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REACTIONS OF PRIMARY PHOSPHINES WITH TETRACYCLONE

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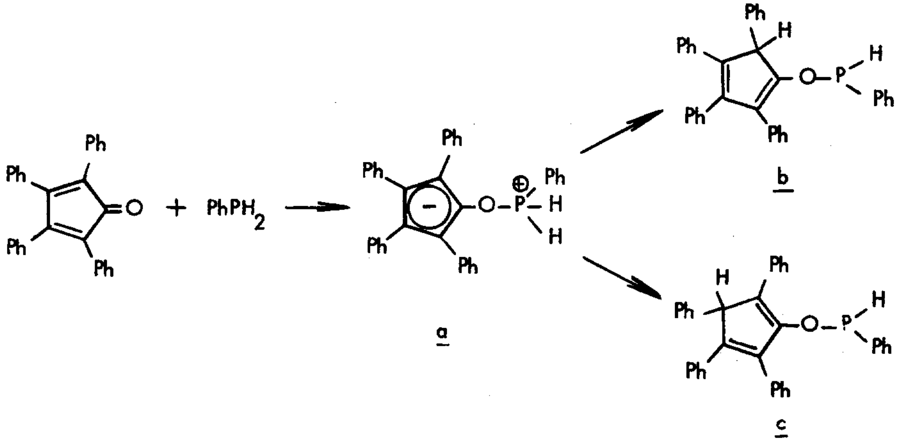
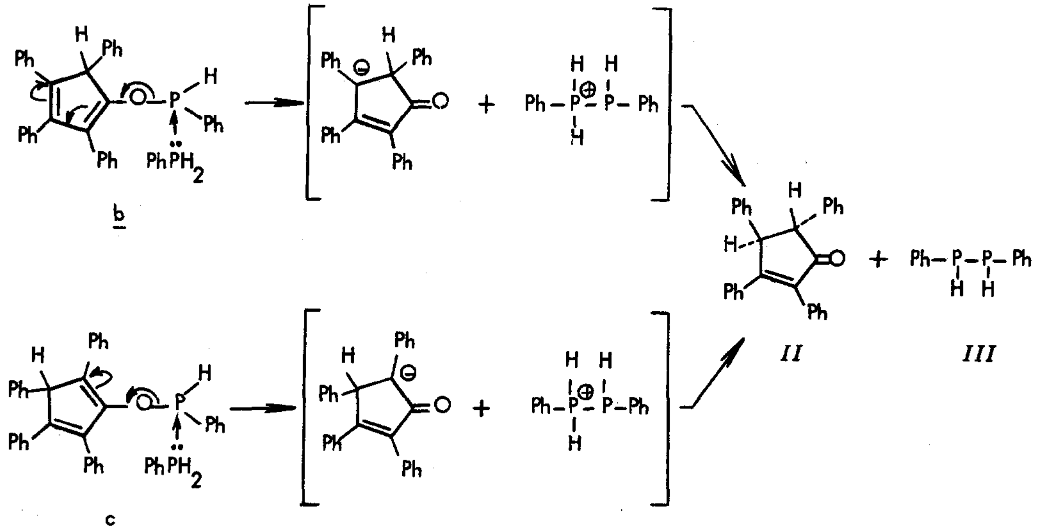
The reaction of tetraphenylcyclopentadienone (tetracyclone) with a variety of trivalent and tetravelent phosphorous compounds (mainly phosphites) has been given in recent literature[1-3]. In the course of our investigation of the addition of primary phosphines to various dienonic compounds[4], the reaction with tetracyclone was investigated and is described here.

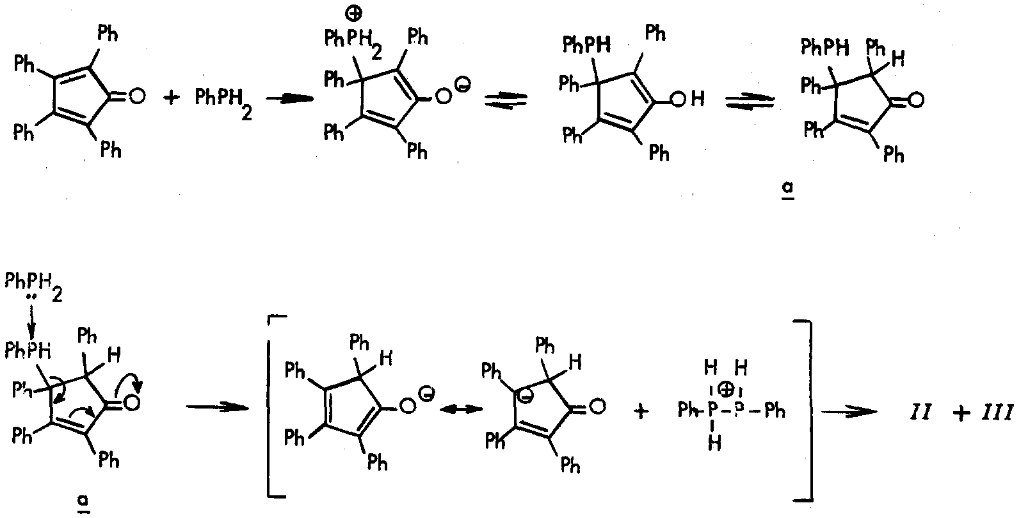
When a solution of tetracyclone (*I*) in phenylphosphine or benzylphosphine is heated at 80° for a few minutes under N_2 atmosphere, or even more easily by performing the reaction in CCl_4 at room temperature, decolorization of the solution occurs. Following removal of the excess phenylphosphine, a crystalline compound (*II*) could be obtained, m.p. 160-161° (pet-ether), m/e 386 $M^{\oplus}$, ν_{max}^{KBr} 3030, 1680, 1610, 1590, 1480, 1440, 1340, 1140, 1060, 1020, 930, 790 cm^{-1}; NMR δ 3.76(d, J=2.5Hz, 1H), 4.56(d, J=2.5Hz, 1H) and 7.3 (m, 20H); this data unequivocally shows that compound *II*, which is obtained almost quantitatively from *I*, is trans-dihydrotetracyclone[5] - a result which resembles the reduction of *I* by Ph_3SnH[6]. The second product of the reaction, i.e. the product from the reacting phenylphosphine, is very sensitive to oxygen and is most probably a mixture of linearic and cyclic polyphosphines (e.g. $(PhP)_4$), which, upon oxidation with HNO_3 yielded phenylphosphonic acid (identical in all respects with an authentic sample)[7,8].

Two possible mechanisms can be suggested for the above reaction. In the first, the oxygen of *I* is initially attacked, while the other begins with a Michael type addition of the phosphine to the unsaturated carbonyl:





mechanism (i)



mechanism (ii)

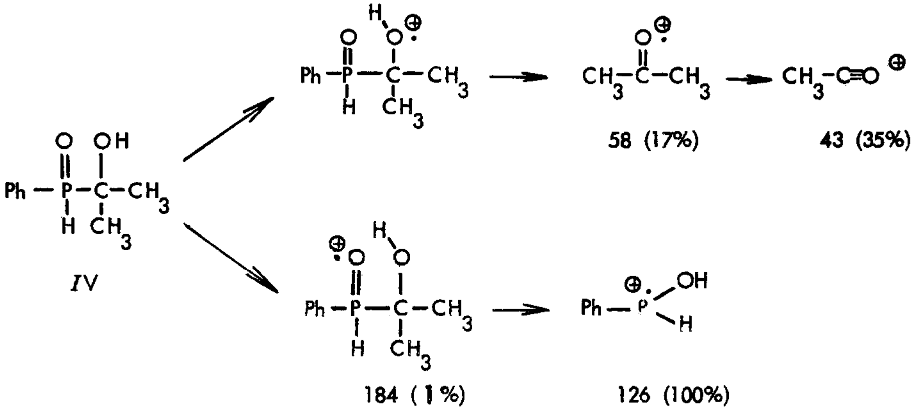
The reaction could be followed by reacting *I* with $PhPH_2$ in CCl_4 in a NMR tube; after decolorization occurred, two new doublets at δ 4.11 and 4.18 (J_{P-H} 215 Hz) could be observed. Of most significance was the fact that the doublets at δ 3.76 and 4.56 belonging to compound *II*, were not observable, thus confirming the existence of an intermediate. The 4.11 and 4.18 doublets attributed to two different PhP(H)-groups, are in accordance with a mixture of b and c in mechanism (i) as well as to the possible isomers of a in (ii).

The intermediate is quite stable at room temperature and only on heating for some time it decomposes, with the consequent formation of compound *II* (this observation was followed by NMR technique). Additional complementary data could be derived from the IR spectrum, in which the C=O absorption of *I* at 1700 cm^{-1} disappeared, during the decolorization, and no other peak which could be attributed to C=O was detectable. Only after heating, the 1680 cm^{-1} band belonging to the carbonyl of *II*, could be observed. The disappearance of the C=O stretching, together with the fact that no -OH band was observed, gives support to the O-attack over the C-one i.e. mechanism (i) rather than (ii). Further support for this assumption was derived from the fact that the intermediate could not be acetylated by Ac_2O [9].

The second step in the reaction seems to be the decomposition of the intermediate by a nucleophilic displacement with the aid of a second phosphine molecule, to yield diphenyldiphosphine (*III*) (a displacement which is similar to the one suggested for the reaction between two molecules of benzoyloxydiphenylphosphine) [10]. Generally the unstable diphosphines are known to undergo quick disproportionation to $(ArP)_n$ and the corresponding phosphines[11], a reaction which most probably occurs also in this case.

An interesting product was obtained when the intermediate was decomposed by boiling in acetone. The acetone which does not react with phenylphosphine nor with $(PhP)_4$ on refluxing or even more drastic conditions, yielded low yields, upon chromatography, of an oily compound (*IV*);
NMR δ 1.40(d, J=15Hz, CH_3); 1.50(d, J=15Hz, CH_3); 3.60(s, O$\underline{H}$); 6.97(d, J=756Hz P(O)$\underline{H}$) and 7.55(m, Ph).
IR $\nu_{max}^{CHCl_3}$ 3600, 3250 (OH), 2950 (C-CH_3), 2300 (P(O)$\underline{H}$), 1590 (Ph); 1435 (Ph-P); 1170 (P=O) cm^{-1}.

This data, together with the fragmentation observed in the mass spectrum suggest that *IV* is α-hydroxyisopropylphenylphosphine oxide.



The low yield of *IV* did not alter even if the whole reaction was performed in acetone, a fact which may indicate that *III* or its initial disproportionation product do react with the acetone. Reactions of this type between diphosphines and carbonylic compounds are known in the literature[12].

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