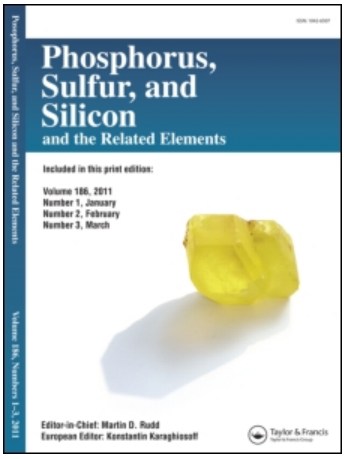

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BASE-PROMOTED REARRANGEMENT OF EPOXIDES IN THE 2- AND 3-PHOSPHABICYCLO[3.3.0]HEPTANE SYSTEMS[1]

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BASE-PROMOTED REARRANGEMENT OF EPOXIDES IN THE 2- AND 3-PHOSPHABICYCLO[3.3.0]HEPTANE SYSTEMS[1]

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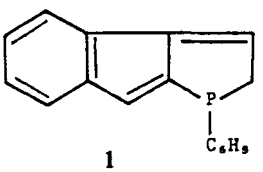
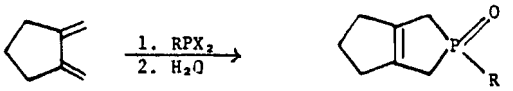
Unsaturated alcohols were formed by the base-catalyzed rearrangement of epoxides of saturated cyclopentaphosphole derivatives. Reaction of the 3a,6a-epoxide of the cyclopenta[*c*]phosphole with cyclohexylamine gave a mixture of the two possible alcohols. The 3a,6a-epoxide of the cylopenta[*b*]phosphole at $-50°$ with n-butyllithium gave only the 3a-hydroxy product, with the double bond in the cyclopentane ring (6,6a), but at higher temperatures migration of the double bond to the 5,6-position occurred. All compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic measurements.

Aromatic character is retained on replacement of a carbanionic center of the pentalenyl dianion with a heteroatom containing a lone pair of electrons. To the present, phosphorus has not been included among the several heteroatoms employed in these anions,[2] although it is not unreasonable to expect this atom also to participate in the delocalization phenomenon. Many of the properties of phospholes suggest phosphorus to be able to provide two electrons to the establishment of a six π-electron system,[3] and the creation of ten π-electron systems is a definite possibility, now being studied in this laboratory.[4] Along with these efforts, we have initiated a program to synthesize derivatives of the rare cyclopenta[*b*]- and cyclopenta[*c*]phosphole systems, possibly suitable for later conversion to phosphapentalenyl anions. The construction of a benzo derivative (**1**) of the cyclopenta[*b*]phosphole system was recently described,[5] and in this paper are reported a number of functionalized derivatives of the parent bicyclic systems.

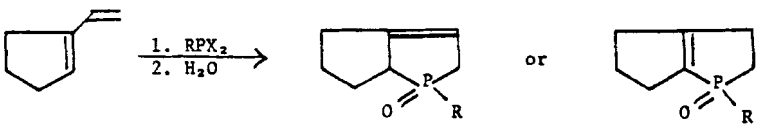


1

Previous work in this laboratory[6,7] has provided a background for further studies in the cyclopentaphosphole systems. It was first discovered[6] that 1,2-dimethylenecyclopentane readily underwent the McCormack cycloaddition with trivalent phosphorus halides to form cyclopenta[*c*]phosphole derivatives (**2**), and later[7] that 1-vinylcyclopentene in the same reaction provided the cyclopenta[*b*]phosphole system (**3** and **4**).

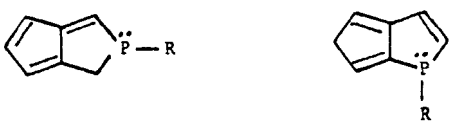


2 R = CH_3
3 R = C_6H_5



4 R = CH_3 5

It was also reported[7] that epoxides could be readily formed from these bicyclic phospholene oxides, and in the present paper we describe our results on the rearrangement of these epoxides with amines or amide ions to form unsaturated alcohols. Such rearrangements were first reported by Arbusov *et al.*,[8] for monocyclic epoxyphospholane oxides; the bicyclic derivatives were later reported[7] also to undergo the rearrangement. The new unsaturated alcohols in the cyclopentaphosphole systems may be considered to have potential as intermediates for the creation of phosphapentalene derivatives such as **6** and **7** (or other tautomeric forms).

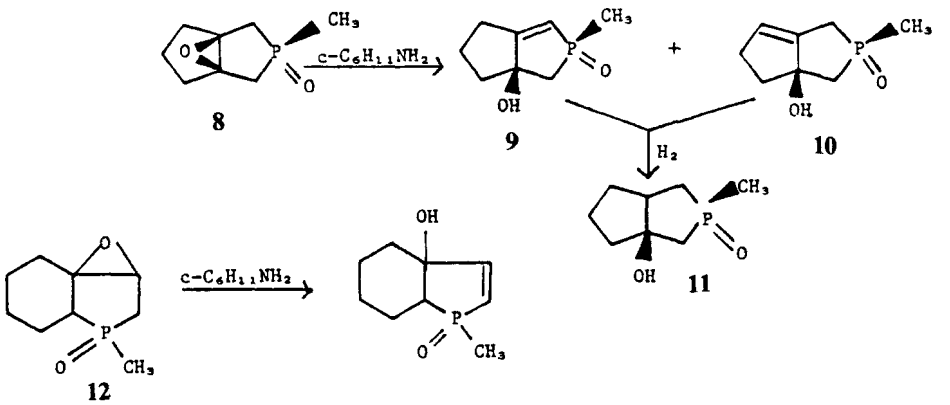


6 **7**

The Cyclopenta[c]phosphole System.

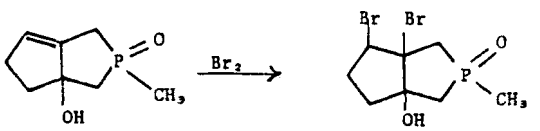
The previously reported[7] epoxide (**8**) of bicyclic phospholene oxide **2** was found to be inert to triethylamine or diazabicycloundecene (DBU), but underwent the desired rearrangement (86% yield) on heating with cyclohexylamine. This amine had previously been used to effect the rearrangement of **12**, also a 3,4-epoxyphospholane derivative; in that case, as well as the present, the rearrangement was the exclusive reaction occurring. Opening of the epoxide ring to form an amino alcohol is apparently retarded by the steric congestion at the oxygen-substituted carbons. However, spectral examination of the product from the cyclopenta derivative **8** did show that a mixture of isomeric alcohols had been formed.

Thus, in the ^{13}C NMR spectrum there were two doublets in the region expected for the carbon of a tertiary alcohol (δ 84.30, J_{PC} = 10.6 Hz, and 88.85, J_{PC} = 4.8), and there were two doublets in the characteristic upfield region for P—CH_3 groups (δ 19.43, J_{PC} = 60.5, and δ 19.82, J_{PC} = 63.3 Hz). The isomers differed markedly in the sp^2 carbon region. One of them clearly possessed the double bond in conjugation



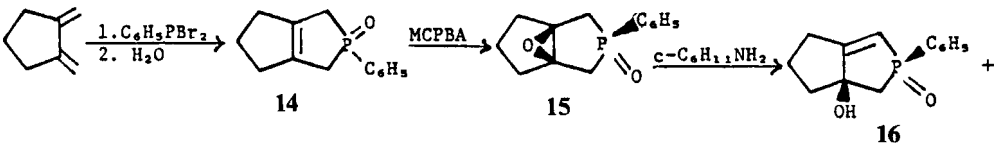
with phosphoryl, since it displayed a signal in the expected downfield region (δ 171.56, J_{PC} = 20.5 Hz). The carbon attached to P was easily recognized at δ 116.66 from its large coupling constant (94.5 Hz). This isomer is therefore assigned structure **9**, which is the expected product of the reaction. The other isomer is assigned structure **10**; its sp^2 carbon signals occurred at δ 127.31 (J = 10.6) and δ 143.29 (J = 8.8). The latter shift arises from the carbon common to the two rings. The ^{1}H NMR spectra in the olefinic proton region showed the expected doublet (δ 5.71, J = 26 Hz) for the proton located at the α-carbon of **9**, with the singlet for the proton of **10** overlapping at δ 5.54. The isomer composition was dependent on the reaction conditions, but generally **9** was in excess. To prove that the two reaction products differed only in the location of the double bond, the mixture was hydrogenated, whereupon a single saturated product was obtained that had the spectral features for **11**.

The mixture of **9** and **10** was very hygroscopic and could not be crystallized; attempts to separate the mixture by chromatographic techniques were also unsuccessful. However, a valuable reactivity difference existed between the isomers; **10** was much more reactive to bromine than was **9**, and when the isomer mixture was treated with 0.5 equivalent of bromine, only the dibromide **13**, a white solid, was obtained. It was insoluble in acetone, which allowed separation from the soluble, unreacted alcohol **9**. The crude **9** has still defied crystallization attempts, however. Compound **13** is potentially of value in the synthesis of a phosphapentalene, although its chemistry has not yet been studied.

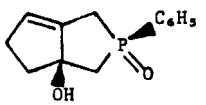


Very similar results were obtained with the P-phenyl derivatives. The starting bicyclic phospholene oxide (**14**) was obtained in the usual way[6] from 1,2-dimethylenecyclopentane and phenylphosphonous dibromide, although the yield was poor (14% after hydrolysis of the cycloadduct formed after 14 days). Epoxidation,

however, proceeded smoothly to form a single diastereoisomer, presumably[7] of structure **15**, in 81% yield. This product was isomerized by cyclohexylamine to give a mixture of alcohols **16** (slightly in excess) and **17** in 84% yield.

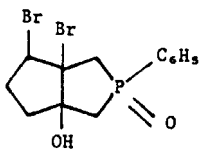


14 **15** **16**



17

As found for the P-methyl system, there were two olefinic proton signals in the NMR spectrum; isomer **16** provided a doublet (J_{PH} = 23 Hz) at δ 5.73 while **17** provided an unresolved multiplet at δ 5.66. In addition, the two isomers gave well-separated ^{31}P signals (δ +65.8 and +74.2). The difference in reactivity of the isomers towards bromine was of value in the separation of the mixture. Treatment with 0.5 equivalent of bromine caused only a reaction with the isomer **17** with the cyclopentene structure. This reaction product **18** proved to be readily soluble in acetone, while the unreacted isomer **16** crystallized on cooling the solution. It was recovered in analytically pure form after one recrystallization from hot acetone.

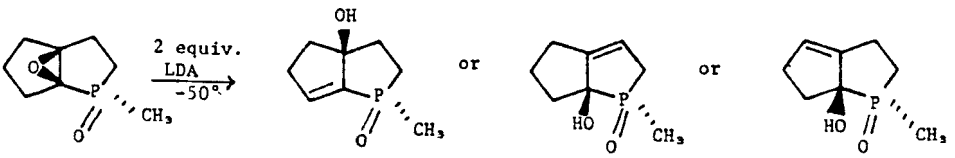


18

The Cyclopenta[b]phosphole System.

The starting material for these studies was the known[7] epoxide **19**. The best conditions for effecting its rearrangement to an allylic alcohol consisted of reaction at −55° with two equivalents of lithium diethylamide, a reagent preferred for rearrangement of cyclohexene oxides.[9] After the mixture was quenched with water, an oily solid could be isolated by extraction with chloroform. The solid was recrystallized from acetone, which provided the product in 49% yield. The product was established as an unsaturated alcohol from its ^1H NMR spectrum, which contained an exchangeable hydroxyl proton at δ 3.46, and a 1H multiplet in the olefinic region (δ 6.5–6.6). The ^{31}P NMR signal was at relatively high field (δ +34.6) for a phospholane derivative, which commonly would have a shift of +60 or more. However, recent work[5] has shown that an exocyclic double bond at the α-position is associated with strong upfield shifting, and that a 5-membered ring fused to the phospholane ring also causes an upfield shift. The value observed for

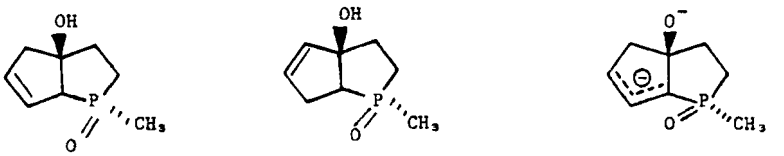
the allylic alcohol is then entirely consistent with structure **20**, where both effects are operative.



19 **20** **21** **22**

The ^{13}C NMR spectrum conclusively supported this structure; the carbinol carbon (δ 91.95) had a coupling constant to ^{31}P of 28.1 Hz, which is too small for the one-bond value expected from **21** or **22**. However, one olefinic carbon (δ 145.28) did possess the large coupling (100 Hz) for direct connection to ^{31}P required by **20**.

When the reaction with two equivalents of LDA was conducted at room temperature, a mixture of two isomers was obtained. One isomer gave the spectral characteristics of **20**. The characteristics of the other did not fit either **21** or **22**. The carbinol carbon at δ 87.10 had a coupling constant to ^{31}P (14.6 Hz) which was again too small for this carbon to be attached directly to phosphorus. Also, there were two olefinic carbons that had small couplings to ^{31}P (δ 125.75, J = 6.75 and δ 131.85, J = 10.4). These data imply that a further rearrangement of **20** has occurred, giving the homoallylic structure **23**. Another possible structure that fits the available data is **24**; while this cannot be eliminated at present, it is certainly a less likely structure. At higher temperature (refluxing THF), the rearrangement was complete. Rearrangements of allylic alcohols in the carbocyclic series are not unknown;[9] they are promoted by the presence of excess base in the reaction mixture which abstracts a proton from the allylic position. The ease with which the present rearrangement occurs may be attributed to the stabilization of the allylic ion (**25**) provided by the phosphoryl group.



23 **24** **25**

In the reaction of epoxide **19** with base, the first equivalent appears to act only to remove a proton, for quenching with water of the solution returned only the starting material. Quenching with D_2O instead of H_2O gave a product with greatly reduced intensity for the ^1H NMR signal of the P—CH_3 group, and this is presumably the site of proton abstraction.

EXPERIMENTAL[10]

Reaction of Epoxide **8** *with Cyclohexylamine.* A solution of 3.60 g (0.021 mol) of epoxide **8** in 60 ml of cyclohexylamine was refluxed for 12 h. The amine was stripped off under vacuum, leaving a dark brown

oil. Trituration with ether gave 3.10 g (86%) of tan solid, which was an approximately 2 : 1 mixture of 2,3,3a,4,5,6-hexahydro-3a-hydroxy-2-methylcyclopenta[*c*]phosphole 2-oxide (**9**) and 1,2,3,3a,4,5-hexahydro-3a-hydroxy-2-methylcyclopenta[*c*]phosphole 2-oxide (**10**); ^{1}H NMR ($CDCl_3$) δ 1.75 (d, $^2J_{PH}$ = 14 Hz, P—CH_3 of **11**), 1.79 (d, $^2J_{PH}$ = 14 Hz, P—CH_3 of **10**), 1.60–2.90 (m, —CH_2—), 4.40 and 4.95 (both s, —OH), 5.54 (m, C=C<u>H</u>— of **11**), 5.71 (d, $^2J_{PH}$ = 26 Hz, P—C<u>H</u>=C of **10**); IR ($CHCl_3$) ν_{OH} 3280 cm^{-1}; ^{13}C NMR, Table I.

3a-Hydroxy-2-methyloctahydrocyclopenta[c]phosphole 2-Oxide (**12**). A solution of 0.20 g (0.001 mol) of the mixture of isomers **10** and **11** in 30 ml of methanol was placed in a Parr bottle with 125 mg of rhodium on alumina. The mixture was treated with hydrogen at 50 psi for 16 h. The solution was filtered and then concentrated to a yellow oil, which slowly solidified. The material was recrystallized from tetrahydrofuran to provide 0.18 g (90%) of white plates; mp 106°C; ^{1}H NMR ($CDCl_3$) δ 1.71 (d, $^2J_{PH}$ = 13 Hz, P—CH_3), 1.88–2.30 (m, —CH_2—), 4.10 ppm (broad s, —OH); ^{13}C NMR, Table I.

Anal. Calcd for $C_8H_{13}OP$: C, 55.20; H, 8.62; P, 17.79. Found: C, 54.86; H, 8.63; P, 17.79.

3a,4-Dibromo-6a-hydroxy-2-methyloctahydrocyclopenta[c]phosphole 2-Oxide (**13**). A solution of 1.12 g (0.0065 mol) of the mixture of isomers **10** and **11** in 50 ml of chloroform was cooled at 0°C under nitrogen. To the solution was added 0.56 g (0.0035 mol) of bromine over a 5-min period. Most of the bromine color disappeared immediately, leaving a light yellow solution. The reaction mixture was stirred at 0°C for 90 min before it was washed with a 20 ml aliquot of saturated sodium thiosulfate solution. The chloroform solution was dried ($MgSO_4$) and then concentrated to a red oil which was triturated with acetone to produce a white solid and a red supernatant solution. The solid was isolated by filtration and identified as the dibromide **13**. It was recrystallized from acetone to provide 0.70 g (0.0021 mol) of white plates, mp 175°C (dec). The low solubility prevented analysis by NMR spectroscopy; IR (KBr) ν_{OH} 3210, $\nu_{P=O}$ 1170 cm^{-1}; mass spectrum, m/e 332 (M^+), 251, 170.

Anal. Calcd for $C_8H_{13}Br_2O_2P$: C, 28.95; H, 3.92; Br, 48.15; P, 9.33. Found: C, 28.83; H, 3.57; Br, 48.26; P, 9.53.

The red supernatant solution was stripped to leave an oil whose ^{1}H NMR spectrum was that of crude **9**.

1,2,3,4,5,6-Hexahydro-2-phenylcyclopenta[c]phosphole 2-Oxide (**14**). A solution of 8.60 g (0.091 mol) of 1,2-dimethylenecyclopentane[6] in 150 ml of hexane was placed in a wide-neck, brown jar. To the solution was added 0.20 g of copper stearate and 24.5 g (0.091 mol) of phenylphosphonous dibromide. The bottle was flushed with nitrogen and sealed. Adduct formation commenced immediately upon mixing of the reagents; the reaction mixture was allowed to stand at room temperature for 14 days. The solid adduct was filtered and crushed in pentane. It was then stirred into 100 g of crushed ice and the resulting aqueous slurry was neutralized with 100 ml of saturated aqueous bicarbonate solution. The aqueous mixture was then extracted with four 125-ml aliquots of chloroform and the extracts were dried ($MgSO_4$) and concentrated to give an off-white solid. This material was extremely hygroscopic and bulb-to-bulb distillation was used for purification, providing 2.70 g (14%) of **14**.

An analytical sample was prepared by sublimation of the distilled material; mp 72°C; ^{1}H NMR ($CDCl_3$) δ 2.04–2.39 (m, —CH_2—), 2.64–2.74 (m, P—<u>CH_2</u>—C=C), 7.36–7.78 ppm (m, aromatic); ^{31}P and ^{13}C NMR Table I.

Anal. Calcd for $C_{13}H_{15}OP$: C, 71.59; H, 6.88; P, 14.42. Found: C, 71.31; H, 7.03; P, 14.20.

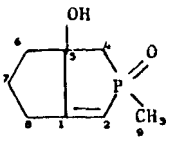
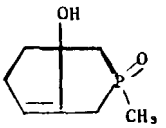
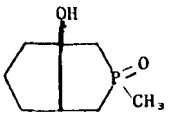
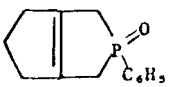
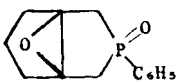
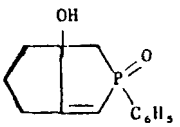
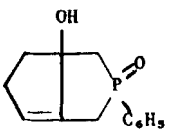
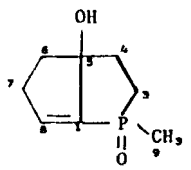
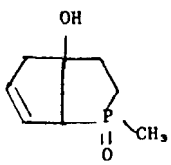
1,5-Epoxy-3-phenyl-3-phosphabicyclo[3.3.0]octane 3-Oxide (**15**). A solution of 2.40 g (0.011 mol) of **14** and 2.38 g (0.011 mol) of 85% *m*-chloroperoxybenzoic acid in 50 ml of methylene chloride was heated at reflux for 42 h. The reaction mixture was then cooled and treated with 25 ml of saturated aqueous bicarbonate solution and then 4.00 g of solid sodium bicarbonate. The mixture was stirred for 1 h and the layers then separated. The aqueous layer was extracted with three 15-ml portions of methylene chloride. Organic layers were combined, dried ($MgSO_4$) and concentrated to a brown oil which quickly solidified. The material was purified by bulb-to-bulb distillation to provide 2.10 g (81%) of **15**, a hygroscopic white solid; bp 110°C (0.05 mm); ^{1}H NMR ($CDCl_3$) δ 1.65–2.70 (m, —CH_2—), 7.40–7.93 (m, aromatic); ^{31}P and ^{13}C NMR Table I.

Anal. Calcd for $C_{13}H_{15}O_2P$: C, 66.61; H, 6.41; P, 13.23. Found: C, 66.41; H, 6.64; P, 13.50.

Reaction of Epoxide **15** *with Cyclohexylamine.* A solution of 1.90 g (0.0081 mol) of **15** in 30 ml of cyclohexylamine was refluxed for 24 h. The amine was stripped off under a vacuum, leaving a brown oily solid. Trituration with ether provided 1.60 g (84%) of white solid, consisting of a 3 : 2 mixture 2,3,3a,4,5,6-hexahydro-3a-hydroxy-2-phenylcyclopenta[*c*]phosphole 2-oxide (**16**) and 1,2,3,3a,4,5-hexahydro-3a-hydroxy-2-phenylcyclopenta[*c*]phosphole 2-oxide (**17**); ^{1}H NMR ($CDCl_3$) δ 1.68–2.82 (m, —CH_2—), 4.72 (broad s, —OH), 5.66 (m, C=C<u>H</u>, **17**), 5.73 (d, $^2J_{PH}$ = 23 Hz, P—C<u>H</u>=C, **16**), 7.36–8.04 ppm (m, aromatic); ^{31}P NMR ($CDCl_3$) δ +65.8 (**17**), +74.2 (**16**); ^{13}C NMR Table I.

TABLE I

^{31}P and ^{13}C NMR spectra of cyclopentaphosphole derivatives[a]

	No.	δ ^{31}P	C-1	C-2 or C-3	C-4	C-5	C-6	C-7	C-8	C-9
	**9**[b]	+79.9	171.67 (20.5)	116.66 (94.5)	c	84.30 (10.6)	c	c	c	19.43[d] (60.5)
	**10**[b]	+76.2	143.29 (8.8)	c	c	88.85 (4.8)	c	c	127.31 (10.6)	18.91[d] (62.5)
	**11**		43.37 (6.9)	33.56 (62.3)	40.41 (64.4)	85.50 (11.7)	41.29 (8.7)	22.74	43.37 (6.9)	17.65 (61.5)
	**14**	+66.5	131.15 (9.8)	33.73 (66.0)	33.73 (66.0)	131.15 (9.8)	32.53 (9.2)	24.21	32.53 (9.2)	
	**15**	+76.0	71.27 (4.2)	34.05 (64.7)	34.05 (64.7)	71.27 (4.2)	29.23 (7.4)	22.83	29.33 (7.4)	
	**16**	+73.4	175.0 (28.1)	116.37 (96.6)	42.31 (66.5)	85.28 (11.9)	40.36 (7.8)	22.92	26.49 (13.7)	
	**17**[c]	+65.8	143.75 (4.95)	30.41 (65.3)	45.45 (67.2)	89.39 (4.95)	c	c	136.49 (4.2)	
	**20**	+34.6	145.28 (100)	30.09 (71.4)	c	91.95 (28.1)	35.65	c	143.04 (9.2)	19.08 (69.6)
	**23**	+54.4	56.25 (67.8)	27.83 (61.7)	35.02 (6.8)	87.19 (14.6)	48.16 (2.1)	131.85[f] (10.4)	125.75[f] (6.8)	16.66 (61.7)

[a] Numbering for the [*c*] series follows that shown for **9**; for the [*b*] series, **20**. Conditions for preparing the spectra are given in ref. 10.

[b] Spectra obtained for a mixture of **9** and **10**.

[c] Overlapping of signals prevented firm assignments.

[d] May be reversed.

[e] Spectra obtained for a mixture of **16** and **17**.

[f] May be reversed.

Isolation of 2,3,3a,4,5,6-Hexahydro-3a-hydroxy-2-phenylcyclopenta[c]phosphole 2-Oxide (**16**). A solution of 1.60 g (0.0068 mol) of a mixture of isomers **16** and **17** in 100 ml of chloroform was cooled to 0°C and treated with 0.55 g (0.0034 mol) of bromine. The mixture was stirred at 0°C for 90 min before it was washed with two 25-ml aliquots of saturated thiosulfate and 25 ml of saturated sodium chloride. The chloroform solution was dried ($MgSO_4$) and concentrated to a dark red oil. The oil was taken up in acetone, and upon cooling the solution, a white solid crystallized. The solid was isolated by filtration and recrystallized from acetone to give 0.60 g of white plates. This represented a 38% recovery of the allylic alcohol **16** from the mixture, and a 32% overall yield from the epoxide **15**; mp 179–181°C; ^{1}H NMR ($CDCl_3$) δ 1.93–2.72 (m, $-CH_2-$), 3.47 (broad s, —OH), 5.76 (d, $^2J_{PH}$ = 23 Hz, P—CH=C), 7.35–8.03 ppm (m, aromatic); ^{31}P and ^{13}C NMR Table I.

Anal. Calcd for $C_{13}H_{15}O_2P$: C, 66.61; H, 6.41; P, 13.23. Found: C, 66.96; H, 6.56; P, 13.18.

Reaction of Epoxide **19** *with Lithium Diethylamide.* (a) To a solution of 1.83 g (0.025 mol) of diethylamine in 10 ml of tetrahydrofuran was added 11 ml of 2.4 M *n*-butyllithium (0.025 mol) over a 5-min period. The solution was stirred at 25°C for 10 min before a solution of 1.70 g (0.010 mol) of epoxide **19** in 5 ml of tetrahydrofuran was added. The addition of the epoxide was accompanied by a vigorous reaction and the formation of a tan solid. The reaction mixture was stirred at room temperature for 3 h and then it was poured into 10 ml of ice water. The aqueous and organic layers were separated and the aqueous layer was extracted with three 5-ml portions of chloroform. The organic solutions were combined and dried ($MgSO_4$) before concentration to a brown oil. Trituration with ether produced 1.0 g (58%) of tan solid which was recrystallized from acetone to provide a mixture of **20** and **23**; mp 131–133°C; ^{1}H NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 13 Hz, P—CH_3), 1.78 (d, $^2J_{PH}$ = 14 Hz, P—CH_3), 1.89–2.97 (m, $-CH_2-$), 5.29 (broad s, —OH), 5.60–5.80 (m, —CH=CH of **23**), 6.48–6.58 (m, P—C=CH— of **20**); ^{31}P NMR ($CDCl_3$) δ +53.4 (**23**), +34.6 (**20**); IR ν_{OH} 3300, $\nu_{C=C}$ 1630 cm^{-1}; ^{13}C NMR Table I.

Anal. Calcd for $C_8H_{13}O_2P$: P, 18.02. Found: P, 18.16.

(b) To reduce the concentration of isomer **20** in the mixture, a solution of 0.90 g (0.0052 mol) of the product from the preceding experiment in 60 ml of THF was stirred with a mixture of 0.95 g (0.013 mol) of diethylamine in 10 ml of THF and 6 ml of 2.2 M *n*-butyllithium (0.013 mol) for 10 min, and then the solution was refluxed for 24 h. It was then poured onto 25 g of crushed ice; the layers were separated and the aqueous layer extracted with three 10-ml portions of chloroform. The organic layers were combined, dried over $MgSO_4$, and concentrated to an oil. This material was triturated with ether to give 0.70 g (74%) of crude **23** whose spectral properties matched those observed in the **20–23** mixture: ^{1}H NMR ($CDCl_3$) δ 1.68 (d, $^2J_{PH}$ = 13 Hz, P—CH_3), 1.20–3.00 (m, $-CH_2-$), 5.72 ppm (broad s, —OH); ^{31}P and ^{13}C NMR, Table I.

(c) To obtain **20**, the rearrangement of **19** was carried out at lower temperature. To a solution of 2.98 g (0.0407 mol) of diethylamine in 20 ml of tetrahydrofuran was added 22.6 ml of 2.4 M *n*-butyllithium (0.0407 mol) over a 10-min period. The mixture was stirred at room temperature for an additional 20 min before it was cooled to −55°C. A solution of 3.50 g (0.0204 mol) of epoxide **19**[7] in 20 ml of tetrahydrofuran was added over a 10-min period. The reaction mixture was stirred vigorously while the temperature was maintained between −45° and −55°C for 1 h. The mixture was then allowed to warm to −5°C over a 2.5 h period; it was cooled to −30°C and quenched with a mixture of 15 ml of tetrahydrofuran and 15 ml of water. The reaction mixture was then warmed to room temperature, the aqueous and organic layers were separated, and the aqueous layer was continuously extracted with chloroform. The extract and the reaction mixture were combined, dried ($MgSO_4$) and concentrated to a yellow, oily solid. The material was readily triturated with ether to a white solid. The solid was recrystallized from acetone to give 1.70 g (49%) of **20** as white plates; mp 132–133°C; ^{1}H NMR ($CDCl_3$) δ 1.78 (d, $^2J_{PH}$ = 14 Hz, P—CH_3), 1.96–3.00 (m, $-CH_2-$), 3.46 (broad s, —OH), 6.52–6.63 (m, P—C=CH—); ^{31}P and ^{13}C NMR, Table I.

REFERENCES

1. Supported by National Science Foundation Grant CHE 7717876. Taken from the Doctoral Dissertation of H. F. Lawson, Duke University, 1980.
2. H. Volz and H. Kowarsch, *Tetrahedron Lett.*, 4375 (1976).
3. For recent reviews, see (a) F. Mathey, "Topics in Phosphorus Chemistry," Vol. 10, M. Grayson and E. J. Griffith, Eds., John Wiley, New York (1980), Chapt. 1; (b) A. N. Hughes, "New Trends in Heterocyclic Chemistry," R. B. Mitra, N. R. Ayyangar, V. N. Gogte, R. M. Acheson and N. Cromwell, Eds., Elsevier, Amsterdam (1979), p. 216; (c) L. D. Quin, "The Heterocyclic Chemistry of Phosphorus," Wiley-Interscience, New York (1981), pp. 406–414.

4. L. D. Quin, E. D. Middlemas and N. S. Rao, *J. Org. Chem.*, **47**, 905 (1982).
5. L. D. Quin, A. N. Hughes, H. F. Lawson and A. L. Good, *Tetrahedron*, in press.
6. E. D. Middlemas and L. D. Quin, *J. Am. Chem. Soc.*, **99**, 8370 (1977).
7. L. D. Quin, C. Symmes, Jr., E. D. Middlemas and H. F. Lawson, *J. Org. Chem.*, **45**, 4688 (1980).
8. B. A. Arbusov, A. P. Rakov and A. O. Vizel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 85 (1970).
9. B. Rickborn and C. L. Kissell, *J. Org. Chem.*, **37**, 2060 (1972).
10. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. All manipulations of cycloadducts were conducted in a glovebag with N_2. Spectra were taken as follows: ^1H, JEOL MH-100 spectrometer, internal Me_4Si reference, $CDCl_3$ solutions; ^{31}P, Bruker HFX-10 at 36.43 MHz, FT proton decoupled, 85% H_3PO_4 external reference with positive values downfield and negative values upfield, $CDCl_3$ solutions; ^{13}C, JEOL FX-60 at 15.0 MHz, FT proton decoupled, internal Me_4Si as reference in $CDCl_3$ solutions as lock.