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CARBON-CARBON CONDENSATIONS VIA OXYPHOSPHORANES FROM THE REACTION OF HEXAFLUOROACETONE WITH TRIPHENYLPHOSPHINE AND WITH DIPHENYLPHOSPHINITE, PHENYLPHOSPHONITE, AND PHOSPHITE ESTERS.

THE OXYPHOSPHORANE FROM TRIPHENYLPHOSPHINE AND PHENANTHRENEQUINONE

Fausto Ramirez[1], C. P. Smith, A. S. Gulati and A. V. Patwardhan
Department of Chemistry, State University of New York
Stony Brook, New York

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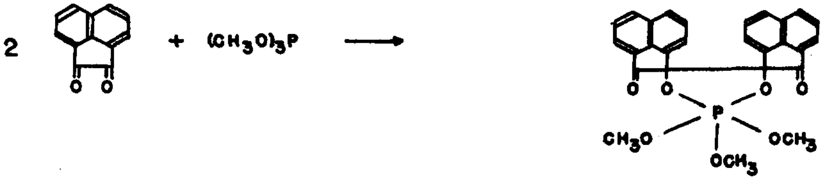
The first 2,2,2-trialkoxy-1,3,2-dioxaphospholane was made from acenaphthenequinone and trimethyl phosphite at 20° [2a].



$\delta\ P^{31} = +\ 48.0$ PPM VS H_3PO_4

An analogous oxyphosphorane, XXIX of Chart 1, was prepared from biacetyl and trimethyl phosphite[2b]. In this case, it could be shown that the carbon-carbon condensation involved a dioxaphospholene XIX as an intermediate[2c,d]. The latter was formed rapidly and was consumed slowly; therefore, it was readily isolated. Other oxyphosphorane condensations were reported subsequently[2e-1]. These reactions appeared to be related to the conversion of phthalic anhydride into biphthalyl by triethyl phosphite at elevated temperatures[3].

The formation of dioxaphospholenes, V-VIII, XII-XIV, and XVIII-XIX, from the reaction of phosphite esters with o-quinones[2], α-diketones[2,4,5], α-ketoaldehydes[2k], and triketones[2k], involves an attack by phosphorus on a carbonyl-oxygen. Probably, this is the initial process, since the attack by the phosphite on the carbonyl-carbon of propionaldehyde did not produce a 1,3,2-dioxaphospholane, but led instead to a 1,4,2-dioxaphospholane, XXX[6].

This Communication describes new developments in oxyphosphorane chemistry. (1) The reaction of triphenylphosphine with phenanthrenequinone at 120° gave the first reported 2,2,2-triphenyl-1,3,2-dioxaphospholene, I. The ^{31}P n.m.r. shift is given in Table 1. Note the positive value of the shift and its relationship to those of related compounds, V-VIII[2]. Several new dioxaphospholenes, II-IV were made from diphenylphosphinite and phenylphosphonite esters.

(2) Benzil and biacetyl failed to react with triphenylphosphine at 120°. However, they reacted with diphenylphosphinite and phenylphosphonite esters. The products were dioxaphospholenes, IX-XI, and XV-XVII; cf. Table 1. The corresponding phosphite-adducts, XII-XIV, and XVIII-XIX[2,4,5] are listed also.

(3) Diphenyl phenylphosphonite was much more reactive than triphenyl phosphite and triphenylphosphine toward α-dicarbonyl compounds. This might be related to the rather large negative value of the ^{31}P n.m.r. shift of the phosphonite; i.e., to the relatively poor shielding of its P-nucleus by electrons (see Table 1).

(4) The formation of adducts from triphenyl phosphite required heating. Since biacetyl is quite reactive as an acceptor in the oxyphosphorane condensation[2], the formation of the 2:1 adduct, XXVIII, was unavoidable

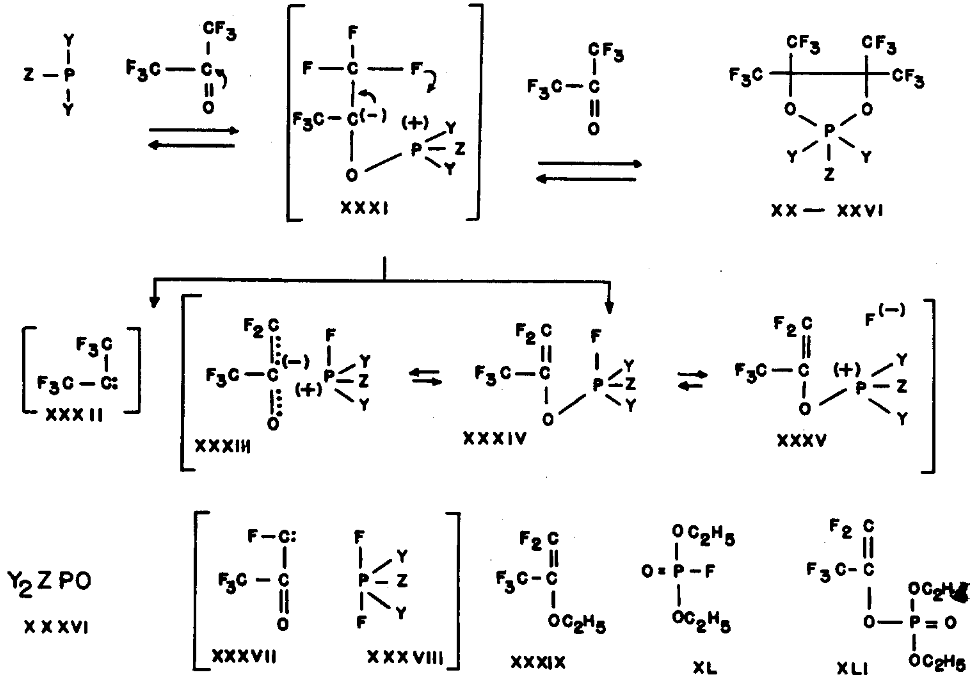
(5) The biacetyl-ethyl diphenylphosphinite adduct, XV, dissociated into its original components at 160° and 0.2 mm.

(6) Hexafluoroacetone (HFA) reacted with triphenylphosphine at low temperatures (-70 to 0°). The product was a dioxaphospholane XX, isolated in 90% yield. This behavior was quite general: the

dioxaphospholanes XXI-XXVI were obtained in 90% yields from the reactions of HFA with phosphinite, phosphonite and phosphite esters at, or below, 0°. The ^{31}P shifts are given in Table 1. The ^{19}F shifts were in the range -8.9 to -10.8 p.p.m. *vs* CF_3COOH; the signals were singlets when examined at 94.1 Mcps, which confirmed the four-bond separation between the F-P nuclei, *i.e.*, the establishment of a new phosphorus-oxygen bond in the adducts.

The phosphine-adduct XX dissociated into triphenylphosphine and 1.5 moles of HFA at 120°. The triethyl phosphite-HFA adduct XXV remained unchanged after 4 hrs. at 140°; however, it released *one mole* of HFA within 4hrs. at 165°. Most of the phosphorus appeared as diethyl phosphorofluoridate (XL; $\delta^{31}P$ +12.0 p.p.m., J_{PF} 972 cps) and triethyl phosphate ($\delta^{31}P$ +1.2 p.p.m.) in a 3:1 ratio; there were also traces of what could be an enol-phosphate (XLI; $\delta^{31}P$ +2.8 p.p.m.). Several phosphorus-free substances were formed in this pyrolysis. One of them, 2-ethoxy-pentafluoropropene, XXXIX, was produced in less than one-half the amount of fluoridate XL; *i.e.*, the latter is formed in more than one way. The other decomposition products will be discussed in the full paper. The elemental analyses, the infrared and the ^{1}H n.m.r. spectra of the substances in Table 1 were determined.

Fluorine atoms next to the carbonyl group in HFA promote the attack by phosphorus on oxygen leading to the *1:1 adducts* XXXI[7]. Under mild conditions, XXXI condenses with more HFA to give the *2:1* adducts XX-XXVI[2]. The stability of the latter depends on the nature of *Y* and *Z* attached to the phosphorus. If a 1:1 adduct, XXXI, Y = Z = OR, is generated at high temperatures, it may break up in several ways, XXXII-XLI. The differences that have been observed in the reactions of α-haloketones with trivalent phosphorus compounds[8] are probably related to the relative stabilities of 1:1 adducts (XXXI), ion-pairs (XXXIII, XXXV) and halophosphoranes[2,9] (XXXIV, XXXVIII). These are related to the nucleophilicity of the halides and the nature of *Y*, *Z*.

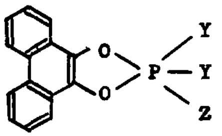


The nature and the number of halogens in the ketone, and the halophilicity of the phosphorus compound, Y_2ZP, will also play a role.

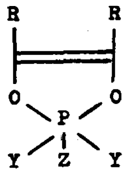
Wiley and Simons[10] found only the ethoxypropene XXXIX and the fluoridate XL in their study of the reaction of HFA with triethyl phosphite; apparently they distilled adduct XXV at 760 mm. Russian investigators reported[11a] the formation of XXV, but gave no ^{31}P n.m.r. data. Later[11b], they stated that the pyrolysis of XXV gave the ethoxypropene XXXIX and tetra-trifluoromethylethylene oxide (the latter by loss of phosphate from XXV). They did not account for the phosphorus and did not mention other products.

The HFA-triphenylphosphine adduct XX is being reported also by Stockel[12]. A 1:1 adduct from o-chloranil and triphenylphosphine has been assigned an open-dipolar structure[13]. This may well be correct because the adduct has a band at 6.88μ in the infrared. We have been

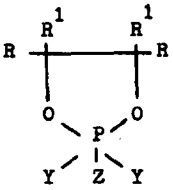
CHART 1



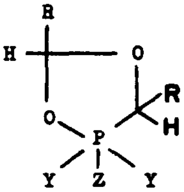
I, Y = Z = C_6H_5
II, Y = C_6H_5; Z = OC_2H_5
III, Y = OC_6H_5; Z = C_6H_5
IV, Y = OC_4H_9-n; Z = C_6H_5
V, Y = Z = OC_6H_5
VI, Y = Z = OC_4H_9-n
VII, Y = Z = OC_2H_5
VIII, Y = Z = OCH_3



IX, R = C_6H_5; Y = C_6H_5; Z = OC_2H_5
X, R = C_6H_5; Y = OC_6H_5; Z = C_6H_5
XI, R = C_6H_5; Y = OC_4H_9-n; Z = C_6H_5
XII, R = C_6H_5; Y = Z = OC_6H_5
XIII, R = C_6H_5; Y = Z = OC_2H_5
XIV, R = C_6H_5; Y = Z = OCH_3
XV, R = CH_3; Y = C_6H_5; Z = OC_2H_5
XVI, R = CH_3; Y = OC_6H_5; Z = C_6H_5
XVII, R = CH_3; Y = OC_4H_9-n; Z = C_6H_5
XVIII, R = CH_3; Y = Z = OC_2H_5
XIX, R = CH_3; Y = Z = OCH_3



XX, R = R^1 = CF_3; Y = Z = C_6H_5
XXI, R = R^1 = CF_3; Y = C_6H_5; Z = OC_2H_5
XXII, R = R^1 = CF_3; Y = OC_6H_5; Z = C_6H_5
XXIII, R = R^1 = CF_3; Y = OC_4H_9-n; Z = C_6H_5
XXIV, R = R^1 = CF_3; Y = Z = OC_6H_5
XXV, R = R^1 = CF_3; Y = Z = OC_2H_5
XXVI, R = R = CF_3; Y = Z = OCH_3
XXVII, R = CH_3; R^1 = CH_3CO; Y = OC_6H_5; Z = C_6H_5
XXVIII, R = CH_3; R^1 = CH_3CO; Y = Z = OC_6H_5
XXIX, R = CH_3; R^1 = CH_3CO; Y = Z = OCH_3

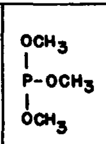
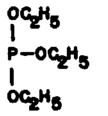
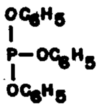
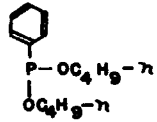
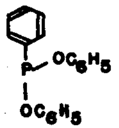
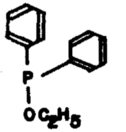
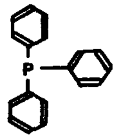


XXX, R = alkyl;
Y = Z = OCH_3
δP^{31} +34.1 ppm

……………………………

unable, however, to detect the ^{31}P n.m.r. signal of this adduct due to insufficient solubility. Triaminooxyphosphonium dipolar ions have been made from the reaction of trisdimethylaminophosphine with o-quinones, vicinal triketones and oxomalonic esters[14].

Table 1. ^{31}P NMR Shifts, in p.p.m. *vs* 85% H_3PO_4, of 1:1 Adducts (1,3,2-Dioxaphospholenes) and of 2:1 Adducts (1,3,2-dioxaphospholanes) From the Reaction of Trivalent Phosphorus Compounds (P^{III}) with Phenanthrenequinone (PQ), Benzil (BZ), Biacetyl (BI) and Hexafluoroacetone (HFA). Solvent: CH_2Cl_2 *M.p. or b.p. (mm).

	 $P(OCH_3)_3$		 $P(OC_2H_5)_3$		 $P(OC_6H_5)_3$									
Compd.	M.P.*	δP^{31}	M.P.*	δP^{31}	M.P.*	δP^{31}	M.P.*	δP^{31}	M.P.*	δP^{31}	M.P.*	δP^{31}	M.P.*	δP^{31}
P^{III}	111 (760)	-140.0	154 (760)	-138.5	184 (0.2)	-127.1	132 (1.7)	-155.0	161 0.1	-157.9	93 (0.1)	-109.8	80	+ 5.7
$P^{III}\cdot PQ^{a}$	74	+ 44.7	74	+ 47.1	147	+ 58.6	52	+ 29.6[b]	142	+ 38.1	147	+ 16.3[c]	165	+15.6
$P^{III}\cdot BZ^{a}$	49	+ 49.5		+ 52.2	99	+ 62.5		+ 36.6		+ 43.2	90	+ 27.0[d]		None
$P^{III}\cdot BI^{e}$	45 (0.5) 31	+ 48.9 + 54.8[f]	62 (0.05)	+ 51.3		+ 64.7[g] + 66.1		+ 36.1		+ 42.4[h] + 48.0		+ 27.7[i]		None
$P^{III}\cdot HFA^{j}$	34 (0.5)	+50.1	33 (0.1)	+ 53.2	55	+ 64.1	99 (0.1)	+ 33.4		+ 40.1	111	+ 19.0[k]	105	+21.6[l]

[a] Forms 1:1 Adducts only. [b] For the $(n\text{-}C_4H_9O)_3P.PQ$ Adduct, δP^{31} = +47.3 ppm. [c] +17.3 ppm in benzene [d] +27.3 ppm in benzene [e] Forms 1:1 Adducts (upper values) and 2:1 Adducts (lower values) [f] For *meso*-isomer of dioxaphospholane with *cis*-acetyl groups; +52.6 ppm for *racemic*-isomer [g] A 1:1 mixture of phosphite and biacetyl gave 1.0 parts of 1:1 adduct (+64.7 ppm), 5.2 parts of *meso*-2:1 adduct (+66.1 ppm) and 0.5 parts of *racemic*-2:1 adduct (+65.3 ppm) after 2 hours at 75°. [h] After 2 hours at 30° obtained 5 parts of 1:1 adduct and 1 part of 2:1 adduct, probably meso-isomer [i] +28.1 ppm in benzene [j] Forms only

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