Catalyst Free Diels-Alder reactions of vinylphosphonates with cyclopentadienones

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Abstract: The unprecedented thermal Diels-Alder reaction of the diethyl vinylphosphonate and diethyl styrylphosphonate with various cyclopentadienones is described. In these Diels-Alder reactions, catalysis was not required and the corresponding cycloadducts derivatives were obtained. The tetraethyl vinylidene-1,1-bis-phosphonate was found to be less reactive than monophosphonates with the same cyclopentadienones.

Keywords: cycloaddition, cyclopentadienones, Diels-Alder reaction, vinylphosphonate, styrylphosphonate, vinylidene-1,1-bisphosphonate.

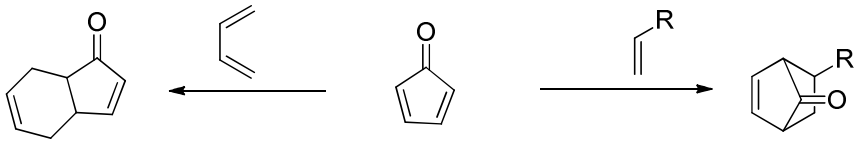
Résumé : Pour la première fois, la réaction thermique de Diels-Alder du vinylphosphonate de diéthyle et du styrylphosphonate de diéthyle avec diverses cyclopentadiénones est décrite. Dans ces réactions de Diels-Alder, aucun catalyseur n'est nécessaire et les produits de cyclo-addition ont été obtenus. Le vinylidène-1,1-bis-phosphonate de tétraéthyle s'est révélé être moins réactif que les monophosphonates avec les mêmes cyclopentadiénones.

Mots clés: cyclo-addition, cyclopentadiénones, réactions de Diels-Alder, vinylphosphonate, styrylphosphonate, vinylidène-1,1-bis-phosphonate

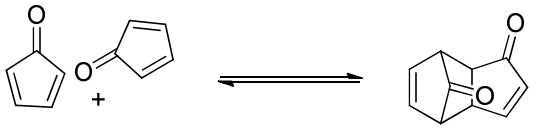
Introduction

The chemistry of cyclopentadienones is old but well documented, as witnessed by the review made by Ogliaruso *et al.*[1] Although not frequently used, cyclopentadienones remain interesting molecules, owing to their dual role of diene and dienophile in the Diels-Alder cycloadditions (Figure 1). An example of this dual role is the self-dimerization of cyclopentadienone.[2]

Figure 1. Dual role of cyclopentadienone in Diels-Alder reactions.

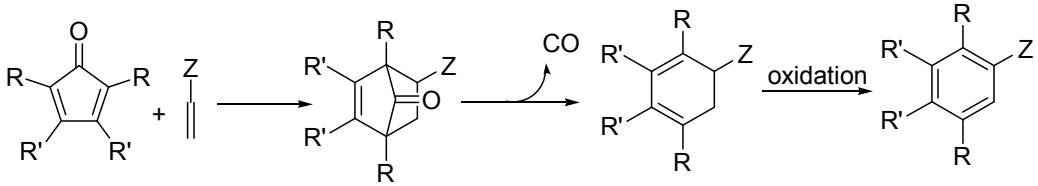


Self-dimerisation of cyclopentadienone.



In contrast to non-substituted cyclopentadienones, which tend to dimerize, tetrasubstituted cyclopentadienones are stable and were extensively studied in the past by Dilthey *et al.*[3] They usually react as dienes with electron poor olefins in Diels-Alder reactions, and the initial product can subsequently be decarbonylated then oxidized, thus leading to a stable aromatic compound (Scheme 1).

Scheme 1. Reaction of tetrasubstituted cyclopentadienones with dienophile olefins followed by decarbonylation and oxidation reactions.



The result of the reaction of tetrasubstituted cyclopentadienones with dienophiles is sensitive to reaction conditions. Generally, the temperature for the decarbonylation reaction is higher than the temperature needed for the Diels-Alder reaction, and the aromatization step takes place under oxidative conditions such as air or an oxidizing agent. Cyclopentadienones are important because their thermal [4+2] Diels-Alder reactions furnish polyaromatic materials which can be of interest for electronic and photovoltaic applications.[4] Although few examples of dienophiles with electron donating groups like vinylidene carbonate have been reported,[5] most of the Diels-Alder reactions of cyclopentadienones described in literature involve olefins bearing electron-withdrawing groups such as COR, COOR, CN, SOR, SO_2R.

To our knowledge, the Diels-Alder cycloaddition of alkenylphosphonate esters with substituted cyclopentadienones has not been reported. Thus, in the context of synthesizing new polyaromatic phosphonated compounds, we are reporting herein the thermal catalyst-free Diels-Alder reaction of various tetrasubstituted cyclopentadienones with diethyl vinyl- and styryl- phosphonates. The phosphonate group is subsequently interesting for the immobilization of organic compounds on the surface of inorganic solids[6] like titanium dioxide for photovoltaic applications.

Experimental

General information

Melting points were determined on Kofler Bank apparatus type WME 50-260°C and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 plates, 40-63 μm thick with F-254 indicator aluminium sheets. Visualization was accomplished by UV light. IR spectra were recorded with Perkin-Elmer spectrophotometer equipped with ATR accessory.
^{31}P NMR spectra were recorded at 161.97 MHz on a Bruker AC 400 spectrometer with $CDCl_3$ as solvent and phosphoric acid as external reference. NMR spectra were recorded at 400 or 500 MHz for ^{1}H NMR and 100.6 or 125

MHz for ^{13}C NMR with a Bruker AC 400 or Bruker AC 500 spectrometer with $CDCl_3$ as solvent and TMS as an internal standard; Chemical shifts (δ) are expressed in ppm and are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet, b = broad).

Mass spectra were recorded on a QTOF Micro (Waters) spectrometer with electrospray ionization (ESI, positive mode), lockspray PEG, infusion introduction at 5μL/min, a source temperature of 80°C and desolvation temperature of 120°C.

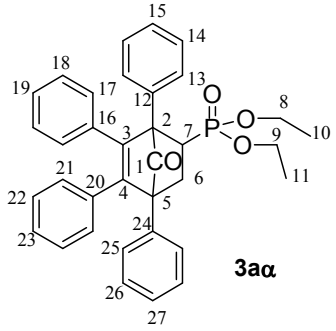
Reagents

Cyclopentadienones (tetracyclone **1a**,[7] phencyclone **1b**,[8] acecyclone **1c**,[9] 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone **1d**,[10] 2,3-dimethyl-3,4-diphenylcyclopentadienone **1e**[11] and 2-methyl-3,4,5-triphenylcyclopentadienone **1f**[12] were prepared by Knoevenagel condensation using potassium hydroxide as base. Diethyl vinylphosphonate **2α**, diethyl 2-*E*-phenyl vinylphosphonate **2β**[13] and tetraethyl vinylidene-1,1-bisphosphonate **2γ**[14] were synthesized according to the literature.

Experimental part

Synthesis of diethyl (7-oxo-1,4,5,6-tetraphenylbicyclo[2.2.1]hepta-5-en-2-yl) phosphonate 3aα

A solution of tetraphenylcyclopentadienone **1a** (0.5 g; 1.3 mmol) was added to diethyl vinylphosphonate **2α** (0.23 g; 1.4 mmol) in 5 mL of toluene. The mixture was refluxed at 110°C for 38 h. The solvent was removed under vacuum and the residue was crystallized from methanol giving a purple solid (0.34 g, 48%), mp=180°C.



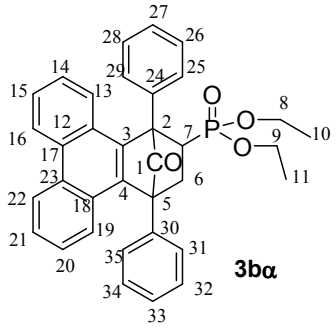
3aα

^{31}P NMR (162 MHz) δ 28.4. ^{1}H NMR (500 MHz) *δ* 7.42 (d, 2H, H_{25}, *J*=7.3 Hz); 7.38-7.22 (m, 8H, H_{13}, H_{14}, H_{15}, H_{26}, H_{27}); 7.12 (t, 1H, H_{23}, *J*=7.0 Hz); 7.08-7.02

(m, 4H, H_{22}, H_{17}); 7.00-6.89 (m, 5H, H_{19}, H_{18}, H_{21}); 4.33-4.17 (m, 3H, H_{8a}, H_9); 4.04 (dq, H_{8b}, $^3J_{HP}$= 16.5 Hz, $^3J_{H8\text{-}H10}$ =7.0 Hz); 3.51 (ddd, 1H, H_7, $^2J_{HP}$=16.5 Hz, $^3J_{H7\text{-}H6a}$=10.0 Hz, $^3J_{H7\text{-}H6b}$ =7.0 Hz); 2.83 (ddd, 1H, H_{6a}, $^2J_{H6\text{-}H6}$=12.0 Hz, $^3J_{H6a\text{-}H7}$=10.0 Hz $^3J_{HP}$=10.0 Hz); 2.69 (ddd, 1H, H_{6b}, $^3J_{HP}$=22.9 Hz, $^2J_{H6\text{-}H6}$=12.0 Hz, $^3J_{H6b\text{-}H7}$ = 7.0 Hz); 1.40 (t, 3H, H_{11}, $^3J_{HH}$=7.0 Hz); 1.19 (t, 3H, H_{10}, $^3J_{HH}$=7.0 Hz). ^{13}C NMR (100 MHz) δ 199.7 (d, C**1**, J=19.2 Hz); 143.8 (C4); 140.1 (d, C3, J=4.7 Hz); 135.1 (C**12**); 134.8 (C**20**); 133.3 (C**16**); 133.2 (C**24**); 130.9 (C**17**); 130.1 (**C13**); 129.9 (**C21**); 129.3 (**C25**); 128.0 (**C26**); 127.7 (C14); 127.6 (**C22**); 127.5 (**C27**); 127.4 (**C23**); 127.2 (**C15**); 127.0 (**C18**); 126.7 (**C19**); 64.9 (d, C**2**, J=2.7 Hz); 62.4 (d, C**8**, J_{CP}=7.0 Hz); 62.3 (d, C**9**, J_{CP}=7.7 Hz); 60.3 (d, C**5**, J_{CP}=2.7 Hz); 34.0 (d, C**7**, J_{CP}=144.2 Hz); 32.1 (d, C**6**, J_{CP}=3.4 Hz); 16.5 (d, C**10**, J_{CP}=5.8 Hz); 16.2 (d, C**11**, J_{CP}=5.8 Hz). IR νmax (neat/cm-1): 2980 (C-H); 1778 (C=O); 1441 (C=C); 1231 (P=O intense); 1050 (P-O-C). ESI-TOF MS m/z (% relative abundance): 521 (M+1, 40). HRMS-ESI calculated for $C_{34}H_{34}O_3P$ 521.2246; found 521.2238.

Synthesis of diethyl (13-oxo- 1,4-diphenyl-1,2,3,4-tetrahydro-1,4-methano-triphenylen-2-yl)phosphonate 3bα

A solution of phencyclone **1b** (0.38 g; 1 mmol) in 10 mL bromobenzene was added to diethyl vinylphosphonate **2α** (0.25 g; 1.5 mmol) in 10 mL of bromobenzene. The mixture was refluxed for 24 h. The solvent was removed under vacuum and the residue was crystallized from ethanol to give a colorless powder (0.22 g, 41%), mp 228°C.

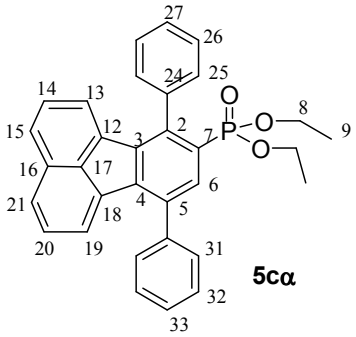


^{31}P NMR (162 MHz) δ 26.5. ^{1}H NMR (500 MHz) δ 8.76 (bd, 1H, H_{22}, J = 8.4 Hz); 8.73 (bd, 1H, H_{16}, J = 8.4 Hz); 8.09 (bd, 1H, H_{25}, J = 7.6 Hz); 7.70 (dt, 1H, H_{31}, J = 7.7 Hz and 1.4 Hz); 7.65 (td, 1H, H_{32}, J = 7.6 Hz and J = 1.5 Hz); 7.64 (td, 1H, H_{26}, J = 7.7 Hz and J = 1.4 Hz); 7.57-7.53 (m, 2H, $H_{15,21}$); 7.50 (tt, 1H, H_{33}, J = 7.5 Hz and J = 1.4 Hz); 7.46 (tt, 1H, H_{27}, J = 7.6 Hz and J = 1.3 Hz); 7.45 (dd, 1H, H_{13}, J = 8.1 Hz and J = 1.3 Hz); 7.43 (td, 1H, H_{34}, J = 7.7 Hz and J = 1.5 Hz); 7.38 (td, 1H, H_{28}, J = 7.6 Hz and J = 1.5 Hz); 7.29 (m, 1H, H_{35}); 7.28

(m, 1H, H_{14}); 7.22 (ddd, 1H, H_{20}, J = 8.3 Hz, 7.1 Hz and J = 1.3 Hz); 7.15 (dt, 1H, H_{29}, J = 7.8 Hz and J = 1.4 Hz); 7.08 (dd, 1H, H_{19}, J = 8.4 Hz and J = 1.1 Hz); 3.79-3.71 (m, 2H, H_8); 3.67 (ddd, 1H, H_7, $J_{H\text{-}P}$ = 14.8 Hz, $J_{H7\text{-}H6}$ = 10.5 Hz and $J_{H7\text{-}H6}$ = 5.5 Hz); 3.41 (dqd, 1H, H_9, $J_{H9a\text{-}H9b}$ = 10.1 Hz, $J_{H9a\text{-}H11}$ = 7.1 Hz and $J_{H\text{-}P}$ = 6.5 Hz); 3.26 (ddd, 1H, H_{6a}, $J_{H6a\text{-}H6b}$ = 11.8 Hz, $J_{H6a\text{-}H7}$ = 10.5 Hz and $J_{H\text{-}P}$ = 10.5 Hz); 3.07 (ddq, 1H, H_{9b}, $J_{H9b\text{-}H9a}$ = 9.9 Hz, $J_{H\text{-}P}$ = 8.6 Hz and $J_{H9a\text{-}H11}$ = 7.1 Hz); 2.60 (ddd, 1H, H_{6b}, $J_{H\text{-}P}$ = 22.7 Hz, $J_{H6b\text{-}H6a}$ = 11.9 Hz and $J_{H6b\text{-}H7}$ = 5.5 Hz); 0.89 (t, 3H, H_{10}, J = 7.1 Hz); 0.54 (t, 3H, H_{11}, J = 7.1 Hz). ^{13}C NMR (100 MHz) δ: 200.1 (d, C1, $^3J_{CP}$=19.1 Hz); 136.7 (C4); 135.8 (C30); 134.8 (d, C3, $^3J_{CP}$ = 7.4 Hz); 134.4(C24); 131.5 (C29); 131.4 (C23); 131.3 (C35); 130.8 (C17); 129.1 (C32); 128.8 (C34); 128.6 (C26); 128.4 (C25); 128.0 (C33); 127.9 (C28); 127.7 (C27); 127.6 (C31); 127.5 (C12); 127.1 (C13); 126.4 (C18); 126.3 (C21); 126.3 (C15); 126.1 (C20); 125.9 (C14); 125.0 (C19); 123.4 (C22); 122.8 (C16); 62.54 (d, C2, $^2J_{CP}$=3.3 Hz); 62.54 (d, C8, $^2J_{CP}$=3.3 Hz); 61.7 (d, C9, $^2J_{CP}$= 6.9 Hz); 59.1 (d, C5, $^3J_{CP}$= 2.3 Hz); 35.6 (d, C7, $^1J_{CP}$= 157.3 Hz); 30.5 (d, C6, $^2J_{CP}$= 3.9 Hz); 15.9 (d, C10, $^3J_{CP}$= 6.1 Hz); 15.4 (d, C11, $^3J_{CP}$= 6.5 Hz). IR νmax (neat/cm^{-1}): 2979 (C-H); 1780 (bridged C=O); 1447 (C=C); 1234 (P=O intense); 1025 (P-O-C intense). ESI-TOF MS m/z (% relative abundance): 547 (M+H, 100). HRMS-ESI calculated for $C_{33}H_{32}O_4P$ 547.2038; found 547.2032.

Synthesis of diethyl (7,10-diphenylfluoranthen-8-yl)phosphonate 5cα

A solution of acecyclone **1c** (0.35 g; 1.0 mmol) in 10 mL bromobenzene was added to diethyl vinylphosphonate **2α** (0.25 g; 1.5 mmol) in 10 mL of bromobenzene. The mixture was refluxed for 24 h. The solvent was removed under vacuum and the residue was flash-chromatographed on silica gel column using (AcOEt/Cyclohexane: 15/85) as eluent to give an orange viscous liquid (0.16 g, 32%).



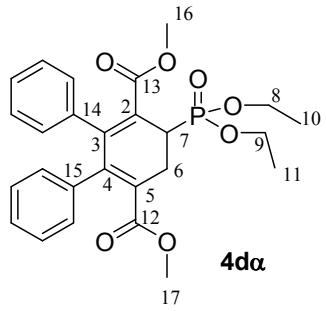
5cα

^{31}P NMR (162 MHz) δ 18.5. ^{1}H NMR (500 MHz) δ 8.04 (d, 1H, H_6, $^3J_{HP}$ = 14.5 Hz); 7.81 (d, 1H, H_{21}, J = 7.5 Hz); 7.75 (d, 1H, H_{15}, J = 8.0 Hz); 7.68 (bd, 2H,

H_{25}, J = 6.5 Hz); 7.61-7.54 (m, 8H, H_{26}, H_{27}, H_{31}, H_{32}, H_{33}); 7.41 (t, 1H, H_{20}, J= 7.5 Hz); 7.35 (d, 1H, H_{19}, J= 7.5 Hz); 7.31 (dd, 1H, H_{14}, J=8.0 Hz and J= 7.0 Hz); 6.40 (d, 1H, H_{13}, J= 7.0 Hz); 4.05-3.89 (m, 4H, H_8); 1.23 (t, 6H, H_9, J=7.5 Hz). ^{13}C NMR (125 MHz) δ 140.2 (d, C**24**, $^3J_{CP}$=8.3 Hz); 140.1 (C**30**); 140.0 (C**4**); 139.2 (d, C**3**, $^3J_{CP}$=18.5 Hz); 138.8 (d, C**5**, $^3J_{CP}$=4.3 Hz); 137.4 (d, C**2**, $^2J_{CP}$=16.3 Hz); 135.8 (d, C1**2**, $^4J_{CP}$=2.4 Hz); 135.0 (C**18**); 134.7 (d, C**6**, $^2J_{CP}$=11.2 Hz); 133.1 (C**17**); 129.8 (C**31**); 129.7 (C**16**); 129.1 (C**25**); 128.8-128.2 (C**26**/C**32**); 128.14-128.09 (C**27**/C**33**); 127.9 (C**14**); 127.8 (C**21**); 127.6 (C**20**); 127.0 (C**15**); 126.1 (d, C**7**, $^1J_{CP}$=188.2 Hz); 124.2 (C**19**); 124.0 (C**13**); 62.0 (d, C**8**, $^2J_{CP}$=5.5 Hz); 16.4 (d, C**9**, $^3J_{CP}$=6.3 Hz). IR νmax (neat/cm^{-1}): 3053; 2979 (C-H); 1442 (C=C); 1225 (P=O intense); 1020 (P-O-C intense). ESI-TOF MS m/z (% relative abundance): 491 (M+H, 100). HRMS-ESI calculated for $C_{32}H_{28}O_3P$ 491.1776; found 491.1762.

Synthesis of dimethyl 4'-(diethoxyphosphoryl)-4',5'-dihydro-(1,1':2'1"-terphenyl)-3',6'-dicarboxylate 4dα

A solution of 3,4-dimethoxycarbonyl-2,5-diphenylcyclopentadienone **1d** (0.2 g, 5.7 mmol) in 10 mL of bromobenzene was added to diethyl vinylphosphonate **2α** (0.1 g, 6.1 mmol) in 10 mL of bromobenzene. The mixture was then refluxed during 24 h. The solvent was removed under vacuum to give a brown viscous liquid. The residue was flash-chromatographed on silica gel column using (AcOEt/Cyclohexane: 15/85) as eluent to give an orange viscous liquid (0.24 g, 89%).



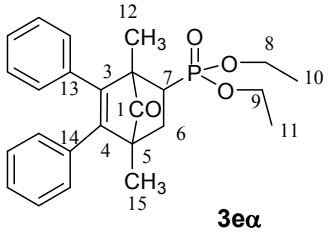
4dα

^{31}P NMR (162 MHz) δ 26.3. ^{1}H NMR (500 MHz) δ 6.97 (m, 6H, H_{arom}, J = 6.9 Hz); 6.68 (m, 4H, H_{arom}); 4.15-4.06 (m, 4H, H_8, H_9); 3.59 (ddd, 1H, H_7, $^2J_{HP}$=26.2 Hz, $^3J_{H7\text{-}H6b}$ = 9.5 Hz, $^3J_{H7\text{-}H6a}$=1.5 Hz); 3.37 (s, 3H, H_{17}); 3.33 (s, 3H, H_{16}); 3.26 (ddd, 1H, H_{6a}, $^2J_{H6a\text{-}H6b}$ =18.0 Hz, $^3J_{HP}$ =17.0 Hz, $^3J_{H6a\text{-}H7}$ =1.5 Hz); 3.01 (ddd, 1H, H_{6b}, $^3J_{HP}$ =52.5 Hz, $^2J_{H6b\text{-}H6a}$=18.0 Hz and $^3J_{H6b\text{-}H7}$= 9.5 Hz); 1.28 (t, 3H, H_{11}, J= 7.2 Hz); 1.25 (t, 3H, H_{10}, J=7.1 Hz). ^{13}C NMR (125 MHz) δ

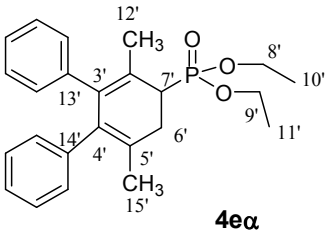
167.8 (d, C**12,** $^{4}J_{CP}$=1.5 Hz); 167.4 (d, C**13,** $^{3}J_{CP}$=3.2 Hz); 147.1 (d, C**3**, $^{3}J_{CP}$=11.4 Hz); 144.6 (d, C**4**, $^{4}J_{CP}$= 5.4 Hz); 137.7 (d, C**14,** $^{4}J_{CP}$=3.6 Hz); 137.6 (C**15**); 128.8 (**C**H_{arom}); 128.6 (**C**H_{arom}); 127.2 (d, C**5,** $^{3}J_{CP}$=10.3 Hz); 127.1 (**C**H_{arom}); 127.0 (**C**H_{arom}); 126.8 (**C**H_{arom}); 126.7 (**C**H_{arom}); 125.4 (d, C**2**, $^{2}J_{CP}$=9.8 Hz); 62.4 (d, C**8,** $^{2}J_{CP}$=1.4 Hz); 62.3 (d, C**9,** $^{2}J_{CP}$=1.4 Hz); 51.7 (C**16**); 51.0 (C**17**); 33.0 (d, C**7**, $^{1}J_{CP}$= 136.4 Hz); 25.1 (d, C**6**, $^{2}J_{CP}$= 5.5 Hz); 16.6 (d, C**10**, $^{3}J_{CP}$= 5.5 Hz); 16.4 (d, C**11**, $^{3}J_{CP}$=6.0 Hz). IR νmax (neat/cm^{-1}): 2985 (C-H); 1705 (C=O ester intense); 1432 (C=C); 1212 (P=O intense); 1018 (P-O-C intense). ESI-TOF MS m/z (% relative abundance): 485 (M+1, 100); 507 (M+Na, 35). HRMS-ESI calculated for $C_{26}H_{30}O_7P$ 485.1729; found 485.1722.

Synthesis of diethyl (1,4-dimethyl-7-oxo-5,6-diphenylbicyclo[2.2.1]hept-5-en-2-yl)phosphonate 3eα and diethyl (3,6-dimethyl-4,5-dihydro[1,1':2',1"]-phosphonate 4eα.

A solution of 2,5-dimethyl-3,4-diphenylcyclopentadienone **1e** dimer (0.4g; 0.77 mmol) in 10 mL of bromobenzene was added to diethyl vinylphosphonate **2α** (0.25 g; 1.6 mmol) in 10 mL of bromobenzene. The mixture was refluxed for 24 h and the solvent was then distilled under vacuum to give a brown viscous liquid. The residue was flash-chromatographed on silica gel column using (AcOEt/Cyclohexane: 15/85) as eluent to give an orange viscous liquid (0.5 g, global yield: 81% which turned to be a mixture of **3eα** and **4eα** in the ratio 45/55 (determined by ^{1}H NMR).



3eα



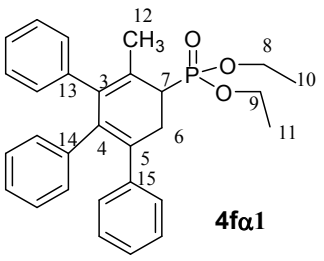
4eα

^{31}P NMR (162 MHz) δ 28.4; 29.5. ^{1}H NMR (500 MHz) δ 7.24-6.85 (m, 16H, H_{arom}); 6.83 (t, 2H, H_{arom}, J=7.0 Hz); 6.74 (t, 2H, H_{arom}, J=7.0 Hz) ; 4.21-3.94 (m, 8H, H_{8}, $H_{9'}$, $H_{8'}$, H_{9}); 2.85 (ddd, 1H, $H_{6a'}$, $^{3}J_{HP}$= 54.6 Hz, $^{2}J_{H6a'\text{-}H6'b}$= 17.3 Hz, $^{3}J_{H6'a\text{-}H7'}$ =9.7 Hz); 2.66 (dd, 1H, $H_{7'}$, $^{2}J_{HP}$=24.6 Hz, $^{3}J_{H7'\text{-}H6'a}$= 9.5 Hz); 2.53 (t, 1H, $H_{6'b}$, $^{2}J_{H6'b\text{-}H6'a}$ =$^{2}J_{HP}$=17.0 Hz); 2.31 (ddd, 1H, H_{7}, $^{2}J_{HP}$= 17.2 Hz, $^{2}J_{H7\text{-}H6a}$= 10.1 Hz, $^{3}J_{H7\text{-}H6b}$ =7.4 Hz); 2.13-1.96 (m, 2H, H_{6}); 1.75 (d, 3H, $H_{12'}$, $^{3}J_{HP}$= 4.7 Hz); 1.65 (s, 3H, $H_{15'}$); 1.41 (s, 3H, H_{12}); 1.35-1.11 (m, 12H, H10, H11, H10', H11'); 1.20 (s, 3H, H_{15}). ^{13}C NMR (125 MHz) δ 203.9 (d, C**1,** $^{3}J_{CP}$=20.1 Hz), 143.2 (C**4**); 140.9 (d, C**3,** $^{3}J_{CP}$ =4.7 Hz); 140.4 (C**13**); 140.3 (C**14**); 140.2 (C**14'**);

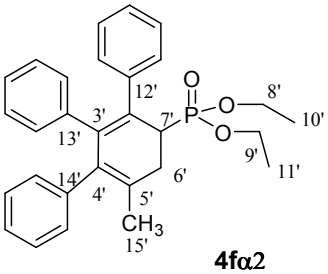
140.1 (C**13'**); 137.8 (d, C**3'**, $^{3}J_{CP}$=12.8 Hz); 134.3 (C**4'**); 131.7 (**C**H$_{arom}$); 130.5 (**C**H$_{arom}$); 130.2 (**C**H$_{arom}$); 130.1 (**C**H$_{arom}$); 129.5 (**C**H$_{arom}$); 128.2 (**C**H$_{arom}$); 127.6 (**C**H$_{arom}$); 127.5 (**C**H$_{arom}$); 127.4 (d, C**5'**, $^{3}J_{CP}$=7.0 Hz); 127.3 (**C**H$_{arom}$); 127.2 (**C**H$_{arom}$); 125.8 (**C**H$_{arom}$);125.6 (**C**H$_{arom}$); 123.8 (d, C**2'**, $^{2}J_{CP}$=11.5 Hz); 62.1 (d, C**8**, $^{2}J_{CP}$=6.9 Hz); 62.1 (d, C**9**, $^{2}J_{CP}$=5.6 Hz); 62.0 (d, C**9'**, $^{2}J_{CP}$=6.8 Hz); 61.9 (d, C**8'**, $^{2}J_{CP}$=7.0 Hz); 54.8 (d, C**2**, $^{2}J_{CP}$=3.1 Hz); 52.2 (d, C**5**, $^{3}J_{CP}$=3.2 Hz); 39.6 (d, C**7'**, $^{1}J_{CP}$=130.2 Hz); 38.7 (d, C**7**, $^{1}J_{CP}$=155.5 Hz); 33.6 (d, C**6,** $^{3}J_{CP}$=2.7 Hz); 30.5 (d, C**6'**, $^{2}J_{CP}$=5.9 Hz); 21.3 (d, C**12'**, $^{3}J_{CP}$=3.1 Hz); 21.1 (d, C**15',** $^{4}J_{CP}$=1.3 Hz); 16.8 (d, C**11'**, $^{3}J_{CP}$=5.9 Hz); 16.5 (d, C**11**, $^{3}J_{CP}$=5.8 Hz); 16.5 (d, C**10'**, $^{3}J_{CP}$=6.5 Hz); 16.4 (d, C**10**, $^{3}J_{CP}$=5.8 Hz), 12.4 (C**12**); 12.2 (C**15**). ESI-TOF MS m/z (% relative abundance): 425 3eα (M+1; 30); 397 4eα (M+1; 21). HRMS-ESI calculated for $C_{24}H_{28}O_3P$ 395.1776; found 395.1778.

Synthesis of diethyl (5'-methyl-6'-phenyl-3',4'-dihydro [1,1':2',1"-terphenyl]-4'yl)3,4,5)phosphonate 4fα1 and diethyl (5'-methyl-6'-phenyl-3',4'-dihydro [1,1':2',1''-terphenyl]-3'yl)3,4,5)phosphonate 4fα2.

A solution of 2-methyl-3,4,5-triphenylcyclopentadienone **1f** (0.2 g, 0.62 mmol) in 10 mL bromobenzene was added to diethyl vinylphosphonate **2α** (0.1 g, 0.62 mmol) in 10 mL bromobenzene. The mixture was refluxed for 24 hours. The solvent was distilled under vacuum giving a brown viscous liquid. The residue was flash-chromatographed on silica gel column using (AcOEt/Cyclohexane: 15/85) as eluent to give an orange viscous liquid (0.21 g, 74%) which is a mixture of ***4fα1*** and ***4fα2*** (60:40).



4fα1



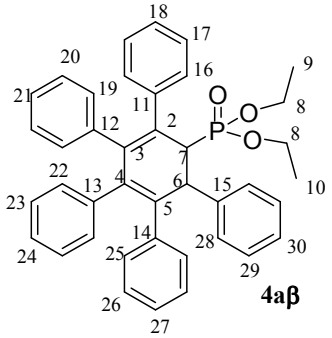
4fα2

NMR ^{31}P (162 MHz) δ 28.8; 29.3. NMR ^{1}H (500 MHz) δ 7.42 (d, 4H, H$_{arom}$, J=8.5 Hz); 7.24-7.14 (m, 4H, H$_{arom}$); 7.07-6.92 (m, 10H, H$_{arom}$); 6.83-6.73 (m, 8H, H$_{arom}$); 6.62-6.57 (m, 4H, H$_{arom}$); 4.20-3.89 (m, 8H, H$_{8}$, H$_{9}$, H$_{8'}$,H$_{9'}$); 3.28 (ddd, 1H, H$_{6a}$, $^{3}J_{HP}$=54.9 Hz, $^{2}J_{H6a\text{-}H6b}$ =16.8 Hz, $^{3}J_{H6a\text{-}H7}$ =8.9 Hz); 3.16 (dd, 1H, H$_{7'}$, $^{2}J_{HP}$=25.2 Hz , $^{3}J_{H7'\text{-}H6'a}$ =9.1 Hz); 3.02 (dddq, 1H, H$_{6'a}$, $^{3}J_{HP}$ =54.5 Hz, $^{2}J_{H6'a\text{-}H6'b}$ =16.6 Hz, $^{3}J_{H6'a\text{-}H7'}$ =8.9 Hz, $^{4}J_{H6'a\text{-}H15'}$ =1.7 Hz); 2.94 (ddd, 1H, H$_{6b}$, $^{3}J_{HP}$ =16.7 Hz, $^{2}J_{H6b\text{-}H6a}$ =16.7 Hz, $^{3}J_{H6b\text{-}H7}$ =1.7 Hz); 2.77 (ddd, 1H, H$_{7}$, $^{2}J_{HP}$= 26.5 Hz, $^{3}J_{H7\text{-}H6a}$ =9.1 Hz, $^{3}J_{H7\text{-}H6b}$ =1.7 Hz); 2.72 (dd, 1H, H$_{6'b}$, $^{3}J_{HP}$ =17.4 Hz, $^{2}J_{H6'b\text{-}H6'a}$

=16.7 Hz); 1.83 (d, 3H, H_{12}, $^4J_{HP}$ = 4.7 Hz); 1.68 (t, 3H, $H_{15'}$, $^4J_{H15'\text{-}H6'a}$ =1.4 Hz); 1.27 (t, 6H, $H_{11, 10'}$, $^3J_{HH}$=7.5 Hz); 1.23 (t, 3H, H_{10}, $^3J_{HH}$ =7.5 Hz); 1.03 (t, 3H, $H_{11'}$, $^3J_{HH}$= 7.5 Hz). NMR ^{13}C (125 MHz) δ 142.3 (d, **C15**, $^4J_{CP}$=1.7 Hz); 141.8 (d, **C13'**, ^4JCP=3.1 Hz); 139.9 (d, **C12'**, ^3JCP=4.0 Hz); 139.8 (**C14**); 139.7 (**C14'**); 139.7 (d, **C3'**, ^3JCP=12.1 Hz); 139.6 (d, C**13**, $^4J_{CP}$=3.9 Hz); 138.4 (d, C**3**, $^3J_{CP}$=13.3 Hz); 136.0 (d, C**4**, $^4J_{CP}$=6.3 Hz); 135.1 (d, C**4'**, $^4J_{CP}$=5.8 Hz); 130.6 (d, C**5**, $^3J_{CP}$=6.7 Hz) ; 130.1 (d, C**5'**, $^3J_{CP}$=7.2 Hz) ; 128.2 (d, C**2'**, $^2J_{CP}$=10.8 Hz) ; 126.3 (d, C**2**, $^2J_{CP}$=11.2 Hz); 131.6 (**C**H_{arom}); 131.6 (**C**H_{arom}); 131.6 (**C**H_{arom}); 130.9(**C**H_{arom}); 130.9 (**C**H_{arom}); 130.2 (**C**H_{arom}); 130.1 (**C**H_{arom}); 130.1(**C**H_{arom}); 130.1 (**C**H_{arom}); 130.0 (**C**H_{arom}); 128.8 (**C**H_{arom}); 127.5 (**C**H_{arom}); 127.4 (**C**H_{arom}); 127.4 (**C**H_{arom}); 127.3 (**C**H_{arom}); 126.9 (**C**H_{arom}); 126.9 (**C**H_{arom}); 126.8 (**C**H_{arom}); 62.2 (d, C**8**, $^2J_{CP}$=7.2 Hz); 61.8 (d, C**9**, $^2J_{CP}$=6.6 Hz); 61.7 (d, C**8'**, $^2J_{CP}$=7.0 Hz); 61.6 (d, C**9'**, $^2J_{CP}$=6.5 Hz); 39.8 (d, C**7**, $^1J_{CP}$=131.4 Hz); 39.2 (d, C**7'**, $^1J_{CP}$=130.1 Hz); 31.3 (d, C**6'**, $^3J_{CP}$=6.2 Hz); 30.8 (d, C**6**, $^3J_{CP}$=6.2 Hz); 21.5 (d, C**12**, $^3J_{CP}$=3.0 Hz); 21.2 (d, C**15'**, $^4J_{CP}$=1.3 Hz); 16.7 (d, C**10**, $^3J_{CP}$=5.7 Hz); 16.6 (d, C**11, C10'**, $^3J_{CP}$=5.7 Hz); 16.3 (d, C**11'**, $^3J_{CP}$=6.0 Hz). IR νmax (neat/cm-1) : 2982 (C-H); 1443 (C=C); 1228 (P=O intense); 1019 (P-O-C intense). ESI-TOF MS m/z (% relative abundance): 459 (M+1, 100). HRMS-ESI calculated for $C_{29}H_{32}O_3P$ 459.2089, found 459.2079.

Synthesis of diethyl (4',5',6'-triphenyl-2',3'-dihydro[1,1',:2',1"-terphenyl]-3-yl) phosphonate 4aβ.

A solution of tetracyclone **1a** (1 g, 2.6 mmol) and diethyl 2-*E*-phenyl vinylphosphonate **2β** (0.78 g, 2.6 mmol) in 2 mL bromobenzene was refluxed for 96 h. The solvent was removed under vacuum and the residue was crystallized from ethanol to give colourless solid. The precipitate was collected and recrystallized in ethanol giving colorless crystals (0.47 g, 31 %), mp 152°C.



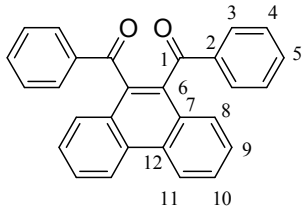
4aβ

NMR ^{31}P (162 MHz) δ 26.7. NMR ^{1}H (500 MHz) δ 7.68 (d, 2H, H_{28}, ^3J = 7.9 Hz); 7.46 (t, 2H, H_{29}, ^3J = 7.9 Hz); 7.36 (t, 1H, H_{30}, ^3J = 7.9 Hz); 7.10 (d, 2H, H_{25}, ^3J = 6.5 Hz); 7.04-6.90 (m, 14H, H_{26}, H_{27}, H_{23}, H_{21}, H_{18}, H_{17}, H_{20}, H_{22}); 6.75

(m, 2H, H_{19}); 6.67 (m, 2H, H_{16}); 4.60 (bd, 1H, H_6, $^3J_{HP}$ = 16.5 Hz); 4.24-4.16 (m, 2H, $H_{8a, H8'a}$); 4.13 (ddq, 1H, H_{8b}, $^2J_{H8b\text{-}H8a}$ = 10.2 Hz, $^3J_{HP}$ = 7.1 Hz, $^3J_{H8b\text{-}H9}$ = 7.0 Hz); 3.89 (ddq, 1H, $H_{8'b}$, $^2J_{H8'b\text{-}H8'a}$ = 10.1 Hz, $^3J_{HP}$ = 7.9 Hz, $^3J_{H8'b\text{-}H10}$ = 7.3 Hz); 3.47 (dd, 1H, H_7, $^2J_{HP}$ = 26.5 Hz, $^3J_{H7\text{-}H6}$ = 1.5 Hz); 1.34 (t, 3H, H_9, J = 7.0 Hz); 1.15 (t, 3H, H_{10}, J = 7.0 Hz). NMR ^{13}C (125 MHz) δ 141.5 (C**14**); 141.4 (d, $^3J_{CP}$ = 5.3 Hz C**11**); 140.8 (d, C**15**, $^3J_{CP}$ = 25.5 Hz); 140.1 (d, C**3**, $^3J_{CP}$= 12.0 Hz); 139.2 (C**13**); 139.1 (d, C**4**/C**12**, $^4J_{CP}$ = 6.2 Hz); 139.0 (d, C**4**/C**12**, $^4J_{CP}$ = 3.9 Hz); 134.6 (d, C**5,** $^3J_{CP}$ = 5.6 Hz); 131.1 (C**22**); 130.9 (d, C**19,** $^5J_{CP}$ = 4.3 Hz); 129.4 (C**25**); 129.3 (d, C**16,** $^4J_{CP}$ = 2.6 Hz); 128.9 (C**29**); 128.1 (C**28**); 127.9 (d, C**2,** $^2J_{CP}$ = 10.8 Hz); 127.5 (C**26**); 127.4 (C**17**); 127.3 (C**30**); 127.1 (C**23**); 127.0 (C**20**); 126.1 (C**27**); 126.3 (C**18**); 125.9 (C**21**); 62.2 (d, C**8**, $^2J_{CP}$=7.0 Hz); 49.0 (d, C**7**, $^1J_{CP}$ = 128.9 Hz); 45.8 (d, C**6**, $^2J_{CP}$=3.3 Hz); 16.7 (d, C**9**, $^3J_{CP}$ = 5.9 Hz); 16.4 (d, C**10**, $^3J_{CP}$ = 5.9 Hz). IR νmax (neat/cm-1): 2978 (C-H); 1442 (C=C); 1245 (P=O intense); 1018 (P-O-C). ESI-TOF MS m/z (% relative abundance): 597 (M+H, 100); 619 (M+Na, 57). ESI-TOF: calculated for $C_{40}H_{38}O_3P$ 597.2559; found 597.565.

Synthesis of diethyl (13-oxo-1,3,4-triphenyl-1,2,3,4-tetrahydro-1,4-methanotriphenylen-2-yl) phosphonate 3bβ.

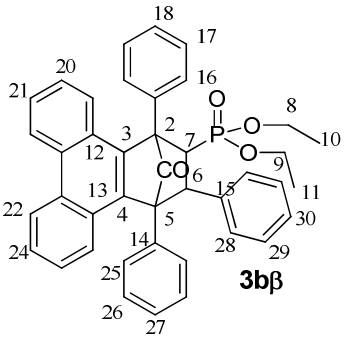
A solution of phencyclone **1b** (0.38 g; 1 mmol) in 10 mL bromobenzene was added to diethyl 2-*E*-phenyl vinylphosphonate **2β** (0.36 g, 1.5 mmol) in 10 mL bromobenzene. The mixture was refluxed for 96 h. The solvent was removed under vacuum and the residue was crystallized from ethanol to give a colorless powder (0.27 g, 70 %), mp 204°C.



^{1}H (400 MHz) δ 8.81 (d, 2H, H_8, ^3J= 8.3 Hz); 7.77 (dd, 4H, H_3, ^3J=8.0 Hz, ^4J = 1.6 Hz); 7.74 (ddd, 2H, H_9, ^3J=8.6 Hz, ^3J=6.8 Hz, ^4J = 1.2 Hz); 7.72 (dd, 2H, H_{11}, ^3J =8.4 Hz, ^4J =0.8 Hz); 7.56-7.49 (m, 4H, $H_{5,10}$); 7.35 (dd, 4H, H_4, ^3J= 8.4 Hz, ^3J=8.0 Hz). NMR ^{13}C (100 MHz) δ 198.4 (C**1**); 137.8 (C**2**); 135.5 (C**6**); 134.0 (C**5**); 130.7 (C**7**); 130.3 (C**3**); 128.7 (C**4**); 128.6 (C**12**); 128.1 (C**9**); 127.6 (C**10**); 127.4 (C**8**); 123.2 (C**11**). IR νmax (neat/cm-1): 3055 (C-H); 1665; 1593 (C=O); 1446 (C=C). ESI-TOF MS m/z (% relative abundance): 387 (M+1, 92);

409 (M+23, 100). HRMS-ESI calculated for $C_{28}H_{19}O_2$ 387.1385, found 387.1371.

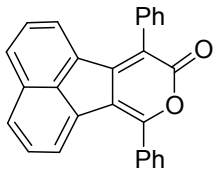
The filtrate, a viscous liquid (<4%) constitution was assigned on the basis of mass spectroscopy to be the bridge carbonyl phosphonated compound ***3bβ*** :



NMR ^{31}P (162 MHz) δ 25.14. ESI-TOF MS m/z (% relative abundance): 623 (M+1, 16); 687 (M+23, 4).

Diels-Alder reaction of acecyclone 1c with diethyl 2-*E*-phenyl vinylphosphonate 2β.

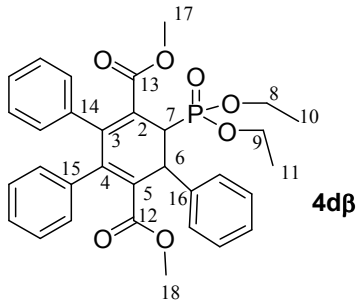
A solution of acecyclone **1c** (0.35 g; 1 mmol) in 10 mL bromobenzene was added to diethyl 2-*E*-phenyl vinylphosphonate **2β** (0.36 g; 1.5 mmol) in 10 mL of bromobenzene. The mixture was refluxed for 96 h. The solvent was removed under vacuum and the residue was crystallized from ethanol to give a green powder (0.17 g), mp > 260°C. The ^{1}H NMR was conform with the structure of the reactants, however the mass spectrum showed clearly the presence of the corresponding lactone.



ESI-TOF MS *m/z* (% relative abundance): 373 (M+1; 80); 395 (M+23; 20). HRMS-ESI: calculated for $C_{27}H_{17}O_2$ 373.1229; found 373.1235.

Synthesis of dimethyl 4'-(diethoxyphosphoryl)-4'5'-dihydro-[1,1':2"-terphenyl]-3'6'- dicarboxylate 4dβ.

A solution of 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone **1d** (0.20 g; 0.57 mmol) in 10 mL bromobenzene was added to diethyl 2-*E*-phenyl vinylphosphonate **2β** (0.14g; 0.57 mmol) in 10 mL bromobenzene. The mixture was refluxed for 4 days then the solvent was distilled under reduced vacuum to give a brown viscous liquid (0.23 g, 72%).



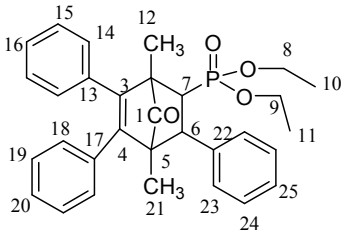
4dβ

NMR ^{31}P (400 MHz) δ 24.92. NMR ^{1}H (500 MHz) δ 7.43 (td, 2H$_{arom}$, J=4.0 Hz, J'=1.0 Hz); 7.38 (d, 2H$_{arom}$, J=9.0 Hz); 7.31 (dd, 4H$_{arom}$, J=6.5 Hz, J'=2.0 Hz); 7.24 (t, 2H$_{arom}$, J=7.0 Hz); 7.04-6.93 (m, 5H$_{arom}$); 4.68 (d, 1H, H$_{\mathbf{6}}$, $^{3}J_{HP}$=19.5 Hz); 4.09-4.02 (m, 4H, H$_{\mathbf{9}}$, H$_{\mathbf{8}}$); 3.81 (dd, 1H, H$_{\mathbf{7}}$, $^{1}J_{HP}$= 27.5 Hz, $^{3}J_{H7\text{-}H6}$=1.0 Hz); 3.24 (s, 3H, H$_{\mathbf{17}}$); 3.20 (s, 3H, H$_{\mathbf{18}}$); 1.28 (td, 6H, H$_{\mathbf{11}}$, H$_{\mathbf{10}}$, $^{3}J_{HH}$=7.0 Hz, $^{3}J_{HP}$= 1.5 Hz). NMR ^{13}C (125 MHz) δ 167.4-167.1 (C**12**/C**13**); 148.8 (d, C**16**, $^{3}J_{CP}$=6.7 Hz); 146.7 (d, C**3**, $^{3}J_{CP}$=11.4 Hz); 145.7 (d, C**4**, $^{3}J_{CP}$=5.4 Hz); 137.4 (d, C**14**, $^{3}J_{CP}$=3.4 Hz); 133.1 (C**15**); 130.3 (C**5**); 129.3 (**C**H$_{arom}$); 129.1 (**C**H$_{arom}$); 128.9 (**C**H$_{arom}$); 128.7 (**C**H$_{arom}$); 128.6 (**C**H$_{arom}$); 128.5 (**C**H$_{arom}$); 128.2 (**C**H$_{arom}$); 127.9 (**C**H$_{arom}$); 127.7 (**C**H$_{arom}$); 126.9 (d, C**2**, $^{2}J_{CP}$=4.6 Hz); 62.6 (d, C**8**, $^{2}J_{CP}$=7.0 Hz); 61.9 (d, C**9**, $^{2}J_{CP}$=5.4 Hz); 51.7 (C**18**); 51.6 (C**17**); 41.8 (d, C**7**, $^{1}J_{CP}$=134.9 Hz); 38.1 (d, C**6**, $^{2}J_{CP}$=3.0 Hz); 16.6 (d, C**10**, $^{3}J_{CP}$=5.6 Hz); 16.5 (d, C**11**, $^{3}J_{CP}$=8.0 Hz). IR ν_{max} (neat/cm^{-1}): 2983 (C-H); 1709 (C=O ester); 1434 (C=C); 1229; 1102; 1050 (C-O ester intense); 1019 (P-O-C intense). ESI-TOF MS *m/z* (% relative abundance): 561 (M+1; 48); 583 (M+23; 15). HRMS-ESI: calculated for $C_{32}H_{34}O_7P$ 561.2042; found 561.2020.

Synthesis of diethyl (1,4-dimethyl-7-oxo-3,5,6- triphenylbicyclo[2,2,1]hept-5-en-2-yl) phosphonate 3eβ

A solution of 2,5- dimethyl-3,4-diphenylcyclopentadienone **1e** (0.2 g; 0.76 mmol) in 10 mL bromobenzene was added to diethyl 2-*E*-phenyl vinylphosphonate **2β** (0.24 g; 1 mmol) in 10 mL bromobenzene. The mixture was refluxed for 96 h. The solvent was removed under vacuum and the residue

was chromatographied on silica gel column using (AcOEt/cyclohexane 20%) as eluent to give a yellow viscous liquid (0.271 g; yield: 67%).

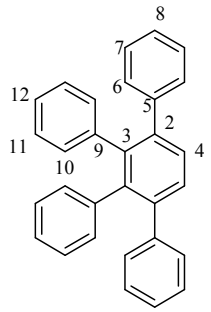


3eβ

NMR ^{31}P (162 MHz) δ 28.5. NMR ^{1}H (400 MHz) δ 7.10-6.98 (m, 9H, **H$_{15,16,19,20,24,25}$**); 7.25-7.15 (m, 6H, **H$_{14,18,23}$**); 3.97-3.75 (m, 3H, H$_{8,8,9}$); 3.63-3.53 (m, 1H, H$_9$); 3.31 (dd, 1H, H$_6$, $^3J_{HP}$= 21.9 Hz; $^3J_{H6-H7}$=7.6 Hz); 2.42 (dd, 1H, H$_7$, $^2J_{HP}$=18.0 Hz, $^3J_{H7-H6}$=7.4 Hz); 1.52 (s, 3H, H$_{12}$); 1.00 (t, 1H, H$_{10}$, $^3J_{H10-H8}$=6.9 Hz); 0.86 (t, 3H, H$_{11}$, $^3J_{H11-H9}$=6.9 Hz); 0.79 (s, 3H, H$_{21}$). NMR ^{13}C (100 MHz) δ 204.6 (d, C**1**, $^3J_{CP}$=20.7 Hz); 143.6 (C**4**); 142.0 (d, C**3**, $^3J_{CP}$=4.7 Hz); 140.2 (d, C**22**, $^3J_{CP}$=3.7 Hz); 134.6 (C**13**); 134.0 (C**17**); 130.4 (**C14**); 129.6 (**C18**); 128.7 (**C15**); 128.1 (**C19,23**); 127.5; (**C24**); 127.4 (**C25**); 127.3 (C**16**); 127.1 (**C20**); 61.9 (d, C**8**, $^2J_{CP}$=5.8 Hz); 61.8 (d, C**9**, $^2J_{CP}$=6.2 Hz); 56.4 (d, C**5**, $^3J_{CP}$=4.7 Hz); 54.8 (d, C**2**, $^2J_{CP}$=2.6 Hz); 51.1 (d, C**6,** $^2J_{CP}$=0.8 Hz); 48.4 (d, C**7**, $^1J_{CP}$=152.0 Hz); 16.1 (d, C**10**, $^3J_{CP}$=6.2 Hz); 15.8 (d, C**11**, $^3J_{CP}$=6.4 Hz); 12.4 (C**12**); 10.1 (C**21**). IR νmax (neat/cm-1): 2983 (C-H); 1770 (C=O); 1443 (C=C); 1240; 1102; 1048 (C-O ester intense); 1021 (P-O-C intense). ESI-TOF MS m/z (% relative abundance): 501 (M+1; 100); 523 (M+23; 90).

Diels-Alder reactions of tetraphenylcyclopentadienone 1a with tetraethyl vinylidenebisphosphonate 2γ

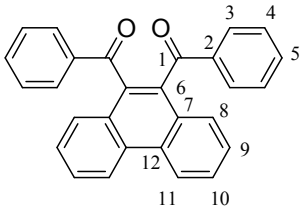
A solution of tetracyclone **1a** (0.14 g; 0.37 mmol) in 10 mL bromobenzene was added to tetraethyl vinylidenebisphosphonate **2γ** (0.11g; 0.37 mmol) in 10 mL bromobenzene. The mixture was refluxed for 96 h. The solvent was distilled under vacuum and the residue was crystallized in a brown solid m=0.13 g (92 %).



IR νmax (neat/cm-1): 3055 (C-H); 1691; 1598; 1441 (C=C). NMR ^{1}H (400 MHz) δ 7.54 (s, 2H, H4); 7.22-7.12 (m, 10H, H7,10,12); 6.97-6.93 (m, 6H, H8,11); 6.85-6.82 (m, 4H, H6). NMR ^{13}C (100 MHz) δ 141.9 (C5); 140.9 (C3); 140.4 (C2); 139.9(C9); 131.6 (C6); 129.9 (C10); 129.4 (C4); 127.5 (C7); 126.9 (C11); 126.2 (C12); 125.6 (C8).

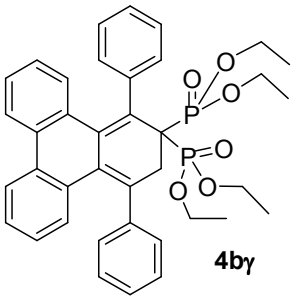
Diels-Alder reactions of phencyclone 1b with tetraethyl vinylidenebisphosphonate 2γ.

A solution of phencyclone **1b** (0.38 g; 1 mmol) in 5 mL bromobenzene was added to tetraethyl vinylidenebisphosphonate **2γ** (0.20 g; 1.5 mmol) in 5 mL bromobenzene. The mixture was refluxed for 96 h. The solvent was distilled under vacuum to give a residue which was crystallized in methanol, as colorless crystals (0.18 g, 46%). mp= 204°C which turned out to be the phenanthrene-9,10-diylbisphenylcarbonyle.



HRMS-ESI calculated for $C_{28}H_{19}O_2$ 387.1385, found 387.1371.

The filtrate after evaporation of solvent gave a viscous liquid (< 3%). The constitution was assigned on the basis of mass spectrum analysis to be a bisphosphonated compound which structure may be:



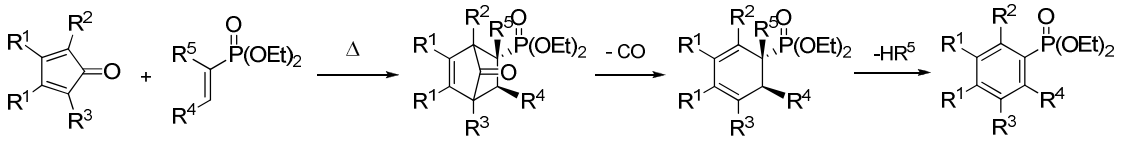
4bγ

NMR ^{31}P (162 MHz) δ 21.3. ESI-TOF MS *m/z* (% relative abundance): 655 (M+1, 27).

Results and discussion

We have studied the Diels-Alder reaction of diethyl vinylphosphonate **2α**, diethyl 2-styrylphosphonate **2β** and tetraethyl vinylidene-bis-phosphonate **2γ** with the stable tetrasubstituted cyclopentadienones **1a-f**.

Scheme 2. Formation of various cyclic phosphonated compounds **3**, **4**, **5** from reaction of tetrasubstituted cyclopentadienones with phosphonated olefins.



1a-f **3** **4** **5**

The Diels-Alder reaction of vinylphosphonates with dienes were described in particulary for the vinylphosphonates bearing an other electron-withdrawing groups (CN, COR, COOR…).[15] Likewise, tetraalkyl vinylidene-1,1-bis-phosphonates are also known to react as dienophiles with electron rich diene systems, but are generally less reactive in cycloadditions probably due to their steric hindrance.[16]

In Diels-Alder reaction of vinylphosphonates with cyclopentadienones, several phosphonated products could be generated, such as carbonylated **3**, decarbonylated **4** or aromatic compounds **5** (Scheme 2). The control of the reaction depends on the reaction temperature, compounds of general structure **3** can be generally isolated through a simple heating. If the temperature is increased however, compound **3** is converted in compound **4**, and eventually in compound **5** if heating is prolonged under oxidative conditions.

In preliminary experiments, we have used refluxing toluene (110°C), but the kinetics were oftentimes too slow, thus turning towards the use of bromobenzene (bp 156°C) as solvent. We have also tested nitrobenzene (bp 210°C) as solvent because its oxidant properties could facilitate the

aromatization step, but it led to many by-products. Additionally, in some cases, an extended heating under argon has led to elimination of the phosphonate group. All isolated products were fully identified using IR, proton, carbon and phosphorus NMR spectroscopies (especially HMBC and HSQC experiments), as well as mass spectrometry.

a) Reactions with diethyl vinylphosphonate 2α

The main results of vinylphosphonate **2α** with cyclopentadienones **1a-f** are summarized in the Table 1**.**

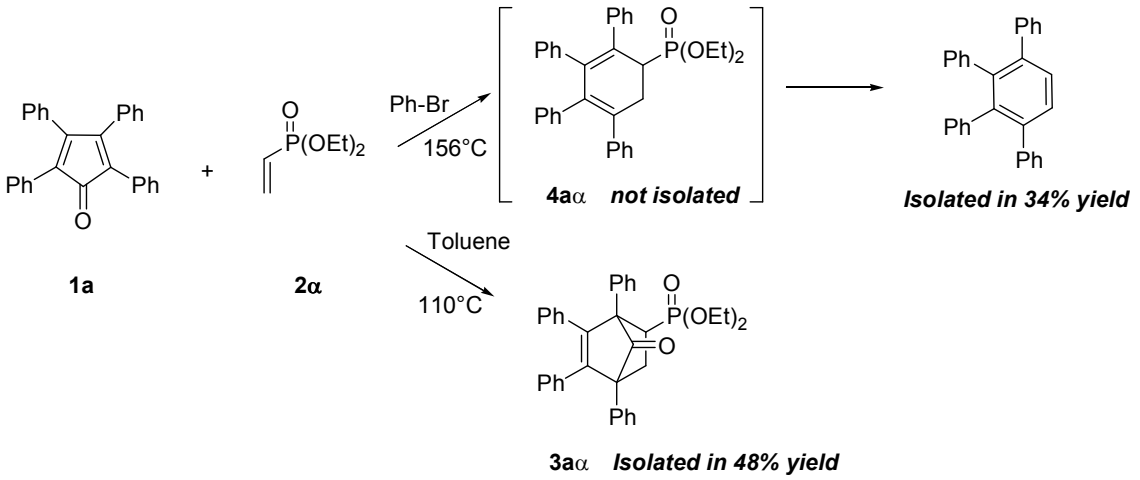
Table 1: Cycloadducts synthesis from cyclopentadienones **1a-f** and vinyl phosphonate **2α** in refluxing bromobenzene.

Entry	Cyclone	T(°C)	Time (h)	Products	Yield (%)	Ratio
1	**1a**	110	24	**3aα**	48*	
2	**1b**	156	24	**3bα**	41	
3	**1c**	156	24	**5cα**	32	
4	**1d**	156	24	**4dα**	89	
5	**1e**	156	24	**3eα+4eα**	81	45:55**
6	**1f**	156	24	**4fα1+4fα2**	74	60:40**

* Reaction was carried out in toluene as solvent. ** determinated by ^{1}H NMR.

When a solution containing tetracyclone **1a** and a slight excess of diethyl vinylphosphonate **2α** in bromobenzene was stirred at reflux for 24 hours, the 1,2,3,4-tetraphenylbenzene was obtained as the sole product in a low 34% yield accompanied by insoluble materials, suggesting that the temperature was too high. Our suspicions were partly confirmed when refluxing toluene for 38 hours

was used (110°C) instead of bromobenzene (156°C), thus obtaining the 2,3,4,5-tetraphenylcyclohexa-2,4-dienylphosphonate **3aα** in a 48% yield (Scheme 3).



Scheme 3. Reaction of tetracyclone **1a** with diethyl vinylphosphonate **2α** in bromobenzene and toluene.

The structure of **3aα** was assigned mainly on the basis of the ^{13}C NMR spectrum, in which the bridged carbon is at 199.7 ppm. The IR spectrum showed also a characteristic carbonyl band at 1778 cm^{-1} suggesting the presence of a bridged carbonyl group.

The Diels-Alder cycloadditions of vinylphosphonate were carried out in refluxing bromobenzene as solvent for the next reactions. When phencyclone **1b** was refluxed with diethyl vinylphosphonate **2α** in bromobenzene, the deep black- green color associated with **1b** gradually faded to a pale yellow solution providing the carbonylated bridge product (41%). Likewise, the structure of **3bα** was mainly determined by ^{13}C NMR (200.1 ppm) and IR spectrum (1780 cm^{-1}).

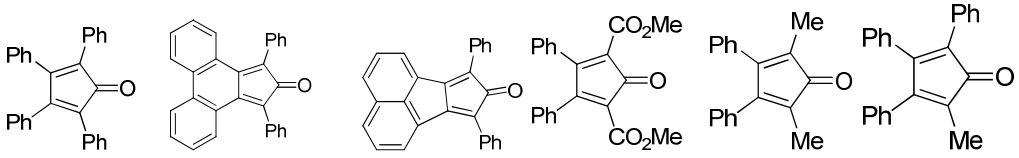
In the same conditions, acecyclone **1c** reacted with diethyl vinylphosphonate **2α** giving the corresponding aromatic decarbonylated cycloadduct **5cα** (32%). Probably, the fusion of acenaphthylene ring to the bicyclo[2.2.1]-hepten-7-one

system causes a considerable increase in strain energy derived from distortion of the external angle, thus inducing fast decarbonylation.

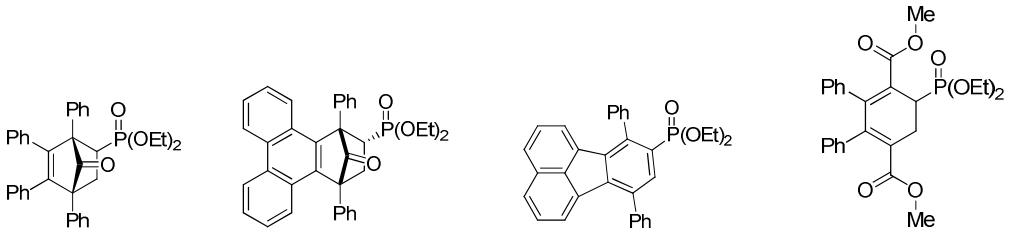
When reacting with diethyl vinylphosphonate **2α**, cyclopentadienone **1d** produced the decarbonylated cycloadduct **4dα** as the sole product in 89% yield, whereas the cyclone **1e** led to a mixture of carbonylated and decarbonylated products **3eα** and **4eα** respectively, in 81% overall yield. It is noteworthy that mass spectrum showed the presence of the corresponding aromatic **5eα** whereas it is not visible in NMR. The conditions of ESI-TOF promote probably the aromatization step during the analysis.

Cyclopentadienone **1f** gave a mixture of regioisomers **4fα1** and **4fα2** in a 60/40 ratio, with no carbonylated product however.

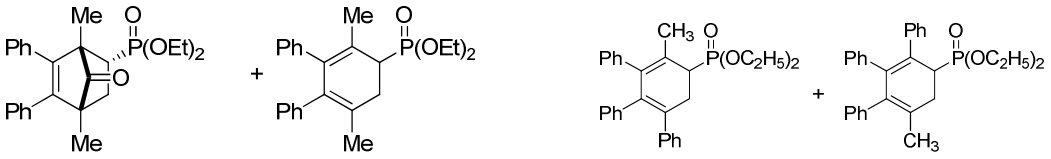
The literature reports the Diels-Alder reaction of vinylphosphonate with dienes as being catalyzed by Lewis acids (BF_3, $GaCl_3$),[17] yet attempts to use boron trifluoride (hard Lewis acid) or bismuth trichloride (soft Lewis acid) as catalyst in cycloaddition of vinyl phosphonate **2α** with cyclopentadienones **1a** or **1d** were unsuccessful, no increase of yield was observed.



1a **1b** **1c** **1d** **1e** **1f**



3aα **3bα** **5cα** **4dα**



3eα + 4eα **4fα1 + 4fα2**

b) Reaction with diethyl 2-*E*-styrylphosphonate 2β

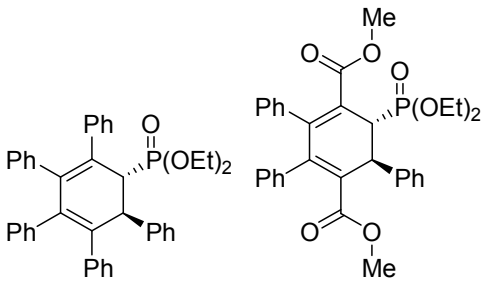
To our knowledge, the Diels-Alder reaction of diethyl 2-*E*-styrylphosphonate **2β** has never been reported. Only few styrylphosphonates bearing a carbonyl group have been described.[18]

The Diels-Alder reaction of diethyl 2-*E*-styrylphosphonate **2β** with cyclopentadienones **1a** and **1d** afforded, besides some unreacted starting material, the decarbonylated cycloadducts **4aβ** and **4dβ** in 31% and 72% respectively (Table 2). On the other hand, the cyclopentadienone **1e** gave the carbonylated compound **3eβ**.

Table 2. Cycloadducts synthesis from cyclopentadienones **1a, 1d** and **1e** with vinyl phosphonate **2β** in refluxing bromobenzene.

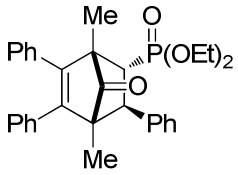
Entry	Cyclone	T(°C)	Time (h)	Products	Yield (%)
1	**1a**	156	24	**4aβ**	31
2	**1d**	156	24	**4dβ**	72
3	**1e**	156	24	**3eβ**	67
4	**1f**	156	24		0

*: ratio assigned on the basis of NMR analysis



4aβ

4dβ

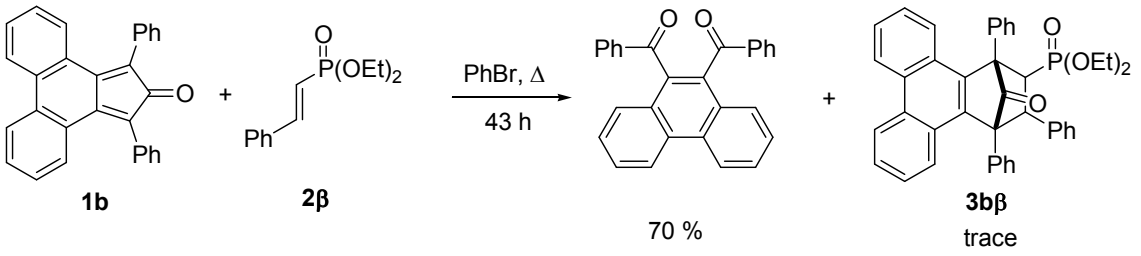


3eβ

Finally, cyclopentadienone **1f** failed to add to diethyl 2-*E*-phenyl-vinylphosphonate **2β,** even after extended heating time (6 days) in bromobenzene.

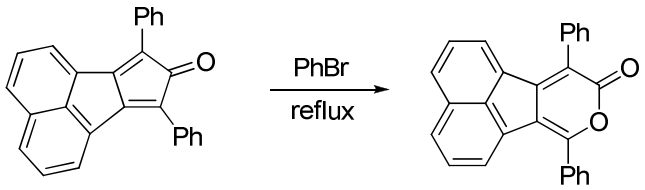
Cycloaddition of phencyclone **1b** with a small excess of diethyl *E*-styrylphosphonate **2β** in the same conditions afforded the corresponding bridge carbonylated cycloadduct **3bβ** in only trace, along with the diketonic compound phenanthrene-9,10-diylbisphenylcarbonyle 70% (Scheme 4) resulting from an oxidation process of phencyclone by air.

Scheme 4. Reaction of phencyclone **1b** with diethyl 2-*E*-styrylphosphonate **2β** in refluxing bromobenzene.



Interestingly, the reaction of acecyclone **1c** in the same conditions provided a different compound that turned out to be a lactone instead, after mass spectrum identification (Scheme 5). Dilthey *et al.*[19] have already described this oxidation reaction with phencyclone **1b** and acecyclone **1c** in 1938, but it is only recently that a mechanism of oxidation was postuled.[20] Under argon atmosphere starting products were recovered.

Scheme 5. Aerobic oxidation of **1c** in extended heating in bromobenzene.



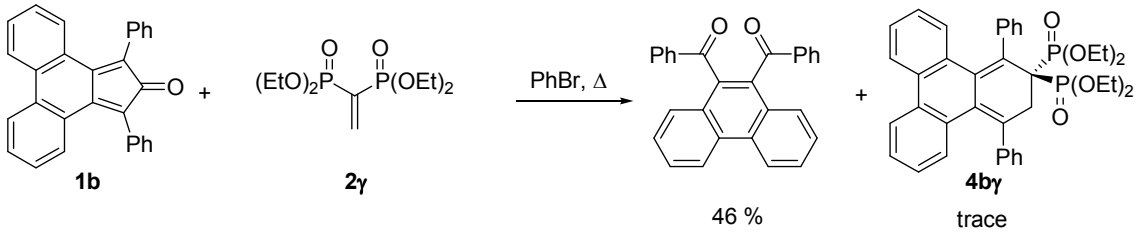
c) Tetraethyl vinylidene-1,1-bisphosphonate 2γ.

The Diels-Alder cycloaddition of the tetraethyl vinylidene-1,1-bisphosphonate **2γ** has been tested with the cyclopentadienones **1a-c** in the same conditions as previously described. Thus, heating of **2γ** with tetraphenylcyclopentadienone **1a** in refluxing bromobenzene for 96 hours furnished a brown solid. Unfortunately, ^{31}P NMR spectra displayed no signal at all, while suggesting after further investigation the formation of the 1,2,3,4-tetraphenylbenzene.

On the other hand, the Diels-Alder reaction of phencyclone **1b** with an excess of vinylidene-bis-phosphonate **2γ** upon heating in bromobenzene during 96 hours led to the formation of a colorless solid which turned out to be the phenanthrene-

9,10-diylbisphenylcarbonyle, resulting from oxidation process of phencyclone by air (Scheme 6). However, next to this solid, the analysis of the filtrate by ^{31}P NMR showed a new phosphorus signal at 21.3 ppm different from the corresponding one in vinylidene-bis-phosphonate (δ ^{31}P =13.1 ppm). Further analysis showed the formation of the diphosphonated compound **4bγ** in poor yield (3 %).

Scheme 6. Reaction of phencyclone **1b** with tetraethylvinylidenebisphosphonate **2γ** in refluxing bromobenzene.



Conclusion

The reactions of the cyclopentadienones with unsaturated phosphonates have never been described. New polycyclic phosphonate compounds were obtained from cyclopentadienones **1a-f** with vinyl and styryl phosphonates **2α** and **2β** using thermal Diels-Alder reaction. Cycloadditions of tetraethyl vinylidenebisphosphonate **2γ** with cyclopentadienones **1a-c** were generally unsuccessful with poor yield, but opened the field for further investigation. Thanks to the phosphonate group, the new polycyclic molecules might used for surface modification,[21] immobilization of catalysts, for metal cation coordination[22] or for electronic or photovoltaic applications.[23]

Acknowledgments

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