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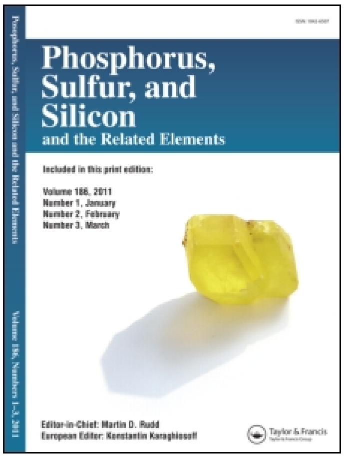

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Reactivity of Phosphaalkenes

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REACTIVITY OF PHOSPHAALKENES

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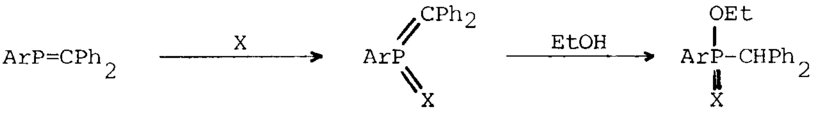
Abstract The reaction of triarylphosphaalkenes with oxidants (O_2, S_8, Se, Te, H_2O_2), with orthoquinones, and with Pt(O)- and Ni(O)-complexes is described.

In recent years, the synthesis and structural properties of phosphaalkenes have been investigated with increasing intensity[1]. In contrast, their chemical reactivity is less well known. We are engaged in a systematic study of the chemical behaviour of triarylphosphaalkenes and wish to report on progress in three areas.

OXIDATION REACTIONS

Mesityl(diphenylmethylene)phosphine (MesP=CPh_2, 1) and 2,6-dimethylphenyl(diphenylmethylene)phosphine (XyP=CPh_2, 2) were reacted with O_2, S_8, Se, Te and H_2O_2. While Te shows no reaction, the other reagents attacked phosphorus at the lone pair to give the "phosphaalkene oxide" (= methyleneoxophosphorane) 3a (X = O) or the thio or seleno analogue 3b (X = S) or 3c (X = Se), respectively. 3 Is unstable: 3a has never been detected directly, 3b could be observed spectroscopically, and 3c was isolable but readily decomposed under reversal of its formation reaction. However, 3 could be intercepted, e.g. by addition of ethanol to furnish 4.



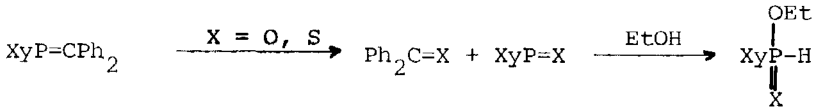
1: Ar=Mes

2: Ar=Xy

3

4

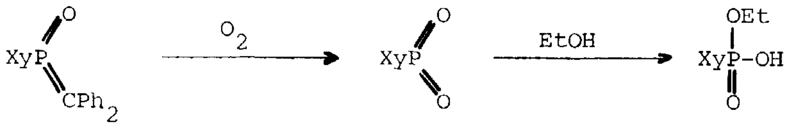
In the case of X = O and X = S, a second, less important mode of reaction consisted in the cleavage of the P=C bond. Besides benzophenone (or thiobenzophenone, respectively), the phosphene oxide 5a (X = O) or sulfide 5b (X = S) were the unstable primary products; they were intercepted with ethanol to yield 6.



$$XyP{=}CPh_2 \xrightarrow{X\,=\,O,\,S} Ph_2C{=}X + XyP{=}X \xrightarrow{EtOH} XyP(OEt)(H){=}X$$

2 5 6

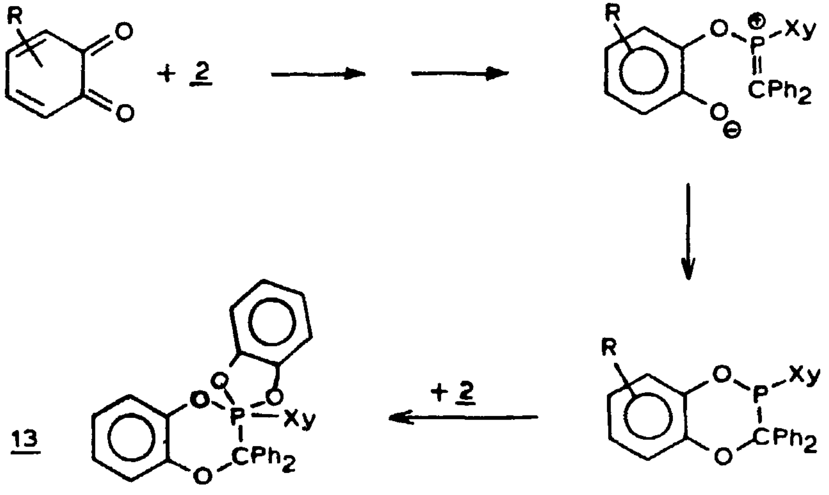
Finally, oxygen, contrary to sulfur, was able to compete with ethanol for 3a', cleaving the P=C bond to furnish the intermediate dioxophosphorane 7 which ethanol was converted to 8.



3a' 7 8

REACTIONS WITH ORTHO-QUINONES

Earlier, we had found that 1 and 2 are unreactive towards a variety of dienes; they did give [4+2] additions with 1,3-dipoles[2]. We now observed a formal [4+2] reaction of 2 with the ortho-quinones tetrachloro-o-benzoquinone (9), 3,5-di-tert-butyl-o-benzoquinone (10) and phenanthrenequinone (11), leading to the six-membered ring adducts 12a, 12b, and 12c, respectively.



14

12

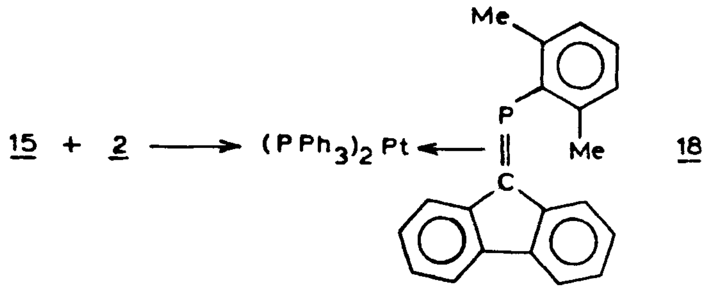
13

The reaction rate decreased from 9 to 11; the more reactive quinones tended to add to the primary adduct 12 under formation of a phosphorane 13. Because of the low regiochemical preference observed in the reaction with 10, and in analogy with the reaction of ortho-quinones with tertiary phosphines, we conclude that this addition is not concerted, but a multistep reaction, which is probably initiated by single electron transfer from 2 to the quinone followed by the formation of the zwitterionic intermediate 14.

PLATINUM(O) AND Ni(O) COMPLEXES

Recently, we described the reaction of 1 with {Pt(PPh$_3$)$_2$ · CH$_2$=CH$_2$} (15) to furnish the red complex Pt(PPh$_3$)$_2$ · 1} (16); in the crystalline state, 16 possesses the structure 16a with σ-bonded (end-on) 1, whereas the ^{31}P NMR parameters in toluene-d_8 were better reconciled with π-coordination (16b; side-on)^3. The solid state ^{31}P NMR spectrum confirmed the NMR parameters of the σ-complex to be different from those of 16b. A detailed study of the ^{31}P and ^{195}Pt NMR spectra in toluene-d_8 solution (Table 1), including their temperature dependance, revealed the equilibrium 16a $\rightleftarrows$ 16b with $\Delta H = -3.9$ kcal.mol^{-1} and $\Delta S = -15$ kcal.mol^{-1}.degree^{-1}. To our knowlegde, this is the first example of such a η_1/η_2 equilibrium of two-coordinate phosphorus. Theoretical calculations on models confirm the greater stability of the η^2-complex.

In order to investigate the influence of steric factors on η_2-coordination, we synthesized the "flatter" o,o'-biphenylenephosphaalkene 17 and its Pt(PPh$_3$)$_2$ complex 18.



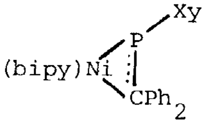
18 Is an off-white solid, but dissolves in toluene-d_8 with red colour which is possibly indicative for a minor quantity of the η_1-complex; however, in the NMR spectra (Table 1), only the signals of the η_2-complex could be discerned. Thus again, η_2-coordination is preferred; in 18, it is practically undisturbed by steric hindrance, whereas in 16 the non-planarity of the two phenyl groups on carbon destabilizes the π-complex (16) sufficiently so that the σ-complex (16a) can compete.

TABLE 1 NMR spectra of 16a, 16b, and 18

			^{31}P				^{195}Pt		
cpd.	state	T °C	δ{ppm} P_A	P_B	P_C (sp^2)	J(PtPc) {Hz}	T °C	δ{ppm}	J(PtPc) {Hz}
16a	solid	25	50.0	40.5	247	4720	-	-	-
16a	C_7D_8	-70	48.0	48.0	247.5	4964	-40	-4410	4940
16b	C_7D_8	-70	25.0	22.4	-30.3	499	-40	-4847	500
18	C_7D_8	-55	25.2	26.3	-34.7	319	25	-4885	320

Depending on the co-ligand on nickel(O), we encounter η^1-coordination (19) or η^2-coordination (20: $\delta(^{31}P) = -16.1$ ppm; $\delta(^{13}C) = -70.6$ ppm). According to the X-ray structure, 20 has an extremely long "P-C" bond of 183.2(6) pm.

$(CO)_3Ni \cdot MesP{=}CPh_2$ 19



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