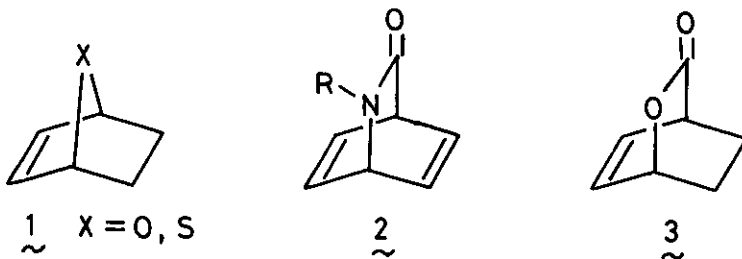


HIGH PRESSURE APPROACH TO THE SYNTHESIS OF 7-PHOSPHANORBORNADIENES FROM λ^5 -PHOSPHOLE OXIDES AND DIALKYL ACETYLENEDICARBOXYLATES

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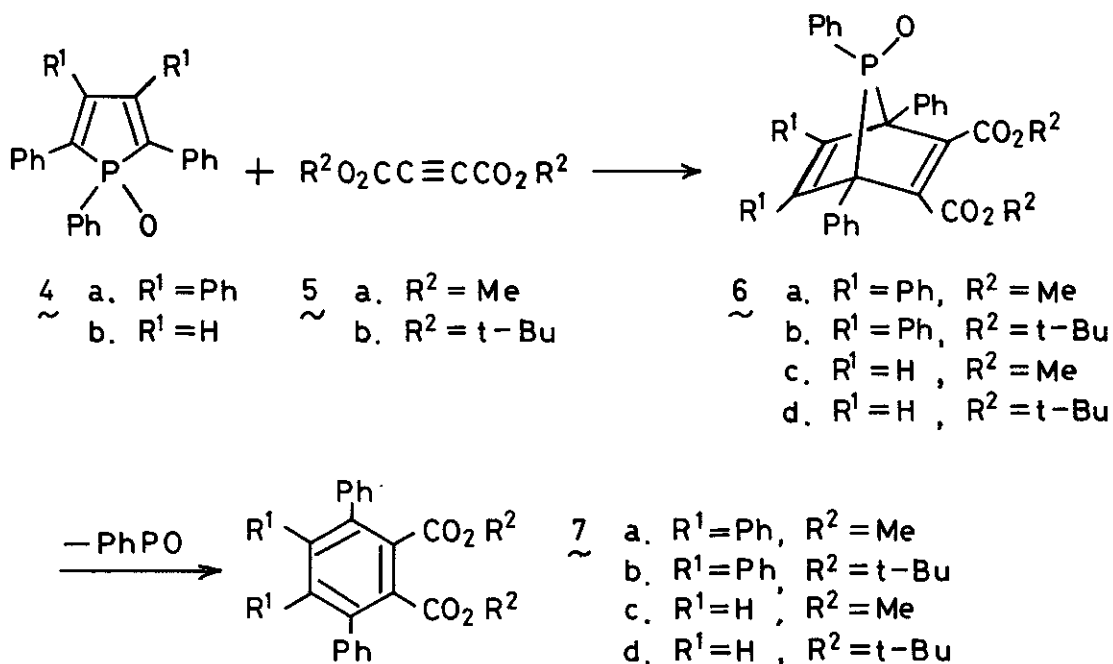
Abstract— Reactions of 1,2,3,4,5-pentaphenylphosphole oxide (4a) with dimethyl and di-*t*-butyl acetylenedicarboxylates (5a, b) under high pressure afford the tetraphenylphthalates (7a, b) along with the 7-phosphanorbornadiene derivatives (6a, b). The latter adducts have proven too unstable to be submitted to deoxygenation under conventional conditions.

7-Phosphanorbornenes have attracted a considerable attention because of their unusual properties. For example, they display a ^{31}P resonance at very low field for a phosphine and easy syn to anti isomerization at phosphorus in protic solvents.¹ Attempts to synthesize even more interesting 7-phosphanorbornadienes by reaction of an acetylenic dienophile with a monomeric λ^5 -phosphole derivative² have been unsuccessful, leading to loss of the phosphorus bridge in the adduct.³ Recently, this loss was avoided by using λ^5 -phosphole-P $\text{M}(\text{CO})_5$ complexes [$\text{M}=\text{Cr}, \text{Mo}, \text{W}$] in place of phosphole oxides.¹ In view of the recent successful formation of 7-oxa- and 7-thia-bicyclo[2.2.1]heptenes (1) from furans⁴ and thiophene,⁵ 7-aza-8-oxobicyclo[2.2.2]-



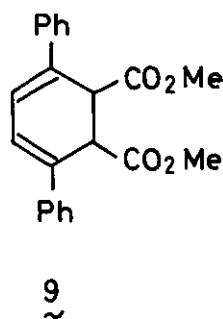
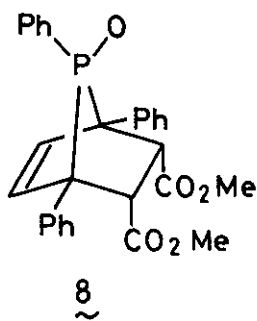
octadienes (isoquinuclidienones) (2) from 2-pyridones,⁶ and 7-oxa-8-oxobicyclo-[2.2.2]octenes (3) from 2-pyrones⁷ at high pressures, it was anticipated that elevated pressures might induce the Diels-Alder reaction of a monomeric phosphole oxide with an acetylenic dienophile under milder conditions, e.g. at lower temperature thus leading to the adduct without loss of the phosphorus bridge. The present report describes formation of such a primary adduct from 1,2,3,4,5-pentaphenylphosphole-1-oxide and dimethyl or di-*t*-butyl acetylenedicarboxylate, albeit not in pure state owing to their instability.

Reaction of 1,2,3,4,5-pentaphenylphosphole-1-oxide (4a) with dimethyl acetylenedicarboxylate (5a) at 10 kbar and room temperature (ca. 16-18 °C)⁸ resulted in the formation of the mixture of the 7-phosphanorbornadiene P-oxide (6a) and dimethyl 3,4,5,6-tetraphenylphthalate (7a).⁹ The primary adduct (6a) decomposed gradually during chromatographic separation and therefore could not be isolated in pure form.



However, the ¹³C- and ³¹P-NMR spectra of this crude product (6a) (ca. 16% yield based on ¹H-NMR) show doublets at 69.9 ppm ($J_{C-P}=53$ Hz at 90 MHz) and 105.5 ppm (from external H₃PO₄) probably due to the bridgehead carbon and the phosphorus, respectively. The crude product (6a) was completely converted to 7a upon heating in refluxing benzene or on standing at room temperature. A similar crude adduct (6b)¹⁰ and di-*t*-butyl 3,4,5,6-tetraphenylphthalate (7b)¹¹ were obtained from 4a and

di-*t*-butyl acetylenedicarboxylate (5b) at 9 kbar. It has been claimed that the 7-phosphanorbornadiene P-oxide (6c) was prepared as a stable solid (mp 187-188 °C) in an indirect route involving the reaction of 1,2,5-triphenylphosphole-1-oxide (4b) with bromomaleic anhydride followed by esterification with MeOH-conc.H₂SO₄.¹² The "6c" was also reported to undergo cheletropic extrusion of the phosphorus bridge upon an attempted deoxygenation with trichlorosilane giving dimethyl 3,6-diphenyl-1,2-dihydrophthalate (9).¹² In contrast, high pressure reaction of 4b with 5a produced only dimethyl 3,6-diphenylphthalate (7c)¹³ as an isolable product along with the recovered (4b) in 68% and 31% yields respectively. An examination by ¹³C- and ³¹P-NMR of the crude reaction mixture immediately after release of pressure did not indicate any evidence of the presence of 6c. Analogous attempts to isolate the 7-phosphanorbornadiene P-oxide (6d) from 4b and 5b by employing high pressure technique were unsuccessful resulting in loss of Ph-P-O to produce 7d¹⁴ in 60% yield. Thus, it is probably dimethyl 7-phosphanorbornene-5,6-dicarboxylate P-oxide (8) that has been previously described as 6c. Indeed, the adduct 8¹⁵ obtained from 4b and dimethyl maleate at 8 kbar had mp 189-190 °C. Furthermore, attempted deoxygenation of 8 with trichlorosilane under the reported conditions¹² gave dimethyl 3,6-diphenyl-1,2-dihydrophthalate (9)¹⁶ in virtually quantitative yield.



The difference in thermal stability between pentaphenyl adducts (6a, b) and triphenyl adducts (6c, d) may be due to the greater steric hindrance involved in the formation of tetraphenylphthalates (7a, b) from the former.

Further efforts are continuing to obtain a more stable 7-phosphanorbornadiene system by using sterically hindered dienophiles.

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 c) General Procedure: A mixture of phosphole-1-oxide (1 mmol) and acetylenedicarboxylic acid ester (2 mmol) is diluted to 8 ml with dichloromethane in Teflon tube and stored at 9-10 kbar and room temperature (ca. 16-18 °C) for 4 days. After release of pressure, the reaction mixture is immediately subjected to column chromatography on SiO₂ with benzene-ethyl acetate.
9. Mp 274 °C [lit. mp 261 °C: W. Dilthey, J. Thewalt, and O. Trosken, Chem. Ber. 67, 1959 (1935)]; IR(KBr) 1720 cm⁻¹; ¹H-NMR(CDCl₃) δ 3.47(s, 6H, CH₃), 6.50-7.25(complex, 2OH, aromatic-H); ¹³C-NMR(CDCl₃) δ 52.2(q, CH₃), 125.9, 126.8, 127.4, 129.7, 130.8(d, aromatic CH), 132.2, 138.6, 138.7, 139.3, 143.2(s, aromatic C), 168.6(s, C=O).
10. About 10% yield from ¹H-NMR analysis; ¹³C-NMR(CDCl₃) δ 68.3(d, J_{C-P}=54 Hz at 90 MHz); ³¹P-NMR(CDCl₃) 104.7 ppm from external H₃PO₄. The stereochemical assignment of 6a,b at the phosphorus atoms is only based upon steric consideration.¹

11. Mp 259-260 °C; IR(KBr) 1715 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 1.16(s, 18H, CH_3), 6.50-7.25(complex, 20H, aromatic-H); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 27.4(q, CH_3), 82.1(s, $(\text{CH}_3)_3\text{C}$) 125.7, 126.5, 126.7, 127.2, 130.3, 130.9(d, aromatic- CH), 133.2, 138.5, 138.9, 139.0, 142.3(s, aromatic-C), 167.4(s, C=O).
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13. Mp 191-192 °C[lit. mp 191 °C: K. Alder and M. Guenzl-Schumacher, Chem. Ber., 92, 822 (1959).]; IR(KBr) 1710, 1738 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 3.60(s, 6H, CH_3), 7.43(s, 10H, aromatic-H), 7.53(s, 2H, aromatic-H); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 52.3(q, CH_3) 127.7, 128.2, 128.4, 131.6(d, aromatic- CH), 132.1, 139.7, 139.9(s, aromatic-C), 167.3(s, C=O).
14. Mp 178-180 °C; IR(KBr) 1715 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 1.26(s, 18H, CH_3), 7.43 (s, 12H, aromatic-H); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 27.5(q, CH_3), 82.2(s, $(\text{CH}_3)_3\text{C}$), 127.4, 128.1, 128.8, 130.7(d, aromatic- CH), 133.3, 139.4, 140.3(s, aromatic-C), 167.3 (s, C=O).
15. Mp 189-190 °C; IR(KBr) 1725, 1740(sh) cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 3.47(s, 6H, CH_3), 4.68(d, $J_{\text{P-H}}=1.80$ Hz at 90 MHz, 2H, CH), 6.93-7.75(complex, 17H, $\text{CH}=\text{}$ and aromatic-H); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 51.8(q, CH_3), 55.1(d, $J_{\text{P-C}_2}=13.2$ Hz, CH), 58.8 (d, $J_{\text{P-C}}=64.7$ Hz, bridge head C), 127.0-134.1(complex, aromatic and C=C carbons), 170.3(d, $J_{\text{P-C}_3}=16.2$ Hz, C=O). The stereochemical assignment of 8 at the phosphorus is tentative being based on steric consideration.
16. Mp 115-116 °C[lit.¹² mp 116 °C]; IR(KBr) 1740, 1720(sh) cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 3.56(s, 6H, CH_3), 4.26(s, 2H, CH), 6.49(s, 2H, $\text{CH}=\text{}$), 7.15-7.60(complex, 10H, aromatic-H); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 46.8(q, CH_3), 52.1(d, CH), 123.9, 125.4, 128.3 128.5(d, aromatic- CH and $\text{CH}=\text{}$), 133.4, 139.3(s, aromatic-C and $\text{C}=\text{}$), 171.7(s, C=O).
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