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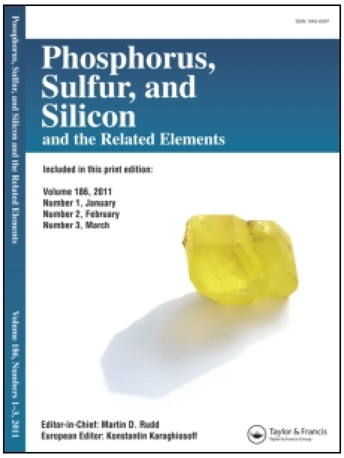

Phosphorus, Sulfur, and Silicon and the Related Elements

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THE DIELS-ALDER REACTION OF DIPHENYL(1,2-PROPADIENYL)PHOSPHINE OXIDE AND DIPHENYL(1-PROPYNYL)PHOSPHINE OXIDE WITH CYCLOPENTADIENE

Michel Maffei[a]
[a] Laboratoire des Organo-Phosphorés, Marseille, France

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THE DIELS-ALDER REACTION OF DIPHENYL(1,2-PROPADIENYL)PHOSPHINE OXIDE AND DIPHENYL(1-PROPYNYL)PHOSPHINE OXIDE WITH CYCLOPENTADIENE

Michel Maffei
Laboratoire des Organo-Phosphorés, Marseille, France

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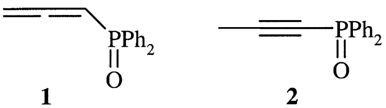
The Diels-Alder reaction of diphenyl(1,2-propadienyl)phosphine oxide ***1*** *and diphenyl(1-propynyl)phosphine oxide* **2** *with cyclopentadiene is reported.* ***1*** *reacts smoothly at room temperature in the presence of one equivalent of aluminum trichloride to give the corresponding adducts* endo ***3a*** *and* exo ***3b*** *(90:10 ratio) whose structure was attributed on the basis of their* ^{13}C *NMR spectra, whereas* **2** *is a poor dienophile, affording the corresponding adduct in low yield even under harsh conditions.*

Keywords: Cyclopentadiene; Diels-Alder reaction; diphenyl(1,2-propadienyl)phosphine; diphenyl(1-propynyl) phosphine oxide; organophosphorus dienophiles

The Diels-Alder reaction is a powerful method for the synthesis of bicyclic compounds. In this area, the use of organophosphorus dienophiles is well documented.[1] However, cycloaddition reactions of allenic[2,3] or acetylenic[4,5] dienophiles bearing a phosphorus containing electron withdrawing group has been much less studied.

Herein are reported the Diels-Alder reactions of diphenyl(1,2-propadienyl)phosphine oxide **1** and diphenyl(1-propynyl)phosphine oxide **2** with cyclopentadiene.



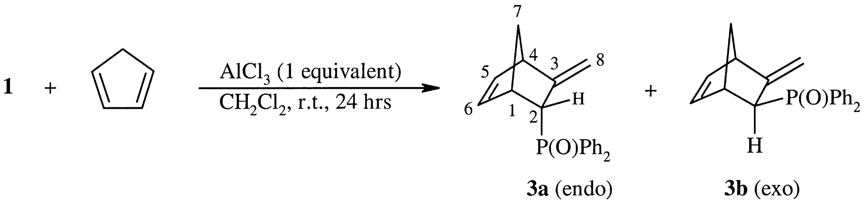
1 **2**

FORMULAE 1 and 2

Address correspondence to Michel Maffei, Laboratoire des Organo-Phosphorés (UMR 6009 du CNRS), Case 552, Faculté des Sciences de Saint Jérôme, Avenue Escadrille Normandie-Niémen, 13397 Marseille Cedex 20, France. E-mail: michel.maffei@univ.u-3mrs.fr

A recent article[3] describes the Diels-Alder reaction of **1** with cyclopentadiene (85 h at 80°C) to yield a single isomer in 64% yield, whose *endo* structure was assigned on the basis of NMR data.

In contrast with this report, **1** was found to react smoothly with cyclopentadiene at room temperature in the presence of one equivalent of aluminum trichloride, giving rise to a (90:10) mixture of *endo* **3a** and *exo* **3b** isomers.



SCHEME 1

The *endo* isomer was isolated after two recrystallizations from toluene, whereas treatment of the same 90:10 *endo*/*exo* mixture with sodium ethoxide led to epimerization at the carbon α to phosphorus and afforded a 20:80 mixture of **3a**/**3b** from which spectral data for *exo* **3b** were deduced. These structures were unambiguously attributed by examination of ^{13}C NMR data, using the characteristic values of three bond carbon-phosphorus coupling constants which depend on the configuration, and follow a Karplus relation.[1b,6]

Thus, for the *endo* isomer **3a**, the dihedral angle PC_2-C_1C_7 is close to 180°, so the $^3J_{PC7}$ coupling constant is at a maximum (10.8 Hz). In the case of the *exo* isomer **3b**, $J_{PC7} = 0$, which is consistent with a dihedral angle PC_2-C_1C_7 close to 90°. Therefore, the major isomer produced in the $AlCl_3$-promoted Diels-Alder reaction is *endo* **3a**, according to previous results described with related dienophiles.[1b,c] These data also suggest that the major isomer produced in the thermal cycloaddition[3] might be the *exo* rather than the *endo* isomer.

In contrast with **1**, diphenyl(1-propynyl)phosphine oxide **2** was found to be a poor dienophile. Its synthesis was carried out in 73% yield by prototropic isomerization of **1**, by analogy with acetylenic phosphonates,[5] upon reaction with a catalytic amount of potassium *tert*-butoxide in THF. Its low reactivity as dienophile (Scheme 2) was exemplified by the different experiments listed in Table I.

The conversion of **2** into **4** was rather low in the presence of one equivalent of aluminum trichloride at room temperature (entries 1 and 2), or in refluxing toluene (entry 3) or xylene (entry 5), and did not greatly

4

SCHEME 2

increase on prolonged heating (compare entries 3 and 4). Even performing the reaction in a steel bomb under rather harsh conditions did not promote a complete reaction, whereas several by products arising from decomposition of **2** were formed. However, from this last experiment (entry 7), the adduct **4** could eventually be isolated in 17% yield.

These miscellaneous results are consistent with the generally low reactivity of acetylenic organophosphorus dienophiles reported in the literature: only dienophiles possessing a second electron withdrawing group (phosphonate,[4a,4b,4e] ester,[4c] sulfone or sulfoxide,[4d]) give satisfactory results.

The use of adducts **3** in synthesis is currently under progress.

EXPERIMENTAL

THF was distilled from sodium and dichloromethane from calcium hydride prior to use. Cyclopentadiene was prepared by cracking of dicyclopentadiene immediately prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AC 200 spectrometer.

TABLE I Diels-Alder Reaction Between **2** and Cyclopentadiene Under Different Conditions.

Entry	Conditions[a]	Time (h)	Conversion of **2** into **4** (%)[b]
1	$AlCl_3$ (1 equiv.), room temperature	24	20
2	ibid.	48	35
3	Refluxing toluene	24	20
4	ibid.	48	35
5	Refluxing xylene	24	40
6	Sealed tube, 140°C, no solvent	24	55[c]
7	Steel bomb, 220°C, 90 bars[d]	4	70[c]

[a] Cyclopentadiene (2 equiv. with respect to **2**) was added every 12 h, except for entries 6 and 7.

[b] Determined by ^{31}P NMR analysis of the crude product.

[c] Several by products were formed.

[d] Dicyclopentadiene was used.

Chemical shifts were measured from chloroform ($\delta = 7.26$ ppm for ^{1}H and $\delta = 77$ ppm for ^{13}C). 85% H_3PO_4 as external standard was used for ^{31}P chemical shifts. Elemental analyses were performed by the Service de Microanalyse de la Faculté de St. Jérôme. Melting points were measured on a Büchi apparatus and are uncorrected. Diphenyl(1,2-propadienyl)phosphine oxide **1**[7] was prepared as previously reported.

((3-Methylene)bicyclo[2.2.1]hept-5-en-2yl)diphenyl Phosphine Oxide 3

To a cooled (0°C) suspension of aluminum trichloride (3.85 g, 28.9 mmol) in dichloromethane (5 mL) under argon was added dropwise a solution of **1** (7 g, 29.1 mmol) in dichloromethane (25 mL), and the mixture was allowed to reach room temperature with stirring (ca. 1 h). The brown yellow solution was cooled again to 0°C, and cyclopentadiene (4 g, 60 mmol) was added dropwise via syringe. The mixture was stirred at room temperature for 12 h, cyclopentadiene (4 g) was added, and the solution was stirred for another 12 h. After cooling to 0°C, the mixture was quenched by dropwise addition of saturated NH_4Cl (20 mL), diluted with dichloromethane (20 mL), and the layers were decanted. The organic layer was washed with 1N HCl (2 × 10 mL), saturated $NaHCO_3$ (10 mL), brine (20 mL), and dried over $MgSO_4$. Filtration and removal of solvent afforded a yellowish solid which was recrystallized from toluene/cyclohexane (1:1) to yield 7.3 g (82%) of a white solid, m.p. 157–161°C. ^{31}P NMR analysis showed the presence of two signals corresponding to **3a** and **3b** in a 90:10 ratio. $C_{20}H_{19}OP$: calcd. C 78.43, H 6.21; found C 78.63, H 6.38.

A portion of this mixture was recrystallized twice from toluene to afford pure **3a**, m.p. 170°C.

*Endo **3a***. (numbering refers to Scheme 1) ^{1} H NMR: 1.47(d, J = 9 Hz, 1H, H_{7a}); 1.57 (d, J = 9 Hz, 1H, H_{7b}); 3.12, 3.26 (2 s br., 1H each, H_1 and H_4); 3.57 (m br., 1H, H_2); 4.26 and 4.96 (2 s br., 1H each, H_{8a} and H_{8b}); 6.02 (d, J = 2.5 Hz, H_5 or H_6); 6.05(d, J = 2.5 Hz, H_5 or H_6); 7.42–7.49 (m, 6H aromatics); 7.77–7.90 (m, 4H aromatics). ^{13} C NMR: 45.0 (d, J = 78 Hz, C_2); 45.4 (s, C_1 or C_4); 51.1 (d, J = 10.8 Hz, C_7); 53.1 (s, C_1 or C_4); 106.9 (s, C_8); 128.2, 128.5, 131.5, 131.6, 132.5, 134.3 (aromatics); 134.4 (d, J = 3.8 Hz, C_5 or C_6); 133.7 (s, C_5 or C_6); 146.5 (s, C_3). ^{31} P NMR: 29.1.

*Exo **3b***. To a solution of sodium ethoxide in ethanol (prepared by adding 500 mg of sodium metal in 10 mL of absolute ethanol) was added 1 g of the **3a/3b** mixture, and the mixture was stirred at 40°C overnight. After cooling to room temperature, the red solution was quenched with 10 mL of saturated NH_4Cl, and the mixture was concentrated in vacuo.

Dichloromethane (20 mL) was added, the layers were decanted and the organic layer was washed with water, brine, and dried over $MgSO_4$. Filtration and removal of solvent afforded a yellowish solid which was recrystallized from toluene to afford a (20:80) mixture of **3a/3b** (m.p. 155–156°C) from which spectral data for **3b** were deduced. ^{1}H NMR: 1.44 (d, J = 8.3 Hz, H_{7a}); 2.24 (d, J = 8.7 Hz, H_{7b}); 2.93, 3.10, 3.27 (3 br.s., 1H each, H_1, H_2, H_4); 4.06, 4.98 (2 br.s., 1H each, H_{8a} and H_{8b}); 6.23 (s, 2H, H_5 and H_6); 7.43–7.49 (m, 6H aromatics); 7.81–7.88 (m, 4H aromatics). ^{13}C NMR: 43.0 (d, J = 67 Hz, C_2); 45.2 (s, C_1 or C_4); 47.3 (s, C_7); 51.9 (s, C_1 or C_4); 108.1 (s, C_8); 128.5, 128.7, 130.8, 131.3, 131.5, 133.8 (aromatics); 137.1 (d, J = 16 Hz, C_5 or C_6); 137.9 (s, C_5 or C_6); 146.2 (s, C_3). ^{31}P NMR: 29.8.

Diphenyl(1-propynyl)phosphine Oxide 2

To a solution of **1** (4.8 g, 20 mmol) in THF (20 mL) was added solid potassium *tert*-butoxide (78 mg, 0.7 mmol) at room temperature. The mixture turned immediately deep red while a slight heat evolution was noticed. After stirring at room temperature for one hour, 1N HCl (10 mL) was added and most of the THF was removed in vacuo. Dichloromethane (100 mL) was added, and the layers were decanted. The organic layer was washed with brine (20 mL) and dried over $MgSO_4$. Filtration and removal of solvent left a red oil which solidified upon standing at room temperature overnight. This was recrystallized from ethyl acetate/cyclohexane (1:1) to yield 3.5 g (73%) of a pale yellow solid, m.p. 91–92°C. ^{1}H NMR: 2.05 (d, J = 3.5 Hz, 3H); 7.46 (m, 6H); 7.81 (m, 4H). ^{13}C NMR: 4.9 (d, J = 3.0 Hz, CH_3); 74.4 (d, J = 176 Hz); 105.5 (d, J = 31.8 Hz); 128.5, 130.8, 132.0, 135.2 (aromatics). ^{31}P NMR: 6.4. $C_{15}H_{13}OP$: calcd. C 75.00, H 5.42; found C 75.05, H 5.51.

Diphenyl(3-methyl-norborna-2,5-dienyl)phosphine Oxide 4

A mixture of **2** (2.4 g, 10 mmol) and dicyclopentadiene (4 g, 30 mmol) was heated at 220°C under 90 bar with shaking for 4 h in a steel bomb. ^{31}P NMR analysis of the reddish very viscous oil thus obtained showed the presence of a major signal ($\delta = 23.9$ ppm, 70%), unreacted **2** (10%), and several other products ($\delta = 22$ ppm, 27 ppm, 28.7 ppm, and 32.3 ppm). This mixture was subjected to column chromatography. Initially, petroleum ether (400 mL) was used as eluent to separate the cyclopentadiene. Further elution with ether (400 mL) yielded a unseparable mixture of **4**, unreacted **2**, and byproducts, and final elution with ethyl acetate (500 mL) gave 520 mg (17%) of pure **4** as a very viscous yellowish oil that did not solidify. ^{1}H NMR: (numbering refers to Scheme 1) 1.98 (d, J = 0.7 Hz, 3H, H_8); 2.06–2.12 (m, 2H, H_7); 3.49, 3.57 (2 br.s., 1H each, H_1 and H_4); 6.63, 6.72 (2 br.s., 1H each, H_5 and H_6); 7.40–7.77 (m, 10H). ^{13}C NMR: 17.2 (d, J = 3.6 Hz, CH_3); 53.9 (d, J = 12.5 Hz, C_1 or C_4); 59.0 (d, J = 12.7 Hz, C_1 or C_4); 71.0 (d, J = 5 Hz, C_7); 127.9, 128.4, 130.8, 131.1 (aromatics); 140.1 (d, J = 2 Hz, C_5 or C_6); 142.9 (s, C_5 or C_6). ^{31} P NMR: 23.9. $C_{20}H_{19}OP$: calcd. C 78.43, H 6.21. Found C 78.71, H 6.44. MS (ESI) : $m/z = 307$ [$M + H^+$].

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