[2 + 2] Cycloadditions between Electron-poor Phospha-alkene Complexes and Electron-rich Alkenes or Alkynes: A New Route to Phosphetane and 1,2-Dihydrophosphete Rings

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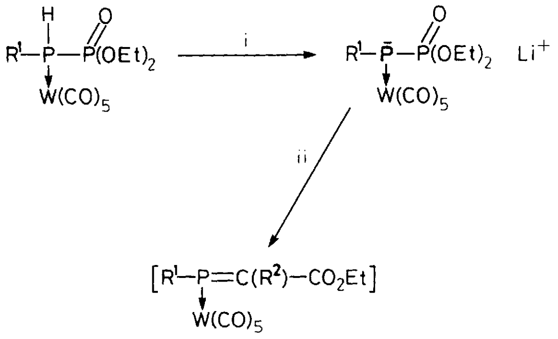
Ethoxycarbonyl-*C*-substituted phospha-alkene P–W(CO)$_5$ complexes instantly react at low temperature with enamines, enol ethers, ynamines, and ethoxyacetylene to yield the corresponding phosphetane and 1,2-dihydrophosphete [2 + 2] cycloadducts.

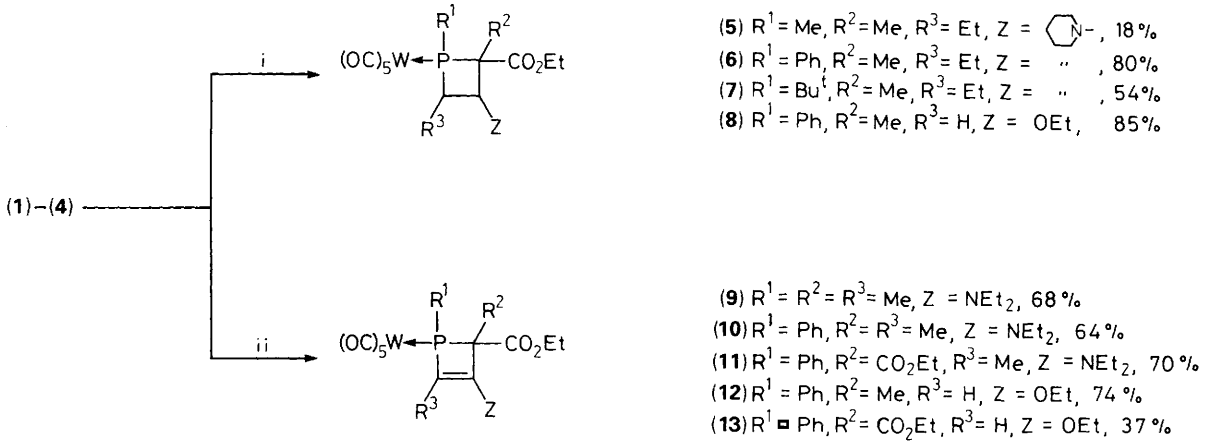
One of the classical approaches toward cyclobutanes and cyclobutenes, *i.e.* [2 + 2] cycloaddition between electron-rich and electron-poor alkenes or alkynes,[1] has no equivalent in organophosphorus chemistry at present. To date, there is only one general synthesis of phosphetanes which involves the addition of $RPCl_2$–$AlCl_3$ complexes to highly substituted alkenes.[2] Very recently another approach has been described which relies on the insertion of phosphenium ions into cyclopropanes.[3] Alternatively, the much more recently discovered 1,2-dihydrophosphete ring has been synthesized unambiguously by cyclisation of 1-phosphadienes[4] or by CO insertion into phosphirenes.[5] We wish to report here the cycloaddition of unstable electron-poor phospha-alkene complexes with enamines, enol ethers, ynamines, and ethoxyacetylene leading to the corresponding phosphetanes and 1,2-dihydrophosphetes.

Phospha-alkene complexes (**1**)—(**4**) were first prepared at low temperature using the so-called phospha-Wittig reaction[6] (Scheme 1). The complexes thus obtained were immediately allowed to react *in situ* with either enamines, enol ethers,

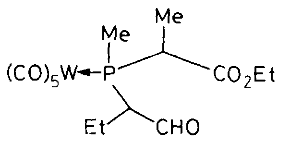


(**1**) $R^1 = R^2 = Me$
(**2**) $R^1 = Ph$, $R^2 = Me$
(**3**) $R^1 = Bu^t$, $R^2 = Me$
(**4**) $R^1 = Ph$, $R^2 = CO_2Et$

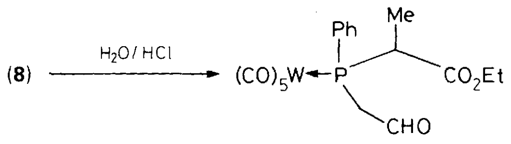
Scheme 1. *Reagents and conditions*: i, BuLi (1 equiv.), tetrahydrofuran (THF), −70 °C, 5 min.; ii, R'C(O)–CO_2Et, −70 °C, 2 min.



Scheme 2. *Reagents and conditions*: i, *trans*-R^2–CH=CH-Z, $-70 \rightarrow 25$ °C, 10 min; ii, $R^2C{\equiv}CZ$, $-70 \rightarrow 25$ °C, 10 min.



(14)



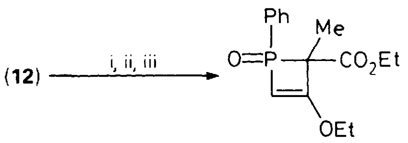
(15)

Scheme 3. *Conditions*: 3 M HCl, THF, 25 °C, 5 min, 100% yield.

ynamines, or ethoxyacetylene to yield the expected four-membered rings (Scheme 2).†

All the products were purified by chromatography on silica gel. The main product of the reaction leading to (**5**) is the open chain adduct (**14**) (mixture of three isomers: 40% yield). Complexes (**5**), (**6**), (**7**), and (**8**) were obtained as mixtures of two isomers; only the major isomer was fully characterized. Both isomers of (**9**) and (**10**) were obtained and characterized separately. Only one isomer of (**12**) was detected.

Highly polarized C–C bent bonds in cyclobutanes have been shown previously to be cleaved by water.[7] A similar cleavage occurs when (**8**) is allowed to stand in dilute acid (Scheme 3).



(16) (>50%)

Scheme 4. *Reagents and conditions*: i, $C_5H_5NH^+$ Br_3^- (1 equiv.), CH_2Cl_2, -20 °C, 5 min; ii, 2,2′-bipyridyl (2 equiv.), 25 °C, 1 h; iii, H_2O, 25 °C.

Finally, we investigated the possibility of cleaving the P–W bond of a complex such as (**12**) without cleavage of the four-membered ring. The 1,2-dihydrophosphete oxide (**16**) was thus obtained by a procedure described previously (Scheme 4).[4b,5a]

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† *Spectral data*: ^{31}P NMR of compounds (**5**)—(**16**) (C_6D_6); (**5**) δ 11.8; (**6**) δ 37.1; (**7**) δ 59.8; (**8**) δ -18.4; (**9 a,b**) δ -21.5, 20.2; (**10 a,b**) δ -0.05, 34.8; (**11**) δ 42.5; (**12**) δ -13.3; (**13**) δ -24.6; (**14 a,b**) δ 3.4, -2.4; (**15 a,b**) δ 6.3, 3.3; (**16**) δ (MeOH) 19.1 p.p.m.

For compound (**6**): ^{1}H NMR (200 MHz, C_6D_6) δ 1.20 [3H, d, ^3J(H–P) 12.9 Hz, P–C–CH_3], 2.50 (m, PCH–), 3.73 [1H, dd, ^3J(H–H) 11.4, ^3J(H–P) 3.3 Hz, CH–N]; ^{13}C NMR (50 MHz, C_6D_6) δ 17.33 [d, ^2J(C–P) 4.0 Hz, P–C–CH_3], 41.43 [d, ^1J(C–P) 27.7 Hz, PCH], 50.69 [d, ^1J(C–P) 23.1 Hz, P–*C*–CH_3], 65.27 (s, *C*H–N), 173.16 (s, CO_2Et); IR (decalin) ν (CO) 2075 m, 1955sh, 1950sh, 1940vs, ν (*CO*$_2$Et) 1725 cm^{-1}; mass spectrum: *m/z* (^{184}W) 643 (*M*$-$CO, 10%), 392 [WP(Ph)=C(Me)CO_2Et, 100%].

(**10a**): ^{1}H NMR (C_6D_6) δ 1.64 [6H, d, ^3J(H–P) 12.4 Hz, P–C–C*H*$_3$ + P–C(C*H*$_3$)=]; ^{13}C NMR (C_6D_6) δ 77.25 [d, ^1J(C–P) 50.8 Hz, P–*C*(Me)(CO_2Et)], 95.87 [d, ^1J(C–P) 43.3 Hz, P–*C*(Me)=], 151.35 [d, ^2J(C–P) 4.3 Hz, =*C*–N], 153.02 [d, ^2J(C–P) 8.0 Hz, *C*O$_2$Et].

(**10b**): ^{1}H NMR (C_6D_6) δ 1.02 [d, ^3J(H–P) 12.8 Hz, P–C–C*H*$_3$], 1.99 [d, ^3J(H–P) 13.9 Hz, P–C(C*H*$_3$)=]; ^{13}C NMR (C_6D_6) δ 52.14 [d, ^1J(C–P) 26.2 Hz, P–*C*(Me)(CO_2Et)], 93.34 [d, ^{1}(C-P) 54.3 Hz, P–*C*(Me)=], 149.25 (s, *C*H–N), 172.12 (s, *C*O$_2$Et); mass spectrum: *m/z* (^{184}W) 643 (*M*, 11%), 503 (*M*$-$5CO, 100%).

Compound (**15 a,b**): ^{1}H NMR (C_6D_6) δ 9.27 [dt, ^3J(H–P) 4.6, ^3J(H–H) 2.4 Hz, CHO] (major isomer), δ 9.37 [dt, ^3J(H–P) 5.4, ^3J(H–H) 2.8 Hz, CHO] (minor isomer); mass spectrum: *m/z* (^{184}W) 548 (*M*$-$CO, 12%), 436 (*M*$-$5CO, 100%).

(**16**): ^{1}H NMR (CD_3OD) δ 1.59 [d, ^3J(H–P) 11.4 Hz, P–C(C*H*$_3$)], 4.78 [d, ^2J(H–P) 37 Hz, P–C*H*=]; ^{13}C NMR (CD_3OD) δ 7.81 (s, P–C–*C*H$_3$), 67.74 [d, ^1J(C–P) 116.2 Hz, P–*C*H=], 80.08 [d, ^1J(C–P) 116.8 Hz, P–*C*–CH_3]; mass spectrum: *m/z* 294 (*M*, 100%).

Satisfactory elemental analyses were obtained for compounds (**6**), (**10 a,b**), (**15 a,b**), and (**16**).

References

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