The 1-Methyl-3-phospholanol System. Synthesis and Stereochemistry[1]

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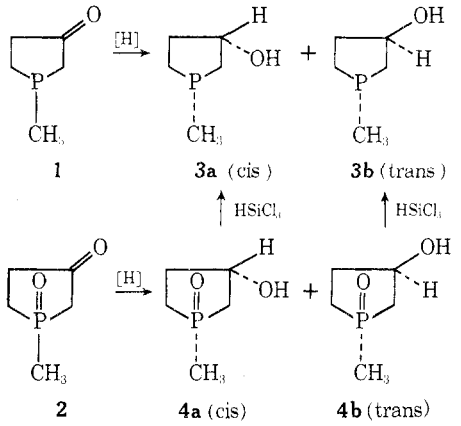
1-Methyl-3-phospholanol (cis, trans) has been prepared by reduction of 1-methyl-3-phospholanone with several agents, preferably lithium aluminum hydride, as well as by P-deoxygenation of the alcohol mixture formed on catalytic hydrogenation of 1-methyl-3-phospholanone 1-oxide. The phospholanol mixture is easily analyzed by the well-separated (13 Hz) PCH_3 nmr signals; the downfield signal is attributed to the cis isomer, which predominated (84%) from the various reductions of the phospholanone. The route *via* the phospholanone oxide gave predominantly the trans alcohol (63%). The conformational equilibrium for the cis isomer appears to be dominated by the diaxial conformer. Addition of methylmagnesium iodide to the phospholanone follows a similar steric path, and gives mostly the cis isomer.

It is now well established by X-ray studies[2] that the replacement of carbon by trivalent phosphorus in a six-membered ring does not alter the chair shape of the ring greatly, in spite of the longer C–P bonds and smaller C–P–C angle. However, the conformational tendency of an exocyclic substituent on phosphorus is quite different from that when on carbon.[3,4] For example, in 1-methylphosphorinane, there is a predominance of the axial methyl conformer at room temperature,[4] and in both the cis and trans forms of 1-methyl-4-phosphorinanol the hydroxy group is largely equatorial and the methyl group is either axial (cis) or equatorial (trans).[3,5] No prior consideration has been given to the conformational consequences of replacing a carbon in cyclopentane with phosphorus, however, mostly because of the lack of access to suitable model compounds for such studies. We recently prepared 1-methyl-3-phospholanone[6] and its 1-oxide,[7] and recognized that these compounds would be useful starting points for stereochemical study of the phospholane ring, in that cis and trans isomers would result from additions to the carbonyl group. The isomer ratio as well as nmr spectral properties could be expected to provide stereochemical information, and this is shown to be true in this paper.

Synthesis of 3-Phospholanols. These alcohols can be approached by two paths from the ketones available. The

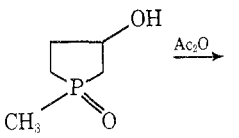


1 3a (cis) 3b (trans)

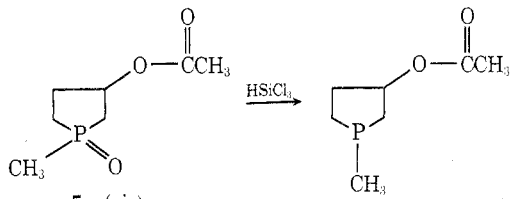
2 4a (cis) 4b (trans)

reduction of ketophospholane 1 proceeded especially well (84%) with lithium aluminum hydride; yields were distinctly inferior with two other systems tried (sodium–ethanol, 13%; aluminum isopropoxide, 54%), although these experiments were performed only once.

The high enolic character[6,7] of β-keto oxide 2 interfered with hydride reduction (sodium borohydride or lithium aluminum hydride). However, catalytic hydrogenation proceeded smoothly to give a mixture of alcohols **4a** and **4b**. These compounds were very difficult to work with in that they were extremely hygroscopic. They could be acetylated, however, and, though still hygroscopic, the acetates were more readily handled. The acetates were reduced with trichlorosilane to the corresponding phosphines (**6a** and **6b**).



4a (cis)
4b (trans)



5a (cis)
5b (trans)

6a (cis)
6b (trans)

Deoxygenation of the alcohol oxides **4a** and **4b** occurred in 37% yield. As will be noted later, the ratio of alcohols **3a** and **3b** is quite different from that obtained by reduction of the ketophosphine, a point which would have utility if the pure isomers were desired. That a separation of the isomer mixture is feasible was demonstrated by subjecting a 1:1 cis–trans mixture to fractional distillation with a spinning-band column. The first fraction was the cis isomer in 95% or greater purity; the pot residue was about 85% trans. The separation was not further perfected, however.

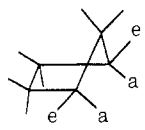
Structure Assignment. The ^1H nmr spectrum (neat) of the 3-phospholanol mixture contained two sharp, well-separated PCH_3 doublets (**3a**, δ 1.71; **3b**, δ 1.49), which permitted easy analysis of the mixture. The signals are of additional importance, however, in that their chemical-shift difference is attributable to the orientation of the methyl and hydroxyl groups. The hydroxyl group is well known to deshield cis methyl groups.[8] This effect also prevails in the 1-methyl-4-phosphorinanols.[9] Accordingly, structure **3a** is assigned to that compound with the more deshielded PCH_3.

The ^{31}P nmr signals of the isomers are sufficiently well separated (1.5 ppm) that under conditions of proton decoupling they may be used to analyze a mixture. The trans isomer has the more upfield signal (**3b**, δ ^{31}P +40.3; **3a**, δ +38.8), but the structural significance of this order of signals is not yet apparent.

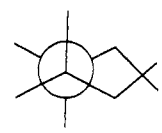
The 3-phospholanols were found to experience a strong upfield shift of all ^1H nmr signals on addition of benzene.

The most readily observed signal was that for PCH_3, where it was seen that the signal associated with the cis compound (**3a**) was less susceptible to this effect than that of the trans. This allowed a greater spread to develop between the PCH_3 signals of the isomer mixture. Thus, in a 40% benzene solution, **3a** had $\delta(PCH_3)$ 1.30, while **3b** had δ 0.95. The difference (21 Hz) is substantially greater than seen for the neat sample (13 Hz). The same effect holds for the 1-methyl-4-phosphorinanols,[9] although the shifts are much smaller since the complexed solvent (at OH[10]) is more removed from the PCH_3 group. The geometry of the complex would also be quite different.

Conformational Aspects. The conformation of the five-membered ring is usually discussed in terms of an envelope (A) or twist envelope (B) shape, shown in Newman projection. These forms are flexible, and pseudo-rotation,



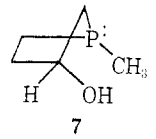
A



B

which is rapid, causes puckering at all ring positions. Similar shapes appear to be adopted by heterocyclic rings, including some heterosubstituted phospholanes (1,3,2-dioxa-,[11] 1,3,2-dithia-,[12] 1,3,2-oxathia-,[12a,13] 1,3,2-oxaza[14]). Models show that it is reasonable to depict the parent phospholane ring in the same manner. For convenience, substituents occupying the a positions in structure A will be referred to as axial, and those in the e positions as equatorial.

One nmr property of the 3-phospholanols is of particular importance in a conformational sense: the large difference (13 Hz) in chemical shifts for the PCH_3 groups in the cis and trans form [$\Delta\delta(PCH_3)$], as caused by hydroxyl deshielding, is in the range commonly found for 1,3-methyl and hydroxyl when fixed rigidly in the diaxial relation.[15] In the flexible 3-methylcyclopentanol system, the difference between isomers is only 4 Hz[16] (with cis downfield). The implication is clear that in the *cis*-3-phospholanol system the CH_3 and OH groups are, on the average, closer together than they are in *cis*-3-methylcyclopentanol. This may be expressed by envelope structure **7**, or twist envelope **8**; presumably these predominate in the conformational equilibrium with other puckered structures (*e.g.*, **9** and **10**).



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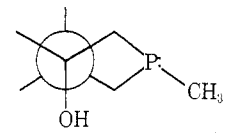

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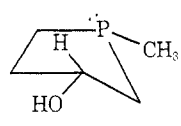

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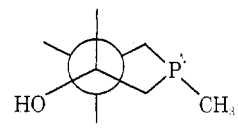

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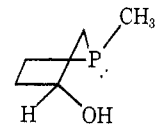
Indeed, the size of $\Delta\delta(PCH_3)$ suggests that the *cis*-3-phospholanol may exist exclusively as **7** (or **8**), with no ring flexing, but this view would require a stronger defense than can now be developed.

In the isomeric *trans*-1-methyl-3-phospholanol, either the hydroxy group or the methyl group may be axial, and the other equatorial, as represented by **11** and **12**. No information is available on the conformational preference in this compound.



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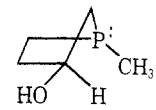

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The importance of the diaxial conformation **7** (or **8**) for the cis isomer suggests that nonbonded 1,3 interactions must play only a small role in the phospholane system, and this is supported by the fact that the cis and trans phospholanols are of nearly equal concentration (51 and 49%, respectively) in the mixture formed on equilibration at 135° *via* pyramidal inversion at phosphorus. This low energy difference between cis and trans forms is paralleled in the cyclopentane system; in 1,3-dimethylcyclopentane, cis is more stable than trans by 0.53 kcal/mol[17] and, for 3-methylcyclopentanol, $\Delta G°$ for cis $\rightleftharpoons$ trans is -0.2 kcal/mol.[18] Carbon-13 shifts for these same 1,3-disubstituted cyclopentanes also reveal the absence of strong steric interaction.[19] The spectra for an isomer pair are very similar, comparable carbons differing at most by only 1.9 ppm. In the cyclohexane system, the more severe 1,3-nonbonded interactions involving an axial substituent can cause differences of about 5 ppm at the ring carbons involved. The ^{31}P shifts for the corresponding phospholane derivatives reveal the same situation to hold true. For the 1-methyl-3-phospholanols, $\Delta\delta(^{31}P)$ is 1.5 ppm and, for the 1,3-dimethylphospholanes, it is 0.4 ppm;[20] in isomeric *P*-methylphosphorinane derivatives, $\Delta\delta(^{31}P)$ can be several parts per million (6 ppm in the 4-hydroxy compounds[9] and 7 ppm in the 4-hydroxy-4-*tert*-butyl compounds[3]).

That diaxial structures such as **7** or **8** can have special importance in phospholanes is not out of keeping with the character of phosphorus in six-membered rings. It has already been noted[3,4] that 1,3 interactions of PCH_3 are markedly reduced in this system, and an axial orientation is not disfavored at room temperature. Since 1,3 interactions are generally weaker in five-membered rings, it follows that structure **7** (or **8**) may be quite stable. It perhaps is relevant also that the known[21] preference of the hydroxy group for axial orientation in cyclopentanol is maintained in this structure. It is also relevant that in some of the five-membered cyclic phosphite derivatives[11-13] the substituent on phosphorus seems to adopt the axial position. However, the lone pairs on the heteroatoms attached to phosphorus, which may play a role in controlling the structure, are absent in the phospholane system.

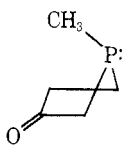
Stereochemistry of Phospholanol Formation. When 3-methyl-[18] or 3-*tert*-butylcyclopentanone[22] are reduced under kinetically controlled conditions, the alcohol mixture formed is richer in the cis isomer. Equilibration, however, leads to a slight predominance of trans in each case (*tert*-butyl, 52%; methyl 57%). That the cis isomer forms faster has been explained by hindrance provided by the substituent on that face of the ring to which it is attached, making it more favorable for hydrogen to be delivered from the opposite side. When 1-methyl-3-phospholanone is reduced, the cis isomer also predominates, but to an extent much larger than that seen for the cyclopentanones. Data are compared in Table I. That these percentages for **3a** and **3b** result from kinetic control is indicated by the adjustment of the cis–trans composition to nearly 1:1 on equilibration at 135° *via* pyramidal inversion at phosphorus. At least at this temperature, which is not greatly different from that of the aluminum isopropoxide reduction (80–90°), it is seen that there is little energy difference between the two isomers.

Table I
Per Cent Cis Alcohol Formed in Various Reductions

Compd	$LiAlH_4$	Na–ROH	$Al(O\text{-}i\text{-}C_3H_7)_3$
3-Methylcyclopentanone[18]	60	53[a]	*b*
3-*tert*-Butylcyclopentanone[22]	60	56[c]	59
1-Methyl-3-phospholanone[d]	81	79[c]	80

[a] R = H. [b] Conditions used allowed equilibration to occur. [c] R = C_2H_5. [d] Nmr analysis, by integration of CH_3 doublets.

The significantly higher content of cis product from the phospholanone may be taken to indicate that approach to the carbonyl is more hindered than in the 3-alkyl cyclopentanones. This is consistent with the concept that a P substituent on the phospholane ring experiences only weak nonbonded interactions when axially oriented, allowing contributions from structures such as **13** to be important relative to the equatorially substituted form, **14**.



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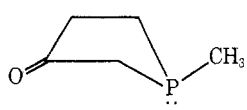

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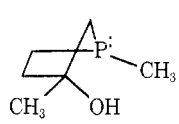
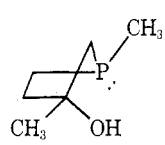
In some preliminary work[23] on the addition of Grignard reagents to ketone **1**, we have found that methylmagnesium iodide gives predominantly the cis alcohol (88.2%). This was established again with the aid of the cis deshielding of PCH_3 by hydroxyl (in benzene, major isomer, δ 1.25; minor, δ 0.91). The mixture showed only one CCH_3 signal, implying that this group has the same orientation in both isomers. Structures **15** and **16** (or twist



15 (cis)

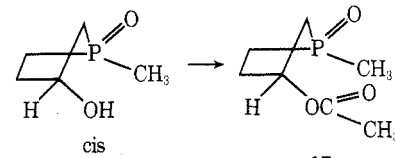


16 (trans)

forms) accommodate these facts, and are in keeping with the concept of low preference by PCH_3 for a particular location. Again, the proportion of cis isomer formed exceeded that from addition to 3-*tert*-butylcyclopentanone, which gave 51% cis alcohol. A steric block to one face of the phospholanone ring is indicated, as proposed to explain the large amount of cis product on reduction.

Stereochemistry of Reduction of 1-Methyl-3-phospholanone 1-Oxide. Catalytic hydrogenation of ketone **2** gave an alcohol mixture again readily analyzed by well-separated PCH_3 signals ($\Delta\delta$ 10 Hz). The cis structure (**4a**) was assigned to the isomer with the downfield PCH_3 signal. This time, however, the trans isomer predominated (60:40); this was confirmed by deoxygenation with trichlorosilane, which gave the phospholanols in the same ratio. Little can be said about the significance of the steric result with the oxide, since it is not known if the keto or the enol form is the species undergoing reduction.

Acetylation of the alcohol oxide mixture gave the isomeric acetates **5a** and **5b**, again recognized from their differing PCH_3 signals. However, the signals were reversed in position from the alcohols, the more intense now being downfield. This suggests that the acetate group has a specific shielding effect on the PCH_3 of the cis compound, moving the signal from δ 2.30 in the alcohol to 2.16 in the acetate. The trans signal was but slightly affected, shifting from δ 2.17 to 2.22. If the shielding effect can be associated with anisotropy of the ester carbonyl group, then only the cis isomer should allow positioning of the two groups in the appropriate relation, as expressed by conformer **17**. Instances of such shielding of methyl by acetoxy



cis

17

groups are found among rigid five-membered rings with diaxial geometry, as in the D ring of steroids.[15a]

The shielding by acetate is found also in the corresponding phosphines **6a** and **6b**. The ratio of isomers, as seen by the nmr spectrum, was the same as in the starting oxide mixture. The major isomer (60%) was downfield (δ 1.58), as was the major isomer in the oxide mixture. Since this is the trans isomer, the shielding by acetate in the cis isomer is demonstrated.

Experimental Section[24]

Synthesis of 1-Methyl-3-phospholanol (3) from 1-Methyl-3-phospholanone 1-Oxide (2). A mixture of 8.5 g (64.4 mmol) of ketone **2**, 1 g of Raney nickel, and 100 ml of 95% ethanol was hydrogenated in a Parr apparatus (48 hr at 50 psi). Norit was added and the mixture was filtered through Celite. The filtrate was evaporated to dryness, providing crude *cis*- and *trans*-1-methyl-3-phospholanol 1-oxide (**4**): nmr ($CDCl_3$) δ 2.17 (d, $^2J_{PH}$ = 12.8 Hz, cis PCH_3, 35%), 2.30 (d, $^2J_{PH}$ = 13.8 Hz, trans PCH_3, 65%), 2.3–3.1 (6 H, m), 4.6–5.4 (CHOH, m). The product was extremely hygroscopic.

The alcohol mixture was dissolved in 200 ml of benzene containing 15 ml of triethylamine. The solution was chilled to 0° and treated with 17.4 g (12.8 mmol) of trichlorosilane in 60 ml of benzene over a 30-min period. The reaction was completed with 2 hr of reflux. The mixture was chilled again for hydrolysis with 10 *N* NaOH, added to obtain complete dissolution of the initially precipitated solid. The benzene layer was recovered, and the aqueous layer was extracted with benzene. The combined benzene solutions were dried ($MgSO_4$) and distilled to give 2.8 g (37%) of 1-methyl-3-phospholanol (**3**, cis:trans 37:63): bp 93–95° (17 mm); nmr (neat) δ 1.49 (d, $^2J_{PH}$ = 2.8 Hz, trans PCH_3), 1.71 (d, $^2J_{PH}$ = 2.5 Hz, cis PCH_3), 1.82–2.9 (6 H, m), 4.7–5.3 (CHOH, m); nmr (40% in benzene) δ 0.98 (trans PCH_3) and 1.30 (cis PCH_3); $\delta(^{31}P)$ +38.8 (cis) and +40.3 (trans); ir (neat) ν_{OH} 3250 cm^{-1}.

The methiodide of the alcohol mixture was prepared in benzene and recrystallized from methanol–ether.

Anal. Calcd for $C_6H_{14}IOP$: C, 27.69; H, 5.43; P, 11.91. Found: C, 27.85; H, 5.57; P, 11.72.

Reduction of 1-Methyl-3-phospholanone (1) with Lithium Aluminum Hydride. A slurry of 0.30 g (7.9 mmol) of lithium aluminum hydride in 20 ml of tetrahydrofuran at reflux was treated dropwise (20 min) with a solution of 1.26 g (10.9 mmol) of ketone **1** in 20 ml of THF. The mixture was then refluxed for 4 hr, chilled in an ice bath, and hydrolyzed cautiously with 1 ml of water, followed by 1 ml of 15% NaOH and more water (6 ml). The mixture was filtered. The filtrate was washed with 30 ml of saturated NaCl solution, then dried ($MgSO_4$) and distilled to give 1.07 g (83.6%) at 96–97° (15 mm). The product contained by ^1H nmr analysis 81% *cis*- and 19% *trans*-1-methyl-3-phospholanol (**3**).

Reduction of 1-Methyl-3-phospholanone (1) with Aluminum Isopropoxide. A mixture of 3.0 g (14.7 mmol) of aluminum isopropoxide and 120 ml of isopropyl alcohol at reflux was treated dropwise (30 min) with a solution of 1.45 g (12.5 mmol) of ketone **1** in 20 ml of isopropyl alcohol. The mixture was refluxed for 12 hr, and then 20 ml of solvent was removed by distillation. This distillate gave a strong positive test for acetone with 2,4-dinitrophenylhydrazine. The reaction was continued, with occasional removal of distillate for the acetone test. When the test was negative, the reaction was terminated and the volume was reduced to about 30 ml by distillation. The mixture was cooled and stirred with 1 ml of water for 1 hr, and then overnight with 30 ml of 1 *N* NaOH. The mixture was extracted with one 200-ml and two 50-ml portions of benzene. The benzene extract was dried

($MgSO_4$) and distilled to give 0.80 g (54%) of 4 at 96–100° (16 mm) (by ^1H nmr, 80% cis, 20% trans).

Reduction of 1-Methyl-3-phospholanone (1) with Sodium and Ethanol. Sodium sand (2.0 g, 87 mmol) in 100 ml of toluene at 5–10° was treated with 3.36 g (29.2 mmol) of ketone 1 in 4.0 g (87 mmol) of absolute ethanol at such a rate as to keep the temperature below 10°. After 2.5 hr at 10°, 15 ml of water was cautiously added. The toluene layer was removed, and the aqueous layer was extracted with two 40-ml portions of benzene. The organic fractions were combined and dried ($MgSO_4$); distillation gave 0.41 g (12.7%) of 4 containing a trace of starting ketone 1. The ^1H nmr spectrum showed the composition 79% *cis*- and 21% *trans*-1-methyl-3-phospholanol (3).

Thermal Equilibration of 1-Methyl-3-phospholanol Isomers. A neat specimen (78.7% cis, 21.3% trans) was heated in an oil bath maintained at 135°. The specimen was then placed in benzene and its ^1H nmr spectrum was recorded for determination of the isomer composition by the PCH_3 signal size. After 35 hr, the composition was 67% cis, 33% trans. After an additional 107 hr, the composition of the dark material was 51% cis, 49% trans. Further heating caused tar formation, and the experiment was terminated.

1-Methyl-3-acetoxyphospholane 1-Oxide (5) and 1-Methyl-3-acetoxyphospholane (6). Ten grams (75.8 mmol) of 1-methyl-3-phospholanone 1-oxide (2) was hydrogenated as above. The product was dissolved in 35 ml of pyridine, cooled to 0°, and treated with 5.86 g (74.7 mmol) of acetyl chloride. After 2 hr, the mixture was warmed to room temperature and the precipitated pyridine hydrochloride was filtered off. The filtrate was evaporated to dryness, placed in 30 ml of 1 *N* HCl, and extracted with six 50-ml portions of $CHCl_3$. The extracts were dried ($MgSO_4$) and distilled, giving 6.6 g (50.5%) at 126–128° (0.17 mm) which solidified on standing. The product was a mixture of cis (34%) and trans (66%) isomers: nmr ($CDCl_3$) δ 2.16 (d, $^2J_{PH}$ = 13.5 Hz, cis PCH_3), 2.22 (d, $^2J_{PH}$ = 13.5 Hz, trans PCH_3), 2.38–3.12 (complex m, ring CH_2), 2.51 and 2.54 (s, CH_3CO), 5.34–6.25 (complex m, OCH). The oxide mixture is very hygroscopic and difficult to purify. Analytical results are only partly satisfactory.

Anal. Calcd for $C_7H_{13}O_3P$: C, 47.71; H, 7.44. Found: C, 46.91; H, 7.75.

The oxide mixture was deoxygenated as described previously with trichlorosilane–triethylamine. Distillation gave 3.46 g (82.8%) of colorless liquid at 105–110° (12 mm); nmr ($CDCl_3$) δ 1.44 (d, $^2J_{PH}$ = 2.92 Hz, PCH_3 of cis isomer, 34%), 1.58 (d, $^2J_{PH}$ = 2.80 Hz, PCH_3 of trans isomer, 66%), 1.79–2.92 (complex m, ring CH_2), 2.44 and 2.45 (s, CH_3CO), 5.84 (m, OCH); ir (neat) $\nu_{C=O}$ 1740, ν_{CO} 1240 cm^{-1}. Various attempts to form quaternary salts for analysis of the isomer mixture have so far given only intractable oils.

Registry No.—1, 49849-35-6; 2, 21229-61-8; 3a, 51015-54-4; 3b, 51015-55-5; 3 methiodide, 51015-53-3; 4a, 51015-58-8; 4b, 51015-59-9; 5a, 51015-60-2; 5b, 51015-61-3; 6a, 51015-62-4; 6b, 51015-63-5.

References and Notes

(1) Taken from the Ph.D. Dissertation of R. C. Stocks, 1973. Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute. The National Science Foundation provided funds toward the purchase of the Bruker spectrometer (Grant No. GP 10301).
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The Stereochemical Elucidation of the Birch Reduction Product of [2.2]Paracyclophane[1a]

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The tetrahydro Birch reduction product of [2.2]paracyclophane is shown to be the *dl* stereoisomer (**2b**), with the olefins of the upper deck only partially overlapping with the olefins of the lower deck. This stereochemical elucidation is accomplished primarily by means of a complete proton nmr analysis of the tetraepoxide derivative **3**. The *dl* stereochemistry is in agreement with CNDO calculations performed on likely carbanion intermediates.

It has been recently shown[2,3] that the Birch reduction of [2.2]paracyclophane (1) gives the tetrahydro product **2** in which reduction has gone 2,5 in each deck. Although the structure elucidation of each deck of **2** was straightforward,[2,3] it was not possible to establish the overall stereochemistry of **2**, *i.e.*, whether the product was meso (**2a**) with each olefin in the upper deck overlying a corresponding olefin in the lower deck, or was *dl* (**2b**) with the olefins