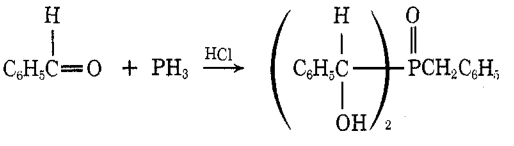
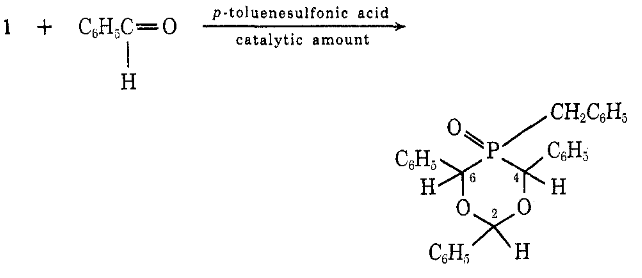
It has been reported by Buckler[2] that the reaction of benzaldehyde with phosphine in the presence of HCl proceeds with the transfer of oxygen from carbon to phosphorus to yield benzylbis(α-hydroxybenzyl)phosphine oxide **1**.



$$C_6H_5\overset{H}{C}{=}O + PH_3 \xrightarrow{HCl} \left(C_6H_5\overset{H}{\underset{OH}{C}}\right)_2 \overset{O}{\overset{\|}{P}}CH_2C_6H_5$$

1

It was further shown that the reaction of **1** with benzaldehyde under conditions suitable for acetal formation led to the title compounds which are represented by the general structure **2**.



2

2 was obtained as a mixture of stereoisomers, two of which were isolated in pure form by fractional crystallization. **2** represents one of only several examples of 1,3,5-dioxaphosphorinanes which have been prepared.[3,4] To our knowledge there have been no reports on the stereochemistry of these products. Furthermore, there has been a great deal of interest in recent years in the preparation and stereochemistry of 1,3,2-dioxaphosphorinanes.[5-7] This interest has prompted us to report our studies on the title compounds.

Discussion and Results

An examination of **1** revealed the possibility of two meso forms and one *d,l* pair. These are shown in Figure 1. Ph stands for phenyl and Bz for benzyl, and the configuration about each carbon is designated.[8] The nmr spectra for **1** showed it to be the *d,l* form as the benzyl methyne protons appeared as a doublet of doublets and the benzyl methylene protons as the AB portion of an ABX pattern. The meso form of **1** would be expected to show doublets for both the benzyl methyne and benzyl methylene protons. Raising the temperature of **1** to 100° caused no change in its nmr spectra.

For **2** there is the possibility of 16 isomers. Assuming rapid ring inversion, these can be reduced to eight sets of different nmr signals. Furthermore, since there are two sets of mirror pairs, only six sets of nmr signals are potentially observable. Table I lists the eight possibilities; the groups shown are in the equatorial positions. The groups are taken in order moving clockwise from phosphorus.

TABLE I
ISOMERIC POSSIBILITIES OF 2

Isomer no.	Configuration (equatorial)		
I	O, Ph, Ph, Ph		
II	O, H, Ph, Ph		
III	O, H, H, Ph		
IV	O, H, H, H	*d,l*	*d,l*
V	O, Ph, H, Ph	pair	pair
VI	O, Ph, H, H		
VII	O, Ph, Ph, H		
VIII	O, H, Ph, H		

Preparation of **1** and **2** and fractional crystallization of **2** proceeded essentially as described by Buckler.[2] Two isomers were obtained and shown to have markedly different ir and nmr spectra. Table II shows the important ir bands for the two isomers. The ir spectra were essentially identical up to the 7.0-μ region, but

TABLE II
INFRARED BANDS FOR BOTH ISOMERS

Spectral region, μ	Bands for **2a**	Bands for **2s**
2.5–3.0		
3.0–4.0	3.28 (m), 3.45 (m)	3.28 (m), 3.45 (m)
4.0–5.0		
5.0–6.0		
6.0–7.0	6.25 (m), 6.7 (s), 6.9 (s)	6.25 (m), 6.7 (s), 6.9 (s)
7.0–8.0	7.32 (s), 7.85 (m)	7.26 (s)
8.0–9.0	8.22 (vs), 8.33 (vs), 8.60 (s), 8.99 (vs)	8.4 (vs)
9.0–10.0	9.09 (vs), 9.37 (s), 9.8 (vs), 9.92 (s)	9.20 (vs), 9.39 (vs), 9.72 (s)
10.0–11.0	10.6 (m), 10.85 (m)	9.8–10.1 (vs), 10.68–10.96 (vs)
11.0–12.0	11.48 (m)	11.48 (m)
12.0–13.0	12.41 (m)	
13.0–14.0	13.10 (vs), 13.20 (s), 13.62 (m)	13.0 (vs), 13.2 (s), 13.85 (s)
14.0–15.0	14.15 (s), 14.4 (vs)	14.3 (vs)

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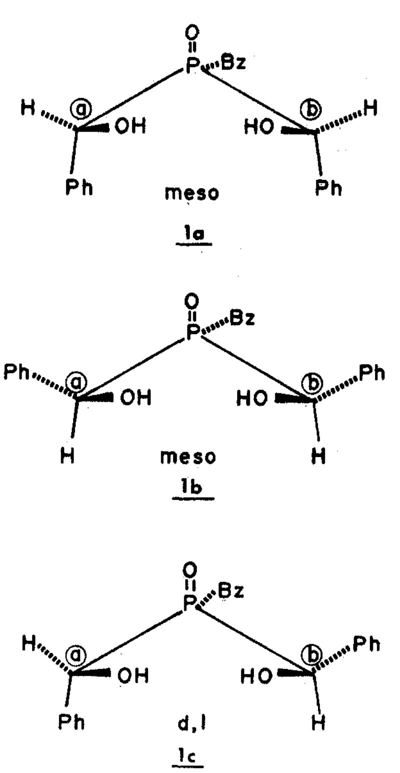

Figure 1.—Isomeric possibilities for **1**: **1a**, C_a has *S* and C_b *R* configuration; **1b**, C_a has *R* and C_b *S* configuration; **1c**, C_a has *S* and C_b *S* configuration. In mirror image of **1c** both carbons have *R* configuration.

from there to 17 μ they differed dramatically. Of particular interest were the numerous differences in the 8-10-μ region where the P=O and C-O-C absorptions are expected. There were no differences in the >C-H stretching or aromatic >C=C< and >C-H bending regions but minor differences could be seen in the substituted benzene region.

The nmr spectra of the two isomers are shown in Figure 2. **2a** exhibited a relatively complex spectrum with different protons at C_4 and C_6 (two overlapping AX patterns). The proton at C_2 appeared as a singlet. The benzylic protons at phosphorus appeared as the AB portion of an ABX pattern. Analysis of this portion of the spectrum gave values of 15 Hz for J_{AB}, 22.5 Hz for $2D_+$, 30.5 Hz for $2D_-$, and 13 Hz for $\frac{1}{2}|J_{AX} + J_{BX}|$.[9,10]

Solving simultaneously the equations

$$D_+ = \tfrac{1}{2}\{[(V_A - V_B) + \tfrac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}^2\}^{1/2}$$

$$D_- = \tfrac{1}{2}\{[(V_A - V_B) - \tfrac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}^2\}^{1/2}$$

yields values for $(J_{AX} - J_{BX})$ of ±43.3 and ±9.8. Solving for J_{AX} and J_{BX} gives one set of values in which $|J_{AX}|$ or $|J_{BX}|$ is 34.65 which is unrealistically high. The other solution $[(J_{AX} - J_{BX}) = \pm 9.8)]$ gives values of ±17.9 and ±8.1 for J_{AX} and J_{BX}. Neither value can be assigned to a particular coupling constant as **2a** was not soluble enough for a ^{31}P nmr spectra to be obtained. Thus the X portion of the spectra could not be observed. However, the values of ±17.9 and ±8.1 are what would be expected for P-CH coupling in phosphorus-methylene compounds.[11-14]

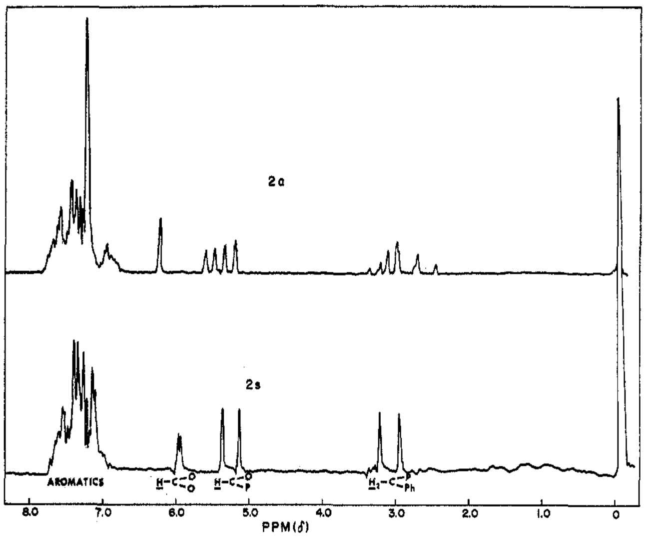

Figure 2.—Nmr spectra of isomeric 1,3,5-dioxaphosphorinanes.

The spectra showed conclusively that **2a** was one of the *d,l* pairs II-VII or III-VI since the benzyl protons were nonequivalent. This could occur only if there was no symmetry plane between the benzyl protons[15] as is the case in the *d,l* pairs. All of the other isomers have a symmetry plane through the 2,5 positions and of course through the benzyl methylenes.

Studies of 1,3,2-dioxaphosphorinanes[5-7] and very recent studies on phosphacyclohexane[16] and its derivatives have shown that the favorable position for substituents on phosphorus is axial while the electron pair (phosphines), oxygen (oxides), or sulfur (sulfides) occupy the equatorial position.

Alkyl and aryl substituents on phosphorus exhibit this strong preference for the axial conformation despite the fact that severe 1,3 interactions are possible. In the 1,3,5-dioxaphosphorinane system there is no possibility of 1,3 interactions involving the substituent on phosphorus. For this reason the preference for the axial conformation by the substituent on phosphorus should be more pronounced and the benzyl group on phosphorus should be axial.

The proton at C_2 shows no discernible coupling to phosphorus. If the proton were in the equatorial position, a coupling of about 1-2 Hz would be expected as a planar zigzag arrangement[17] exists between the phosphorus and the equatorial proton. The phosphorus coupling to the axial proton would be expected to be less than 1 Hz.[18] The structure of **2a** can therefore be designated as shown which is the *d,l* pair II-VII. Thus, two of the three phenyl groups attached to carbon occupy the favored equatorial positions.

2s exhibits a highly symmetrical nmr indicating that the phenyl groups at C_4 and C_6 are either both axial or both equatorial. Isomers I, IV, V, and VIII would be

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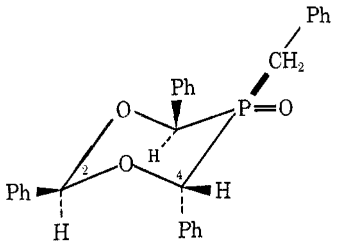
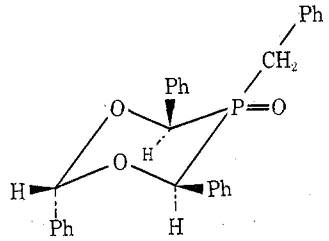


2a

expected to give symmetrical nmr spectra since they each have a plane of symmetry through the 2,5-ring positions. However, an examination of molecular models showed isomers IV and VIII to be extremely crowded with severe 1,3 interactions between the phenyl groups at C_4 and C_6. These interactions would favor the diequatorial configuration at C_4 and C_6. The proton at C_2 shows a doublet (J = 2 Hz). The only coupling which would give a doublet would be to phosphorus. This long-range coupling would be expected to be greater than 1 Hz only if the proton were equatorial.[17,18] Thus, the structure of **2s** is that of



2s

isomer V. Again two of the three phenyl groups attached to carbon are in the equatorial positions.

The two isomers isolated are the only ones which have two bulky groups equatorial and two axial. All the rest have three bulky groups, either axial or equatorial.

The reasons for obtaining only these two isomers and the mechanism necessary to produce the meso ring system from *d,l* starting material are now under investigation and will be reported in a subsequent publication.

Experimental Section

Reagent grade chemicals were used as supplied. Phosphine was generated by addition of water to a suspension of aluminum phosphide in dioxane. The benzene and benzaldehyde were dried over Linde Molecular Sieve 4A. Ir spectra were run as KBr disks on a Perkin-Elmer 137 with NaCl optics; nmr spectra were run in $CDCl_3$ on a Varian A-60.

Benzylbis(α-hydroxybenzyl)phosphine Oxide.—The preparation was carried out identically with Buckler's work.[2] However, after running the experiment several times, the maximum yield of crystalline solid was 35%: mp 150–152°; nmr (DMSO-d_6) δ 3.18 (m, 2 H, PCH_2Ph), 5.17 (d, J = 9 Hz, 1 H, HC(O)P), 5.3 (d, J = 12 Hz, 1 H, HC(O)P), 6.48 (m, 2 H, OH), 6.73–7.78 (m, 15 H, aromatics).

5-Benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane 5-Oxide (2).—A solution of 35 ml of benzaldehyde, 120 ml of dry benzene, and a crystal of *p*-toluenesulfonic acid was prepared and 17.6 g (0.05 mol) of **1** was added. The mixture was heated under reflux until the water in the Dean-Stark trap did not increase over several hours reflux. Only 0.55 ml of water was collected (theoretical, 0.90 ml), and this took 7 days of reflux (Buckler reported 20 hr). The resulting solution was dried *in vacuo* and the residue mixed with 150 ml of anhydrous ether. The white solid present was collected (11.6 g, 52.8% yield), mp 158–200°, as a mixture of isomers **2**. The pure isomers were obtained by mixing **2** with 450 ml of ethyl acetate, heating, and filtering. The ethyl acetate soluble material after crystallization was recrystallized further from 2-propanol (three times) to yield 2.32 g of a white solid: mp 198–200° (**2a**); nmr ($CDCl_3$) δ 2.9 (m, 2 H, PCH_2Ph), 5.36 (d, $J_{\text{P-H}}$ = 17 Hz, 1 H, eq HC(O)P), 5.50 (d, $J_{\text{P-H}}$ = 16 Hz, 1 H, ax HC(O)P), 6.25 (s, 1 H, HC(O)O), 7.87–6.78 (m, 20 H, aromatics).

The ethyl acetate insoluble portion was then recrystallized four times from dioxane to yield 0.3 g of a white solid: mp 216–220° (**2s**); nmr ($CDCl_3$) δ 3.5 (d, $J_{\text{P-H}}$ = 16 Hz, 2 H, PCH_2Ph), 5.32 (d, $J_{\text{P-H}}$ = 14 Hz, 2 H, HC(O)P), 6.02 (d, $J_{\text{P-H}}$ = 2 Hz, 1 H, HC(O)O), 7.85–6.88 (m, 2 OH aromatics).

Registry No.—**1**, 36871-68-8; **2a**, 36871-89-3; **2s**, 36871-90-6.

Use of Polymethylhydrosiloxane as a Selective, Neutral Reducing Agent for Aldehydes, Ketones, Olefins, and Aromatic Nitro Compounds

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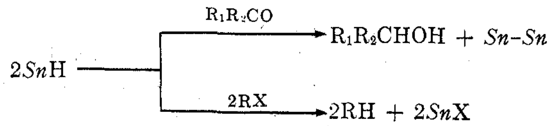
Several reports of the reductions of a variety of functional groups by silyl hydrides under mild conditions and in high yields prompted this work. The present study was aimed at determining the scope and utility of siloxane hydrides as general reducing agents for organic compounds under mild, neutral conditions.

Recently Grady and Kuivila[1] reported reductions of halocarbons and a ketone by tin hydrides, generated *in situ* from reaction of polymethylhydrosiloxane (PMHS) and organostannoxanes. Stoichiometric quantities of stannoxane were required. Earlier work of Nitzsche and Wick[2] had described reductions of several ketones and aromatic nitro compounds with methylhydrosiloxanes and catalytic quantities of dialkyltin diacylates or other organometallics in protic solvents. In view of Grady and Kuivila's work[1] and earlier reports of the reactions of stannoxanes and alkoxystannanes with silyl hydrides,[3] it is likely that tin hydrides are the active reducing agents, being rapidly consumed and regenerated *in situ*.

$$\mathit{Sn}\text{O}\mathit{Sn} + \frac{2}{n}[\text{MeHSiO}]_n \longrightarrow \frac{2}{n}[\text{MeSiO}_{1.5}]_n + 2\mathit{Sn}\text{H}$$



Sn = organotin

The organotin hydrides are versatile reagents which reduce a variety of functional groups.[4] However,

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