Reaction of *o*-Hydroxyphenyl Alkyl Ketones with Phosphorus Trichloride. Formation of 1,3,2-Dioxaphosphorinans *via* α-Proton Abstraction

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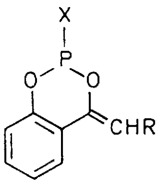
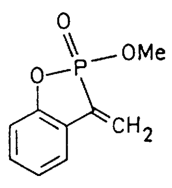
Summary Treatment of PCl_3 with *o*-$HOC_6H_4COCH_2R$ (R = H or Et) and NEt_3 affords 2-chloro-1,3,2-dioxaphosphorinans, which can be readily converted into the corresponding 2-alkoxy derivatives; evidence is presented for the formation of analogous derivatives on similar reaction of acetylacetone and PCl_3.

As part of a general study of the influence of transition metals on the photochemistry of organic molecules, we attempted the synthesis of tertiary aryl phosphites of the type $P(OC_6H_4COCH_2R)_3$ (R = H, Me, *etc.*,) by reaction of PCl_3 with *o*-$HOC_6H_4COCH_2R$ in the presence of an appropriate base.[1] Mass and ^1H n.m.r. spectral data, however, indicated the product of the reaction involving PCl_3 with three-fold molar amounts of *o*-HOC_6H_4COMe and NEt_3 to be the 1,3,2-dioxaphosphorinan (I; R = H; X = *o*-OC_6H_4-COMe) and not P(*o*-$OC_6H_4COMe)_3$.

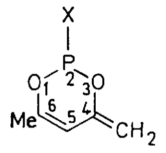
Although this species could not be isolated in a sufficiently pure form for complete characterisation, the 2-chloro-1,3,2-dioxaphosphorinan (I; R = H; X = Cl) was readily obtained by reaction of *o*-HOC_6H_4COMe, PCl_3, and NEt_3 in a molar ratio of 1:2·5:2·5. This was, in turn, treated with various alcohols and phenol in the presence of NEt_3 to give the corresponding 2-alkoxy and 2-phenoxy derivatives (I; R = H; X = OMe, OPr^i, OBu^t, OCH_2Ph, and OPh) (see Table), which were characterised by elemental analysis as well as by i.r. and ^1H n.m.r. spectroscopy and accurate mass determination of the molecular ions. The n.m.r. spectra of these derivatives contained, besides peaks associated with the phenylene and 2-alkoxy- and 2-phenoxy-groups, two broad resonances in the regions δ 4·6—4·9 and 5·0—5·3, readily assigned to the exocyclic methylene group. The absence of peaks between 1650 and 1750 cm^{-1} in the i.r. spectra of these compounds is also consistent with the proposed structure (I). Reaction of (I; R = H; X = OMe) with $[Fe(cp)(CO)_2I]$ (cp=η-C_5H_5) in refluxing benzene afforded a single product, the spectroscopic data of which



(I)



(II)



(III)

are consistent with it being $[\mathrm{Fe(cp)(CO)(MeO\overline{PC_6H_4COCH_2})\text{-}I}]$ [ν(C=O), 1977 cm^{-1} in CH_2Cl_2; δ 3·76 (d, *J* 11·6 Hz, OMe), 4,34 (s, C_5H_5) and 4·36 and 5·13 (d, *J* 2 Hz, =CH_2)]. The formation of this complex provides support for structure (I) as opposed to the other possible structure (II), since the latter would not be expected to give rise to a stable substituted derivative of $[\mathrm{Fe(cp)(CO)_2I}]$. Further evidence against structure (II) is the absence of any band corresponding to P=O in the i.r. spectra of the products. In addition, treatment of the derivatives (I; R = H; X =OMe and OPh) in ether with anhydrous HCl regenerated the ketone fragment, *o*-OC_6H_4COMe, as indicated by the disappearance of the resonances due to the exocyclic methylene group, and the appearance of a singlet at δ 2·64 due to the methyl ketone, in the ^1H n.m.r. spectra. The reaction of *o*-$HOC_6H_4COPr^n$, PCl_3, and NEt_3 in a molar ratio of 1:2·5:2·5 also afforded the 2-chloro-1,3,2-dioxaphosphorinan (I; R = Et; X = Cl), which was characterised as the methoxy derivative, (I; R = Et; X = OMe), formed by reaction with methanol in the presence of NEt_3 (see Table).

TABLE

Compound		B.p./°C (mmHg)	Isolated yield (%)
(I; R=H)	X = Cl	72—76 (0·3)	45[a]
	X = OMe	64—67 (0·35)	65[b]
	X = $OCHMe_2$	73—78 (0·27)	65[b]
	X = $OCMe_3$	83—88 (0·20)	55[b]
	X = OPh	123—127 (0·30)	57[b]
	X = OCH_2Ph	140—144 (0·30)	34[b]
(I; R = Et; X = Cl)		c	c
(I; R = Et; X = OMe)		93—98 (0·27)	55[b]
(III; X = Cl)		28—38 (0·35)	20[a]
(III; X = OMe)		23 (0·55)	15[d]

[a] Based on ketone. [b] Based on (I; X = Cl; R = H or Et). [c] Product not distilled. [d] Based on (III; X = Cl).

Although there is no n.m.r. evidence for the presence of the enol tautomer of *o*-$HOC_6H_4COCH_2R$ in solution, (I; R = H or Et; X = Cl) may be considered as having been formed from *o*-$HOC_6H_4C(OH)$=CHR by proton abstraction from the two hydroxy groups. Attempts were thus made to establish whether an analogous dioxaphosphorinan can be formed by reaction of PCl_3 with acetylacetone in the presence of NEt_3; reaction under similar conditions to those used above did, in fact, afford a product, proposed to be the 2-chloro derivative (III; X = Cl), on the basis of ^1H n.m.r. evidence [δ 5·50 (d, *J* 3 Hz, 5-H), 4·50 and 4·35 (br s, =CH_2), and 1·92 (s, Me)]. Treatment of (III; X = Cl) with methanol in the presence of NEt_3 afforded an unstable product (*m/e* 160) postulated to be the 2-methoxy derivative (III; X = OMe), on the basis of n.m.r. evidence [δ 5·38 (d, *J* 3 Hz, 5-H), 4·34 and 4·12 (br s, =CH_2), 3·65 (d, *J* 11 Hz, OMe), and 1·90 (s, Me)] (see Table). The coupling of 3 Hz observed between ^{31}P and the 5-H in (III; X = Cl or OMe) is similar to that observed for ^4J (POC=CH) in *transoid* enolic phosphates;[2] the signals due to the =CH_2-hydrogens, however, appear as broad singlets ($\omega_{\frac{1}{2}}$ 4 Hz), indicating weaker coupling of these protons to the phosphorus. Similar line broadening is observed for the exocyclic methylene hydrogen signals of the dioxaphosphorinans (I; R=H; X=Cl or OR′), while, in the case of (I; R = Et; X = Cl or OMe), the olefinic proton signal appears as a triplet (*J* 7 Hz) further split by coupling to phosphorus (*J* 2 Hz).

The formation of dienolate anions has been invoked in the treatment of β-diketones with strong bases,[3] but the isolation of a dienolic derivative of a β-diketone has, to the best of our knowledge, not previously been reported. In this respect, the reactions of acetylacetone with BCl_3, $AlCl_3$, and $SiCl_4$ have been shown to afford $[\mathrm{B(acac)_2}]^+$, $[\mathrm{Al(acac)_3}]$, and $[\mathrm{Si(acac)_3}]^+$ (acac = acetylacetonate) respectively, with no α-proton abstraction being reported.[4]

The synthesis of the 2-methoxy derivative (I; R = H; X = OMe) illustrates a typical reaction procedure. *o*-Hydroxyacetophenone (0·15 mol) in ether (100 ml) was added dropwise with stirring to a solution of NEt_3 (0·375 mol) and PCl_3 (0·375 mol) in ether (300 ml). After stirring the mixture for 2 h the precipitate of NEt_3.HCl was filtered off through glass wool and the ether removed under reduced pressure. Distillation of the residue gave the 2-chloro derivative (I; R = H, X = Cl) (45%), b.p. 72—76 °C at 0·3 mmHg. NEt_3 (0·02 mol) was added to a solution of the 2-chloro derivative (0·02 mol) in ether (25 ml), followed by the dropwise addition of a solution of MeOH (0·06 mol) in ether (10 ml). After stirring the mixture for 2 h it was filtered through glass wool and the ether was removed under reduced pressure. Distillation of the residue gave the 2-methoxy derivative (65%), b.p. 64—67 °C at 0·35 mmHg. All operations were carried out under anhydrous conditions and under nitrogen.

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