PERKIN 2

Reactions of phosphine with hexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecan-10-one derivatives

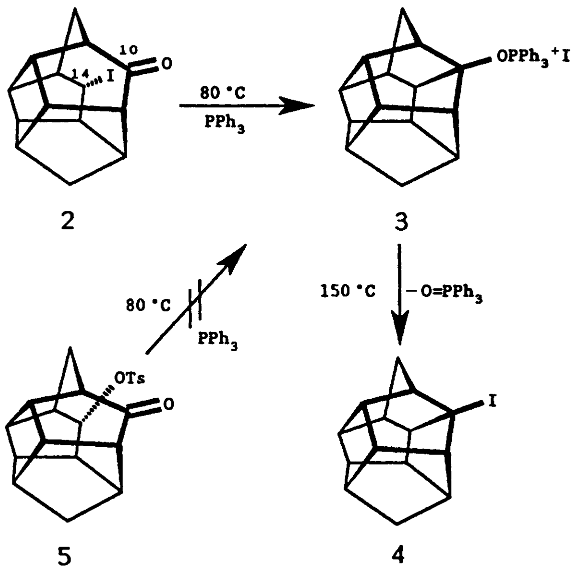
Tahsin J. Chow,[*,a,b] **Lih-Pyng Li,**[b] **Vincent Y. R. Lee,**[b] **Kuan-Jiuh Lin**[a] **and Chong-Yow Chen**[b]

[a] *Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China*
[b] *Department of Chemistry, National Chung Cheng University, Chia-Yi, Taiwan, Republic of China*

Iodoketone 2 reacts with triphenylphosphine or triethyl phosphite to form phosphonium salts 3 and 7 which fragment to an iodide 4 upon heating. The mechanism of C–C bond formation induced by phosphine and phosphite is discussed. A 1,3,2-dioxaphospholane 8 was synthesized from diketone 1 in two steps through an intermediate diol 10, although an attempt for a direct condensation of 1 and triphenylphosphine was unsuccessful. The reaction is rationalized with the aid of semi-empirical calculations. Crystal diffraction analyses for 3 and 8 are reported and some of their bonding parameters are compared with the calculated values.

Introduction

Transannular interaction was shown to exist in the cage-shaped hydrocarbon hexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecan-10,14-dione **1** system.[1] The π-orbitals of C(10) and C(14) of **1** overlap with each other due to their close proximity.[2a] Bond formation between C(10) and C(14) proceeds readily either by photolysis or by metallic reductions.[2b] In connection with this work, formation of the C(10)–C(14) bond has also been observed in the reaction of 14-iodo-10-ketone **2**[2c] with triphenylphosphine. Phosphines and phosphites, owing to their high affinity with oxygen, have been used to induce intermolecular pinacol type C–C coupling for ketones with strong electron-withdrawing substituents.[3,4] In these reactions the polarity of carbonyl groups are inverted (umpolung) while the negative charge developed on carbon is delocalized towards the α-substituents.[5] For ketones with α-halogen substituents, formation of a double bond along with dehalogenation has been reported.[6] In the case of **2**, phosphine induced C(10)–C(14) coupling might be assisted by the overlapping of their π-orbitals and therefore the possibility of this reaction is explored.



Scheme 1

Results and discussion

Reaction of 2 with phosphine and phosphite

Heating **2** with PPh$_3$ in benzene at 80 °C caused the precipitation of a phosphonium salt **3** in 82% yield. Subsequent heating of **3** at a higher temperature (150 °C) in CDCl$_3$ (sealed tube) for 2 h induced its fragmentation to an iodide **4** in 83% yield (Scheme 1). The overall effect on the conversion of **2** into **4** is the deoxygenation of C=O along with the formation of a C–C bond.[7] Compound **3** is stable at ambient temperature and can be purified by recrystallization in methanol as pale yellow prisms with mp 185–186 °C. The ^{1}H-decoupled ^{13}C NMR spectrum shows 18 signals including 12 singlets and 6 doublets (C–P couplings). In the ^{31}P NMR spectrum the phosphorus shows an absorption at δ 55.2 indicating its cationic character. The substituents around the phosphonium centre form a tetrahedral geometry as indicated by crystal diffraction analysis. The iodide in the solid state is located adjacent to the alkoxy group, which is illustrated by the ORTEP drawing shown in Fig. 1. Upon heating, it expels a molecule of O=PPh$_3$ to form **4**. In the presence of excess hydroxide, anion exchange occurred, *e.g.* treatment of **3** in 5% NaOH at room temperature for 30 min yielded the corresponding tertiary alcohol[2c] quantitatively.

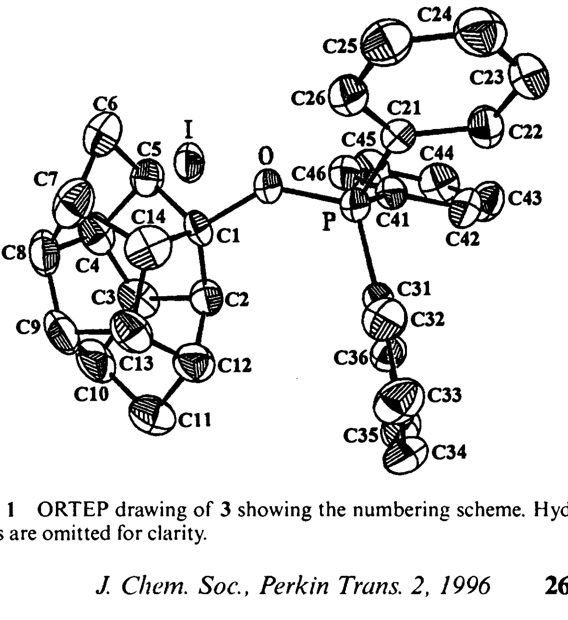
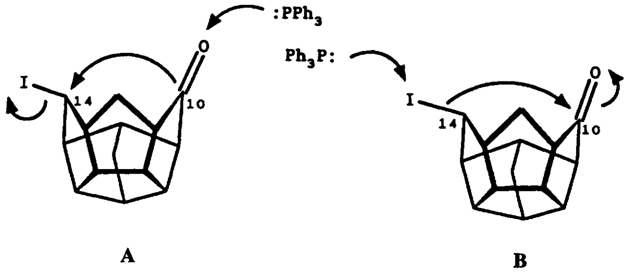


Fig. 1 ORTEP drawing of **3** showing the numbering scheme. Hydrogens are omitted for clarity.

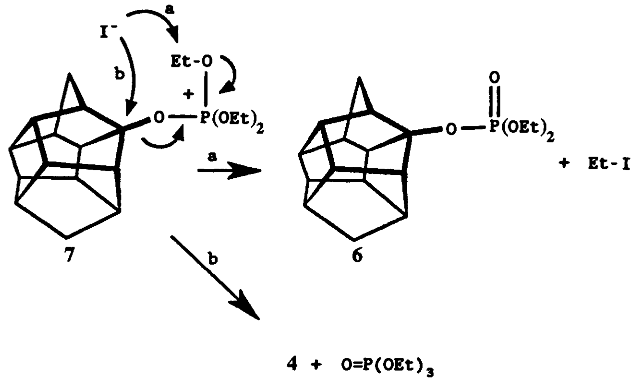
In a normal mode of reaction, the carbonyl carbon of **2** is susceptible to nucleophilic attack, such as by OH^- or a metal hydride. As a consequence the carbonyl oxygen attacks the C(14)–I from the *endo*-side to form a C(10)–O–C(14) linkage.[8] However, in the present reaction with PPh_3, no such product was observed. The nucleophile seeks a site to attack other than the carbonyl carbon. Two possible pathways are feasible as shown in Scheme 2. (A) The phosphorus could approach the oxygen of **2** with its lone pair entering the π^* orbital of C=O and the electronic density on C(10) would be enhanced.[5,9] A successive attack by C(10) on C(14)–I generates a bridging C–C linkage. (B) The phosphorus attacks the iodide instead to produce an anion at C(14). Nucleophilic attack by C(14) on C(10) closes the ring to yield an alkoxide intermediate which rearranges to the phosphonium salt **3**. This can be viewed as a reversal of the ring-opening process.



Scheme 2

It is not apparent as to which of the two pathways occurs in the case of **2**, so that the reaction of 14-tosylate ketone **5** with triphenylphosphine was examined. The tosylate was prepared from **2** and silver tosylate, but heating **5** with triphenylphosphine did not give any C–C coupled product. This result supports pathway B as the mechanism for the formation of **3** from **2**, since an *exo* attack on **5** by phosphine cannot proceed effectively due to steric hindrance. If the reaction went through pathway A, adduct **3** should be obtained where C–C bond is formed *via* endo attack.

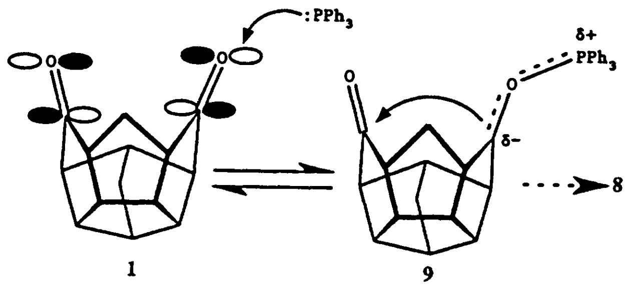
The reaction of **2** with triethyl phosphite was also examined; in this reaction a neutral phosphate **6** was isolated along with a minor yield of iodide **4**. In the ^{13}C NMR spectrum of **6**, the tertiary carbon C(1)–O shows a doublet at δ 106 ($J = 7.5$ Hz) which is shifted to a significantly higher field than that of **3** at δ 114 ($J = 31$ Hz). In the ^{31}P NMR spectrum a multiplet appears at δ −4.5 which is also shifted to a much higher field compared with that of **3** (δ 55.2).[10] Both **4** and **6** were formed presumably through a common intermediate, *i.e.* the phosphonium salt **7**, which fragments upon losing either a molecule of ethyl iodide (to yield **6**) or a molecule of triethylphosphate (to yield **4**) (Scheme 3). The mechanism of this reaction is similar to that of triphenylphosphine (pathway B) since no reaction was observed by heating **5** with triethyl phosphite under the same conditions.



Scheme 3

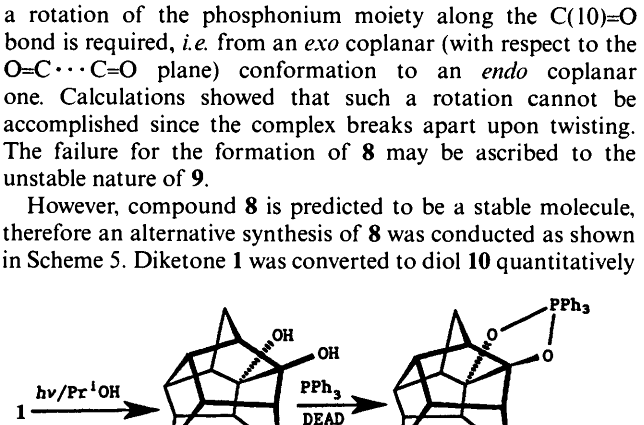
Reaction of 1 with phosphines

In previous studies we have shown that C–C coupling in **1** can be achieved readily by photoexcitation or through a radical anion produced by reactive metals.[2b] These reactions are initiated by putting an electron into the π^* orbital of C=O.[1h] In the reaction with phosphine, such as pathway A in Scheme 2, the umpolung of CO appears as a transient state. Our attempt to make a 1,3,2-dioxaphospholane ring **8** by heating **1** and PPh_3 was unsuccessful.[4h] This reaction has been analysed by a semi-empirical model (PM3)[11] which suggests the existence of an intermediate **9** (Scheme 4). Calculations of the heat of formation of **9** show that it stays at a local minimum on the potential energy surface. In the most stable conformation, the phosphine is kept co-planar with the O=C(10)···C(14)=O plane, on which the original π^* orbital of C=O is located (Fig. 2). The heats of formation of (**1** + PPh_3), **9** and **8** are calculated (PM3) to be 69.9, 107.1 and 89.5 kJ mol^{-1} respectively. As indicated by these values, the conversion **1** into **8** should be endothermic, whereas from **9** to **8** exothermic. In the transformation of **9** to **8** a rotation of the phosphonium moiety along the C(10)=O bond is required, *i.e.* from an *exo* coplanar (with respect to the O=C···C=O plane) conformation to an *endo* coplanar one. Calculations showed that such a rotation cannot be accomplished since the complex breaks apart upon twisting. The failure for the formation of **8** may be ascribed to the unstable nature of **9**.



Scheme 4

However, compound **8** is predicted to be a stable molecule, therefore an alternative synthesis of **8** was conducted as shown in Scheme 5. Diketone **1** was converted to diol **10** quantitatively by UV irradiation in propan-2-ol.[2b] Treatment of **10** with PPh_3 and diethyl azodicarboxylate gave **8** in 83% yield. It is stable as expected under ambient conditions and melts at 241–242 °C. The structure of **8** possesses a plane of symmetry as analysed by both NMR spectroscopy and by X-ray crystal diffraction analysis.



Scheme 5

Crystal structures of 3 and 8

Structures of **3** and **8** were solved by X-ray diffraction analyses. Their crystallographic parameters are listed in Table 1† and their ORTEP drawings in Figs. 1 and 3. The packing pattern of

---

† Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/34.

Table 1 Crystallographic and refinement data of compounds **3** and **8**

	3	**8**
Empirical formula	$C_{32}H_{30}IOP$	$C_{23}H_{29}O_2P$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pnma*
Cell dimensions		
a/Å	10.313(2)	16.627(2)
b/Å	10.314(4)	12.310(2)
c/Å	24.110(7)	11.426(3)
β/degrees	93.470(20)	
v/Å	2559.8(12)	2338.4(7)
Crystal size/mm	0.15 × 0.15 × 0.20	0.25 × 0.35 × 0.46
Formula weight	588.46	476.55
z	4	4
F(000)	1192	956
D(calc)/g cm^{-3}	1.527	1.354
μ/mm^{-1}	1.32	0.14
λ/Å	0.71069	0.71069
2θ (max)/degrees	45	45
Diffractometer	Nonius CAD-4	Nonius CAD-4
Scan mode	$\theta/2\theta$	$\theta/2\theta$
hkl mode	$-11 < h < 11$ $0 < k < 11$ $0 < l < 25$	$0 < h < 17$ $0 < k < 13$ $0 < l < 12$
No. unique reflections	3038	1603
No. obsns $I_0 > 2\sigma(I_0)$	2416	1375
Atoms refined	65	38
Parameters	376	233
R[a]	0.033	0.028
R_w[b]	0.035	0.034
Goodness of fit[c]	2.05	2.48
Maximum Δ/σ	0.001	0.001
D-map maximum, e/Å^3	0.740	0.190
D-map minimum, e/Å^3	−0.750	−0.280

[a] $R = \Sigma||F_0|F_c||/\Sigma|F_o|$. [b] $[w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma|F_o| + 5 \times 10^{-5}|F_o|^2]$. [c] $[\Sigma w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$.

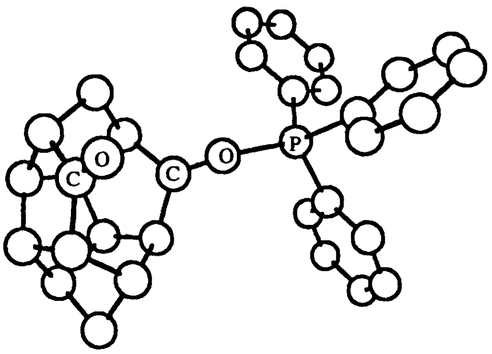


Fig. 2 Computer optimized geometry of **9** by PM3 implanted in MOPAC 6.0. It is indicated that the phosphorus atom is coplanar with the O=C···C=O plane.

3 in unit cell viewed along [100] direction is shown in Fig. 4, in which the position of iodide in the crystal lattice is better illustrated.

The structural parameters of **3** and **8** were compared with those calculated by PM3, on which our rationale of mechanism is based. The molecular geometries were allowed to be fully optimised in calculations. Only the cationic moiety of **3** (gas phase) was computed since the model is not suitable for estimating ion pairs. Selected bond lengths and angles of the crystals and those derived from calculations are compared in Tables 2 and 3. The molecular geometries are reasonably well estimated by this model. A few structural features of **3** and **8** are worthy of a mention. The O–P bond of **3** (1.55 Å) is found to be shorter than that of **8** (1.69 Å), but the O–C(1) bond of the former (1.48 Å) is longer than that of the latter (1.42 Å). The calculated O–P bonds are significantly longer (1.68 Å for **3** and 1.78 Å for **8**) than the experimental values, while the calculated O–C(1) bonds are shorter (1.41 Å for **3** and 1.38 Å for **8**) than the experimental values. The three C–C bond lengths around C(1) are found to be unequal, *i.e.* 1.56, 1.54 and 1.51 Å in **3** and 1.55, 1.53 and 1.52 Å in **8**, depending on their relative positions to the phosphorus grouping, however, all values are about 0.034 Å (averaged) shorter than those estimated by the theoretical model. Despite some deviations the PM3 model gave a fair description of the overall structures of these molecules.

Table 2 Selected bond distances (Å) and angles (°) of compound **3** and the corresponding values calculated by PM3[a]

	Crystal data	Calculated
P–O	1.553(3)	1.68
O–C(1)	1.480(5)	1.41
P–C(21)	1.783(5)	1.75
P–C(31)	1.772(5)	1.75
P–C(41)	1.781(5)	1.75
P–O–C(1)	136.0(3)	133.3
O–P–C(21)	102.9(2)	103.1
O–P–C(31)	114.4(2)	112.1
O–P–C(41)	110.0(2)	109.0
C(1)–C(2)	1.507(8)	1.55
C(1)–C(5)	1.537(7)	1.57
C(1)–C(14)	1.556(7)	1.58
C(2)–C(1)–C(5)	110.2(4)	106.5
C(2)–C(1)–C(14)	105.4(4)	105.2
C(5)–C(1)–C(14)	102.8(4)	102.7
P–O–C(1)–C(2)	−19.3(2)	86.0
P–O–C(1)–C(5)	−144.5(4)	−155.8
P–O–C(1)–C(14)	103.1(4)	−39.7

[a] Only the cationic moiety is included in the calculation with key word CHARGE=1. Geometry is fully optimized by PM3.

Table 3 Selected bond distances (Å) and angles (°) of compound **8** and the corresponding values calculated by PM3

	Crystal data	Calculated[a]
P–O	1.685(1)	1.76, 1.79
P–C(10)	1.874(2)	1.85, 1.91
P–C(16)	1.809(3)	1.83
O–C(1)	1.417(2)	1.38, 1.38
C(1)–C(1a)	1.551(4)	1.59
C(1)–C(8)	1.529(3)	1.56
C(1)–C(2)	1.523(3)	1.55
O–P–Oa	88.65(6)	87.6
C(1)–P–C(10a)	89.18	89.3
P–O–C(1)	118.0(1)	117.2, 117.7
O–C(1)–C(1a)	106.5(1)	107.9, 108.7

[a] Geometry is fully optimized by PM3 without symmetry restrictions. Values from the two equatorial phenyl groups are not averaged.

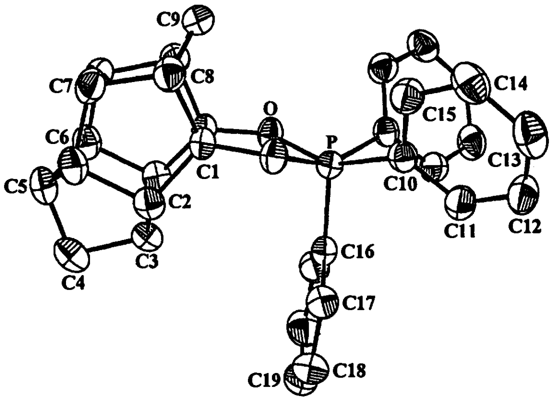


Fig. 3 ORTEP drawing of **8** showing the numbering scheme. Hydrogens are omitted for clarity. The molecule lies on a plane of symmetry containing atoms C(4), C(9), P and C(16).

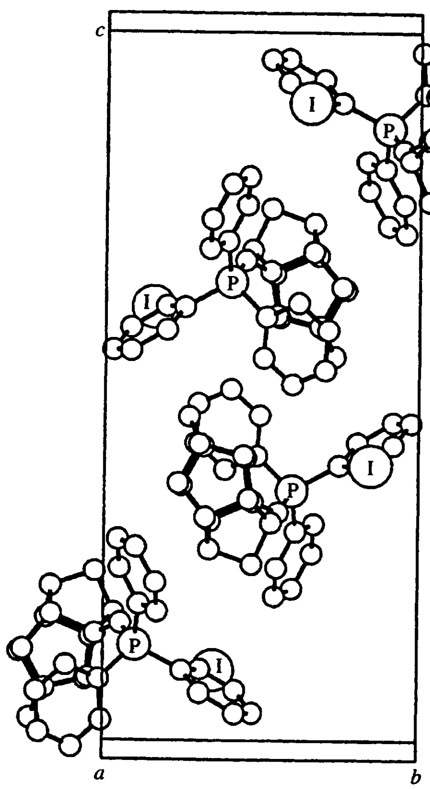


Fig. 4 Packing pattern of **3** in a unit cell viewed along the [100] direction. Hydrogens are omitted for clarity.

Conclusions

A C–C coupling was found in the reaction of triphenylphosphine with compound **2** (14-iodo-10-ketone), although a similar reaction did not proceed with **1** (10,14-diketone). The mechanism of the former was believed to proceed through nucleophilic attack from C(14) to C(10) instead of going through a C(10)=O umpolung intermediate. Semi-empirical calculations on the phosphine adducts of **1** and **2** were found to comply reasonably well with their crystal parameters.

Experimental

General

^{1}H and ^{13}C NMR spectra were obtained either on a Brucker AMX-500 or a Varian Gemini-200 FT spectrometer. Chemical shifts on ^{1}H were measured downfield from TMS in δ units, while those of ^{13}C spectra were calibrated with respect to the central peak of $CDCl_3$ at δ 76.90 as an internal reference. IR spectra were recorded on a Perkin-Elmer 682 IR spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 2400 EA instrument. Mass spectra were recorded on a Fisons VG Trio-2000 spectrometer. Melting points were measured by a Thomas-Hoover mp apparatus and were uncorrected.

Heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecanyltriphenylphosphonium iodide (3)

To a round-bottom flask fitted with a condenser was added freshly distilled benzene, compound **2**^{2c} (0.78 g, 2.39 mmol) and triphenylphosphine (0.75 g, 2.86 mmol) under a nitrogen atmosphere. The solution was heated to reflux for 2 days and precipitates formed gradually. The precipitates were collected by filtration, washed with ethyl acetate and recrystallized from ethyl acetate–methanol. The light yellow crystals weighed 1.08 g (1.84 mmol, 77%), mp 180–182 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.57 (1 H, d, J = 11 Hz), 1.67 (1 H, d, J = 11 Hz), 1.78 (1 H, d, J = 11 Hz), 2.06 (1 H, d, J = 11 Hz), 2.20 (1 H, d, J = 5 Hz), 2.25 (1 H, d, J = 5 Hz), 2.27–2.43 (6 H, m), 2.53–2.59 (1 H, m), 2.64 (1 H, m), 2.84 (1 H, t, J = 5.5 Hz), 7.74–7.79 (12 H, m), 7.84–7.89 (3 H, m); ^{13}C NMR ($CDCl_3$, 50 MHz, ^{1}H-decoupled) δ 41.07, 42.37, 48.75, 49.33, 49.57, 50.51, 51.20, 51.29, 51.70, 53.10, 54.00, 55.27, 64.61 (d, J = 14 Hz), 114.10 (d, J = 31 Hz), 120.38 (d, J = 266 Hz), 130.54 (d, J = 34 Hz), 133.09 (d, J = 29 Hz), 136.26 (d, J = 6.5 Hz); ν(KBr)cm^{-1} 3444 (br), 2970, 1594, 1451, 1325; m/z (CI) (relative intensity) 184 (100%), 279 (25), 462 (80) (Found: C, 65.33; H, 5.19. Calc. for $C_{32}H_{30}IOP$: C, 65.31; H, 5.14%).

1-Iodoheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane (4)

Compound **3** (91 mg, 0.155 mmol) was dissolved in $CDCl_3$ and sealed in an NMR tube. The tube was immersed in an oil bath heated to 160 °C for 4 h and the solution darkened gradually. Compound **4** was isolated as a white solid by a silica gel column chromatograph eluted with hexane (40 mg, 0.13 mmol, 83%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.81 (2 H, s), 1.86 (1 H, d, J = 11 Hz), 2.26 (1 H, d, J = 11 Hz), 2.30–2.50 (8 H, m), 2.83–3.00 (2 H, m), 3.06 (1 H, m); ^{13}C NMR ($CDCl_3$, 50 MHz, ^{1}H-decoupled) δ 29.60, 41.11, 41.68, 48.76, 50.96, 51.23, 51.98, 52.10, 52.18, 53.04, 53.38, 62.22, 66.01, 68.30; ν(KBr)/cm^{-1} 2955, 1465, 1298; m/z (EI) (relative intensity) 310 (10, M$^+$), 183 (100, M$^+$−I).

10-Oxohexacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}]tetradecan-14-yl *p*-toluenesulfonate (5)

To a two-neck round-bottom flask fitted with a nitrogen inlet and a septum silver *p*-toluenesulfonate (155 mg, 0.55 mmol) in CH_3CN (10 ml) was injected through a syringe. The solution was kept at −5 °C and away from light, then **2** (180 mg, 0.55 mmol) in CH_3CN (3 ml) was injected. The reaction mixture was stirred at 0 °C for 2 h and then was allowed to warm up gradually to room temperature for another 18 h. The reaction was quenched by the addition of cold water, the resulting mixture was extracted with diethyl ether (3 × 10 ml). The ether layers were combined, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Products were isolated on a silica gel chromatograph eluted with hexane–ethyl acetate (3:2) to yield **5** (147 mg, 0.40 mmol, 72%) and a minor amount of a hemiketal^{2c} (8.4 mg, 0.039 mmol, 7.1%) resulted from hydrolysis of **2**. Physical data of **5**: mp 134–136 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.68 (2 H, m), 1.95 (1 H, dt, J = 7, 13 Hz), 2.20 (1 H, d, J = 13 Hz), 2.37 (1 H, m), 2.44 (3 H, s), 2.55–2.61 (3 H, m), 2.75–2.90 (3 H, m), 2.90–3.05 (1 H, m), 3.05–3.20 (2 H, m), 4.28 (1 H, d, J = 2 Hz), 7.34 (2 H, d, J = 8 Hz), 7.74 (2 H, d, J = 8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ^{1}H-decoupled) δ 21.56, 42.22, 42.73, 46.21, 47.76, 51.51, 52.09, 53.92, 56.17, 56.76, 57.07, 57.26, 65.73, 90.79, 127.80, 129.74, 133.40, 144.54, 226.83; m/z (EI) (relative intensity) 155 (10%), 170 (30), 198 (100), 215 (2.8), 370 (M$^+$, 1.0); ν($CDCl_3$)/cm^{-1} 1722, 1601, 1361 (Found: C, 67.61; H, 5.85. Calc. for $C_{21}H_{22}O_4S$: C, 68.08; H, 5.99%).

Diethylheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecanylphosphate (6)

To a two-neck round-bottom flask fitted with a condenser and a nitrogen inlet–outlet was added **2** (200 mg, 0.61 mmol) and $P(OEt)_3$ (0.628 ml, 3.67 mmol) in toluene. The solution was heated at reflux for 52 h under a nitrogen atmosphere, then was evaporated *in vacuo*. Products were isolated by a silica gel chromatograph eluted with hexane to collect **4** (40 mg, 0.13 mmol, 21%) and **6** (138 mg, 0.41 mmol, 67%). Physical data of **6**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.32 (6 H, t, J = 7.2 Hz), 1.78 (3 H, s), 1.80 (1 H, d, J = 11 Hz), 2.08 (1 H, d, J = 11 Hz), 2.40–2.70 (7 H, m), 2.75–2.95 (3 H, m), 4.05 (2 H, q, J = 7.2 Hz), 4.09 (2 H, q, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ^{1}H-decoupled) δ 16.08 (d, J = 7.0 Hz), 40.89, 42.53, 49.19, 49.65, 49.81, 50.78, 51.51, 51.92, 52.29, 53.37, 54.03 (d, J = 3.6 Hz), 55.35, 62.41 (d, J = 6.3 Hz), 63.27 (d, J = 6.0 Hz), 106.05 (d, J = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 80 MHz) δ −4.48 (tm, J = 7.3 Hz); m/z (CI) (relative intensity) 89 (100%), 111 (43), 139 (23), 182 (23), 200 (6.5), 210 (2.7), 336 (M^+, 1.4); ν(KBr)/cm^{-1} 2960, 1576, 1447, 1212, 1046.

Heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecan-1,2-dioxytriphenylphosphorane (8)

To a round-bottom flask fitted with a condenser was added diol **10**[2b] (325 mg, 0.15 mmol), followed by a benzene (3 ml) solution of PPh_3 (40 mg, 0.15 mmol) and a benzene (1 ml) solution of diethyl azodicarboxylate (0.50 ml). The reaction mixture was stirred under a nitrogen atmosphere for 3 h at room temperature. It was dried *in vacuo* and compound **8** (59.5 mg, 0.125 mmol, 83%) was recrystallized from $CHCl_3$, mp 244–246 °C. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.27 (1 H, m), 1.48 (2 H, s), 1.80 (1 H, d, $J = 11$ Hz), 2.10 (1 H, d, $J = 11$ Hz), 2.28–2.40 (5 H, m), 2.45 (2 H, m), 2.59 (2 H, m), 7.18–7.26 (9 H, m), 7.50–7.65 (6 H, m); ^{13}C NMR ($CDCl_3$, 50 MHz, ^1H-decoupled) δ 39.34, 42.30, 47.54, 49.31, 49.72, 51.25, 52.20, 54.02, 96.10, 127.24 (d, $J = 13$ Hz), 127.91, 131.97 (d, $J = 9$ Hz), 146.72 (d, $J = 117$ Hz); *m/z* (CI) (relative intensity) 262 (100%), 399 (81), 476 (M^+, 0.41); ν(KBr)/cm^{-1} 3000, 2880, 1450, 1390 (Found: C, 80.10; H, 6.21. Calc. for $C_{32}H_{29}O_2P$: C, 80.65; H, 6.13%).

Acknowledgements

This work was supported in part by the National Science Council of The Republic of China.

References

1 (*a*) T. J. Chow, C.-C. Wei, T.-K. Wu, H.-D. Martin and B. Mayer, *J. Org. Chem.*, 1995, **60**, 5651; (*b*) B. Albert, D. Elsäßer, D. Heckel, S. Kopmeier, H.-D. Martin, B. Mayer, T. J. Chow, T.-K. Wu and S.-K. Yeh, *Chem. Ber.*, 1991, **124**, 803.

2 (*a*) T. J. Chow, T.-K. Wu and H.-J. Shih, *J. Chem. Soc., Chem. Commun.*, 1989, 490; (*b*) T. J. Chow, T.-K. Wu and S.-K. Yeh, *Tetrahedron Lett.*, 1989, **30**, 1279; (*c*) T. J. Chow and T.-K. Wu, *J. Org. Chem.*, 1988, **53**, 1102.

3 (*a*) R. F. Stockel, *Tetrahedron Lett.*, 1966, 2833; (*b*) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, 1976, **98**, 2895.

4 (*a*) F. Ramirez, S. B. Bhatia and G. P. Smith, *Tetrahedron*, 1967, **23**, 2067; (*b*) F. Ramirez, *Acc. Chem. Res.*, 1968, 168; (*c*) F. Ramirez, N. Ramanathan, N. B. Desai, N. Ramanathan and C. V. Greco, *J. Am. Chem. Soc.*, 1963, **85**, 3056; (*d*) F. Ramirez, N. Ramanathan and N. B. Desai, *J. Am. Chem. Soc.*, 1963, **85**, 3456; (*e*) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, 1956, **78**, 5614.

5 R. F. Stockel, *J. Chem. Soc., Chem. Commun.*, 1968, 1594.

6 (*a*) S. Trippett, *J. Chem. Soc.*, 1962, 2337; (*b*) F. W. Lichtenthaler, *Chem. Rev.*, 1961, **61**, 608; (*c*) N. Perkow, K. Ullerich and F. Meyer, *Naturwiss.*, 1952, **39**, 353.

7 C. Guo and X. Lu, *J. Chem. Soc., Chem. Commun.*, 1993, 394.

8 T. J. Chow and T.-K. Wu, *J. Org. Chem.*, 1991, **56**, 6833.

9 F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, 1963, **85**, 3252.

10 M. Murry, R. Schmutzler, E. Gründemann and H. Teichmann, *J. Chem. Soc. (B)*, 1971, 1714.

11 J. J. P. Stewart, *J. Computer-Aided Mol. Design*, 1990, **4**, 1. MOPAC 6.0 program was distributed by QCPE, Indiana U.

Paper 6/03536A
Received 21*st May* 1996
Accepted 1*st August* 1996