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An Improved Preparation of Diphenylmethylenecyclopropanes and their Use in Intramolecular Palladium Catalysed [3+2] Cycloadditions

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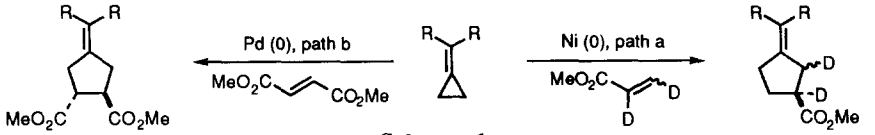
Abstract: *The synthesis and intramolecular palladium catalysed cycloaddition reactions of diphenylmethylenecyclopropanes **1** and **2** containing olefinic and acetylenic acceptors are described. This strategy provides a useful entry into some highly functionalised bicyclo[3.3.0]octane systems.*

The discovery of a nickel catalysed [3+2] cycloaddition of methylenecyclopropane with methyl acrylate to yield the corresponding methylenecyclopentane represented a significant step towards the elaboration of a useful 'Diels-Alder like' strategy for the construction of cyclopentanoids.[1] Binger and coworkers have undertaken extensive studies on this cycloaddition process from which they have made a number of interesting and important discoveries.[2] Palladium or nickel catalysts facilitate this cycloaddition process although the regiochemical outcome of the reactions are highly dependant on the nature of the metal and its associated ligands. Nickel catalysts, particularly in the absence of phosphine ligands, favour formation of products derived from cleavage of the proximal bond of the cyclopropane (Scheme 1, path a), whereas palladium catalysts yield cycloadducts derived from distal bond cleavage (Scheme 1, path b). A further important feature of this reaction stems from the fact that reactions involving geometrically defined olefinic acceptors often provide products in which the initial alkene geometry has been preserved.[2] The ability to control both the regio- and stereochemical outcome of this process suggest that it might provide a powerful method for cyclopentanoid synthesis. However, problems associated with a lack of regiochemical control and competitive dimerisation reactions of the alkylidinecyclopropanes have prevented its widespread application in organic synthesis.

We reasoned that an intramolecular variant of this reaction in which the reaction components were tethered together might alleviate such problems and hence provide an efficient route into polycyclic systems. In this paper, we disclose in full detail our initial studies directed towards realising this objective.[3,4]



Scheme 1

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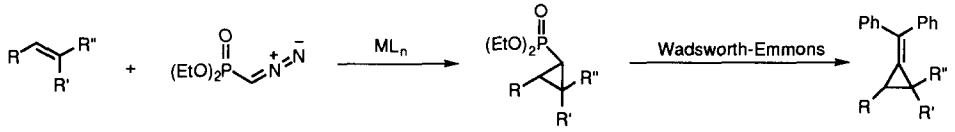
RESULTS AND DISCUSSION

Substrate Design and Synthesis.

Intermolecular precedent suggested that diphenylmethylenecyclopropane derivatives would provide excellent substrates for this intramolecular transition metal catalysed [3+2] cycloaddition process. Such compounds readily undergo regiospecific distal cleavage of the cyclopropane ring in the presence of palladium catalysts.[2] Furthermore, the tetrasubstituted double bond complexes poorly to the catalyst limiting competitive dimerisation of the diphenylmethylenecyclopropane. In designing substrates for our initial investigations, we elected to further bias the system towards cyclisation by incorporating a *gem*-dimethyl substituent into the substrates such that they might benefit from the Thorpe-Ingold effect.[5] With these ideas in mind, we chose to study the palladium catalysed cycloadditions of **1** and **2** (Figure 1).

Figure 1

In order to construct the desired precursors, a modified cyclopropanation / Wadsworth-Emmons strategy for the synthesis of diphenylmethylenecyclopropanes was developed (Scheme 2).[6] Although a number of routes to the intermediate cyclopropylphosphonates had been described in the literature when we undertook this work, they suffered from low chemical yields and/or involved multiple step sequences.[7] Perhaps the most attractive of these approaches was reported by Seyferth.[7a] This one step method involved the decomposition of diazomethylphosphonates to the corresponding carbenes in the presence of metallic copper and subsequent trapping of the resulting carbene with an appropriate alkene. The main drawback with this procedure was the low yield of the desired cyclopropylphosphonates obtained in this reaction even in the presence of a vast excess of the alkene trap. Competitive dimerisation of the carbene intermediate producing 1,2-bis(dialkylphosphono)-ethene was a significant and unwanted side reaction in this process.



Scheme 2

We reasoned that the slow addition of the diazomethylphosphonate to a homogeneous transition metal salt might provide a metal carbenoid species capable of facilitating this reaction in a more efficient fashion. Although the use of rhodium acetate or rhodium pivalate initiated smooth decompostion of diethyl diazomethylphosphonate (DAMP) at room temperature, rapid deactivation of the catalyst occurred. Further experimentation led us to copper (I) triflate which proved to be a particularly effective catalyst for this reaction.[8] Thus, slow addition of DAMP *via* a syringe pump to a well stirred solution of the alkene and cuprous triflate (2-5 mol%) in dichloromethane smoothly furnished the corresponding cyclopropylphosphonates. The scope of this reaction has been surveyed using a variety of mono- and disubstituted alkenes and representative examples are presented (Table 1). Notably, only a two to three fold excess of the alkene is required using this procedure and the unreacted olefin can be recovered and recycled if necessary.

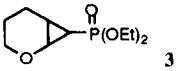
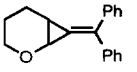
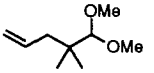
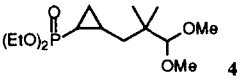
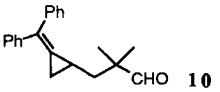
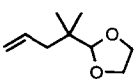
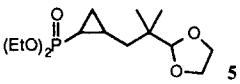
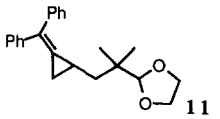
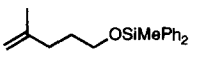
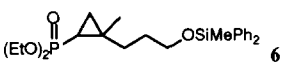
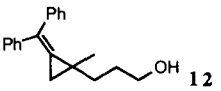
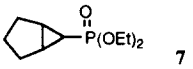
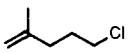
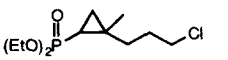
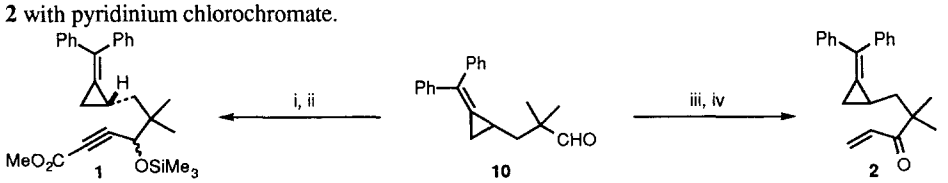
Alkene	*Cyclopropylphosphonate*	*Yield (%)#*	*Diphenylmethylene-cyclopropane*	*Yield (%)*
	 3	71	 9	63
	 4	46¶ (65)	 10	52§
	 5	73	 11	76
	 6	46¶ (98)	 12	40§
	 7	62	-	-
	 8	79	-	-

Table 1. # Yields based upon DAMP unless otherwise indicated. Yields in parentheses refer to those based upon recovered olefin. ¶ Yield based upon alkene. § A deprotection step is included in the work up.

The optimal experimental conditions for the Wadsworth-Emmons reaction were found to be highly dependant on the substrate employed. Thus, whereas reaction of **3** with benzophenone using n-butyllithium as the base furnished **9** directly, formation of **10** and **11** was best accomplished through isolation of the intermediate β-hydroxyphosphonate and subsequent exchange of the lithium counterion for sodium. In this regard, we found that sodium hydride in DMF at 90°C gives better yields than sodium hydride and 18-crown-6 in tetrahydrofuran which has been employed in similar systems by Hirao.[7b] In the conversion of **6** to **12**, isolation of the β-hydroxyphosphonate proved impractical and better results were obtained by direct addition of sodium *tert*-butoxide to the initially formed lithium alkoxide.

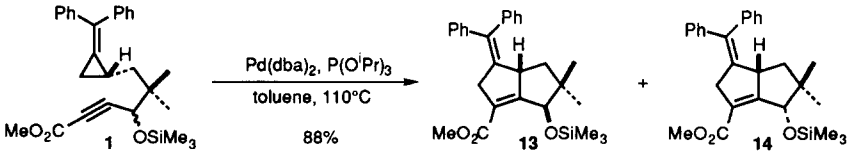
Using this protocol we were able to synthesize reasonable quantities of aldehyde **10** in a concise and reasonably efficient 4 step sequence from 2,2-dimethyl-4-pentenal.[9] The synthesis of acetylenic ester **1** from **10** was achieved using a simple one pot process. Thus, treatment of this aldehyde with the lithium anion derived from deprotonation of methyl propriolate with butyllithium followed by *in situ* silylation with trimethylsilyl chloride gave **1** in 97% yield as a 1:1 mixture of diastereomers (Scheme 3). Conversely, treatment of **10** with vinyl magnesium bromide furnished the homologated allylic alcohol which was oxidised to enone **2** with pyridinium chlorochromate.



Scheme 3. (i) Li-C≡CCO$_2$Me, THF, -78°C; (ii) TMSCl, -78°C to rt, 97%; (iii) vinylmagnesium bromide, 0°C, Et$_2$O, 61%; (iv) PCC, CH_2Cl_2, 76%.

Cycloaddition Studies.

With precursors **1** and **2** in hand, the stage was set to examine the key intramolecular cycloaddition reactions. A catalyst derived from mixing bis(dibenzylidineacetone)palladium (0) with triisopropylphosphite in a 1:1 molar ratio was used for most of our initial studies. Thermolysis of the substrate in a sealed tube under argon with 5-20 mol% of this catalyst mixture was found to be an effective method of performing the cycloaddition reactions.[10] Treatment of acetylenic ester **1**, prepared as a 1:1 mixture of diasteromers, with this catalyst system smoothly provided bicyclic adducts **13** (50%) and **14** (38%) (Scheme 4). Some problems were encountered in the purification of the less polar adduct **13** which was contaminated with traces of unreacted starting material. While column chromatography failed to provide **13** free from this contaminant, pure material could be obtained by simply resubjecting the semi-purified cycloadduct to the above cyclisation protocol.



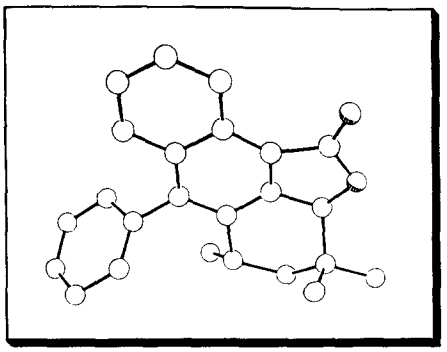
Scheme 4

Interestingly, the conversion of **1** into cycloadducts **13** and **14** could also be accomplished using tetrakis(triphenylphosphine) palladium (0) at room temperature using mild sonication albeit rather slowly (*ca* 60% conversion after 100 hours). While this catalyst is not normally considered to be one of the most reactive in this area,[2] the temperature and pressure effects induced by cavitation in conjunction with the intramolecular nature of this particular cyclisation combine to facilitate cyclisation in this instance.

The bicyclic nature of **13** and **14** and the relative stereochemistry of the bridgehead hydrogen atom (H-6a) and the trimethylsiloxy substitutent attached to C-4 were assigned upon the basis of nOe measurements made on both diastereomers (Figure 2). Most significantly for **14**, an nOe enhancement of H-4 is observed upon irradiation of H-6a, similarly irradiation of H-4 results in an enhancement of H-6a. No nOe's are observed between these two hydrogen atoms in cycloadduct **13**. On the basis of these measurements, bicycles **13** and **14** were assigned the *trans* and *cis* stereochemistries respectively.

Figure 2. Selected nOe data for **13** and **14**.

It is of interest to compare the results of the palladium catalysed reaction of **1** with those obtained in the purely thermal reaction. Simple thermolysis of the same material in toluene lead to extensive decomposition of the substrate from which a low yield of lignan **15** could be isolated after brief treatment with tetrabutylammonium fluoride. The structure of this lignan was unambigously determined using single crystal x-ray diffraction (Figure 3).[11]



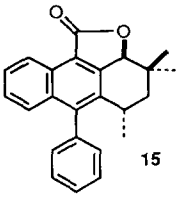
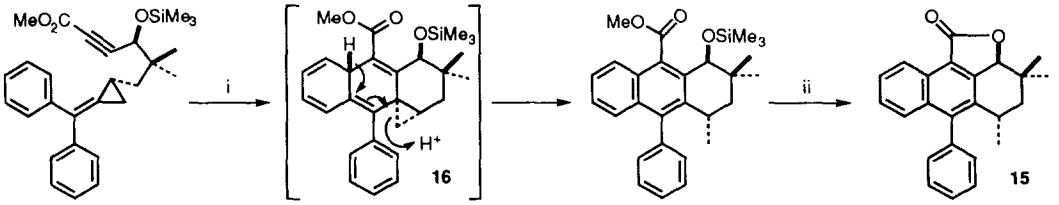


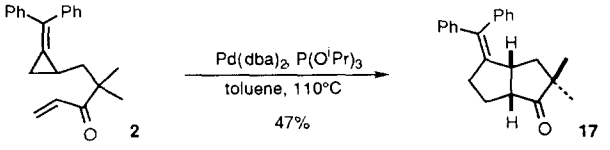
Figure 3. X-ray crystal structure of **15**.

A mechanistic rationale for this transformation can be proposed based upon the known intermolecular Diels-Alder reaction of diphenylmethylenecyclopropane with tetracyanoethylene (Scheme 5).[12] Thus, intramolecular Diels-Alder reaction between the acetylenic ester and a diene consisting of the exocyclic double bond of the cyclopropane and one of the aromatic double bonds would furnish pentacycle **16**. Further steps involving prototropic migration to relieve strain and rearomatise the system and subsequent fluoride induced lactonisation account for the formation of this adduct. No cycloadducts derived from the other diastereomer of **1** were isolated from this thermal reaction. However, this does not necessarily indicate any intrisic difference in the reactivity of the two diastereomers in this Diels-Alder cyclisation but may simply reflect difficulties associated with isolation of these materials from the reaction mixture.



Scheme 5. (i) 140-150°C, sealed tube (ii) TBAF, THF, 20% based upon indicated diastereomer.

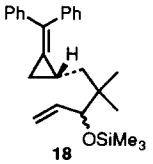
Subjection of enone **2** to the palladium catalysed cyclisation conditions afforded bicyclic ketone **17** *via* distal cleavage of the diphenylmethylenecyclopropane, albeit in only 31% yield. All spectroscopic data were consistent with this structure, and a series of selective decoupling experiments enabled complete assignment of the ^{1}H nmr spectrum. Surprisingly, the major product of this intramolecular cyclisation appeared to be a dimer. Whilst the elucidation of the structure of this material was precluded, the dimeric nature of this material was readily established by mass spectrometry. To prevent dimerisation, and hence favour formation of the monomer, the reaction was repeated under relatively high dilution conditions (0.025M). Under these conditions, bicyclic ketone **17** was produced in an improved 47% yield (Scheme 6).



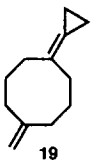
Scheme 6

The successful conversion of enone **2** into bicycle **17** highlights a clear difference between the inter- and intramolecular [3+2] cycloaddition reactions. In contrast to the intramolecular cyclisation described herein, intermolecular reactions involving molecules such as acrolein, which can adopt a *cisoid* conformation, fail to give cycloadducts.[2] These acceptors form a strong bond to the palladium, which presumably prevents interaction of the metal with the alkylidinecyclopropane. The strong affinity between acyclic enones and palladium may account for the formation of the dimer in the intramolecular reaction. Prior to cycloaddition, two enone ligands may be bound to the metal centre. As a consequence, the effective concentration of the enone would be very large, increasing the likelihood of dimerisation.

It was also of interest to examine the behaviour of a simple unactivated alkene in these reactions. To this end, the allylic alcohol produced by addition of vinyl magnesium bromide to **10** (see Scheme 3) was converted to the corresponding trimethylsilyl ether derivative **18** and subjected to the same cyclisation procedure used for the conversion of **2** into **17** (Figure 4). Unfortunately, this substrate was inert under these reaction conditions and starting material was recovered in greater than 90% yield. By way of contrast, almost immediately following our initial communication, an excellent example of an intramolecular palladium catalysed [3+2] cycloaddition of a methylenecyclopropane onto an unactivated olefinic acceptor was described by Nakamura and coworkers.[13] The successful conversion of **19** into **20** accomplished by Nakamura may be accounted for by the enforced propinquity and reduced conformational freedom of **19** compared with **18**.



18


19


20

Figure 4

The foregoing results clearly demonstrate that palladium catalysed intramolecular cycloadditions of diphenylmethylenecyclopropanes can be successfully used to construct functionalised bicyclo[3.3.0]octanes in a regiocontrolled fashion *via* distal cleavage of the cyclopropane ring. These studies have established that both acetylenic and olefinic acceptors can be tolerated in this cycloaddition protocol. Interestingly, the exact location of this electron withdrawing group relative to the acceptor is not critically important in these cycloaddition reactions. Thus, cyclisations can be accomplished either when this group forms an integral part of the tether (*ie* **2**) or when it is located as an additional substituent outside of the linking chain (*ie* **1**). The obtention of an approximately 1:1 ratio of diastereomeric cycloadducts **13** and **14** from **1**, itself prepared as a 1:1 mixture of diastereomers, provides some presumptive evidence that these intramolecular cyclisations are highly stereoselective with respect to the relative configurations of peripheral substituents.

In summary, we have developed a synthetically useful cyclopropanation / Wadsworth-Emmons approach to diphenylmethylenecyclopropanes, and established that the intramolecular palladium catalysed [3+2] cycloaddition reactions of these compounds can be exploited to prepare a variety of functionalised bicyclo[3.3.0]octane systems. While the key cyclisation step is reasonably efficient some drawbacks associated with the introduction and manipulation of the diphenylmethylene substituent are apparent. Further cycloaddition studies based upon the related methylenecyclopropane systems are described in the following article which further probes the scope and limitations of this cycloaddition reaction.

EXPERIMENTAL

General. ^1H nmr spectra were recorded at 90 MHz on a Jeol FX-90Q instrument, at 250 MHz on a Bruker WM-250 instrument, and at 500 MHz Bruker AM-500 instrument with either tetramethylsilane or residual protic solvent as the internal standard. ^{13}C and ^{31}P nmr spectra were recorded at 22.5 MHz and 36.2 MHz respectively on a Jeol FX-90Q instrument. Infrared spectra were recorded on a Perkin Elmer 983G spectrometer. Mass Spectra were recorded on VG 7070B, VG 12-253 and VG ZAB-E instruments under EI conditions. Diethyl ether, and tetrahydrofuran were distilled from sodium - benzophenone ketyl under argon immediately prior to use. Toluene was distilled from sodium under argon immediately prior to use. All other solvents and reagents were purified by standard means. All reactions were performed using oven dried glassware under an atmosphere of argon unless otherwise stated.

1,1-Dimethoxy-2,2-dimethyl-4-pentene (21). To a solution of 2,2-dimethyl-4-pentenal[9] (8.44 g, 75 mmol) in MeOH (120 ml) was added acidic resin amberlyst 15H (2.5 g) and the reaction stirred at room temperature for 18 h. After filtration, the solvent was removed at reduced pressure. Distillation of the residue afforded **21** (6.88 g, 58%) as a clear liquid (b.p. 164°C); ν_{max} (film) 2977, 2830, 1386, 1186, 1112, 1078, 967 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 5.65 (1H, m), 4.82 (2H, m), 3.66 (1H, s), 3.35 (6H, s), 1.87 (2H, d, 7.7 Hz), 0.70 (6H, s); ^{13}C NMR (22.5 MHz; $CDCl_3$) 135.0, 116.8, 113.3, 58.1, 42.4, 39.5, 7.0; *m / z* 157(M^+-H), 143 (M^+-Me), 127, 117, 75; Found: C 68.28, H 11.44%; $C_9H_{18}O_2$ requires C 68.31, H 11.46%.

2-(1,1-Dimethyl-3-butenyl)-1,3-dioxolane (22). A mixture of 2,2-dimethyl-4-pentenal[9] (8.16 g. 72.7 mmol), ethylene glycol (22.4 g, 362 mmol), benzene (370 ml), and pyridinium *p*-toluene sulphonate (1.08 g, 4.3 mmol) were heated at reflux under Dean-Stark conditions until water evolution ceased (*ca* 6 hours). On cooling, the reaction was poured into saturated aqueous $NaHCO_3$ (200 ml), the organic phase separated, washed with brine (100 ml), and dried over $MgSO_4$. Removal of the solvent under reduced pressure and subsequent distillation gave **22** (8.66 g, 76%) as a colourless liquid (b.p. 177-178 °C). ν_{max} (film) 2974, 2877, 1472, 1395, 1111, 997, 962, 947, 914 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 5.80 (1H, m), 5.00 (2H, m), 4.56 (1H, s), 3.88 (4H, m), 2.20 (2H, d, 7.2 Hz), 0.90 (6H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$) 134.7, 117.0, 109.5, 65.2, 41.9, 37.3, 21.5, 21.2; *m / z* 115 (M^+-H), 141(M^+-Me), 113, 99, 81, 73 ($C_3H_5O_2^+$); Found: C 69.33, H 10.42%; $C_9H_{16}O_2$ requires: C 69.19, H 10.32%.

5-Diphenylmethylsilyloxy-2-pentanone (23). To a solution of chlorodiphenylmethylsilane (25.6 g, 110 mmol), DMAP (0.50 g, 4.0 mmol), and triethylamine (15.3 ml, 120 mmol) in DCM (250 ml) at 0°C was added 5-hydroxy-2-pentanone (10.2 g, 100 mmol) and the reaction stirred briefly before standing at 4°C for 24 hours. The mixture was poured into water (250 ml) and the organic phase separated. The aqueous phase was extracted with DCM and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure and column chromtography of the residue (15% ether / petrol) gave **23** (17.5 g, 59%) as a colourless oil. ν_{max} (film) 2956, 1714, 1428, 1255, 1118, 791, 765, 733, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 6.94 (4H, m), 6.77 (6H, m), 3.07 (2H, t, 6.0 Hz), 1.86 (2H, t, 7.2 Hz), 1.43 (3H, s), 1.19 (2H, m), 0.00 (3H, s).

5-Diphenylmethylsilyloxy-2-methyl-1-pentene (24). To a slurry of methyltriphenylphosphonium bromide (8.93 g, 25 mmol) in THF (100 ml) at -78°C was added n-butyllithium (1.25 M in hexanes, 20.0 ml,

25 mmol) and the resulting yellow solution allowed to warm to room temperature when a red homogeneous solution formed. **23** (6.77 g, 22.7 mmol) in THF (5 ml) was added and the mixture stirred for 0.5 hr at room temperature. Benzoic acid (300 mg, 2.46 mmol) was added and the reaction stirred for a further 18 hrs. After addition of petroleum ether (150 ml) the mixture was filtered through a glass wool plug. The filtrate was washed with brine, dried over Na_2SO_4 and the solvent removed *in vacuo*. Column chromatography (5% ether / petrol) gave **24** (5.20 g, 77%) as a colourless oil. ν_{max} (film) 2941, 2857, 1640, 1420, 1253, 1118, 790, 734, 699 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) 6.90 (4H, m), 6.70 (6H, m), 4.04 (2H, bs), 3.07 (2H, t, 7.0 Hz), 1.40 (2H, t, 7.2 Hz), 1.08 (2H, m), 1.04 (3H, s), 0.00 (3H, s); *m / z* 296 (M^+), 281, 255, 240, 203, 199, 137, 105, 82, 67, 56, 41; Found: C 77.16, H 8.39%; $C_{19}H_{24}OSi$ requires: C 76.97, H 8.16%.

Diethyl 2-oxabicyclo[4.1.0]hept-7-yl-phosphonate (3). To a stirred solution of dihydropyran (5 ml, 54.8 mmol) and copper (I) triflate.benzene complex[8] (58 mg, 0.11 mmol) in THF (5 ml) was added DAMP[7a](1.03 g.5.78 mmol) dropwise over 1 h (*CAUTION*: nitrogen evolution is vigorous). The mixture was stirred until nitrogen evolution ceased then diluted with ether and poured into water. The organic layer was dried over $MgSO_4$, concentrated under reduced pressure and the residue subjected to short path distillation (150°C, 0.1 mmHg) to afford **3** (950 mg 71%) as a colourless oil. ν_{max} (film) 2981, 2934, 1239, 1106, 1029, 960, 860 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 4.30-3.20 (7H, m), 2.10 (2H, m), 1.30 (8H, m); ^{31}P NMR (36.2 MHz; $CDCl_3$) 25.1; *m / z* 234 (M^+), 206, 178, 138, 97; Observed (M^+): 234.1028; $C_{10}H_{19}O_4P$ requires 234.1021.

Diethyl [2-(3,3-dimethoxy-2,2-dimethylpropyl)cyclopropyl]-phosphonate (4). To a stirred solution of **21** (5.50 g, 34.8 mmol) and copper (I) triflate.benzene complex[8] (100 mg, 0.20 mmol) in DCM (2 ml) at 8°C was added a solution of DAMP[7a] (2.19 g, 12.3 mmol) in DCM (2 ml) dropwise *via* a syringe pump over 22 hours. After stirring for a further 2 hours, the homogeneous green solution was allowed to warm to room temperature. Removal of the solvent under reduced pressure and subsequent column chromatography (ether) gave less polar recovered starting material **21** (4.13 g, 75%); and more polar **4** (1.73 g, 76% based upon recovered alkene) as a colourless oil and as a 1:1 mixture of diastereomers; ν_{max} (film) 2979, 1244, 1108, 1071, 1030, 962 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 4.0 (5H, m), 3.44 (6H, s), 2.0-0.50 (6H, m), 1.27 (6H, t, 7Hz), 0.90 (6H, s); ^{31}P NMR (36.2 MHz; $CDCl_3$) 29.3, 29.1; *m / z* 308 (M^+), 293 (M^+-Me), 277, 248, 233, 208, 195, 166, 139, 107, 75; Found: C 54.42, H 9.70%; $C_{14}H_{29}O_5P$ requires C 54.53, H 9.48%.

Diethyl [2-[2-(1,3-dioxolan-2-yl)-2-methylpropyl]cyclopropyl]-phosphonate (5). To a mixture of **22** (1.87 g, 12.0 mmol) and copper (I) triflate.benzene complex[8] (80 mg, 0.16 mmol) in DCM (3 ml) at 8°C was added a solution of DAMP[7a] (820 mg, 4.6 mmol) in DCM (3 ml) dropwise with stirring *via* a syringe pump over 30 h. After stirring for a further 18 h at room temperature, the solvent was removed under reduced pressure and the residue chromatographed (diethyl ether) to afford **5** (1.03 g, 73%) as a colourless oil and as a 1:1 mixture of diastereoisomers. ν_{max} (film) 2978, 2878, 1244, 1108, 1033, 959, 731 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 4.28 (1H, s), 3.53 (4H, m), 1.60-0.30 (6H, m), 1.00 (6H, t, 7.2Hz), 0.64 (6H, s); ^{31}P NMR (36.2 MHz; $CDCl_3$) 29.4, 29.2 (1:1 ratio); *m / z* 306(M^+), 234, 153, 134, 73 ($C_3H_5O_2$); Observed (M^+): 306.1606; $C_{14}H_{27}O_5P$ requires 306.1596.

Diethyl [2-methyl-2-[3-(methyldiphenylsilyl)oxy]propyl]cyclopropyl]-phosphonate (6). To a stirred solution of **24** (3.0 g, 10.1 mmol) and copper (I) triflate.benzene complex[8] (190 mg, 0.38 mmol) in DCM (2.5 ml) at 0°C was added a solution of DAMP[7a] (3.0 g, 16.9 mmol) in DCM (7.5 ml) dropwise over 72 hours *via* a syringe pump. After stirring for a further 18 hr at room temperature, the mixture was concentrated under reduced pressure and the residue chromatographed (30% ether / petrol → 100% ether) to afford recovered **24** (1.06 g, 35%) and **6** (2.86 g, 64%) as a colourless oil and as a mixture of diastereomers. ν_{max} (film) 2978, 2958, 1428, 1246, 1118, 1094, 1059, 1030, 958, 791, 737, 701 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 6.95 (4H, m), 6.75 (6H, m), 3.40 (4H, m), 3.08 (2H, m), 1.06-0.45 (16H, m), 0.00 (3H, s); ^{31}P NMR (36.2 MHz; $CDCl_3$) 28.7, 28.6; *m / z* 446 (M^+), 431, 403, 369, 232, 197, 95; Found: C 64.45, H 8.16%; $C_{24}H_{35}O_4PSi$ requires C 64.54, H 7.90%.

Diethyl bicyclo[3.1.0]hex-6-yl-phosphonate (7). To a stirred solution of cyclopentene (5 ml, 56.8 mmol) and copper (I) triflate.benzene complex[8] (200 mg, 0.38 mmol) at 0°C was added a solution of DAMP[7a] (2.65 g, 14.9 mmol) in DCM (3 ml) dropwise *via* a syringe pump over 36 hours. After stirring for a further 18 h at room temperature, the mixture was concentrated under reduced pressure. Column chromatography (ether) gave **7** (1.99 g, 62%) as a colourless oil and as a 3:1 mixture of diastereomers. ν_{max} (film) 2937, 2865, 1381, 1246, 1165, 1028, 961, 860, 795 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 4.0 (4H, m), 2.20-0.30 (9H, m), 1.25 (6H, t, 7.2Hz); ^{31}P NMR (36.2 MHz; $CDCl_3$) 28.6, 29.3 (3:1 ratio); *m / z* 218 (M^+), 190, 173, 162, 152, 139, 111, 80; Observed (M^+): 218.1069; $C_{10}H_{19}O_3P$ requires 218.1072.

Diethyl [2-(3-chloropropyl)-2-methylcyclopropyl]-phosphonate (8). To a stirred solution of 5-chloro-2-methyl-1-pentene (2.39 g, 20.1 mmol) and copper (I) triflate.benzene complex[8] (300 mg, 1.03 mmol) in DCM (1.0 ml) at 5°C was added a solution of DAMP[7a] (2.0 g, 11.23 mmol) in DCM (2 ml) dropwise over 72 hours *via* a syringe pump. After stirring for a further 18 hr at room temperature, the mixture was concentrated under reduced pressure and the residue chromatographed (80% ether / petrol) to afford **8** (2.39 g, 79%) as a colourless oil. ν_{max} (film) 2981, 2933, 2907, 1388, 1245, 1097, 1031, 961, 793, 763 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 4.04 (4H, m), 3.50 (2H, m), 1.27 (6H, t, 7 Hz), 2.30-0.50 (16H, m); ^{31}P NMR (36.2 MHz; $CDCl_3$) 28.1; *m / z* 268 (M^+), 233, 205, 177, 163, 149, 135, 111, 95; Observed (M^+): 268.0990; $C_{11}H_{22}ClO_3P$ requires 268.0995.

7-(Diphenylmethylene)-2-oxabicyclo[4.1.0]heptane (9). To a stirred solution of **3** (243 mg, 1.04 mmol) in THF (5 ml) at -78°C was added n-butyllithium (1.4 M in hexanes, 0.82 ml, 1.15 mmol) giving an orange solution. After 20 minutes, a solution of benzophenone (206 mg, 1.1 mmol) in THF (2 ml) was added dropwise giving a green solution. The mixture was stirred at -78°C for 1.5 hours, then allowed to warm to room temperature and quenched by addition of saturated ammonium chloride solution (5 ml). The mixture was then extracted with ether, dried over Na_2SO_4 and the solvent removed *in vacuo*. Column chromatography (2% ether / petrol) gave **9** (170 mg, 63%) as a colourless oil. ν_{max} (film) 2942, 2858, 1614, 1247, 1169, 1137, 764, 733, 700, 631 cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) 7.60 (2H, m), 7.38 (8H, m), 4.20 (1H, d, 7.6Hz), 3.75 (1H, dt, 3.8, 11.4 Hz), 3.51 (1H, m), 2.13 (1H, m), 1.82 (2H, m), 1.48 (2H, m); *m / z* 262 (M^+), 233, 219, 205, 191, 165, 152, 77; Observed (M^+): 262.1358; $C_{19}H_{18}O$ requires 262.1357.

Diethyl [2-(3,3-dimethoxy-2,2-dimethylpropyl)-1-(hydroxydiphenylmethyl)cyclopropyl]-phosphonate (25). To a stirred solution of **4** (1.20 g, 3.84 mmol) and TMEDA (0.64 ml 4.37 mmol) in THF (25 ml) at -78°C was added n-butyllithium (2.5 M in hexanes, 1.70 ml, 4.25 mmol) producing an orange solution. After 20 minutes, a solution of benzophenone (1.50 g, 8.24 mmol) in THF (6 ml) was added dropwise. The mixture was stirred a further 2.5 hours during which time the solution turned first green in colour, then yellow. Glacial acetic acid (0.70 ml, 12 mmol) was added and the mixture allowed to warm to room temperature. The mixture was poured into saturated aqueous $NaHCO_3$, extracted with ether and the extracts dried over $MgSO_4$. Removal of the solvent under reduced pressure and subsequent column chromatography (80% ether / petrol) afforded **25** (1.44 g, 77%) as a 4:1 mixture of diastereomers. The major diastereomer (m.p. 124-126°C) was obtained in pure form by recrystallisation from hot petrol (bp 40-60°C); ν_{max} (film) 3353, 2977, 2829, 1491, 1449, 1388, 1363, 1209, 1053, 964, 759, 704 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 8.20-7.50 (10H, m), 6.14 (1H, s), 4.50-4.00 (5H, m), 3.83 (3H, s), 3.80 (3H, s), 2.20-1.40 (8H, m), 1.24 (3H, s), 1.14 (3H, s), 1.40-0.40 (3H, m); ^{31}P NMR (36.2 MHz; $CDCl_3$) 30.55; *m / z* 490(M^+), 473, 427, 412, 398, 373, 330, 276, 191, 165, 105, 91; Found: C 66.02, H 8.05%; $C_{27}H_{39}O_6P$ requires C 66.10, H 8.01%.

2-(Diphenylmethylene)-α,α-dimethyl-cyclopropanal (10). To a stirred slurry of sodium hydride (272 mg, 60% dispersion, 6.8 mmol) in DMF (100 ml) was added a solution of **22** (2.78 g, 5.67 mmol) in DMF (50 ml). When hydrogen evolution ceased, the resultant alkoxide was heated at 90°C for 2.5 h. On cooling to 0°C, a solution of 10% HCl (20 ml) was added cautiously with stirring and the dark red colour rapidly discharged. Acetal cleavage was completed on stirring at room temperature overnight. The mixture was poured into an equal volume of ice-water and extracted with ether. The combined organic extracts were washed with aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated at reduced pressure. Column chromatography (5% ether / petrol) afforded **10** (1.10 g. 67%) as a colourless oil; ν_{max} (film) 3059, 1725, 1599, 1447, 1318, 1278, 942, 920, 700 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 9.4 (1H, s), 7.4 (10H, m), 1.0 (6H, s), 0.5-2.5 (5H, m); *m / z* 290 (M^+), 272, 219, 206, 182, 165, 105, 91, 77; Observed (M^+): 290.1669; $C_{21}H_{22}O$ requires 290.1671.

Diethyl [2-[2-(1,3-dioxolan-2-yl)-2-methylpropyl]-1-(hydroxydiphenylmethyl)cyclopropyl]-phosphonate (26). To a stirred solution of **5** (599 mg, 1.92 mmol) in THF (12 ml) and TMEDA (0.33 ml, 2.19 mmol) at -78°C was added n-butyllithium (2.5 M in hexanes, 0.85 ml, 2.13 mmol). After 25 minutes, a solution of benzophenone (764 mg.4.2 mmol, 2'.2 eq) in THF (3 ml) was added dropwise over 5 min, turning the orange coloured solution to green. The mixture was stirred at -78°C for a further 5 hours, quenched by addition of glacial acetic acid (0.25 ml. 4.4 mmol) then allowed to warm to room temperature. The solution was poured into saturated $NaHCO_3$ solution and extracted with ether. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. Column chromatography of the residue (ether) afforded **26** (877 mg, 94%) in a 7:1 diastereoisomeric ratio, the major diastereoisomer (772 mg) as a crystalline solid (m.p. 114-117°C). ν_{max} (film) 3353, 2956, 2878, 1473, 1391, 1208, 1108, 1054, 805 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 7.80-7.00 (10H, m), 5.6 (1H, br s), 4.36 (1H, s), 4.10-3.30 (4H, m), 3.76 (4H, m), 1.80-0.50 (5H, m), 1.13 (6H, q, 7.2Hz), 0.82 (3H, s), 0.70 (3H, s); ^{31}P NMR (36.2 MHz; $CDCl_3$) 30.4; *m / z* 448 (M^+), 471, 442, 411, 398, 373, 330, 305, 254, 234, 226, 191, 178, 165, 114, 105, 77; Found: C, 66.29,

H,7.58%; $C_{27}H_{37}O_6P$ requires: C, 66.37, H, 7.63%; the minor isomer (105 mg) as a colourless oil, ^1H NMR (90 MHz; $CDCl_3$) 7.90-7.05 (10H, m), 6.42 (1H, br s), 4.49 (1H, s), 4.05 (2H, m), 3.83 (4H, m), 3.50 (2H, m), 2.12 (1H, d, 12.8Hz), 1.70-0.50 (4H, m), 1.25 (3H, t, 7 Hz), 1.03 (3H, t, 7 Hz), 0.83 (3H, s), 0.80 (3H, s); ^{31}P NMR (36.2 MHz; $CDCl_3$) 31.4.

2-[2-[(Diphenylmethylene)cyclopropyl]-1,1-dimethylethyl]-1,3-dioxalone (11). To a slurry of sodium hydride (60% dispersion, 16 mg, 0.40 mmol) in DMF (8 ml) at room temperature was added a solution of **26** (107 mg, 0.219 mmol) in DMF (2 ml). When hydrogen evolution subsided, the mixture was heated at 90-100°C for 2h, cooled and the dark solution quenched with 10% aqueous HCl (2 ml). The reaction mixture was poured into water (25 ml), extracted with petrol and the combined organic layers dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent column chromatography (5% ether / petrol) gave **11** (55 mg, 81%) as a colourless oil. ν_{max} (film) 2967, 2876, 1491, 1106, 771, 697 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 7.25 (10H, m), 4.54 (1H, s), 3.78 (4H, m), 1.90-0.70 (5H, m), 0.94 (3H, s), 0.90 (3H, s); *m / z* 334 (M^+), 257, 180, 165, 105, 91, 77, 73; Found: C, 82.43, H, 7.89%; $C_{23}H_{26}O_2$ requires: C, 82.59, H, 7.84%.

2-(Diphenylmethylene)-1-methyl-cyclopropanepropanol (12). To a stirred solution of **6** (213 mg, 0.477 mmol) in THF (8 ml) and TMEDA (80 µl, 0.53 mmol) at -125°C was added n-butyllithium (2.5M in hexanes, 0.21 ml, 0.53 mmol) dropwise. After 15 minutes at -120°C, benzophenone (184 mg, 1.0 mmol) in THF (2 ml) was added dropwise. The mixture was stirred for 2 hours at -100°C then warmed to -78°C and stirred for a further 3 hours. A solution of sodium *tert*-butoxide; prepared by stirring NaH (60% dispersion, 40 mg, 1.0 mmol) and *tert*-butanol (225 mg, 3.0 mmol) in THF (2 ml) for 1 hour; was added to the reaction mixture which was subsequently allowed to warm to room temperature. After 36 hours at room temperature, extensive cleavage of the silyl protection was evident by t.l.c. Deprotection was completed by addition of tetrabutylammonium fluoride (1.0 M in THF, 1.0 ml, 1.0 mmol). Aftr 3 hours, the mixture was quenched by cautious addition of 5% aqueous acetic acid (3 ml). The resulting mixture was poured into water, extracted with ether and the combined extracts dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent column chromatography (40% ether / petrol) gave **12** (53 mg, 40%) as a colourless oil. ν_{max} (film) 3360, 2935, 2865, 1598, 1491, 1443, 1059, 771, 755, 697, 610 cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) 7.30 (10H, m), 3.55 (2H, t, 6.1 Hz), 1.80-1.10 (7H, m), 1.29 (3H, s); *m / z* 278 (M^+), 245, 233, 219, 204, 165, 105, 91, 86, 84; Observed (M^+): 278.1674; $C_{20}H_{22}O$ requires: 278.1670.

Methyl 6-[2-(diphenylmethylene)cyclopropyl]-5,5-dimethyl-4-[(trimethylsilyl)oxy]-2-hexynoate (1). To a stirred solution of methyl propiolate (96 mg, 1.14 mmol) in THF (3 ml) at -78°C was added n-butyllithium (1.5 M in hexanes, 0.76 ml, 1.14 mmol). After 1.5 hours, a solution of **10** (83 mg, 286 µmol) in THF (2 ml) was added. After a further hour at -78°C, freshly distilled chlorotrimethylsilane (145 µl, 1.14 mmol) was added and the solution allowed to warm to room temperature. The reaction mixture was poured into water (20 ml), extracted with ether, washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent column chromatography (5% ether / petrol) gave **1** (124 mg, 97%) as a colourless oil and as a 1:1 mixture of distereoisomers; ν_{max} (film) 2959, 2234, 1718, 1253, 1063, 875, 846, 699 cm^{-1}; ^1H NMR (90 MHz; $CDCl_3$) 7.2-7.5 (10H, m), 4.26 (0.5H, s), 4.20 (0.5H, s), 3.80 (1.5H, s), 3.78 (1.5H, s), 1.90 (1H, m), 1.6 (2H, m), 1.50 (1.5H, s), 1.40 (1.5H, s), 1.22 (1H, m), 1.10

(1.5H, s), 1.01 (1.5H, s), 0.94 (1H, m), 0.17 (9H, s); *m / z* 446 (M^+), 431 (M^+-Me), 387 (M^+-CO_2Me), 372, 356, 338, 323, 306, 279, 261, 249, 189, 165, 105; Observed (M^+): 446.2260; $C_{28}H_{34}O_3Si$ requires: 446.2277.

5-[2-(Diphenylmethylene)cyclopropyl]-4,4-dimethyl-1-penten-3-ol (27). To vinyl magnesium bromide (1.0 M in THF, 350 µl, 350 µmol) in THF (1 ml) at 0°C was added a solution of **10** (48.1 mg, 166 µmol) in THF (1 ml) dropwise. After stirring for 30 minutes, saturated NH_4Cl solution (1 ml) was added and the mixture warmed to room temperature. The solution was diluted with water (20 ml) and extracted with ether (3 x 10 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent removed under reduced pressure. Column chromatography (0-10% ether / petrol) gave **27** (32.3 mg, 61%) as a colourless oil and as a 1:1 mixture of diastereomers. ν_{max} (film) 3424, 2962, 1491, 1443, 1032, 993, 770, 751, 696, 664 cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) 7.45-7.25 (10H, m), 6.00-5.84 (1H, m), 5.28-5.14 (2H, m), 3.99 (0.5H, m), 3.86 (0.5H, m), 1.95-1.55 (3H, m), 1.40 (1H, bs), 1.30-0.88 (2H, m), 0.97 (3H, s), 0.95 (3H, s); *m / z* 318 (M^+), 300 (M^+-H_2O), 285 (M^+-H_2O-Me), 219, 218, 205, 91; Observed (M^+): 318.1980; $C_{23}H_{26}O$ requires 318.1984.

5-[2-(Diphenylmethylene)cyclopropyl]-4,4-dimethyl-1-penten-3-one (2). To a stirred solution of pyridinium chlorochromate (52 mg, 240 µmol) in DCM (0.6 ml) was added **27** (43.1 mg, 136 µmol) in DCM (1 ml). After 3 hours, the mixture was diluted with ether and filtered through florisil. Removal of the solvent *in vacuo* and subsequent column chromatography (10% ether / petrol) gave **2** (32.5 mg, 76%) as a colourless oil. ν_{max} (film) 2966, 1689, 1609, 1491, 1443, 1400, 1060, 771, 697 cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) 7.45-7.20 (10H, m), 6.77 (1H, dd, 17, 10 Hz), 6.37 (1H, dd, 17, 2 Hz), 5.65 (1H, dd, 10, 2 Hz), 2.08 (1H, dd, 14, 3 Hz), 1.68-1.50 (2H, m), 1.20 (3H, s), 1.19 (3H, s), 1.16-1.07 (2H, m); *m / z* 316 (M^+), 298 (M^+-H_2O), 255, 245, 231, 218, 91; Observed (M^+): 316.1823; $C_{23}H_{24}O$ requires 316.1827.

***trans*-Methyl 3-(diphenylmethylene)-2,3,3a,4,5,6,-hexahydro-5,5-dimethyl-6-[(trimethylsilyl)oxy]-1-pentalenecarboxylate (13) and *cis*-Methyl 3-(diphenylmethylene)-2,3,3a,4,5,6,-hexahydro-5,5-dimethyl-6-[(trimethylsilyl)oxy]-1-pentalenecarboxylate (14). Method A - Thermally Induced Cyclisation.** To bis(dibenzylideneacetone)palladium (0) (6 mg, 10 µmol) and diphenylmethylenecyclopropane **1** (206 mg, 0.46 mmol) in toluene (5 ml) was added a solution of triisopropylphosphite (1.00 ml of a 0.010 M solution in toluene, 10 µmol). The mixture was stirred briefly, then transfered to a Carius tube and sealed under argon, then heated at 105-110°C for 24 hr. On cooling, the tube was opened and the solvent removed under reduced pressure. Column chromatography (2% ether / petrol) afforded less polar **13** (104 mg, 50%) as a colourless oil contaminated with traces of starting material (this material could be purified further by resubjecting this mixture to the reaction conditions); ν_{max} (film) 2954, 1714, 1441, 1250, 1112, 1075, 1031, 909, 881, 844, 734, 701 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) 7.26 (10H, m, Ph), 4.44 (1H, dd, 6.5, 11 Hz, H-6a) 4.38 (1H, s, H-4), 3.73 (3H, s, CO_2Me), 3.65 (1H, d, 22Hz, H-2), 3.45 (1H, d, 22 Hz, H-2), 1.50 (1H, dd, 13, 11 Hz, H-6_{endo}), 0.91 (3H, s, C-5-Me_{exo}), 0.88 (1H, dd, 6.5, 13 Hz, H-6_{exo}), 0.75 (3H, s, C-5-Me_{endo}), 0.13 (9H, s, $SiMe_3$); ^{13}C NMR (22.5 MHz, $CDC1_3$) 165.7, 142.2, 141.3, 136.2, 128.8, 128.6, 128.4, 128.1, 128.0, 126.4, 126.1, 123.0, 75.7, 52.7, 51.1, 44.8, 42.1, 41.4, 28.9, 23.7, 0.10; Observed (M^+): 446.2278; $C_{28}H_{34}O_3Si$ requires: 446.2277; and more polar **14** (78 mg, 38%) a colourless oil; ν_{max} (film) 2954, 1725, 1491, 1441, 1324, 1297, 1248, 1191, 1092, 1030, 878,

844, 786, 701 cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) 7.24 (10H, m, Ph), 4.28 (1H, br s, H-4), 4.03 (1H, t, 9.5 Hz, H-6a), 3.75 (1H, dd, 21.5, 1.6 Hz, H-2), 3.68 (3H, s, CO_2Me), 3.44 (1H, dd, 21.5, 3.2 Hz, H-2), 1.13 (1H, dd, 12.6, 10.1 Hz, H-6_{exo}), 1.04 (1H, dd, 12.6, 8.5 Hz H-6_{endo}), 0.92 (3H, s, C-5-Me_{exo}), 0.80 (3H, s, C-5-Me_{endo}), 0.13 (9H, s, $SiMe_3$); *m / z* 446 (M^+), 431(M^+-Me), 390, 356, 331, 279, 241, 167, 144, 115, 91; Observed (M^+): 446.2287; $C_{28}H_{34}O_3Si$ requires: 446.2277.

Method B - Sonication Induced Cyclisation. To a solution of **1** (65 mg, 0.146 mmol) in toluene (10 ml) was added palladium tetrakis(triphenylphosphine) (10 mg, 9 μmol) and the mixture was subjected to ultrasonication for an arbitrary period of 100 hours. Removal of the solvent under reduced pressure and subsequent column chromatography (5% ether / petrol) afforded a approximately 1:1 mixture of **1** and **13** (42 mg, 64%) and **14** (23 mg, 35%) identical to materials previously described.

***cis*-2a,3,4,5-Tetrahydro-3,3,5-trimethyl-6-phenyl-1*H*-anthra{1,9-*bc*]furan-1-one (15).** A solution of **1** (22.9 mg, 51.3 μmol) in d_6-benzene (0.6 ml) was sealed in a glass tube under argon and heated to 140-150°C for 5 days. Upon cooling to room temperature, the tube was opened and the solvent removed under reduced pressure. This material was dissolved in THF (1 ml) and treated with tetrabutylammonium fluoride (1.1M in THF, 90 μl, 1.0 mmol) for 3 hours. The reaction mixture was quenched by addition of glacial acetic acid (0.3 ml) poured into water and extracted with ether (3x). The combined organic extracts were washed with saturated $NaHCO_3$ and dried over Na_2SO_4. Removal of the solvent under reduced pressure and subsequent column chromatography (petrol) gave **15** (1.7 mg, 10%). Recrystallisation from 60-80° petrol provided colourless crystals suitable for x-ray diffraction; ν_{max} (film) 2984, 2928, 2871, 1746, 1604, 1570, 1437, 1437, 1423, 1150, 1112, 1035 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) 8.93 (1H, d, 8.2 Hz), 7.65-7.41 (7H, m), 7.07 (1H, m), 5.29 (1H, s), 3.06 (1H, m), 2.02 (1H, dd, 14.6, 8.1 Hz), 1.49 (1H, 14.6, 8.1 Hz), 1.34 (3H, s), 0.96 (3H, d, 6.9 Hz), 0.51 (3H, s); *m / z* 342 (M^+), 286, 271, 258, 229, 215, 149; Observed (M^+): 342.1620; $C_{24}H_{22}O_2$ requires: 342.1621.

X-Ray Crystal Data Parameters (15).[11] $C_{24}H_{22}O_2$, *M* = 342.4, monoclinic, a = 16.487(12), b = 12.654(10), c = 19.595(14)Å, β = 111.10(5)°, U = 3814Å^3, space group $F2_1/c$, *Z* = 8 (2 crystallographically independent molecules), D_c = 1.19gcm^{-3}, μ(Cu-K_α) = 6 cm^{-1}, F(000) = 1480. 3917 independent reflections ($\theta \leq 50°$) were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω-scans. Of these 3034 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The positions of the hydrogen atoms were idealised, C-H = 0.96Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares and converged to give R = 0.054, R_w = 0.063. The maximum residual electron density in the final ΔF map was 0.54 eÅ^{-3} and mean and maximum shift/error in the final refinement were 0.011 and 0.047 respectively.

4-(Diphenylmethylene)hexahydro-2,2-dimethyl-1(2*H*)-pentalenone (17). To bis(dibenzylideneacetone) palladium (6.9 mg, 12 μmol) in toluene (0.5 ml) was added triisopropyl phosphite (0.16M in toluene, 75 μl, 12 μmol) and the resulting solution transfered *via* a cannula to a glass tube with more toluene (0.5 ml). Then **2** (11.6 mg, 37 μmol) in toluene (0.4 ml) and d_6-benzene (50 μl) were added and the

tube cooled to -78°C and sealed. The mixture was heated for 48 hours at 110°C, and on cooling, opened and the solvent removed under reduced pressure. Column chromatography (0-4% ether / petrol) gave **17** (5.4 mg, 47%) as a white solid (m.p. 97-103°C). ν_{max} (film) 2959, 1733, 1598, 1491, 1442, 1379, 1074, 762, 701 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) 7.35-7.12 (10H, m, Ph), 3.42 (1H, m, H-3a), 2.88 (1H, dt, 4.4, 9.3 Hz, H-6a), 2.48-2.37 (2H, m, 2 x H-5), 2.02-1.96 (1H, m, H-6), 1.94-1.86 (1H, m, H-6), 1.83 (1H, dd, 13.3, 8.6 Hz, H-3), 1.51 (1H, dd, 13.3, 7.8 Hz, H-3), 1.05 (3H, s, Me), 0.95 (3H, s, Me); *m / z* 316 (M^+), 242, 167, 149, 91 ; Observed (M^+): 316.1823; $C_{23}H_{24}O$ requires 316.1827.

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