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REACTIONS OF DIMETHYL PHOSPHITE WITH TETRACYCLONE

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The reactions of tervalent phosphorus compounds with carbonyl compounds have contributed greatly to the understanding of organo-phosphorus chemistry (1), and considerable prominence has been given in the recent literature to the reactions of 2,3,4,5-tetraphenylcyclopentadieneone (tetracyclone, Ia) with a variety of tervalent phosphorus compounds (2-6). This paper describes the formation of three products[†] of a type not previously observed in the reactions of tetracyclone and phosphites.

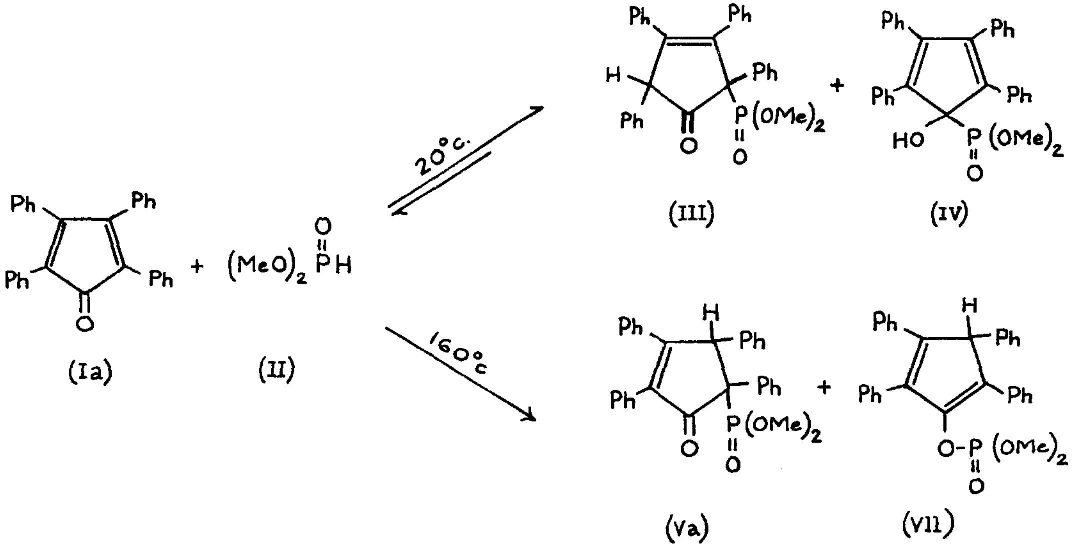
When a suspension of tetracyclone and sodium bicarbonate in ether was stirred at room temperature, in the dark under nitrogen, with dimethyl phosphite (II), a slow reaction resulted in the formation of two products. The more soluble of these was a 1:1 adduct, m.p. 184-186°C; m/e 494 units; λ_{max} 261 nm. (ε, 16000); ν_{max} 1748, 1255, 1060, 1034 cm^{-1}; τ 2.6-3.5 (m, 20H), 4.75 (s, 1H), 6.19 and 6.56 (double d, J_{PH} 10.8 Hz, 6H). The ultraviolet and carbonyl absorptions indicate that this adduct is a non-conjugated ketone, a feature confirmed by the singlet nature of the methine proton, and structure (III) accomodates this data adequately.

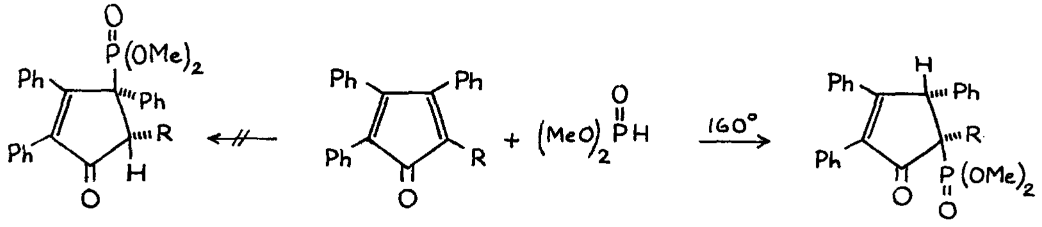
The other product of the room temperature reaction was a very insoluble 1:1 adduct, m.p. 168-171°C; m/e 494 units; λ_{max} 341 nm. (ε, 8400); ν_{max} 3080, 1222, 1060 cm^{-1}. The presence of the hydroxyl group, and the lowering of the phosphoryl frequency to 1222 cm^{-1}(7) are best accounted for by structure (IV). This phosphonate has clearly been formed by attack at the carbonyl carbon, and is a new type of product in the reactions of tetracyclone, although simple carbonyl compounds generally form α-hydroxy phosphoryl structures in reactions with tervalent phosphorus acids, or their anions (8).

When a mixture of tetracyclone (Ia) and dimethyl phosphite (II) was refluxed under nitrogen, the purple colouration of (Ia) rapidly disappeared, and a white 1:1 adduct was readily isolated. This was different from those isolated from the room temperature reaction and gave m.p. 210-212°C; m/e 494 units; λ_{max} 301 nm. (ε, 12700); ν_{max} 1695, 1348, 1262, 1156, 1053 and 1030 cm^{-1}; τ 2.6-3.3 (m, 20H), 5.19 (d, $\underline{J}_{PH}$ 14.0 Hz, 1H), 6.47 and 6.55 (double d, $\underline{J}_{PH}$ 10.5 Hz, 6H). The ultra-violet and infra-red spectra suggest a conjugated ketone chromophore, while the phosphoryl band at 1262 cm^{-1}, and the $\underline{J}_{PH}$ of the methine hydrogen indicate a phosphonate with a vicinal hydrogen <u>cis</u>-fused (4) to the ketonic ring. However, these data could fit either structure (Va) or structure (VIa), although the former seems the more probable, in view of the reaction of 2-methyl-3,4,5-triphenylcyclopentadienone (Ib) and dimethyl phosphite (II) in identical conditions. This produces a 1:1 adduct, in which the methyl group of the ketonic ring appears as a doublet at 8.2τ ($\underline{J}_{PH}$ 15.5 Hz), and to which structure (Vb), and not structure (VIb), can reasonably be assigned.

This reaction also yielded another 1:1 adduct, m.p. 169-171°C, which, from its spectra, appears to be identical to a substance, first reported by Ranganathan and Singh (2), and subsequently shown by Gallacher and Jenkins (5), and by Floyd et al. (6) to have structure (VII), formed by attack of dimethyl phosphite (II) on the carbonyl oxygen of (Ia).

The adducts formed in the room temperature reaction are both converted to tetracyclone by heat or base, and would appear to be the products of kinetically controlled pathways. The dissociation of α-hydroxy phosphoryl compounds to carbonyl compounds has been observed on several previous occasions (9), and represents one way in which products, derived from attack of tervalent phosphorus compounds at the carbonyl carbon, can be converted to those apparently derived from carbonyl oxygen attack.





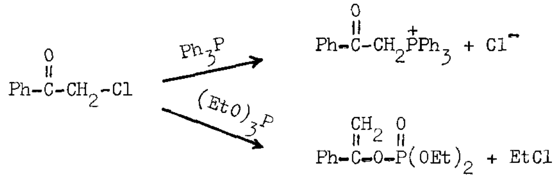
(VI) a ; R = Ph
b ; R = Me

(I) a ; R = Ph
b ; R = Me

(II)

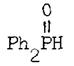
(V) a ; R = Ph
b ; R = Me

The dimethyl phosphite-tetracyclone system thus gives ketonic products, (III) and (Va), resulting from attack at the carbon α- to the carbonyl, analogous to those which have been isolated from the reactions of diphenyl phosphinous acid (VIII) with tetracyclone, and their interconversion is controlled by kinetic and thermodynamic factors similar to those observed for the diphenyl phosphine oxide adducts of tetracyclone(4). However, the formation of (IV) and (VII) is the result of attack by phosphorus at the (relatively) harder carbonyl centre, and analogous adducts were not observed in the diphenyl phosphinous acid-tetracyclone system. It is of interest that the oxygens in dimethyl phosphite would be expected to harden (10) the phosphorus nucleophile, in comparison to the phosphorus of diphenyl phosphinous acid. The consequent change in reaction pathway is therefore not too surprising, and qualitatively similar changes have been reported in reactions of other carbonyl compounds. For example, phenacyl chloride gives phosphonium salts with phosphines (11), but gives enol esters (Perkow Reaction) with phosphites (12).



$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}Cl} \xrightarrow{Ph_3P} \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_2\overset{+}{P}Ph_3 + Cl^-}$$

$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}Cl} \xrightarrow{(EtO)_3P} \mathrm{Ph{-}\overset{CH_2}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{P}}(OEt)_2 + EtCl}$$



$\mathrm{Ph_2\overset{O}{\overset{\|}{P}}H}$

(VIII)

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[†] Satisfactory analytical data have been obtained for all new phosphonates reported.