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ADDITION OF DIPHENYL PHOSPHINOUS ACID TO TETRACYCLONE

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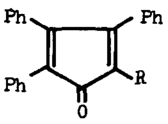
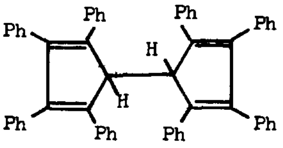
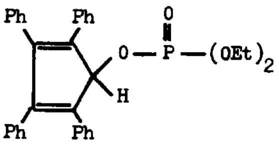
There has been considerable interest recently in reactions between tetracyclone (Ia) and neutral, tervalent phosphorus compounds, which give products arising from attack by phosphorus at the carbonyl oxygen. For example, Anschel (1) has reported the formation of (II) after heating (Ia) with tributyl phosphine, and Ranganathan and Singh (2) have reported the formation of (III) from (Ia) and triethyl phosphite. Although the addition of tervalent $>$P-OH compounds across the double bonds of conjugated ene-one systems is well documented (3), such reactions of tetracyclone have not been reported. This paper describes the formation of three novel phosphine oxides^{+} by reaction of tetracyclone (Ia) with diphenyl phosphinous acid.



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



(II)



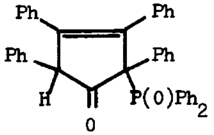
(III)

Thus, when (Ia) was stirred at room temperature under nitrogen with a suspension of the sodium salt of diphenyl phosphinous acid in dioxan, a white, 1:1 adduct (90%) was formed, m.p. 188-189°C; m/e 586, 446, 384, 356, 201, 178 units; λ_{max}^{EtOH} 270 n.m. (ε, 10200): ν_{max} 1740 (C=O), 1205 (P=O) cm.$^{-1}$; τ 1.8-3.5 (m, 30H), 6.80 (S, 1H). This substance is assigned structure (IV) since its carbonyl band is at a high wavenumber (non-conjugated), and its methine proton is a singlet.

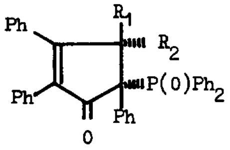
Similar treatment of (Ia) with a solution of diphenyl phosphinous acid, in the presence of hydrogen chloride, lead to the formation of a small amount (10%) of (IV), and of larger amounts (85%) of another white solid, m.p. 107-110°C; m/e 586, 446, 384, 356, 201, 178 units; λ_{max}^{EtOH} 311 n.m. (ε, 9500); ν_{max} 1690, 1350, 1190 (P=O), 1150 cm^{-1}; τ 2.4-3.1 (m, 31H) 4.66

(d, $\underline{J}_{PH}$ 1.5 c/s, 1H). The unassigned infra-red absorptions of this solid are all typical of a 2,3-dihydrotetracyclone, (2,3-dihydrotetracyclone itself absorbs at 1688, 1345 and 1150 cm^{-1}), a partial structure confirmed by the ultra-violet absorption at 311 n.m. It is known that the magnitude of ^{31}P - ^{1}H vicinal coupling is dependent upon the P-C-C-H dihedral angle, in a fashion well established for ^{1}H - ^{1}H and ^{19}F - ^{1}H vicinal couplings (4). The small $\underline{J}_{PH}$ observed above is thus compatible with either structure (Va) or structure (VIa), in which the phosphorus is <u>trans</u> to the methine hydrogen and the P-C-C-H dihedral angle likely to be <u>ca</u>.120°.

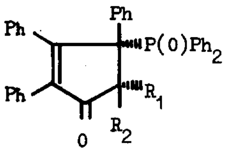
This same (lower m.p.) phosphine oxide was formed when (Ia) was treated with diphenyl phosphinous acid in refluxing diglyme under nitrogen. However, this reaction also gave another phosphine oxide, m.p. 196-197°C; m/e 586, 446, 384, 356, 201, 178 units; λ_{max}^{EtOH} 311 n.m. (ε, 9300); ν_{max} 1680, 1350, 1180 (P=O), 1153 cm^{-1}; τ 1.8-3.2 (m, 30H), 3.80 (d, $\underline{J}_{PH}$ 12 c/s, 1H). These results indicate that this oxide possesses either structure (Vb) or structure (VIb), in both of which the phosphorus and the methine hydrogen are <u>cis</u>, and the P-C-C-H dihedral angle is very small.



(IV)



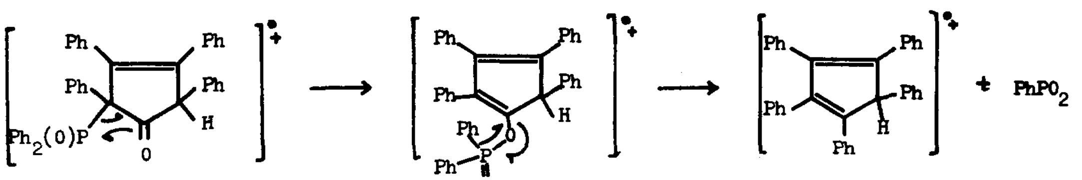
(V) a; R_1 = H,R_2 = Ph
b; R_1 = Ph,R_2 = H



(VI) a; R_1 = H,R_2=Ph
b; R_2 = Ph,R_1 = H.

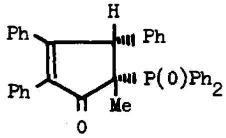
Each of these phosphine oxide adducts of tetracyclone shows a strong M-140 peak in its spectrum, and a metastable peak associated with this fragmentation of the parent ion. Studies conducted in our laboratory (5) on the mass spectra of similar oxides have shown that this fragmentation can be characteristic of β-ketoalkyl diphenyl phosphine oxides, and that it is not observed in the spectra of analogous γ-ketoalkyl diphenyl phosphine oxides. On the basis of this evidence it is probable that the oxides described above have structures (IV), (Va) and (Vb).

The M-140 peaks would seem to be rationalised best by a rearrangement process, illustrated below for adduct (IV), involving an intermediate, (VII), related to an enol phosphinate, from which phenyl "metaphosphonate", (VIII), could be formed. This fragmentation of (VII) is similar to that observed by Occolowitz and Swan (6) in the spectra of vinyl phosphonate esters, and the generation of metaphosphate analogues in a mass spectrometer also has precedent, in the work of Cooks and Gerrard (7).

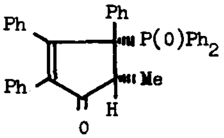


(IV) (VII) (M-140) (VIII)

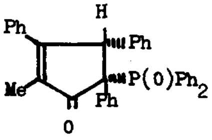
Good confirmation of these assignments came from the structure of the adduct formed by reaction of 2-methyl-3,4,5-triphenylcyclopentadienone (Ib) with diphenyl phosphinous acid, either under basic conditions, or in the presence of hydrogen chloride. This adduct had m.p. 94-97°C; m/e 524; λ_{max}^{EtOH} 302 n.m. (ϵ, 11,000); ν_{max} 1695 (C=O), 1345, 1190 (P=O) 1165 cm^{-1}; τ 1.6-3.4 (m, 25H), 5.44 (1H), 8.18 (d, $J_{P.CH_3}$ 14 c/s, 3H). The observed phosphorus-methyl coupling is more compatible with structure (IX), in which the phosphorus atom and the methyl group are both attached to the 2-position, than with structure (X) or (XI).



(IX)



(X)



(XI)

These cyclopentadienone adducts have therefore all been formed by attack of tervalent phosphorus at the carbon atom α- to the carbonyl group, although the final site of protonation depends largely upon the reaction conditions employed. For example, the formation of (Va) seems to be favoured by acidic conditions, despite the fact that (IV), formed in basic conditions, is quite stable to acid.

In basic conditions, at room temperature, the reaction would appear to be controlled by kinetic factors, which result in protonation of the initial anion so that the carbonyl and olefinic groups of the product are non-conjugated. This type of kinetic control is comparable to that observed in the alkylation or isomerisation of conjugated en-ones in basic media. This explanation is made more likely by the observation that when (IV) is heated in refluxing diglyme under nitrogen, (Ia) is quickly generated, and then a mixture of adducts (Va) and (Vb), similar in composition to that formed directly from (Ia) under the same conditions, is slowly produced.

The regiospecificity of the addition to the 2-position of (Ib) during reaction in basic conditions can readily be explained in terms of the relative stability of the anions leading to the observed product, (IX), and to the other possible β-keto phosphine oxide product, (XI).

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† Satisfactory analytical data have been obtained for all new phosphine oxides reported.