Experimental Section

^1H NMR spectra are at 360 MHz (FT) in $CDCl_3$ solution and ^{13}C NMR spectra at 50 MHz on a Bruker SY 200 instrument. The NOE experiments were carried out by FT NOE difference spectroscopy with previously degassed samples.

Alkaloid Extraction and Purification. *L. oblonga* (Miers) Hook. f. & Thoms. was collected in Malaysia, in Jerantut (Pahang), by one of us (B.D.). Vouchers have been preserved at the Bogor Herbarium in Indonesia and at the Museum National d'Histoire Naturelle (Paris) (no. KL 292). Ground stem barks (10 kg) were first extracted with petroleum ether. After drying, the powder was basified with NH_4OH and extracted by methylene chloride using a Soxhlet apparatus. The organic solution was concentrated and extracted with dilute hydrochloric acid. The aqueous solution was basified and reextracted with methylene chloride to furnish 18.6 g of crude alkaloids.

An initial separation was achieved on a Sephadex LH20 column using $CHCl_3$–CH_3OH (30:70) as eluent. Four fractions were collected. (+)-Clolimalongine (1) and (+)-limalongine (2) were abundant in the two first fractions. Further separations were realized by column chromatography, and preparative TLC on Kieselgel 60 Merck article no. 7734, using C_6H_6–$CHCl_3$–CH_3OH (30:60:10) in an NH_3-saturated tank, furnished 1.2 g of 1 and 0.2 g of 2. Purification of the following fractions led to the isolation of (+)-stepharine (0.9 g), lysicamine (4.5 g), homomoschatoline (5.0 g), imenine (0.3 g), and splendidine (0.1 g).

(+)-Clolimalongine (1): $[\alpha]_D$ +300° (c = 0.1, $CHCl_3$); EIMS, m/z (relative intensity) 369 [$(M + 2)^+$, 1.4], 367 (M^+, $C_{18}H_{22}NO_5Cl$, 4), 332 (18), 304 (6), 196 (12), 195 (100), 194 (20), 152 (30); HR EIMS, m/z 367.1164 ($C_{18}H_{22}NO_5Cl$, calcd 367.1187), 332.1536 ($C_{18}H_{12}NO_5$, calcd 332.1498), 304.1557 ($C_{17}H_{22}NO_4$, calcd 304.1750), 208.0998 ($C_{11}H_{14}NO_3$, calcd 208.0974), 196.0923 ($C_{10}H_{14}NO_3$, calcd 196.0973), 195.0873 ($C_{10}H_{13}NO_3$, calcd 194.0799), 152.0698 ($C_8H_{10}NO_2$, calcd 152.0712); UV (MeOH) λ_{max} 265 (log ϵ = 4.10); IR (KBr) (cm^{-1}) 2920, 1715, 1660, 1620, 1450, 1320, 1300, 940, 820; ^1H NMR and ^{13}C NMR (see around structure 1).

Principal NOEs were H-14 (δ 1.97) to H-14 (δ 1.61) (9.8%), H-14 (δ 1.61) to H-14 (δ 1.97) (9.8%), H-5 (δ 2.19) to H-14 (δ 1.61) (3%), H-14 (δ 1.61) to H-5 (δ 2.19) (3%), H-14 (δ 1.61) to H-15 (δ 2.85) (4%), H-15 (δ 2.85) to H-14 (δ 1.61) (3%), H-14 (δ 1.97) to H-15 (δ 3.05) (1.5%), H-14 (δ 1.97) to H-10 (2.9%), H-10 to H-14 (δ 1.97) (2.7%), H-5 (δ 2.36) to H-5 (δ 2.19) (4.4%), H-5 (δ 2.19) to H-5 (δ 2.36) (2.2%), H-9 (δ 2.80) to H-9 (δ 2.46) (8.8%), H-9 (δ 2.46) to H-9 (δ 2.80) (7.3%), H-9 (δ 2.46) to H-10 (2%), H-10 to H-9 (δ 2.46) (2%), H-1 to H-2 (9%), H-2 to H-1 (2.4%), H-9 (δ 2.80) to H-15 (δ 3.05) (2.5%), H-15 (δ 3.05) to H-9 (δ 2.80) (2.5%), H-15 (δ 2.85) to H-15 (δ 3.05) (5%), H-2 to OMe-3 (9.3%), OMe-3 to H-2 (8.8%).

(+)-Limalongine (2): $[\alpha]_D$ +290° (c = 0.15, $CHCl_3$); EIMS, m/z (relative intensity) 333 (M^+, 73), 332 (12), 318 (90), 305 (41), 304 (5), 290 (69), 289 (11), 262 (43), 260 (42), 234 (29), 195 (90), 194 (100), 167 (45), 152 (83), 134 (30); UV (MeOH) λ_{max} 265 (log ϵ = 3.95); IR (KBr) (cm^{-1}) 2920, 1715, 1660, 1620, 1450, 1320, 1300, 940; ^1H NMR and ^{13}C NMR (see around structure 2).

Principal NOE's were OMe-3 to H-2 (8%), H-2 to OMe-3 (9%), H-15 (δ 3.11) to H-15 (δ 2.89) (5%), H-15 (δ 2.89) to H-15 (δ 3.11) (5%), H-15 (δ 3.11) to H-9 (δ 2.09) (3%), H-9 (δ 2.09) to H-15 (δ 3.11) (2.5%), H-1 (δ 2.67) to H-1 (δ 2.46) (5%), H-1 (δ 2.46) to H-1 (δ 2.67) (7%), H-1 (δ 2.67) to H-2 (10%), H-2 to H-1 (δ 2.67) (9%), H-1 (δ 2.46) to H-2 (8%), H-5 (δ 2.19) to H-5 (δ 2.43) (3%), H-5 (δ 2.43) to H-5 (δ 2.19) (3%), H-5 (δ 2.19) to H-14 (δ 1.56) (4%), H-14 (δ 1.56) to H-5 (δ 2.19) (2.5%), H-10 (δ 1.89) to H-9 (δ 2.09) (2%), H-9 (δ 2.09) to H-10 (δ 1.89) (3%), H-10 (δ 2.10) to H-9 (δ 2.39) (3%), H-9 (δ 2.39) to H-10 (δ 2.10) (2%), H-14 (δ 2.02) to H-14 (δ 1.56) (10%), H-14 (δ 1.56) to H-14 (δ 2.02) (10%), H-14 (δ 2.02) to H-15 (δ 3.11) (5%), H-15 (δ 3.11) to H-14 (δ 2.02) (4%), H-10 (δ 1.89) to H-10 (δ 2.10) (5%), H-10 (δ 2.10) to H-10 (δ 1.89) (6%), H-14 (δ 2.02) to H-10 (δ 1.89) (3%), H-10 (δ 1.89) to H-14 (δ 2.02) (2.8%), H-14 (δ 1.56) to H-1 (δ 2.67) (2.5%), H-1 (δ 2.67) to H-14 (δ 1.56) (2.5%).

Acknowledgment. We are grateful to Professor M. Shamma (Pennsylvania State University) for helpful discussions of this work and Dr. A. J. Freyer (Pennsylvania State University) and Dr. T. Bêcue (SAMM, Faculté de Pharmacie, Châtenay-Malabry, France) for assistance in obtaining NMR and mass spectra.

(8) Cava, M. P.; Buck, K. T.; Noguchi, I.; Srinivasan, M.; Rao, M. G.; Da Rocha, A. I. *Tetrahedron* **1975**, *14*, 1667.

Synthesis and Nuclear Magnetic Resonance Spectroscopic Properties of Some 5,10-Dihydrophenophosphazine Derivatives

Janusz J. Skolimowski, Louis D. Quin,* and Alan N. Hughes

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received December 8, 1988

The 5,10-dihydrophenophosphazine ring system is easily constructed, and its derivatives were among the first heterocyclic phosphorus compounds to be synthesized. A recent review[1] of the chemistry of this ring system reveals that much of the fundamental work was performed some years ago, without significant use of the powerful techniques of ^{13}C and ^{31}P NMR spectroscopy. The only ^{13}C NMR spectral data reported were obtained for the 5,10-dimethyl derivative and its *P*-oxide.[2] The ^{31}P NMR spectra of the same compounds, as well as of the 2,8-dinitro derivative of the former, have been reported,[3] as have data for some thiophosphoryl derivatives[4] and a spirobisphenophosphazinium salt.[5]

In the present work, ^{13}C and ^{31}P NMR techniques were employed effectively in structural studies of the 5,10-dihydrophenophosphazine system. Some new reactions are reported where the spectroscopic properties of the products are used to prove their structure. Information on solution conformations of heterocyclic phosphorus compounds can be obtained with the aid of the stereospecificity in ^{13}C–^{31}P coupling constants,[6] and analysis of the ^{13}C NMR spectra of several derivatives with tricovalent P has provided the first indications of the conformational preferences at phosphorus for this ring system.

5,10-Dihydrophenophosphazine 10-oxide (2) (Scheme I) is the most important member of the family; it is easily synthesized by first reacting diphenylamine with phosphorus trichloride at 220 °C, followed by hydrolysis of the mixture with hot water. The 10-chloro derivative 1 has been proposed as the intermediate that is being hydrolyzed to the secondary phosphine oxide 2. This has been supported by the formation of tertiary phosphines when alkylmetallics are added to such reaction mixtures before hydrolysis,[7] but the phosphinous chloride 1 has never been directly observed in the medium. We have now accomplished this by examination of the reaction mixture with ^{31}P NMR before the hydrolysis. The only significant signal appeared at δ +59.8 (THF), which can be assigned to 1. Addition of *tert*-butyllithium in THF to the mixture resulted in disappearance of this signal and formation of the tertiary phosphine 3, with ^{31}P NMR δ −20.1 ($CDCl_3$). Proof

(1) Freedman, L. D.; Freeman, H. S. *Chem. Rev.* **1987**, *87*, 289.
(2) Negrebetskii, V. V. *Zh. Strukt. Khim.* **1979**, *20*, 459.
(3) Smirnov, A. N.; Yagodina, L. A.; Korolev, B. A.; Bokanov, A. I.; Stepanov, B. I. *Zh. Obshch. Khim.* **1977**, *47*, 2468.
(4) Rozanelskaya, N. A.; Bokanov, A. I.; Negrebetskii, V. V.; Stepanov, B. I. *Zh. Obshch. Khim.* **1981**, *51*, 2222.
(5) Jenkins, R. N.; Freedman, L. D.; Bordner, J. J. *J. Cryst. Mol. Struct.* **1973**, *3*, 103.
(6) Quin, L. D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Chapter 12.
(7) Hellwinkel, D.; Schenk, W.; Blaicher, W. *Chem. Ber.* **1978**, *111*, 1798. Freeman, H. S.; Freedman, L. D. *J. Org. Chem.* **1981**, *46*, 5373.

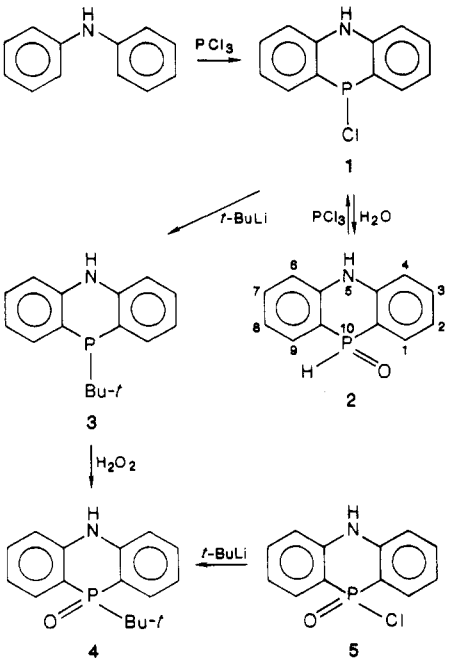
0022-3263/89/1954-3493$01.50/0

Table I. ^{13}C Nuclear Magnetic Resonance Data for 5,10-Dihydrophenophosphazine Derivatives[a]

compd	solvent	C-1,9	C-2,8	C-3,7	C-4,6	C-4a,5a	C-9a,10a
1	$CDCl_3$–PCl_3	135.2 (43.4)	121.2 (14.5)	132.8 (s)	116.1 (s)	140.7 (s)	115 (10)
2	DMSO-d_6 (76 °C)	131.7 (5.2)	120.3 (11.0)	132.9 (5.2)	116.7 (4.5)	142.4 (4.3)	110.6 (97.8)
2[b]	CF_3COOD	134.1 (10.4)	125.0 (17.6)	138.5 (s)	109.0 (s)	145.2 (7.2)	104.4 (159.6)
3[c]	$CDCl_3$	136.6 (36.7)	120.2 (12.6)	130.1 (s)	114.3 (s)	143.2 (2.9)	114.4 (11)
4[d]	DMSO-d_6	131.2 (4.5)	120.2 (9.7)	132.8 (s)	115.7 (6.9)	143.1 (4.6)	107.6 (91.4)
4	CF_3COOD	132.2 (4.3)	124.3 (10.8)	137.7 (s)	108.3 (s)	145.5 (5.3)	104.4 (141.1)
5	DMSO-d_6	128.6 (3.8)	119.6 (11.1)	131.8 (s)	116.2 (7.5)	142.8 (6.6)	104.0 (130.9)
6	$CDCl_3$	134.9 (39.1)	121.4 (13.3)	129.4 (s)	118.0 (s)	143.4 (s)	111.4 (2.7)
9[e]	$CDCl_3$	130.4 (6.3)	120.3 (10.7)	132.4 (s)	115.7 (7.8)	141.9 (5.0)	109.3 (98.4)

[a] Entries are δ_{TMS} (J_{PC}, Hz). Measurements at probe temperature unless otherwise noted to achieve solubilization. [b] Referenced to TFA C=O as 164.2. [c] For *tert*-butyl: P–C, 34.3 (17.1); CH_3, 26.2 (14.1). [d] For *tert*-butyl: P–C, 35.5 (79.7); CH_3, 22.7 (s). [e] P–CH_2, 42.6 (73.2); C_6H_5, 126.2 (3.9), 127.8 (3.5), 129.6 (6.2), 131.6 (7.5).

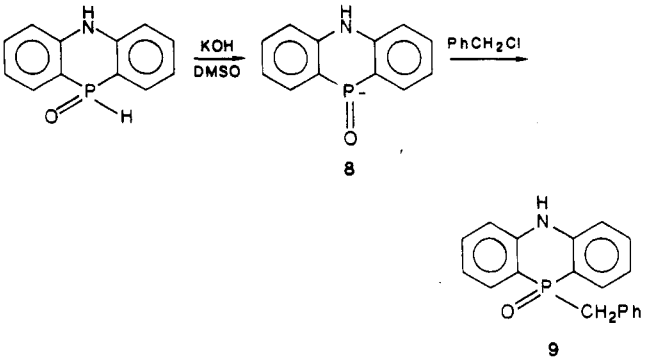
Scheme I



of the structure of **3** also came from its oxidation to phosphine oxide **4**, which was formed independently from the reaction of phosphinyl chloride **5**[8] with *tert*-butyllithium. Attempts to obtain phosphinous chloride **1** in pure form were not successful. The compound is of low stability, and unidentified yellow solids are precipitated during isolation procedures.

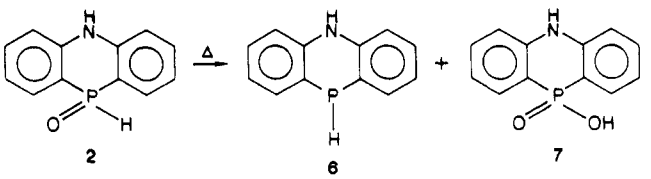
Compound **1** was also synthesized by another method, the reaction of oxide **2** with excess phosphorus trichloride at 10–15 °C. This is a reaction known to convert secondary phosphine oxides to phosphinous chlorides[9] but has never before been applied to this oxide. The reaction product had a ^{31}P NMR signal at δ +60.1 (THF), in agreement with the value for the diphenylamine–PCl_3 reaction intermediate. The development of a simple method for converting the oxide to the chloride could have considerable practical significance, since the chloride would provide access to many valuable derivatives. Due to the instability of the chloride, reactions are preferably performed rapidly on the crude product remaining from vacuum stripping of volatiles (PCl_3, $POCl_3$, and HCl). The ^{13}C NMR spectrum (Table I) was obtained on the crude product and showed the expected differences from that of the oxide **2**. Thus, the large coupling constant (97.8 Hz) observed for $^1J_{PC}$ in the oxide (Table I) was replaced by a smaller value (10 Hz) as expected for a tricovalent derivative. In the ^{31}P NMR

Scheme II



spectrum with proton coupling, the large one-bond PH coupling of 517 Hz observed in the oxide **2** was absent.

A well-known reaction of phosphorus chemistry that appears never to have been performed on oxide **2** is the disproportionation to the phosphine and phosphinic acid.[10] A recent innovation is catalysis by a small amount of CCl_4.[11] The secondary phosphine **6** expected from this reaction with **2** is unknown. We have performed the disproportionation by mixing oxide **2** with CCl_4 and heating in a Kugelrohr apparatus at 200 °C and 0.05 mm, whereupon secondary phosphine **6** sublimed and was collected in quite high purity as seen on ^{31}P and ^{13}C NMR analysis. The yield was 38%. The phosphine, as expected, is highly reactive to oxygen and difficult to preserve. Its structure was conclusively proved, however, by ^{31}P NMR, which gave a signal at δ −105.4 ($CDCl_3$). When P–H coupling was allowed, the signal was split to a doublet with $^1J_{PH}$ = 195.4 Hz. Oxidation of the phosphine with *tert*-butyl hydroperoxide gave the known[8] phosphinic acid **7**.



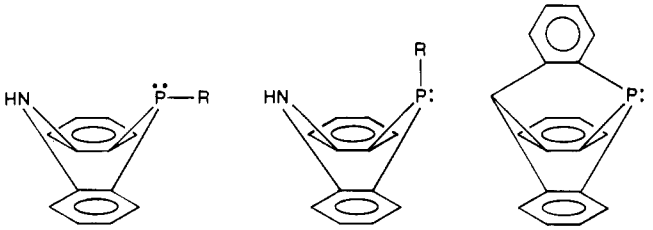
The literature[1] contains several references to syntheses starting with secondary phosphine oxide **2** which depend on anion (**8**) formation, with base, at the P-function, followed by reaction with electrophiles. We have employed the anion **8** in selective P-benzylation to provide a tertiary phosphine oxide for inclusion in the NMR studies (Scheme II). The anion was formed in dimethyl sulfoxide solution with a small (1.2:1) excess of aqueous 50% KOH and was then treated with 1 equiv of benzyl chloride. The ana-

(8) Häring, M. *Helv. Chim. Acta* **1960**, *43*, 1826.
(9) Quin, L. D.; Montgomery, R. E. *J. Org. Chem.* **1965**, *30*, 2393.
(10) Hays, R. *J. Org. Chem.* **1968**, *33*, 3691. Miller, R. C. *J. Org.* Chem. **1959**, *24*, 2013.
(11) Majewski, P. *Synthesis* **1987**, 554.

lytically pure product had a ^{31}P signal in the oxide region (δ +14.1) that was not split when proton coupling was allowed, thus proving the site of benzylation.

The ^{13}C NMR data for seven 5,10-dihydrophenophosphazine derivatives are presented in Table I. The signals for the aromatic carbons are well separated and readily assigned on the basis of chemical shift arguments and ^{31}P and ^{13}C coupling constants. The assignments are in accord with those of Negrebetskii.[2] The strong electron-donating effect of the amino nitrogen is very apparent in these spectra and causes pronounced upfield shifts for the carbons ortho (C-4,6) and para (C-2,8) to it, with the greatest effect at the ortho position.[12] Thus the signals for the para carbons fall in the narrow region of δ 120.2–121.6 when measured in aprotic solvents, regardless of the identity of the phosphorus function. The ortho carbons appear at δ 105–118. The carbons para to phosphorus (C-3,7) generally show no coupling to ^{31}P, since they are connected through four bonds, and their signals are easily recognized. Carbons 1 and 9 (ortho to phosphorus) have modest to strong two-bond coupling to ^{31}P; this coupling is smaller for the P(IV) derivatives than for the P(III) derivatives (vide infra).

The ^{13}C NMR spectra of the three P(III) derivatives **1**, **3**, and **6** have a feature that is valuable in defining, for the first time, the conformation in solution of these tricyclic compounds. In related ring systems, such as the oxygen counterpart dibenzo-1,4-oxaphosphorinane, the boat shape is adopted by the central ring,[13] and for P(III) compounds in the 5,10-dihydrophenophosphazine system, this would lead to two possible conformers (**10** and **11**) that differ in the configuration at P (as usual, it is assumed that pyramidal inversion at N is extremely rapid, in sharp contrast to P where the barrier to inversion is quite high). The



10 **11** **12**

well-known stereospecificity of the two-bond coupling of ^{13}C to ^{31}P in P(III) compounds[6] can be effectively used to show that conformation **11**, with an axial P-substituent, prevails in solution for all three of the compounds, even though the substituents (*t*-Bu, H, Cl) differ drastically in size and electronic character. Two-bond coupling is maximal when the lone pair is in close proximity to ^{13}C and negligible when remote. It is obvious from the data in Table I that the carbons two-bond-related to ^{31}P (C-1,9 and C-4a,5a) have very different coupling constants, with the former being very large (36.7–43.4 Hz), the latter negligible. This is readily explained by structure **11**, since the lone pair is close to C-1,9 and remote from C-4a,5a. The two $^2J_{PC}$ ranges are very similar to those found for phosphatriptycene[14] (**12**, ^2J = 36.5 and ~0 Hz) where the lone pair is oriented in the same sense as in **11**. In structure **10**, the axial lone pair is in similar relation to both sets of carbons, and similar coupling constants would be expected. Support for structure **11** also comes from the magnitude of the three-bond coupling, which is controlled by exactly the same relation.[6] Again this structure has the lone pair close to one set of carbons (C-2,8) and remote from the other (C-4,6); the former carbons show moderate coupling, the latter are singlets.

Table II. ^{31}P Nuclear Magnetic Resonance Data for 5,10-Dihydrophenophosphazine Derivatives

	^{31}P NMR	
compd	solvent	δ
1	THF	+60.1
2	EtOH	−0.5[a]
3	$CDCl_3$	−20.1
4	DMSO	+31.0
5	DMSO	+15.4
6	$CDCl_3$	−105.4[b]
7	DMSO	+10.8
9	$CDCl_3$	+14.1

[a] $^1J_{PH}$ = 517.2 Hz. [b] $^1J_{PH}$ = 195.4 Hz.

Experimental Section

General. A Varian XL-300 NMR spectrometer was used to record FT proton-decoupled ^{13}C and ^{31}P NMR spectra. References were Me_4Si and 85% H_3PO_4, respectively, with positive signs for shifts downfield of these references. Some ^{31}P spectra were also obtained on an IBM NR-80 spectrometer. Reactions involving trivalent phosphorus were conducted in Schlenk tubes in an atmosphere of argon or nitrogen. Solvents were dried before use by standard procedures. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

Synthesis of 5,10-Dihydrophenophosphazine 10-Oxide (2) and Detection of 1 as an Intermediate. Compound **2** was prepared by the reported[8] procedure of heating phosphorus trichloride and diphenylamine (1:1) at 220 °C. This produced a brown solid, which when extracted with THF (freshly dried) gave an extract with a major ^{31}P NMR signal at δ +59.8 attributed to phosphinous chloride **1**. The original solid was heated with water (50 mL for a 0.1-mol run) and the mixture then taken up in 90% ethanol (150 mL). The mixture was filtered at 80 °C to remove some solids, and the filtrate was then cooled to room temperature for hydrolysis by addition of excess 10% KOH. The ethanol solution was filtered to remove some pale yellow solids.[14] Evaporation of the ethanol solution left a solid, which was twice recrystallized from dimethylformamide to give a pure sample of **2**, mp 214–215 °C (lit.[8,15] mp 214–216 °C). In a typical reaction, there was obtained 6.9 g (32%) of **2** from 17 g of diphenylamine. ^{13}C NMR spectrum; Table I. ^{31}P NMR spectrum: Table II.

Synthesis of 10-Chloro-5,10-dihydrophenophosphazine (1). A mixture of 21.5 g (0.1 mol) of phosphine oxide **2** and 35 mL (0.4 mol) of PCl_3 was stirred for 2 h at 10–15 °C under an argon atmosphere. The mixture was evaporated to dryness under reduced pressure. The solid residue was taken up in THF; the solution had a single ^{31}P NMR signal at δ +60.1. Isolation attempts were not successful, due to deposition of yellow solids.

Synthesis of 10-*tert*-Butyl-5,10-dihydrophenophosphazine (3). A solution of 18.7 g (80 mmol) of **1**, prepared by the reaction of **2** with PCl_3, in 200 mL of THF at −50 °C was treated with 100 mL of 1.7 M *tert*-butyllithium in pentane. The resulting red solution was stirred for 2 h at room temperature; it was then cooled to −60 °C and slowly treated with 10 mL of water. Solids were filtered from the yellow mixture, and the filtrate was treated with 2 equiv of ammonium chloride as a saturated aqueous solution. Evaporation of the solution left a colorless solid, from which phosphine **3** was extracted with two portions of hot toluene (150 mL each). The combined extracts were evaporated to dryness, and the residual solid (**3**) was recrystallized from toluene–hexane (4:1): yield, 7.2 g (35.3%); mp 130 °C (with sublimation); ^{13}C NMR, Table I; ^{31}P NMR, Table II.

Anal. Calcd for $C_{16}H_{18}NP$: C, 75.27; H, 7.11; N, 5.48. Found: C, 75.19; H, 7.16; N, 5.46.

(12) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*, English ed.; Springer-Verlag: Berlin, 1983; p C120.

(13) Mann, F. G.; Millar, I. T.; Powell, H. M.; Watkin, D. J. *J. Chem. Soc. Perkin Trans. 2* **1976**, 1383.

(14) Jongsma, C.; DeKleijn, J. P.; Bickelhaupt, F. *Tetrahedron* **1974**, *30*, 3465.

(15) Jenkins, R. N.; Freedman, L. D. *J. Org. Chem.* **1975**, *40*, 766.

Synthesis of 10-*tert*-Butyl-5,10-dihydrophenophosphazine 10-Oxide (4). A suspension of 15 g (60 mmol) of 10-chloro-5,10-dihydrophenophosphazine 10-oxide (**5**)[8] in 250 mL of THF was stirred vigorously at −60 °C while 100 mL of 1.7 M *tert*-butyllithium in pentane was slowly added. The solution was warmed to room temperature and stirred for 4 h. It was cooled again to −60 °C and treated with 40 g of ice. The mixture was warmed to room temperature and the white solid (**4**) recovered by filtration. It was recrystallized from DMSO: yield, 12.6 g (77%); mp 360–363 °C; ^{13}C NMR, Table I; ^{31}P NMR, Table II.

Anal. Calcd for $C_{16}H_{18}NOP$: C, 70.83; H, 6.68; N, 5.16. Found: C, 70.67; H, 6.60; N, 5.08.

The same phosphine oxide (**4**) was formed by oxidation of phosphine **3** (2.55 g) with a mixture of acetone (4 mL) and 30% hydrogen peroxide (2 mL) at room temperature for 1 h. The yield was 2.6 g (96%), mp 366–367 °C; the product had NMR parameters identical with those of the product prepared from **5**.

Synthesis of 5,10-Dihydrophenophosphazine (6). A 4.3-g (20 mmol) sample of secondary phosphine oxide **2** and 1 mL of CCl_4[11] were heated rapidly to 200–220 °C in a Büchi-Kugelrohr apparatus at 0.05 mmHg. A yellow solid (**6**, 0.8 g, 38%) sublimed into the connecting bulb of the apparatus. Phosphinic acid **7**[8] (^{31}P δ +10.8 in DMSO) was isolated from the pot residue by extraction with 10% KOH in ethanol–water, followed by precipitation with 5% HCl. Spectral data for **6** are given in Tables I and II. The sensitivity of the phosphine to oxidation hindered its purification for analysis.

Synthesis of 10-Benzyl-5,10-dihydrophenophosphazine 10-Oxide (10). To a solution of secondary phosphine oxide **2** (2.15 g, 10 mmol) in 20 mL of dimethyl sulfoxide was added 1.6 g of a 50% KOH solution (12 mmol). Benzyl chloride (1.4 mL, 12 mmol) was added dropwise at room temperature and the mixture then heated for 1 h at 50 °C. The solution was diluted with an ice–water mixture and extracted with four 30-mL portions of methylene chloride. The extracts were washed with a saturated sodium chloride solution (two 10-mL portions), dried over sodium sulfate, and rotary-evaporated. The solid residue was chromatographed on silica gel with elution by CH_2Cl_2, and the recovered solid was then recrystallized from 95% ethanol to give 2.1 g (69%) of **9**: mp 216–219 °C; ^{13}C NMR, Table I; ^{31}P NMR, Table II.

Anal. Calcd for $C_{19}H_{16}NOP$: C, 74.74; H, 5.28; N, 4.58. Found: C, 74.57; H, 4.91; N, 4.56.

Acknowledgment. The support of the National Science Foundation for part of this study, through Grant CHE-8405876, is gratefully acknowledged.

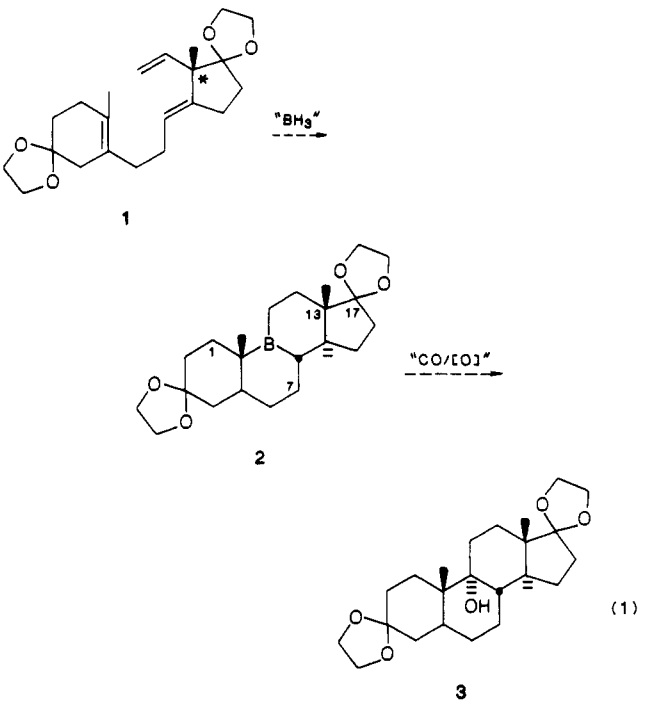
Boron Triene Annulation. Substrate Structural Effects on Steroidal Annulation

T. D. Fulmer and T. A. Bryson*

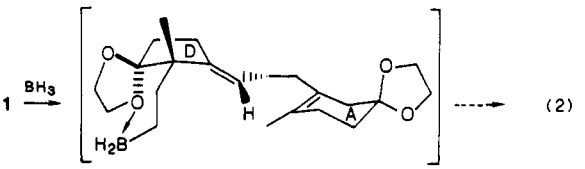
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received January 13, 1989

In principle boron annulation of trienes (e.g. **1**) is well-suited for the synthesis of steroids[1] and other carbocycles.[2] To illustrate, carborane **2** could be formed by successive inter- and intramolecular borane–olefin additions with **1** (eq 1). Carbonylation of boracyclane **2** followed by oxidation would provide the steroid nucleus (**3**) in which the stereochemistry is derived from the defined chiral center in substrate **1**. In practice, attempted boron annulations with variations of triene **1** have generally failed



with the implication that strong Lewis acid–base interactions between boron and the C-17 (steroid numbering system) appended acetal were the likely source of the problem as suggested in eq 2.[3] Variations of triene substrate **1** were sought that would disfavor any *cis*-hydrindane oxygen–boron interactions that could retard further intramolecular olefin additions.



4

negative annulation factor

Moving the ketal group by homologation (eq 3) of the D ring in substrate **1** would disfavor the proposed boron Lewis acid–base complex via an unfavorable pseudoring size while still maintaining the potential annulating stereochemical control at C-13.[4] Investigation of this hypothesis required a new approach to triene synthesis[5] centering on coupling of an allylic halide (**5**) and enone (**6**) as outlined in eq 3.

Attempts to directly alkylate the enolate of **6a** with allylic chlorides resulted in multiple alkylations in low yields. However β-keto sulfone **6b**, obtained from the reaction of the acetal of Hagemann's ester (**8**) and the

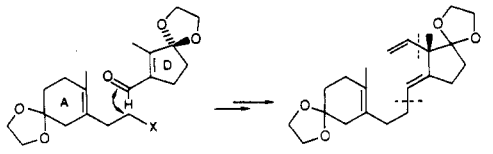
(1) Bryson, T. A.; Reichel, C. J. *Tetrahedron Lett.* **1980**, *21*, 2381–4. Pye, W. E.; Bryson, T. A. *J. Org. Chem.* **1977**, *42*, 3214–5.

(2) Bryson, T. A.; Reichert, C. F.; Pye, W. E. *Tetrahedron* **1981**, *37*, 2441–4. Welch, M. C.; Bryson, T. A. *Tetrahedron Lett.* **1988**, *29*, 521–4. Stevenson, J. W. S.; Bryson, T. A. *Chem. Lett.* **1984**, 5–9. Levine, E.; Bryson, T. A. *Heterocycles* **1982**, *18*, 271–5.

(3) Bonitz, G. H. Ph.D. Dissertation, University of South Carolina, Columbia, SC, 1982; p 125.

(4) Other trienes designed to remedy the proposed cyclic complexation theory added more chiral centers to the "D ring" of the steroid synthon complicating plausible asymmetric approaches to steroids.

(5) Fulmer, T. D. Ph.D. Dissertation, University of South Carolina, Columbia, SC, 1987. The standard approach has been some variation of organometallic A-ring unit addition to D-ring aldehyde, Claisen rearrangement, reduction, and elimination.



0022-3263/89/1954-3496$01.50/0