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SYNTHESIS OF STABLE 7-PHOSPHANORBORNADIENE P-OXIDES

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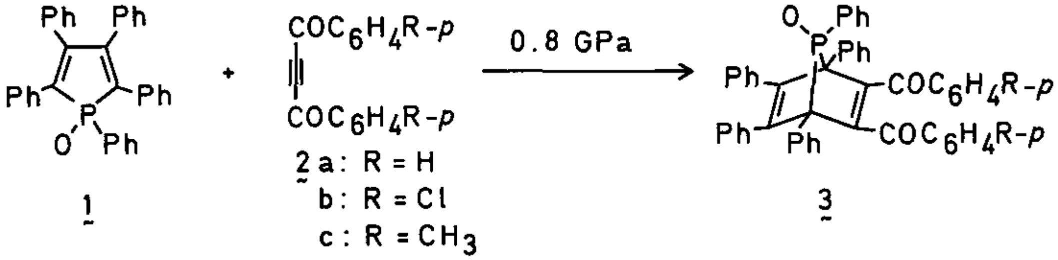
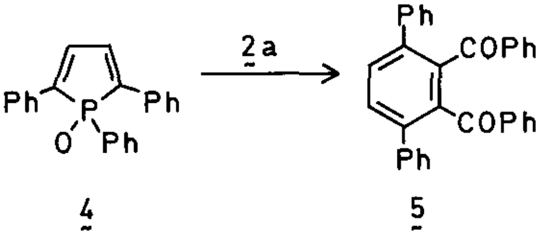
Abstract—Nonbenzo-annelated stable 7-phosphanorbornadiene P-oxides have been prepared for the first time by the high pressure Diels-Alder reaction of 1,2,3,4,5-pentaphenylphosphole oxide with diaroylacetylenes. The P-oxides decompose around 100°C to give the 1,2-diaroyl-3,4,5,6-tetraphenylbenzenes.

Previously, we have reported high pressure approach to the synthesis of 7-phosphanorbornadienes from λ-phosphole oxides and dialkyl acetylenedicarboxylate. For example, reaction of 1,2,3,4,5-pentaphenylphosphole oxide with dimethyl and di-t-butyl acetylenedicarboxylates at high pressure gave the corresponding 7-phosphanorbornadiene P-oxides that, however, decomposed spontaneously on standing at room temperature.[1] Thus, genuine 7-phosphanorbornadiene P-oxides[2] are believed to have a low stability undergoing a cheletropic reaction to give arenes, whereas 7-phosphanorbornenes are normally stable and therefore readily available through the Diels-Alder methodology.[3] The 7-phosphanorbornadiene skeleton has been only stabilized by P-complexation with $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$ and employed to generate a terminal phosphinidene complex, the chemistry of which has been extensively investigated.[4] An alternative simple approach to stable 7-phosphanorbornadiene oxides would consist in employment of more sterically congested dienophiles since the greater steric crowding involved in the formation of a planar arene prevent a cheletropic loss of the phosphorous bridge. The present communication describes a first successful synthesis of the nonbenzo-annelated 7-phosphanorbornadiene P-oxides from 1,2,3,4,5-pentaphenylphosphole oxide and diaroylacetylenes under high pressure conditions.[5]



In a typical experiment, a mixture of 0.25 mmol of 1,2,3,4,5-pentaphosphole (1) and 1 mmol of dibenzoylacetylene (**2a**) was diluted with dichloromethane in an 8 ml of PTFE tube that was compressed at 0.8 GPa and room temperature for 10 days. The resultant mixture was chromatographed on SiO_2 using benzene and benzene-ethyl acetate(8/2) in a gradient fashion, giving the 1:1 adduct **3a**^{6} in 50 % yield. The adduct **3a** decomposed around 100°C to give 1,2-dibenzoyl-3,4,5,6-tetraphenylbenzene. Like the unstable adducts obtained from **1** and dialkyl acetylenedicarboxylate,[1] the ^{13}C- and ^{31}P-nmr spectra of **3a** show a doublet at 71.5 ppm ($\underline{J}_{C-P}$=56 Hz at 90 MHz) and a singlet at 103.2 ppm (from external H_3PO_4) due to the bridgehead carbon and the phosphorus, respectively. 4,4'-Dichloro- and 4,4'-dimethyldibenzoylacetylene (**2b**) and (**2c**) similarly reacted with **1** affording the corresponding 1:1 adducts **3b** and **3c** in moderate yields. The results are summarized in Table 1.

An analogous reaction of triphenylphosphole (**4**) with **2a** produced 1,2-dibenzoyl-3,6-diphenylbenzene (5)[7] in 83 % yield.



The adducts **3** appeared to be stable enough for deoxygenation under conventional conditions. Unfortunately, however, attempts to deoxygenate these adducts to elusive 7-phosphanorbornadienes under variety of conditions failed.

ACKNOWLEDGEMENT

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Table 1. 7-Phosphanorbornadiene P-oxides 3

R	Yield (%)	mp (°C, dec)	^{13}C-nmr (Bridgehead carbon) ($\underline{J}_{C-P}$, Hz)	^{31}P-nmr[a]
H	50	99-101	71.5 (56 Hz)	103.2
CH_3	48	94	71.6 (56 Hz)	102.8
Cl	38	101	71.7 (56 Hz)	104.1

[a] From external H_3PO_4 (ppm)

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2. Only one example is a benzophosphanorbornadiene oxide that has been obtained by Diels-Alder reaction of pentaphenylphosphole with benzyne: J. K. Stille, J. L. Eichenberger, J. Higgins, and M. E. Freeburger, J. Am. Chem. Soc., 1972, **94**, 4761.
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6. The stereochemistry around the phosphorus bridge was tentatively assigned as 3 only based upon steric ground.
7. mp 216-217°C.

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