Tetrahedron. Vol. 28, pp. 4091 to 4098. Pergamon Press 1972 Printed in Great Britain

THE SYNTHESIS OF THE 9-PHOSPHABICYCLO[3.3.1]NONANIC AND 2-PHOSPHA-6-OXAADAMANTANIC SYSTEMS

Y. KASHMAN and E. BENARY

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(*Received in the UK* 24 *February* 1972; *Accepted for publication* 2 *May* 1972)

Abstract— Several derivatives of 2-phospha-6-oxaadamantane (**8**, **9**, **10** and **11**) have been prepared from suitably substituted 9-phosphabicyclo[3.3.1]nonanes. The bicyclo compounds were synthesized by a double Michael addition of a primary phosphine to 2,7-cyclooctadienone. The stereochemistry of the adducts and related compounds was determined by investigation of their NMR spectra.

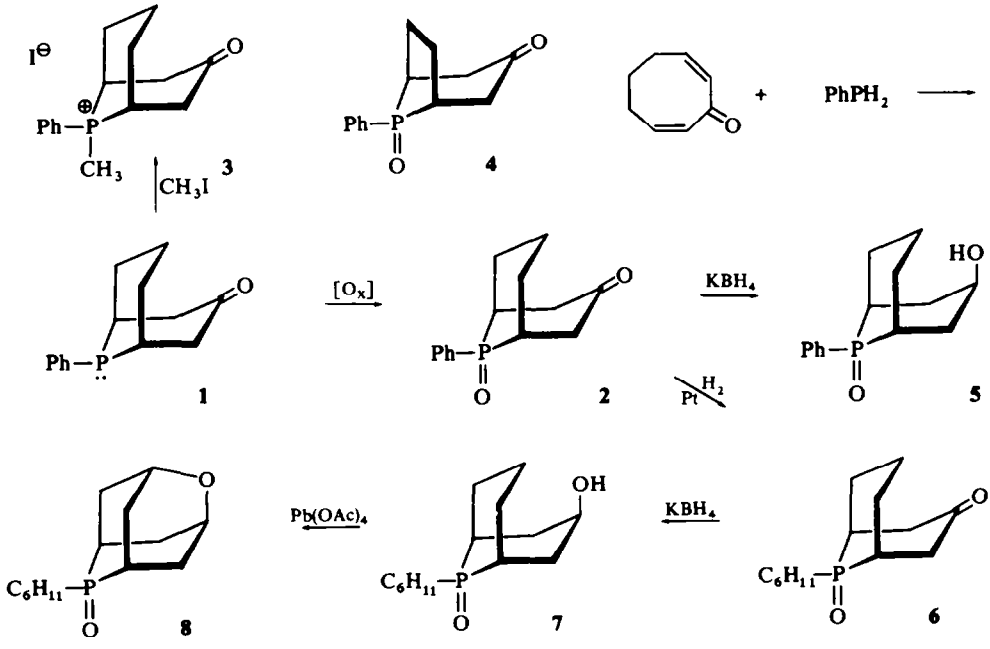
A CONSIDERABLE amount of research has been and is being carried out on the synthesis of the heteroadamantanes—their outstanding biological properties being well known.

We were interested in the examination of phosphaadamantanoic systems as well as their phosphabicyclo[3.3.1]nonanic starting materials. Our interest in the heteroadamantane was focused on the pharmacological as well as spectral properties, the latter originating from the rigid geometry of the adamantane skeleton, which makes it suitable for P=O anisotropy study, by NMR spectroscopy, as well as variation of J_{P-H} with H–P distance and angles. On the other hand, our main concern in bicyclophospha[3.3.1]nonanic systems was the configurational as well as conformational problems arising from the P-atom in comparison to other known bicyclo[3.3.1]nonanes.

The synthesis of the phosphabicyclo[3.3.1]nonanic system consists of a double Michael addition of $PhPH_2$ to 2,7-cyclooctadien-1-one,[1] a reaction which has already been used by us in the preparation of various bicyclo[3.2.1]octanic systems.[2] Actually the addition of the primary phosphine to the dienone at 130° gave, after 8 hr a viscous oil. Following crystallization from acetone, a crystalline adduct (**1**) was obtained in *ca* 50% yield. This crystalline material (**1**) giving rise to only a single spot on a chromatoplate, was found to be only one of the two possible P-epimers. This is best deduced from the NMR spectra of the corresponding methiodide (**3**) (in which only one doublet was observed for the P-C$\underline{H}_3$ group at δ 2·50 d (J_{PH} = 15 Hz)) and from the phosphine oxides (**2**) spectrum (the C_2C_4 protons signals showing on a single isomer *vide infra.*). The proposed 9-phenyl-9-phosphabicyclo[3.3.1]nonan-3-one structure for **1**, was confirmed by the NMR spectrum which shows the proper integration ratio for a one-to-one adduct, between the various regions of the spectra (Table 1) together with a correct elemental analysis and appropriate IR spectrum (Experimental).

The configuration of the P-atom of this adduct (**1**) could be deduced from its phosphine oxide structure (**2**). Following oxidation with H_2O_2, or atmospheric oxygen, **1** was oxidized to **2**, a reaction which is believed to proceed with retention

of configuration.[3] Thus, determination of the configuration of the oxide **2** should also lead to that of the phosphine. Comparison of the NMR spectrum of **2** with that of one of the 8-phenyl-8-oxo-8-phosphabicyclo[3.2.1]nonan-3-ones (**4**)[2a]—in which the P=O is axial to the phosphorinanonic ring, showed great similarity. As in the case of the bicyclo[3.2.1]octanic system, both P-epimers were obtained, the paramagnetic influence of the P=O on the skeleton protons in each isomer could be well established and thus, the distinction between the epimers could be clearly proved.[2a,4] Recently the P-configuration in these isomers was also unequivocally determined on the basis of the X-ray analysis of the corresponding methiodide of **4**.[5] The additional CH_2 group in **2** as compared to **4** is not expected to greatly influence the magnetic anisotropy of the skeleton protons and especially not those belonging to the phosphorinanone ring. Thus, on the ground of the NMR spectra similarity of **2** and **4**[2a] it is reasonable to assume the same P-configuration for the former as for the latter (Table 1). Reduction of compound **2** (which is believed to exist mainly in the chair conformation due to P=O, C=O dipole interaction) by KBH_4 in methanolic solutions yielded **5** which is expected to be the *endo* isomer, as it is known in the case of other bicyclo[3.3.1]nona-3-ones that this isomer is the only one obtainable under such conditions.[6] Compound **5** was, therefore, the suitable epimer for the formation of the adamantane, but unfortunately it was insoluble in apolaric solvents in which the radicalic oxidation processes had to be performed.[7] While checking several experimental conditions for the reduction of **2**, it was found that upon atmospheric hydrogenation at r.t. the phenyl group was surprisingly* the first site to

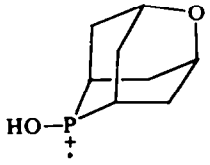


SCHEME 1

* Usually quite drastic conditions are required for such hydrogenations, i.e. the reduction of the phenyl group in phenylmethylpropylphosphine oxide requires 100°, 1500 p.s.i. for 24 hrs.[8]

be reduced, thus leaving the CO unchanged and producing 9-cyclohexyl-9-oxo-9-phosphabicyclo[3.3.1]nonan-3-one (**6**). From the P-irradiated NMR spectrum of **6** the $C_2(C_4)$ proton signals pattern (the AB parts of two equivalent ABX systems) could be clearly observed, (Table 1) and confirmed the system's configuration.

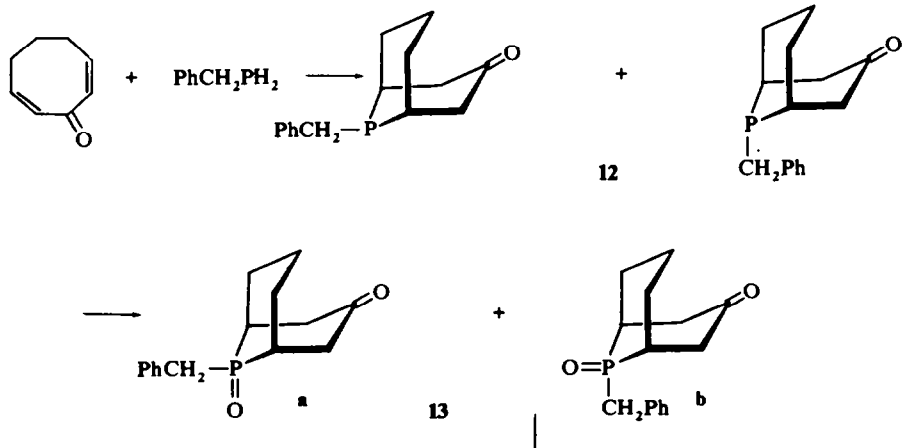
Of interest in this NMR was the observation of the minuteness of the C_6, C_7, C_8 protons signal shift in **6** as compared to **2**, showing the slight influence of the phenyl on these protons in **2**. The consecutive reduction of **6** with KBH_4 which is supposed to give rise to the *endo* isomer, in this case yielded a soluble alcohol **7**, which could be submitted to the transannular oxidation process. Indeed, refluxing of **7** for 3 hr in the presence of $Pb(OAc)_4^9$ yielded, according to TLC, a mixture of three compounds, among which the main one, which was isolated from the reaction mixture following a careful chromatography, being the phospha-oxaadamantane **8**; in the IR spectrum no OH or CO stretching was observable, the NMR spectrum (Table 2) showed the appropriate signals between which the narrow multiplet appearing at δ 3·98(2H) was significant for the two protons near the etheral oxygen bridge. The parent peak in the mass-spectrum, appearing at *m/e* 172, which is attributed to ion **a**, together with the molecular peak at *m/e* 254 (10%), were in full accordance



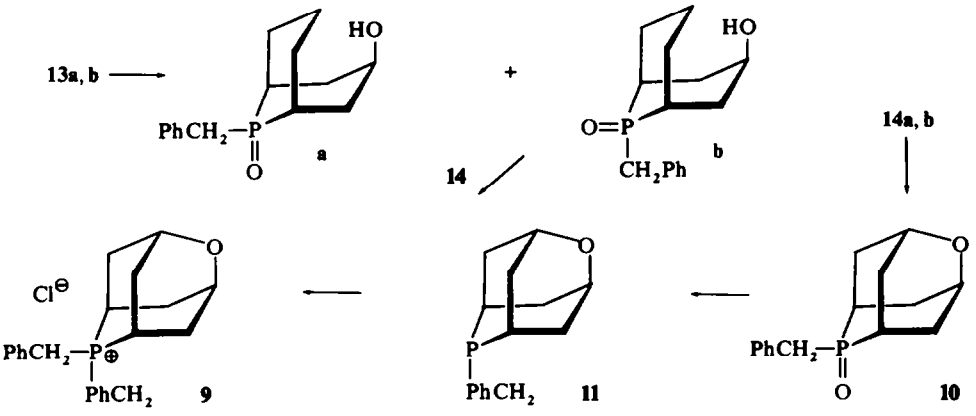
a

with structure **8**. The two additional products which were obtained from the reaction are the expected ketone **6** and the acetate of **7**.[9]

Since a phospha-oxaadamantane of higher symmetry than **8**, would be more suitable for NMR studies, 2,2-dibenzyl-2-phosphonium-6-oxaadamantane chloride (**9**) was prepared.



SCHEME 2



SCHEME 2 (*cont.*)

The addition of $PhCH_2PH_2$ to 2,7-cyclooctadien-1-one yielded in this case, apart from some oligomeric substance, two phosphines. As crystallization was unsuccessful, the phosphines had to be purified by careful chromatography under nitrogen atmosphere. This resulted in two fractions. The first to be eluted was a mixture of the phosphines (**12**) while the second to be eluted by the use of a more polar solvent was the corresponding pair of oxides **13** (NMR: δ 3·38d (J_{PH} = 14 Hz) and δ 3·41d (J_{PH} = 14 Hz) $PC\underline{H}_2Ph$). The spectral data of the 9-benzyl-9-phosphabicyclo[3.3.1]nonan-3-one (**12**) P-epimeric phosphine pair confirmed their structure; the NMR spectrum showed the expected integration ratio between the phenyl, (δ 7·16–7·46 m (5H)), the pair of benzylic (δ 2·98d (J_{PH} = 10 Hz) and δ 3·06d (J_{PH} = 10 Hz) and the alicyclic protons (δ 1·40–3·14 m). The mass spectrum showed the molecular ion at *m/e* 246, 8% intensity of the base peak being *m/e* 155 $(M\text{-}PhCH_2]^+$. Upon chromatography of **13a** and **13b** (obtained either directly from the chromatography or by the oxidation of **12**) **13a** could be obtained in a pure state. The configuration of the P-atom in **13a** was deduced as described above for **2** according to the $C_2(C_4)$ protons pattern (δ 3·26 dd (J = 18; 4 Hz) and δ 2·60 dd (J = 18, <1 Hz) as well as the $P\text{-}C\underline{H}_2$ chemical shift value[2a] (δ 3·41d (J_{PH} = 14.Hz)), and was found to be the same (as in **2**).

Reduction of **13** with KBH_4 in MeOH yielded the two P-epimeric *endo* alcohols **14a** and **14b**, which have the same *Rf* in TLC (NMR: δ 3·70 m and 4·20 m (C-3-H); δ 3·21d (J = 14 Hz) and 3·27d (J = 14 Hz) $P\text{-}C\underline{H}_2Ph$). This pair could be partly separated by crystallization, upon which two different types of crystals were obtained m.p. 215°, ν_{max}^{KBr} 3220, 1600, 1450, 1140, 1100, 1020, 900, 770, 690 cm^{-1} and m.p. 135° ν_{max}^{KBr} 3300, 1600, 1450, 1140, 1040, 1040, 940, 900, 820, 770 cm^{-1}) the former being the major one. The closure of **14a** to the phosphaoxaadamantane **9** (*vide infra*) proved its *endo* configuration.

Cyclization of each one of the two *endo* P-epimeric alcohols (**14a** and **14b**) is supposed to yield the same oxa-phosphaadamantane **10**, thus the transannular reaction with lead tetraacetate was performed on their mixture. The main product of this reaction was the expected **10**, which was accompanied by the parent ketones (**13a**; **13b** in *ca* 20% yield) and small amounts of the acetate of **14**. The reasonably high

yield of the ketones obtained may be explained by the strain released between C_3 and C_7 on changing the hybridization at C-3 from sp^3 to sp^2. In order to obtain the dibenzylphosphonium salt (**9**) the P=O group in **10** was reduced by trichlorosilane in benzene solution[10] to yield the corresponding phosphine **11** which then, on refluxing in CH_3CN with benzyl chloride gave **9**. The higher symmetry of this compound in comparison to **8** and **10** could be well observed in the NMR spectrum after irradiation of the phosphorus atom (Table 2).

After having shown the advantage of complexation of phosphoryl bearing compounds by $Eu(dpm)_3$ for stereochemical elucidation,[4] we checked the influence of $Eu(dpm)_3$ on the NMR spectra of compounds **9** and **10** in $CDCl_3$. As a result of this complexation the spectra was indeed expanded but, unfortunately, not to a first order one, as the difference between the chemical shift of the particular interesting methylene groups remained too small. Other derivatives of these phospha-oxa-adamantone are now under investigation for the NMR study.

TABLE 1

Comp.	H_1;H_5	H_2H_4;H_2,H_4,	$2H_6$;$2H_7$;$2H_8$	Aromatic Protons	Other Protons	Solvent
1	3·02–3·12	2·54–3·02	1·22–2·50	7·32	—	*a*
2	2·54–3·10	3·30–3·65(2H) 2·54–3·10(2H) 3·40dd(J = 18;4)*	1·40–2·30	7·5–7·9	—	*a*
3	3·60–4·00	2·70–3·44	1·20–2·60	7·8–8·4	2·50d(J = 15) P—C$\underline{H}_3$	*b*
5	1·30–3·60	1·30–3·60	1·30–3·60	7·2–7·7	4·98m(C-3-$\underline{H}$)	*c*
6	2·40–2·91	3·1–3·4(2H) 2·4–2·9(2H) 3·52dd(J = 18;4)† 2·85dd(J = 18; <1)	1·60–2·20	—	1·60–2·20($C_6\underline{H}_{11}$)	*a*
7	1·20–2·80	1·20–2·80	1·20–2·80	—	1·20–2·80(C_6H_{11}) 4·70m(C-3-$\underline{H}$)	*a*

All spectra are recorded on a HA-100 instrument.
Solvents: *a.* $CDCl_3$ *b.* d_6-DMSO *c.* CF_3CO_2H.
* The A part of two equivalent ABX systems obtained by additional irradiation of the P-atom.
† The AB part of two equivalent ABX systems obtained by additional irradiation of the P-atom.

TABLE 2

Comp.	H_1;H_3	H_5:H_7	$2H_4$;$2H_8$ $2H_9$;$2H_{10}$	Aromatic Protons	Other Protons
8*	1·20–2·74	3·80–4·16	1·20–2·74	—	1·20–2·74($C_6\underline{H}_{11}$)
9†	2·00–3·37	3·85–4·20	2·00–3·37	6·85–7·50	4·42d(J = 14) Ph-C$\underline{H}_2$
‡	2·90–3·20	3·80–4·10	1·90–2·70	6·85–7·50	4·42s Ph-C$\underline{H}_2$
10†	1·80–2·80	3·88–4·10	1·80–2·80	7·20–7·50	3·30d(J = 12) Ph-C$\underline{H}_2$
11	1·20–2·30	3·88–4·38	1·20–3·00	7·20–7·90	3·35d(J = 12) PhC$\underline{H}_2$

* Spectrum recorded on a 100 Mc—Instrument.
† Spectrum recorded on a 60 Mc—Instrument.
‡ P-irradiated.

EXPERIMENTAL

M.ps were taken on a Unimelt Thomas & Hoover's Capillary m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer Infracord model 337 spectrophotometer. NMR spectra were taken either on a Varian HA-100 spectrometer or a JEOL JNM-C-60HL spectrometer on 5–10% solns in $CDCl_3$ (unless otherwise indicated), containing TMS as an internal standard. Mass spectra were taken with a Hitachi–Perkin–Elmer RMU 6 instrument.

9-Phenyl-9-phosphabicyclo[3.31]*nonan-3-one* (**1**)

A mixture of cycloocta-2,7-dien-1-one (6·1 g) and phenylphosphine (5·8 g) was heated for 8 hr under N_2 at 130–135° on an oil bath. When the reaction was over, depending on the IR spectrum of the mixture (i.e. disappearance of the band at 1650 cm^{-1} and appearance of the CO band at 1700 cm^{-1}) the soln was cooled to room temp and the unreacted reactants were removed under vacuum. The residue was dissolved in acetone from which **1** crystallized out, m.p. 133–135° (50%), $\gamma_{max}^{CHCl_3}$ 3030, 1700, 1450, 1090, 900 cm^{-1}. (Found: C, 72·25; H, 7·38; P, 13·10; $M^{\oplus}$232 (100%). $C_{14}H_{17}OP$ requires: C, 72·40; H, 7·38; P, 13·34%; $M^{\oplus}$232).

9-Phenyl-9-methyl-9-phosphonium-bicyclo[3.3.1]*nonan-3-one iodide* (**3**)

Compound **1** (200 mg) was dissolved in acetone (5 ml) and MeI (200 mg) was added, with stirring. The phosphonium salt precipitated out immediately as a white ppt. The salt was crystallized from water yielding 290 mg m.p. 250° dec. ν_{max}^{KBr} 3090, 1700, 1580, 1440, 1150, 1110, 1090, 940, 900, 740, 630 cm^{-1}. (Found: C, 47·93; H, 5·29; I, 33·91. $C_{15}H_{20}$ IOP required: C, 48·14; H, 5·39; I, 33·91%).

9-Phenyl-9-oxo-9-phosphabicyclo[3.3.1]*nonan*-3-one **2**)

Compound **1** (2 g) was dissolved in chloroform (30 ml) and 30% H_2O_2 (1·5 g) was added, dropwise, to the cooled soln. The heterogeneous mixture was stirred vigorously for 2 hr diluted with more chloroform and washed several times with a 5% $FeSO_4$ soln until a negative KI test was obtained, then washed again with water dried over $MgSO_4$. Evaporation left a crystalline residue (1·7 g) which was crystallized from acetonitrile, m.p. 250° dec; ν_{max}^{KBr} 3040, 1700, 1450, 1150, 1110, 1090, 1060, 895, 760, 740, 725, 690 cm^{-1}. Mass spectra: *m/e* 248 (100%, M^+); 234 (15%); 221 (50%); 220 (30%) 208 (30%); 125 (50%). (Found: C, 67·49; H, 6·86; P, 12·60. $C_{14}H_{17}O_2P$ requires, 6·90; P, 12·47%).

endo-9-*Phenyl-9-oxo-9-phosphabicyclo*[3.3.1]*nonan-3-ol* (**5**)

Compound **2** (0·7 g) was dissolved in MeOH (10 ml), and KBH_4 (0·7 g) was added with stirring portionwise to the refluxed soln during 6 hr. After cooling, the excess reagent was decomposed by the addition of a few drops of AcOH. The soln diluted with more chloroform, washed, with water dried over $MgSO_4$. The residue obtained after evaporation was crystallized from MeOH EtOAc, (0·6 g) m.p. 204–206°; ν_{max}^{KBr} 3250, 1430, 1140, 1100, 1040, 940, 900, 830, 750, 725 cm^{-1}. (Found: C, 67·12; H, 7·51; P, 12·66, $M^{\oplus}$250 (93%) $C_{14}H_{19}O_2P$ requires: C,67·18; H, 7·65; P, 12·37% $M^{\oplus}$250).

9-Cyclohexyl-9-oxo-9-phosphabicyclo[3.3.1] *nonan-3-one* (**6**)

Compound **2** (4 g) in AcOH (50 ml) was hydrogenated over 10% PtO_2 on charcoal at atm pressure and room temp for 48 hr. The product obtained following evaporation of the acid was crystallized from benzene–hexane, ν_{max}^{KBr} 3600, 3310, 1700, 1450, 1140, 1055, 1040, 950, 920, 895, 850, 775, 750 cm^{-1}. (Found: C, 61·35; H, 8·78; P, 10·96; $M^{\oplus}$254 (40%). $C_{14}H_{23}O_2P \cdot H_2O$ requires: C, 62·20; H, 8·57; P, 11·45%; $M^{\oplus}$ 254).

endo-9-*Cyclohexyl-9-oxo-9-phosphabicyclo*[3.31]*nonan-3-ol* (**7**)

Compound **6** was reduced with KBH_4, as was described for the preparation of **5**, to yield 1·8 g of **7**, m.p. 181–183°; ν_{max}^{KBr} 3320, 3210, 1450, 1140, 945, 905, 880, 830, 815, 740 cm^{-1}. (Found: C, 65·64; H, 9·64; P, 11·93 $M^{\oplus}$256 (40%). $C_{14}H_{25}O_2P$ requires: C,65·60; H, 9·83; P, 12·08%, $M^{\oplus}$256).

2-Cyclohexy-2-oxo-2-phospha-6-oxaadamantane (**8**)

A mixture of dry benzene (30 ml), $CaCO_3$ (2 g dried over P_2O_5 at 100°, 0·1 mm) and Pb $(OAc)_4$ (4 g dried over P_2O_5 at 100° 0·1 mm) was heated for 15 min at reflux in a flask fitted with condenser and drying tube. Compound **7** (600 mg) in benzene (20 ml) was then added and refluxing was continued for 3 hr. The mixture was cooled and water (10 ml) added with stirring during 5 hr. After filtration, the soln was dried and evaporated, the residue (320 mg) chromatographed on a silica gel column. Elution with $CHCl_3$–

MeOH (95·5) gave a very hygroscopic material (120 mg) m.p. 144–146° (Et_2O), $\nu_{max}^{CHCl_3}$ 1450, 1150, 1090, 1025, 100, 940, 855 cm^{-1} (Found: $M^{\oplus}$ 254 (50%); $C_{14}H_{20}O_2P$ requires: $M^{\oplus}$ 254).

9-*Benzyl*-9-*phosphabicyclo*[3.3.1]*nonan*-3-*one* (**12**)

A mixture of 2,7-cyclooctadienone (5·5 g) together with benzylphosphine (6 g) was heated for 24 hr under N_2 atm at 130–135° on an oil bath. Following removal of the unreacted reactants, under high vacuum, the residue was purified by chromatography under N_2 on a silica gel column. Elution with chloroform yielded **12** as an hygroscopic oil, $\nu_{max}^{CHCl_3}$ 3040, 1700, 1600, 1450, 1030, 940, 900 cm^{-1}. (Found: $M^{\oplus}$ 246 (78%); $C_{15}H_{19}OP$ requires $M^{\oplus}$ 246).

Further elution with $CHCl_3$–MeOH (95;5) yielded the corresponding oxides **13** which were also very hygroscopic, $\nu_{max}^{CHCl_3}$ 3050, 3030, 1700, 1600, 1450, 1150, 1090, 1055, 1030, 900, 830 cm^{-1}. Mass spectra *m/e* 262 (100%, M^+), 234 (10%) and 171 (7%, $C_8H_{12}O_2P^{\oplus}$).

9-*Benzyl*-9-*oxo*-9-*phosphabicyclo*[3.3.1]*nonan*-3-*one* (**13**)

Compound **12** was oxidized under the same conditions as described for **1** yielding **13** which was identical in all respects with the compound obtained by air oxidation.

endo-9-*Benzyl*-9-*oxo*-9-*phosphabicyclo*[3.3.1]*nonan*-3-*ol* (**14**)

Compound **13** (1·5 g) was reduced by KBH_4 as described for **4** yielding **14a** and **14b** (1·3 g); the mixture was separated by factional crystallization from MeOH–C_6H_6: **14a** m.p. 215°; ν_{max}^{KBr} 3220, 1600, 1450, 1140, 1100, 1020, 900, 770, 690 cm^{-1}. Mass spectra: *m/e* 264 (100%, $M^{\oplus}$·); 247 (44%, $C_{15}H_{20}OP^+$) (Found: C, 68·06; H, 7·84, P, 11·64. $C_{15}H_{21}O_2P$ requires: C, 68·16; H, 8·01; P. 11·71%). **14b** m.p. 135°; ν_{max}^{KBr} 3300, 1600, 1450, 1140, 1040, 940, 900, 820, 770, 700 cm^{-1}. Mass spectra: *m/e* 264 (100%, M^+·); 247 (38%, $C_{15}H_{20}OP^{\oplus}$·).

2-*Benzyl*-2-*oxo*-2-*phospha*-6-*oxaadamantane* (**10**)

Compound **14** (750 mg) was oxidized by $Pb(OAc)_4$ as described for **7**. Elution with $CHCl_3$–MeOH (95;5) from a silica gel column yielded **10** (500 mg) m.p. 184° (acetone-hexane); $\nu_{max}^{CHCl_3}$ 1450, 1150, 1020, 970, 940, 850 cm^{-1}. (Found: C, 67·68; H, 7·32; P, 12·24; $M^{\oplus}$ 262 (100%). $C_{15}H_{19}O_2P$ requires: C, 67·69, H, H, 7·30; P. 11·81%, $M^{\oplus}$ 262).

2-*Benzyl*-2-*phospha*-6-*oxaadamantane* (**11**)

Compound **10** (110 mg) was dissolved in benzene (10 ml) under N_2 atm. To the stirred soln trichlorosilane (0·3 ml) in benzene (2 ml) was added dropwise. After heating at 60–80° for 3·5 hr water (5 ml) was added, the soln was filtered, washed with 10% $NaHCO_3$, water, then dried (Na_2SO_4). Compound **11** (65 mg) which was obtained upon evaporation of the solvent was not crystallized, ν_{max}^{neat} 1430, 1020, 855 cm^{-1} mass spectrum: *m/e* 246 (30%, M^+·); 155 (20%, $C_8H_{12}OP^+$); 91 (100%, $PhCH_2^+$).

2,2-*Dibenzyl*-2-*phosphonium*-6-*oxaadamantane chloride* (**9**)

Compound **11** (60 mg) was dissolved in freshly distilled acetonitrile (10 ml), and freshly distilled benzyl chloride (50 mg) was added. The mixture was refluxed under N_2 overnight. After evaporating the solvent the residue was crystallized from MeOH-EtOAc m.p. 248–250°; ν_{max}^{KBr} 1590, 1450, 1235, 1190, 1090, 1040, 1025, 1000, 940, 850, 830, 790, 770 cm^{-1}. (Found: C, 70·43; H, 7·11; P, 6·97. $C_{22}H_{26}OPCl$ requires: C, 70·86 H, 7·06; P, 6·30%).

REFERENCES

1 [a] R. P. Welcher and N. E. Pay, *J. Org. Chem.* **27**, 1824 (1962);
[b] E. W. Garbisch, *J. Org. Chem.* **30**, 2109 (1965)
2 [a] Y. Kashman and O. Awerbouch, *Tetrahedron* **26**, 4213 (1970);
[b] Y. Kashman and S. Cherkez, *Ibid*, **28**, 155 (1972)
3 L. Horner, *Pure Appl. Chem.* **9**, 225 (1964)
4 Y. Kashman and O. Awerbouch, *Tetrahedron* **27**, 5593 (1971)
5 U. Shmueli and Z. Zurr, *Israel J. Chem.* **9**, 5 (1971)
6 [a] L. L. Zirkle, F. R. Gerns, A. M. Parloff and A. Burger, *J. Org. Chem.* **26**, 395 (1961);
[b] H. O. House, H. C. Müller, C. G. Piff and P. P. Wickhaum, *Ibid.* 2407 (1963)

[7] [a] K. Heusler, J. Kalvoka, *Angew. Chem. Inter Edit.* **3**, 525 (1964);
[b] M. L. Mihailovic, Z. Cekovic, V. Andrevic, R. Matic and D. Jeremic, *Tetrahedron* **24**, 4947 (1968)
[8] P. M. Rylander, *Catalytic Hydrogenation over Platinum Metals* p. 353. Academic Press, New York (1967)
[9] [a] W. A. Ayer, D. A. Law and K. Piers, *Tetrahedron Letters* 2959 (1964)
[b] M. Fisch, S. Smallcombe, J. C. Gramain, M. A. McKervey and J. E. Anderson, *J. Org. Chem.* **35**, 1886 (1970)
[10] W. A. Henderson, S. A. Buckler, *J. Am. Chem. Soc.* **82**, 5794 (1960)