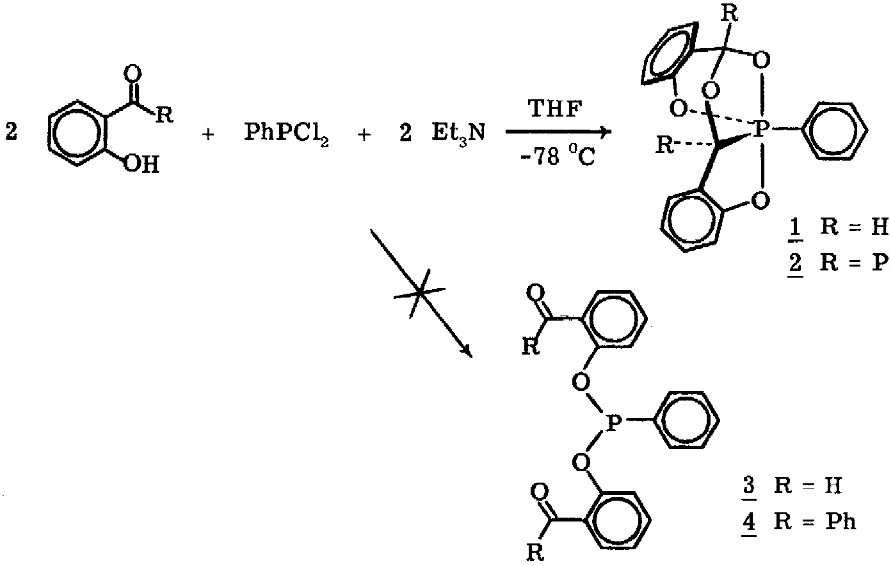
Tetrahedron Letters Vol. 21, pp 4331 - 4334
0040-4039/80/1101-4331$02.00/0

AN EXTREMELY FACILE FORMATION OF TRIOXYDIALKYL PHOSPHORANES FROM THE REACTION OF PHENYLDICHLOROPHOSPHINE AND 2-KETOPHENOLS

Stephen D. Harper and A. J. Arduengo*
School of Chemical Sciences, University of Illinois, Urbana, IL 61801

We wish to report the isolation and characterization of tricyclic 10-P-5[1] species 1 and 2 from the reaction of salicylaldehyde or o-hydroxybenzophenone with phenyldichlorophosphine at -78° in the presence of triethylamine. The 2 : 1 adducts are obtained in ca. 80% yield on warming to room temperature. No evidence for the formation of phosphonous diesters 3 and 4 (8-P-3) in these reactions was found. The formation of 1 and 2 occurs with greater facility than the cyclizations reported by Ramirez and co-workers.[2] In contrast to the previously reported[3] reactions of trialkyl phosphites and diaryl ketones the production of 2 provides the first example of a diaryl ketone which will undergo this type of head to tail oxidative cyclization. Phosphite esters have been reacted with o-quinones, α-diketones, and hexafluoroacetone to give a tail to tail cycloadduct,[4] but diaryl ketones have only given products of more complex reactions.[3]



1 R = H
2 R = Ph

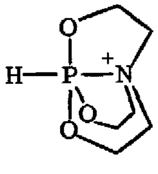
3 R = H
4 R = Ph

Colorless prisms of phosphorane 1 (mp 160-163°, with decomposition) are obtained by recrystallization from anhydrous ethyl acetate. Anal. Calcd for $C_{20}H_{15}O_4P$: C, 68.57; H, 4.32; P, 8.84. Found: C, 68.41; H, 4.22; P, 8.83. No C=O band was visible in the infrared spectrum. ^1H NMR ($CDCl_3$) δ 5.11 (d, 1 H, J_{HP} = 2 Hz), 6.26 (d, 1 H, J_{HP} = 12 Hz), 6.77-7.67 (m, 11 H), 8.10-8.42 (m, 2 H); ^{31}P NMR ($CDCl_3$) -7.9; mass spectrum m/e (rel intensity)

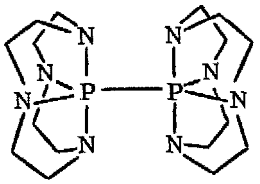
350 (M^+ 44), 321 (33), 230 (40), 229 (100), 210 (63), 181 (61), 166 (27), 165 (93), 121 (29), 77 (27).

Phosphorane 2 is obtained as colorless crystals (mp 177-178°, with decomposition) from anhydrous ethyl acetate. Anal. Calcd for $C_{32}H_{23}O_4P$: C, 76.48; H, 4.61; P, 6.17. Found: C, 76.27; H, 4.60; P, 5.89. No C=O band was visible in the infrared spectrum. ^1H NMR ($CDCl_3$) 6.53-7.97 (m); ^{31}P NMR ($CDCl_3$) -14.0; mass spectrum m/e (rel intensity) 502 (M^+ 100), 321 (48), 305 (44), 181 (64), 152 (27), 105 (44), 77 (53), 28 (22).

The 10-P-5 nature of the phosphorus in the reaction products is confirmed by the ^{31}P NMR shifts of these compounds. The incorporation of phosphorus in two 5-membered rings and one 6-membered ring causes the resonances to appear only slightly upfield of 85% H_3PO_4, in analogy to trends noted for other oxyphosphoranes (Table I). Large positive ^{31}P NMR shifts would be expected for 8-P-3 species such as 3 and 4.



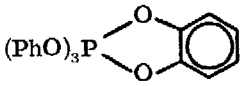
5



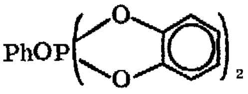
6

$(PhO)_5P$

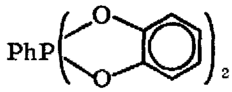
7



8



9



10

$PhP(OPh)_2$

11

Table I. ^{31}P NMR Shifts of Sample 8-P-3 and 10-P-5 Species.

Compound	$\delta^{31}P^*$	Compound	$\delta^{31}P^*$
1	-7.9	8	-60.0[d]
2	-14.0	9	-29.8[d]
5	-20.9[a]	10	-9.0[e]
6	-36.8[b]	11	+164.9[f]
7	-85.7[c]		

*^{31}P shifts are reported in ppm δ relative to 85% H_3PO_4. Negative shifts are upfield of the reference.

[a] D. S. Milbrath and J. G. Verkade, J. Am. Chem. Soc., 99, 6607 (1977).

[b] J. E. Richman, R. O. Day, and R. R. Holmes, J. Am. Chem. Soc., 102, 3955 (1980).

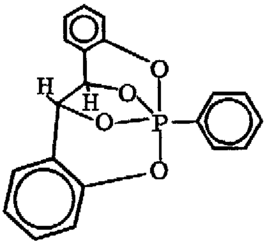
[c] F. Ramirez, A. J. Bigler, and C. P. Smith, J. Am. Chem. Soc., 90, 3507 (1968).

[d] F. Ramirez, A. J. Bigler, and C. P. Smith, Tetrahedron, 24, 5041 (1968).

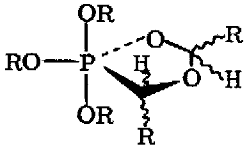
[e] M. Wieber and W. R. Hoos, Monatsh. Chem., 101, 776 (1970).

[f] K. Moedritzer, L. Maier, and L. C. D. Groenweghe, J. Chem. Eng. Data, 7, 307 (1962).

The 2 :1 salicylaldehyde :phenyldichlorophosphine adduct clearly has structure 1 rather than the tail to tail structure 12. The methine protons in the adduct exhibit two different ^1H resonances which are both doublets with different coupling constants to phosphorus. The proton doublet at δ 6.26 (J_{HP} = 12 Hz) is assigned to the methine proton of the acetal carbon. The strong phosphorus proton coupling to this acetal proton is probably the result of the antiperiplanar relationship between the proton and phosphorus. The proton resonance at δ 5.11 (J_{HP} = 2 Hz) is assigned to the methine proton on the carbon directly bonded to phosphorus. Further evidence is provided by the observation of two doublets in the ^{13}C NMR spectrum.[5] One is centered at 65.4 ppm with a coupling constant of 120.85 Hz and may be attributed to a tertiary carbon bonded directly to a 10-P-5 phosphorus. A P-C coupling constant of 128.1 Hz[6] is observed for $(CH_3)_3PF_2$. The other doublet is centered at 97.3 ppm with a coupling constant of 4.27 Hz and is assigned to the acetal carbon. The relative positions of the proton and carbon resonances are also supported by partially decoupled ^{13}C spectra. When the proton at δ 5.11 is irradiated while observing the carbon spectrum the carbon resonance at δ 65.4 appears as a doublet coupled only to phosphorus. Irradiating the downfield component of the proton doublet at δ 6.26 gives a carbon spectrum in which the resonance at δ 97.3 appears as a doublet coupled only to phosphorus.[7]



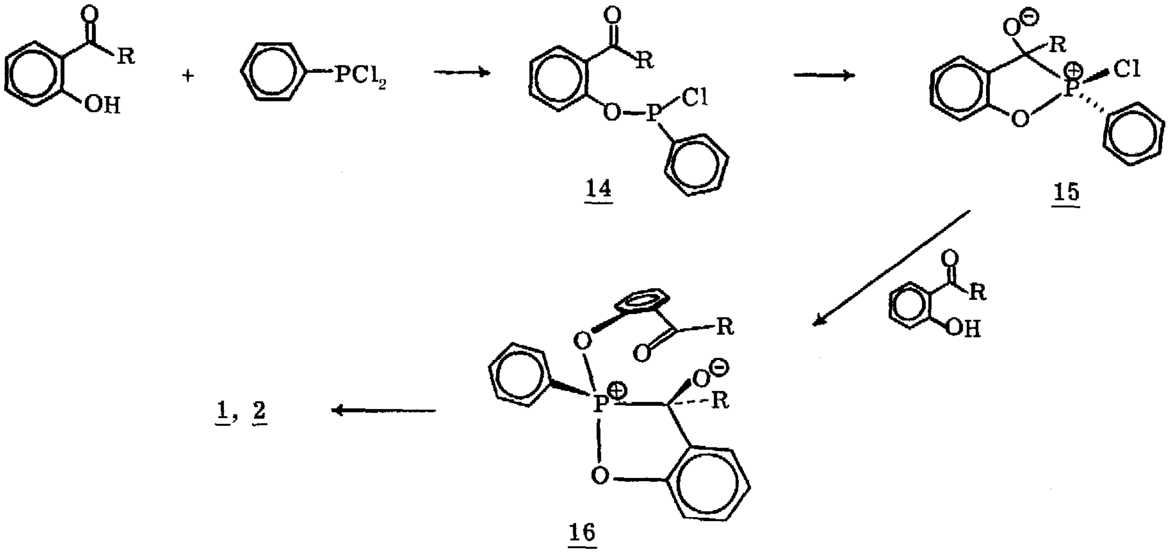
12



13

Ramirez and co-workers[2] have reported the isolation of 2 : 1 adducts of trialkyl phosphites and aliphatic aldehydes having structures of type 13. Formation of these products in good yield requires days to weeks at room temperature. The first step of the mechanism was postulated to be slow addition of the phosphite phosphorus to the carbonyl carbon of the aldehyde to form a zwitterionic intermediate which could then react with a second molecule of aldehyde to yield the phosphorane, 13. The formation of the tricyclic phosphoranes 1 and 2 may proceed in a manner analogous to that postulated by Ramirez for 13 though entropic factors greatly enhance the rate of formation.

Remarkably, when 1 equivalent of salicylaldehyde or o-hydroxybenzophenone is added to 1 equivalent of phenyldichlorophosphine, the 2 : 1 adducts 1 and 2 are again obtained (ca. 80% yield based on the limiting aldehyde or ketone). In spite of the fact that the dichlorophosphine is in excess under the reaction conditions, no 1 : 1 adducts could be detected or isolated from the reaction mixtures. Chlorophosphonite esters [RP(OR')Cl] may normally be obtained in good yield by reaction of phosphonous dichloride, alcohol, and tertiary amine in a 1 : 1 : 1 ratio.[8] This suggests that the trivalent phosphorus in intermediate 14 undergoes nucleophilic addition to the carbonyl carbon to yield chlorophosphonium species[9] 15. The reaction of a second hydroxy compound with the chlorophosphonium species, 15, would then occur rapidly to give 16. Intramolecular addition of the carbonyl group in 16 across the 1,3 phosphorus-oxygen dipole yields phosphoranes 1 and 2. When the reaction is conducted in the presence of p-tolualdehyde, there is no inclusion of p-tolualdehyde in the product which suggests that reaction at the hydroxy center is important for inclusion of the second molecule of aldehyde or ketone in the product phosphorane.



These reactions provide novel and interesting examples of oxidative cyclization of 8-P-3 species with carbonyl compounds to yield tricyclic 10-P-5 species with remarkable facility. We are currently investigating these reactions in more complicated systems as well as attempting to extend this work to other pnitogens.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and the National Science Foundation (NSF CHE 78-14-7720862) for their support of this research.

REFERENCES AND NOTES

1. This N-X-L nomenclature system has been previously described in the literature and provides a convenient means of identifying bonding schemes. (See C. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Alegria, and J. K. Kochi, J. Am. Chem. Soc., in press (1980).)
2. F. Ramirez, A. V. Patwardhan, and S. R. Heller, J. Am. Chem. Soc., 86, 514 (1964).
3. A. C. Poshkus and J. E. Herweh, J. Org. Chem., 29, 2567 (1964).
4. F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, Tetrahedron Lett., 2151 (1966) and references therein.
5. $CDCl_3$ solvent: Shifts reported in ppm δ from internal TMS.
6. H. Dreeskamp, C. Schumann, and R. Schmutzler, Chem. Commun., 671 (1970).
7. We are grateful to the referees for encouraging the inclusion of this experiment.
8. A. W. Frank in "Organic Phosphorus Compounds", G. M. Kosolapoff and L. Maier, Eds., Wiley-Interscience, New York, 1972, Volume 4, p. 268.
9. A number of relatively stable chlorophosphonium salts have been isolated: P. Beck in "Organic Phosphorus Compounds", G. M. Kosolapoff and L. Maier, Eds., Wiley-Interscience, New York, 1972, Volume 2, p. 204.

(Received in USA 22 July 1980)