THE JOURNAL OF Organic Chemistry®

VOLUME 41, NUMBER 4

FEBRUARY 20, 1976

Stereochemistry, Conformations, and Carbon-13 Nuclear Magnetic Resonance Spectra of 9-Phenyl-9-phosphabicyclo[3.3.1]nonane Derivatives

John R. Wiseman* and Herman O. Krabbenhoft

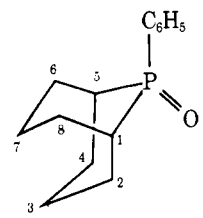
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104

Received July 8, 1975

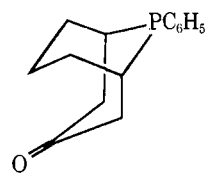
Reaction of phenylphosphine with cycloocta-2,7-dienone followed by oxidation produces the syn (3) and anti (5) isomers of 9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 9-oxide. Sodium borohydride reduction of 3 and 5 produces syn-endo alcohol 6 and anti alcohol 7, respectively. Reaction of 6 and 7 with concentrated hydrobromic acid gives syn and anti olefins 8 and 9. In a reaction with sulfuric acid, syn alcohol 6 is converted to anti olefin 9. Both 8 and 9 are reduced to 9-phenyl-9-phosphabicyclo[3.3.1]nonane 9-oxide (1) by catalytic hydrogenation. Stereochemical assignments for 8 and 9 (and the other compounds reported) are made based on (1) faster rate of catalytic hydrogenation of 8 over 9, (2) greater thermodynamic stability of 9 than 8 and (3) ^{13}C NMR spectra. Alcohol 6 is shown to have a chair–boat conformation which avoids interaction of the endo 3-hydroxyl group with carbon 7. The dependence of vicinal (three-bond) ^{13}C–^{31}P coupling constants upon dihedral angle is discussed.

Until recently polycyclic compounds containing phosphorus as a bridging[1] or a bridgehead[2] atom were rather uncommon. In connection with other studies we required 9-phenyl-9-phosphabicyclo[3.3.1]nonane 9-oxide (1). During the course of the synthesis of bridged phosphine oxide 1 we discovered some interesting chemistry pertaining to the stereochemistry about the phosphorus atom in various derivatives. In this report we describe some of our results and the stereochemical assignments in the 9-phosphabicyclo-[3.3.1]nonane system.

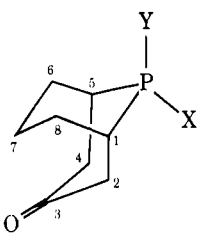
Kashman and Benary have reported that treatment of cycloocta-2,7-dienone[3] with phenylphosphine gives the phosphinone 2.[4] The stereochemistry at the phosphorus atom was inferred from the similarity of the proton NMR spectra of phosphinone oxides 3 and 4,[5] the configuration of the latter having been established by an x-ray analysis.[6] We have confirmed the stereochemical assignment of 3, and we have isolated and characterized its isomer 5.



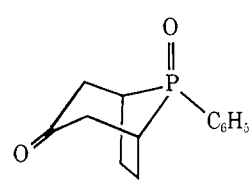
1



2



3, X = O; Y = C_6H_5
5, X = C_6H_5; Y = O



4

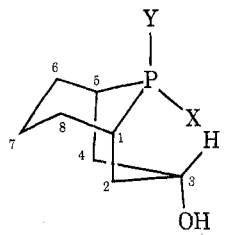
Results and Discussion

Synthesis and Chemistry. We utilized the double Michael addition procedure of Kashman[4] with the following results. Treatment of cycloocta-2,7-dienone[3] with 1 equiv of phenylphosphine afforded a white solid which was not purified, but oxidized directly with hydrogen peroxide. The oxidation product was shown to be a mixture of isomeric phosphine oxides 3 and 5 which could be separated by fractional crystallization. The first isomer to crystallize was the syn phosphinone oxide 3; the mother liquor contained mostly the anti isomer 5. Each isomer was purified by a subsequent recrystallization. The combined yield of purified 3 and 5 was approximately 50%, and the ratio of 3 to 5 was about 1:1.7. The infrared spectra of phosphinone oxides 3 and 5 are virtually identical, each displaying strong absorption bands at 1700 and 1160 cm^{-1} for the carbonyl and phosphonyl chromophores, respectively. The proton NMR spectra, however, are quite different. The NMR spectrum of 3 correlated well with the tabulated data of Kashman and Benary;[4] 5 has not been described previously. The melting point reported[4] for the syn isomer 3 is 250°, with decomposition. We found that 3 melts at 305–306°, with decomposition, and that 5 has a melting point of 201.5–204°. Because of the large discrepancy in the melting points found for 3, additional information was sought to support the structural assignments. Mass spectrometry and

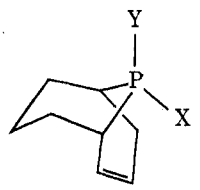
correct combustion analyses showed that **3** and **5** are isomeric and monomeric. The small ranges observed in the melting points of **3** and **5** indicated that they were isomerically pure, and the purity of each was substantiated by its ^{13}C NMR spectrum. Each spectrum was uncontaminated by signals from the other isomer. Furthermore, the gross structures of **3** and **5** were confirmed, since each spectrum displayed five signals for the five different types of nonaromatic carbon atoms in the 9-phosphabicyclo[3.3.1]nonan-3-one ring system. In addition, the ^{13}C NMR spectra indicated the syn and anti relationships of the phosphonyl and carbonyl oxygen atoms (see below).

The syn phosphinone oxide **3** and the anti phosphinone oxide **5** were each converted into the corresponding endo alcohols **6** and **7** by reduction with sodium borohydride in yields of 91 and 95%, respectively. Alternatively, the crude mixture of **3** and **5** was reduced, and the alcohols **6** and **7** were separated by fractional crystallization.

Ketones **3** and **5** should have double chair conformations and should be attacked by borohydride on the exo face. Therefore, alcohols **6** and **7** are assigned the endo configuration. The endo configuration of alcohol **6** was verified by ^{13}C NMR spectroscopy (see below). We were unable to obtain a ^{13}C NMR spectrum of **7** because it was not sufficiently soluble in the common organic solvents.



6, X = O; Y = C_6H_5
7, X = C_6H_5; Y = O

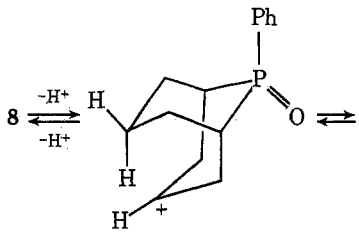


8, X = O; Y = C_6H_5
9, X = C_6H_5; Y = O

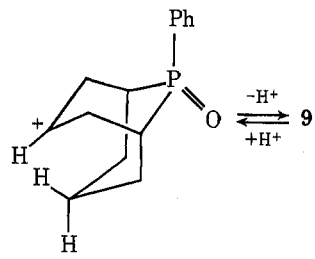
Alcohols **6** and **7** were dehydrated to olefins **8** and **9** in yields of 88 and 77%, respectively, by treatment with refluxing concentrated hydrobromic acid. The olefins **8** and **9** provided a chemical basis for the assignment of the syn and anti configurations at the phosphorus atom of all of the phosphine oxides prepared in the study. During attempts to convert **8** and **9** into 9-phenyl-9-phosphabicyclo-[3.3.1]nonane 9-oxide (**1**) by catalytic reduction at 1 atm using a platinum catalyst, one of the olefins was reduced only partially (about 50%) after 18 h, while the other alkene took up the theoretical volume of hydrogen by the end of 1 h. The *less* reactive isomer was assigned the anti structure **9**, since it should be somewhat resistant to hydrogenation owing to the steric bulk of the phenyl group which inhibits effective adsorption of the substrate onto the catalyst. Isomer **8** is not so hindered[7] and undergoes hydrogenation readily. The product of the reduction of **8** and **9** was phosphine oxide **1**. Subsequent experiments showed that the olefin **9** was quantitatively converted into **1** when the reduction was conducted at 4 atm pressure. Having determined the stereochemical configurations of the phosphorus substituents for the alkenes **8** and **9**, the configurations of the alcohols **6** and **7** and the ketones **3** and **5** are also established.

An interesting and useful result was observed during the scale-up of the synthesis of **1**. In the dehydration step, 57% sulfuric acid was substituted for the concentrated hydrobromic acid employed previously. As expected, alcohol **7** gave olefin **9**, but **6** also afforded olefin **9** in good yield. Evidently, olefin **9** must be more stable than **8** since **8** is converted into **9** under the reaction conditions. Inspection of molecular models reveals that **9** should be more stable than **8**. In the case of **8**, where the phenyl group is anti to the carbon double bond, the ortho hydrogens of the phenyl ring interact strongly with the axial hydrogens at carbons 6 and 8.[8] In olefin **9**, these interactions are diminished by removal of one of the hydrogens and flattening of the unsaturated bridge syn to the phenyl group. Thus, the dehydration experiment provides additional support for the configurational assignments made above.

The conversion of **8** into **9** could occur by either or both of the following pathways. Transannular hydride shifts are

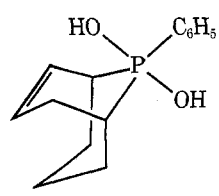


10

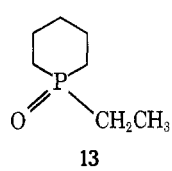


11

common in medium-sized rings[9] and have been observed to occur between the 3 and 7 positions of bicyclo[3.3.1]nonane derivatives.[10] Accordingly, such a shift, interconverting ions **10** and **11**, would account for the net transformation of **8** into **9**. Alternatively, the formation of **8** from **9** may be explained as an acid-catalyzed epimerization of the phosphorus atom via the pentacoordinate intermediate **12**. Wetzel and Kenyon[2b] have studied the acid-catalyzed oxygen exchange of phosphine oxides, including **13**. The rate con-



12



13

stant[2b] for oxygen exchange of **13** in approximately 57% sulfuric acid is nearly large enough to account for the epimerization of the phosphorus atom of **8**, assuming that **8** would react at the same rate as **13**.

Finally, we briefly comment on the reaction of phosphine oxide **1** with methyllithium. The reaction was quenched with methyl iodide, and the ethyl derivative **14** was obtained in 77% yield. The mechanism depicted in Scheme I is proposed to account for this result. Such a mechanism is in accord with the results of Seyferth and co-workers.[11] A similar intermediate was invoked by Turnblom and Katz[1] with phenylphosphahomocubane oxide, phenylphosphahomocuneane oxide, and other phosphine oxides.

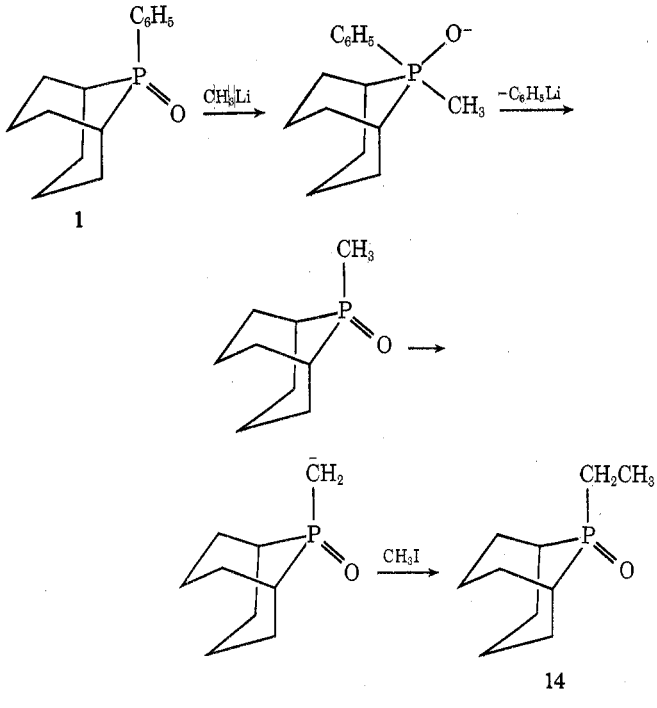
^{13}C NMR Spectra. Chemical Shifts. ^{13}C NMR spectroscopy provides additional evidence for the stereochemical assignments in the previous section. Table I records chemical shift data for the phosphine oxides **1**, **3**, **5**, and **6**; Table II contains ^{31}P–^{13}C coupling constants for these compounds. Assignments of shielding values (downfield from internal Me_4Si) of the wide-band proton noise de-

Table I
Chemical Shifts of 9-Phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxides

Compd	Aliphatic carbons[a]					Aromatic carbons			
	C-1	C-2	C-3	C-6	C-7	α	o	m	p
1	28.5	26.3	21.6	29.7	20.9	(130.5)[b]	129.6	128.9	131.4
3	30.8	42.8	208.3	29.1	17.1	(128.3)[c]	130.0	129.4	132.4
5	29.3	44.9	207.0	27.0	18.2	129.7	129.7	128.9	132.5
6	27.6	34.5	61.4	30.8	15.6	130.2	129.8	129.1	131.6

[a] See structural formulas for numbering of carbon atoms. [b] The α carbon resonates as a doublet due to coupling with phosphorus, but one of the peaks is obscured by the other aromatic signals. The value cited was calculated from the visible peak (132.3 ppm) assuming a P—C coupling constant of 96 Hz (Table II). [c] As in footnote b; the visible peak occurs at 126.4 ppm.

Scheme I



1 14

coupled spectra of ketones **3** and **5** were made as follows. The carbonyl carbons and those adjacent to the carbonyl group are readily recognized because of their characteristic shielding regions.[12] The bridgehead carbon signals are also easily discerned owing to the relatively large phosphorus–carbon coupling constants.[2a] Carbons 6(8) and 7 are assigned on the basis of relative peak heights and similar chemical shifts for other bicyclo[3.3.1]nonane compounds.[13] The aromatic carbons were assigned based upon the results of Gray and Cremer.[14] A particularly informative feature of the spectra of ketones **3** and **5** is the deshielding of carbons 2(4) and 6(8) when they are syn to the phenyl group. We have previously demonstrated that steric interactions between a methyl carbon and carbons 2(4) and 6(8) of 9-*tert*-butyl-9-azabicyclo[3.3.1]nonan-3-one (**15**) result in carbons 2(4) and 6(8) being deshielded by approximately 3 ppm.[15] In the case of the 3-keto phosphine oxides **3** and **5**, the ortho carbons of the phenyl groups interact sterically with the carbons 2 and 4 or 6 and 8 when they are in a syn relationship.[8] Thus, isomer **3** should have carbons 6 and 8 more deshielded than the corresponding carbons of 5; and ketone **5** should have its carbons 2 and 4 more downfield than those of **3**. The δ steric shift is 2.1 ppm in each instance, and is in good agreement with our earlier observations[15] and those of others.[16] Coupling constants between the bridgehead protons and phosphorus atoms were found to be 18 Hz for both **3** and **5**. The coupling constants were

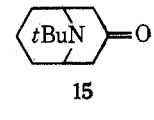
Table II
^{31}P–^{13}C Coupling Constants of
9-Phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxides

Compd	C-1	C-3	C-7	α	o	m
1	60	8	6	*a*	8	10
3	62	7		*a*	9	12
5	62	7		95	*a*	*a*
6	63	20	7	96	9	12

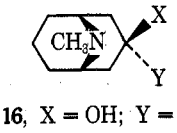
[a] The coupling constant of phosphorus was obscured by the other aromatic resonance signals.

determined after exchanging the protons adjacent to the carbonyl group for deuterium in order to simplify the spectra.

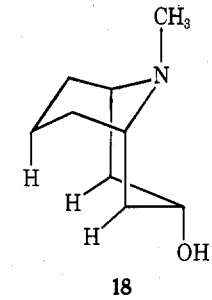
The carbons of alcohol **6** were assigned in the same manner as used with ketones **3** and **5**. Unfortunately, alcohol **7** was not sufficiently soluble in common organic solvents to permit obtaining its spectrum. The spectrum of **6** did allow us to assign unequivocally the endo configuration of the C-3 hydroxy group. We have shown by direct comparison of the ^{13}C NMR spectra of the *exo*- and *endo*-3-hydroxy-9-methyl-9-azabicyclo[3.3.1]nonanes (**16** and **17**) that in the endo isomer carbon atom 7 resonates at a rather high field (14.5 ppm) as a result of the gauche interactions brought about by the chair–boat conformation **18**,[15] which predomi-



15



16, X = OH; Y = H
17, X = H; Y = OH



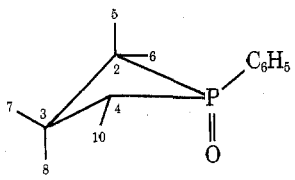
18

nates over the chair–chair conformation in order to relieve transannular steric interactions.[17] Since carbon 7 of alcohol **6** is also quite shielded (15.6 ppm), we conclude that the C-3 hydroxy group is situated endo and that the predominant conformation of **6** in solution is the chair–boat.

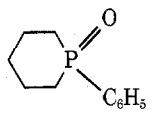
The carbon-13 chemical shifts of phosphine oxide **1** were assigned as follows. The bridgehead carbons were again readily assigned as a result of the large ^{31}P–^{13}C coupling constants. The remaining two most downfield aliphatic signals are attributed to carbons 2(4) and 6(8) based on the shieldings of ketones **3** and **5**. The most downfield signal is assigned to carbon 6(8) since it experiences the same steric interactions with the ortho carbons of the syn phenyl group that were observed with the ketones **3** and **5**. The two upfield signals are due to carbons 3 and 7. Based on the chemical shifts of carbons 7 for ketones **3** and **5**, the most shielded resonance of **1** is assigned to carbon 7.

Vicinal ^{13}C–^{31}P Coupling Constants. A large body of data exists on ^{13}C–^{31}P coupling constants,[12,14] but there are few examples where the angular dependence of the three-bond (vicinal) ^{13}C–^{31}P coupling constant has been examined in compounds with rigid and predictable geometries.[2a,14] Wetzel and Kenyon[2a] have pointed out that these coupling constants can be expected to show a dependence on dihedral angle similar to that observed in proton–proton[18] and ^{13}C–^{13}C vicinal coupling.[19] The ^{13}C–^{31}P coupling constant should be maximal when the dihedral angle formed by the bonds connecting the atoms is 0 or 180° and should be minimal when the dihedral angle is near 90°.

Gray and Cremer[14] have recorded the ^{13}C NMR spectra of an extensive series of polymethylphosphetane oxides, sulfides, and salts. Among these 1-phenyl-2,2,3,3,4-pentamethylphosphetane 1-oxide (**19**) is of interest because it



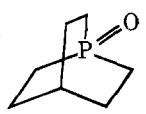
19



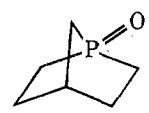
20

has a preferred conformation with C_7 equatorial and C_8 axial. The dihedral angle between the planes P–C_2–C_3 and C_2–C_3–C_7 is near 150° while the dihedral angle between planes P–C_2–C_3 and C_2–C_3–C_8 is near 100°. The ^{13}C–^{31}P coupling constants for C_7 and C_8 are 24.9 and 1.6 Hz, respectively. Six other pentamethylphosphetane oxides and salts differing in substituents on phosphorus show similar coupling constants of phosphorous to C_7 and C_8. In several other compounds which have greater conformational mobility the coupling constants for C_7 and/or C_8 are near an average value of 14–15 Hz.[14] Conformationally mobile phosphonium salts also have vicinal ^{13}C–^{31}P coupling constants of 12–15 Hz.[12] Compound **20** has a coupling constant of C_4 to P of 6.8 Hz;[14] the relevant dihedral angle along the C_2–C_3 bond is about 60°.

Bicyclic phosphine oxides **21** and **22**[2a] have unusually high coupling constants between the bridgehead carbon and phosphorus atoms of 47 and 35 Hz, respectively. These



21



22

rigid ring systems have fixed geometries with the dihedral angles of 0° along the C_2–C_3 bond. Each compound has three coupling paths linking the bridgehead atoms, two three-bond paths for **21** and two three-bond paths plus a two-bond path for **22**.[2a]

The three-bond ^{13}C–^{31}P coupling constants shown in Table II support the assignment of a chair–boat conformation for compound **6**. In compounds **1**, **3**, and **5**, which have double-chair conformations, the dihedral angle between the P–C_1–C_2 and C_1–C_2–C_3 planes is about 60°. In these compounds the three-bond ^{13}C–^{31}P coupling constants are 6–8 Hz, similar to that of **20**. In compound **6**, the relevant dihedral angle is close to 0° and the coupling constant is 20 Hz. Significantly, the coupling constant between C_7 and phosphorus in compound **6** is 7 Hz, showing that the unsubstituted ring remains in the chair form.

Experimental Section

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance spectra were obtained on a Varian Associates T-60 instrument; ^{13}C magnetic resonance spectra were obtained on a JEOL JNM PS-100 spectrometer interfaced with a Digilab Nova 1200 computer. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Mass spectra were obtained on an Associated Electrical Industries MS-902. Vapor phase chromatographic analyses and collections were performed on a Varian Aerograph Model 90-P instrument. Elemental analyses were carried out by Spang Microanalytical Laboratory.

Unless specified otherwise, spectral data were obtained as follows: NMR, solutions in deuteriochloroform (units in parts per million downfield from internal Me_4Si); ir, solutions in chloroform (units in cm^{-1}); MS, 70 eV.

9-Phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (1). A mixture of alkenes **8** and **9** (6.96 g, 30.0 mmol) in 300 ml of methanol was hydrogenated over platinum (557 mg of PtO_2) at room temperature under 4 atm pressure on a Parr 22 apparatus. After 1 h the required amount of hydrogen had been taken up. The mixture was filtered through Celite and concentrated to afford 6.46 g (92%) of **1**, which was purified by crystallization (benzene–cyclohexane) and sublimination (175–178°, 0.015 Torr): mp 181–183°; ir, 3050, 1590, 1150, 1115 cm^{-1}; NMR 7.83–7.35 (5 H), 3.0–1.2 ppm (14 H).

Anal. Calcd for $C_{14}H_{19}OP$: C, 71.78; H, 8.17; P, 13.22. Found: C, 71.60; H, 8.26; P, 13.05.

***syn*-9-Phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 9-Oxide (3) and *anti*-9-Phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 9-Oxide (5).** The procedure of Kashman and Benary was used.[4] An equimolar solution of cycloocta-2,7-dienone[3] and phenylphosphine was heated under nitrogen at ~135° until the infrared spectrum showed the complete disappearance of the dienone carbonyl band. The reaction mixture was then cooled to room temperature, taken up in chloroform, cooled in an ice–water bath, and oxidized by the dropwise addition of excess aqueous 30% hydrogen peroxide solution. After stirring for an additional 3 h, the layers were separated; the aqueous layer was extracted with chloroform. The combined organic layers were washed once with half-saturated aqueous sodium bisulfite solution, dried (Na_2SO_4), and concentrated to provide a white solid. Crystallization from acetonitrile gave the syn isomer **3**; concentration of the mother liquor gave the anti isomer **5**. The ratio of **3** to **5** was 1:1.7 (one experiment), and the overall yield from the cycloocta-2,7-dienone was 48–59% (three experiments). The syn isomer **3** was purified by recrystallization from acetonitrile–benzene (mp 305–306° dec): ir 1700, 1590, 1160, 1115 cm^{-1}, NMR 8.0–7.3 (5 H), 3.8–1.3 ppm (12 H).

Anal. Calcd for $C_{14}H_{17}O_2P$: C, 67.73; H, 6.90; P, 12.48. Found: C, 67.74; H, 6.96; P, 12.36.

The anti isomer **5** was recrystallized from benzene–cyclohexane (mp 201.5–204°): ir 1700, 1590, 1160, 1120 cm^{-1}; NMR 8.0–7.3 (5 H), 3.2–1.4 ppm (12 H).

Anal. Calcd for $C_{14}H_{17}O_2P$: C, 67.73; H, 6.90; P, 12.48. Found: C, 67.85; H, 7.01; P, 12.47.

***syn*-2,2,4,4-Tetradeuterio-9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 9-Oxide (3-d_4).** A solution of 565 mg (2.3 mmol) of **3** in 20 ml of NaOD–D_2O solution (prepared from 20 ml of D_2O and 200 mg of Na) was heated on a steam bath under nitrogen for 6 h. After cooling, the aqueous solution was extracted with methylene chloride; the combined extracts were dried (Na_2SO_4) and concentrated to give 415 mg (74%) of **3**-d_4 (mp 290–293° dec). NMR indicated 96% exchange; ir 1700 cm^{-1}; NMR 2.88 (d, J_{P-H} = 18 Hz, 2 H), 2.3–1.3 ppm (6 H); MS *m/e* 254.

***anti*-2,2,4,4-Tetradeuterio-9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one 9-Oxide (5-d_4).** The above procedure was used to prepare **5**-d_4 (mp 203–206° dec) in 96% yield. NMR indicated 96% exchange; ir 1695 cm^{-1}; NMR 3.1–1.4 ppm (8 H); MS *m/e* 254.

***endo*-3-Hydroxy-*syn*-9-phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (6) and *endo*-3-Hydroxy-*anti*-9-phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (7).** To a methanolic solution of the crude mixture of **3** and **5**, cooled in an ice–water bath, was added, in portions, an equal weight of sodium borohydride. After stirring for about 10 h, the reaction mixture was processed by extraction with methylene chloride, drying over sodium sulfate, and concentration to provide an 85% yield (two experiments) of a mixture of **6** and **7**. Crystallization of the crude mixture from methanol–ethyl acetate provided the anti isomer **7**; concentration of the mother liquor gave the syn isomer **6**. The anti isomer **7** was recrystallized from methanol–ethyl acetate (mp 303–306° dec): ir (KBr) 3250, 1140, 1100 cm^{-1}; NMR (TFA) 8.2–7.6 (5 H), 4.2 –1.6 ppm (13 H).

Anal. Calcd for $C_{14}H_{19}O_2P$: C, 67.19; H, 7.65; P, 12.38. Found: C, 67.30; H, 7.74; P, 12.42.

The syn isomer **6** was purified by recrystallization from acetonitrile (mp 198–201°): ir (KBr) 3350, 1150, 1110 cm^{-1}; NMR (TFA) 8.1–7.6 (5 H), 5.3–4.7 (1 H), 3.6–1.4 ppm (12 H).

Anal. Calcd for $C_{14}H_{19}O_2P$: C, 67.19; H, 7.65; P, 12.38. Found: C, 67.36; H, 7.59; P, 12.21.

In separate experiments pure **3** was reduced to **6** (91% yield) and pure **5** was reduced to **7** (95% yield).

***syn*-9-Phenyl-9-phosphabicyclo[3.3.1]non-2-ene 9-Oxide (8).** A solution of 1.18 g (4.75 mmol) of syn-endo hydroxy oxide **6** in 60 ml of concentrated hydrobromic acid was refluxed for 6 h, then allowed to cool to room temperature overnight, cooled in an ice–salt bath, and basicified with 25% aqueous sodium hydroxide. The resulting solution was extracted with methylene chloride and the combined extracts were dried (Na_2SO_4) and concentrated to provide 0.96 g (88%) of **8** (mp 160–163°): ir 1640, 1590, 1160, 1120 cm^{-1}; NMR 8.0–7.3 (5 H), 6.4–5.3 (2 H), 3.4–1.2 ppm (10 H).

Anal. Calcd for $C_{14}H_{17}OP$: C, 72.40; H, 7.38; P, 13.34. Found: C, 72.35; H, 7.47; P, 13.13.

***anti*-9-Phenyl-9-phosphabicyclo[3.3.1]non-2-ene 9-Oxide (9).** The above procedure was employed to provide a 77% yield of **9** (mp 145–148°) from **7**: ir 1640, 1590, 1150, 1120 cm^{-1}; NMR 8.0–7.3 (5 H), 6.4–5.5 (2 H), 3.4–1.1 ppm (10 H).

Anal. Calcd for $C_{14}H_{17}OP$: C, 72.40; H, 7.38; P, 13.34. Found: C, 72.24; H, 7.26.

Dehydration of *endo-syn*-3-Hydroxy-9-phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (6) with Sulfuric Acid. A solution of 10.00 g (0.042 mol) of syn hydroxy phosphine oxide **6** in 57% sulfuric acid (prepared from 120 ml of water and 160 ml of concentrated sulfuric acid) was heated to boiling for 12 hr. The solution was cooled, saturated with sodium chloride, and extracted several times with dichloromethane. The dichloromethane extracts were combined and evaporated to yield 6.55 g (71% yield) of a slightly yellow solid. The NMR spectrum of the solid was identical with that of *anti*-9-phenyl-9-phosphabicyclo[3.3.1]non-2-ene 9-oxide (**9**) (see previous experiment).

In a similar experiment starting with 7.08 g of anti hydroxy phosphine oxide **7**, 4.025 g (61%) of olefin **9** was produced.

The acidic aqueous solutions from both of the above experiments were combined and extracted repeatedly with dichloromethane. Evaporation of the dichloromethane extracts yielded an additional 2.76 g of **9** bringing the combined yields for the two experiments to 84%.

9-Ethyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (14). To a mixture of 234 mg (1.0 mmol) of phosphine oxide **1** in 10 ml of ether (freshly distilled from lithium aluminum hydride) cooled in an ice bath was added 2 mmol of methyllithium in ether. After 15 min (during which time the solution became yellow), excess methyl iodide was added and the reaction mixture was allowed to warm to room temperature. The mixture was then poured into water, the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic phases were dried (Na_2SO_4) and concentrated to give 143 mg of yellow solid material. Preparative VPC (4% SE-30 on Chromosorb G, 3 ft × 0.25 in.) afforded 30 mg of **14** (mp 131–133°): ir 1150 cm^{-1}; NMR 3.0–1.1 ppm; MS *m/e* 186.

Anal. Calcd for $C_{10}H_{19}OP$: C, 64.49; H, 10.28; P, 16.63. Found: C, 64.30; H, 10.28; P, 16.72.

Acknowledgment. This research was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—**1**, 57458-74-9; **3**, 37759-01-6; **3**-d_4, 57495-99-5; **5**, 57458-75-0; **5**-d_4, 57458-76-1; **6**, 37759-02-7; **7**, 57458-77-2; **8**, 57458-78-3; **9**, 57458-79-4; **14**, 57458-80-7.

References and Notes

(1) E. W. Turnblom and T. J. Katz, *J. Am. Chem. Soc.*, **95**, 4294 (1973), and references cited therein.
(2) (a) R. B. Wetzel and G. L. Kenyon, *J. Am. Chem. Soc.*, **96**, 5189 (1974), and references cited therein; (b) *ibid.*, **96**, 5199 (1973); (c) C. Jongsma, J. P. deKlein, and F. Bickelhaupt, *Tetrahedron*, **30**, 3465 (1974).
(3) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).
(4) Y. Kashman and E. Benary, *Tetrahedron*, **28**, 4091 (1972).
(5) Y. Kashman and O. Awerbouch, *Tetrahedron*, **26**, 4213 (1970).
(6) U. Shmuell and Z. Zurr, *Isr. J. Chem.*, **9**, 5 (1971).
(7) The oxygen should not sterically interfere with adsorption since 9-thiabicyclo[3.3.1]non-2-ene 9,9-dioxide undergoes hydrogenation readily: B. R. Anderson and J. R. Wiseman, unpublished results.
(8) N. L. Allinger and M. T. Tribble, *Tetrahedron Lett.*, 3259 (1971).
(9) For leading references consult A. C. Cope, M. M. Martin, and M. A. McKervey, *Q. Rev., Chem. Soc.*, **20**, 119 (1966).
(10) For leading references see (a) L. Stehelin, L. Kanellias, and G. Ourisson, *J. Org. Chem.*, **38**, 847, 851 (1973); (b) M. P. Doyle and W. Parker, *Chem. Commun.*, 755 (1970).
(11) D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Am. Chem. Soc.*, **86**, 1100 (1964).
(12) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(13) H. O. Krabbenhoft, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1974.
(14) (a) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972); (b) *ibid.*, **37**, 3470 (1972).
(15) J. R. Wiseman and H. O. Krabbenhoft, *J. Org. Chem.*, **40**, 3222 (1975).
(16) (a) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973); (b) J. B. Stothers and C. T. Tan, *Can. J. Chem.*, **52**, 308 (1974).
(17) C.-Y. Chen and R. J. W. LeFevre, *J. Chem. Soc. B*, 539 (1966).
(18) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1969).
(19) (a) J. L. Marshall and D. E. Miller, *J. Am. Chem. Soc.*, **95**, 8303 (1973); (b) D. Doddrell, I. Burfitt, J. B. Grutzner, and M. Barfield, *ibid.*, **96**, 1241 (1974).

Potamogetonin, a New Furanoid Diterpene. Structural Assignment by Carbon-13 and Proton Magnetic Resonance

Cecil R. Smith, Jr.,* Richard V. Madrigal, David Weisleder, and Kenneth L. Mikolajczak

Northern Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604

Robert J. Highet*

National Heart and Lung Institute, Bethesda, Maryland 20014

Received May 16, 1975

Potamogetonin (**1**), a new furanoid diterpene with a labdane skeleton, has been isolated from seeds of *Potamogeton ferrugineus* Hagstr. The structure of **1** has been assigned on the basis of its spectral characteristics, particularly by nuclear magnetic resonance. The proton and carbon-13 chemical shifts of two related diterpenes of known structure, sciadin (**3**) and nepetaefuran (**4**), are correlated with shifts of **1**.

We wish to report the isolation and structure of potamogetonin (**1**), a new member of the growing group of furanoid labdane derivatives.[1] Potamogetonin was isolated from seeds of *Potamogeton ferrugineus* (family Potamogetonaceae).[2] Gas–liquid phase chromatographic (GLC) analysis of the petroleum ether extract of these seeds revealed, in