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(9) (a) Conformational and solvent effects commonly lead to small two-bond phosphorus–hydrogen coupling constants,[9b,c] although larger four-bond than two-bond couplings are unusual: the related molecule $(CH_3)_2PCH_2Si(CH_3)_2Cl$ has ^2J = 1.3 and ^4J = 0.5 Hz.[9d] (b) Horn, H.-G.; Sommer, K. *Spectrochim. Acta, Part A* **1971**, *27*, 1049. (c) Grim, S. O.; Mitchell, J. D. *Inorg. Chem.* **1977**, *16*, 1762, 1770. (d) Grobe, J.; Heyer, G. *J. Organomet. Chem.* **1973**, *61*, 133.

(10) NMR of **6**: δ 0.42 (d, J = 0.9 Hz, 6 H, $Si(CH_3)_2$), 1.82 (br s, 2 H, PCH_2Si), 7.2–7.9 (m, 10 H, $(C_6H_5)_2P$) ppm; NMR of **5**: δ 0.15 (t, J = 0.7 Hz, 6 H), 1.52 (br s, 4 H), 7.2–7.9 (m, 20 H) ppm.

(11) Crude mixture displays NMR signals (THF) at δ 0.07 (d, J = 0.8 Hz) and −0.16 (d, J = 0.9 Hz) ppm. In THF, **6** shows δ 0.28 (d, J = 0.9 Hz) ppm.

(12) (a) **8** was isolated as a red-orange liquid (benzene/alumina(I) chromatography). Calcd for $C_{40}H_{44}P_2Si_2Fe$: C, 68.76; H, 6.35; Si, 8.04; Fe, 7.99. Found: C, 68.69; H, 6.46; Si, 7.97; Fe, 8.13. NMR (benzene-d_6): δ 4.12 and 4.32 (apparent t, 'J' = 1.8 Hz, C_5H_4). (b) **9** was isolated as a white solid from petroleum ether at −40 °C, melting below room temperature. Calcd for $C_{40}H_{44}Cl_2P_2Si_2Zr$: C, 59.68; H, 5.51; Cl, 8.81. Found: C, 59.87; H, 5.64; Cl, 8.68. NMR (benzene-d_6): δ 6.03 and 6.52 (apparent t, 'J' = 2.5 Hz). (c) **10** was isolated as was **9**. Calcd for $C_{25}H_{27}Cl_2PSiZr$: C, 54.73; H, 4.96; Cl, 12.92. Found: C, 54.60; H, 5.11; Cl, 13.09. NMR (benzene-d_6): δ 6.10 (s, C_5H_5), 6.00 and 6.50 (apparent t, 'J' = 2.5 Hz, C_5H_4).

(13) (a) X = Br, brown solid (precipitates from benzene/petroleum ether at 25 °C), darkens above 115 °C: mp 138–142 °C dec; visible (benzene) λ_{max} 411, 507, 845 nm; NMR (benzene-d_6) δ 1.15, 4.15, 4.30, 5.95, 9.50 (all broad; latter three are averaged positions for para, ortho, and meta protons of phenyl rings). (b) X = Cl, red solid (from ethanol): mp 63–66 °C dec; visible (benzene) λ_{max} 484, 838 nm; NMR (benzene-d_6) δ 0.75, 4.15, 4.30, 7.60 (all broad).

(14) (a) The dibromonickel(II) complex of 1,2-bis(diphenylphosphino)ethane is diamagnetic and that of 1,3-bis(diphenylphosphino)propane is ~50% diamagnetic in solution.[14b] (b) Van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, *5*, 1968.

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Reaction between Chlorophosphoranes and Benzyltri-*n*-butylammonium or Trimethylsilyl Azides. Direct Observation of Hexacoordinate Intermediates in Displacement Reactions at Pentacoordinate Phosphorus

Sir:

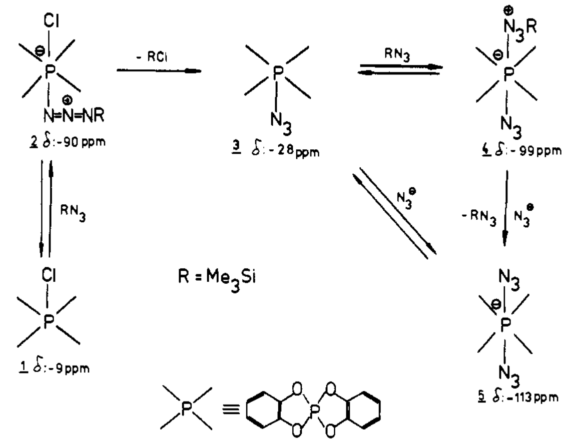
The number of hexacoordinate phosphorus compounds that has been prepared is relatively small. They are formed either from nucleophilic anions and neutral pentacoordinate phosphoranes[1,2]

$$R_5P + Nu^- \rightarrow R_5P^- \text{-} Nu$$

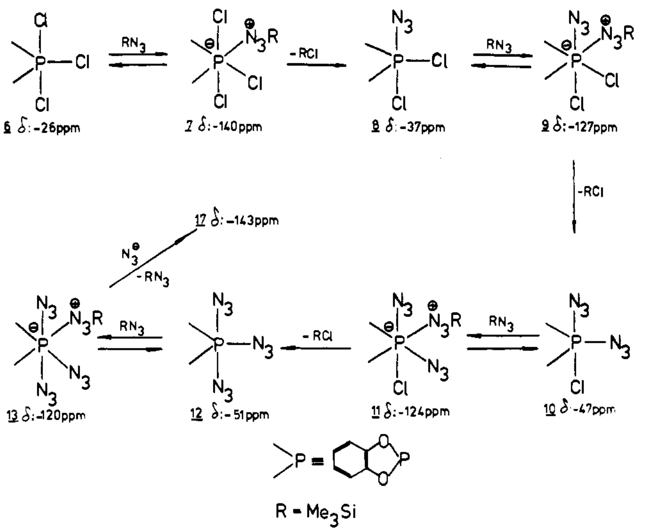
or from phosphoranes and amines.

$$R_5P + NR_3' \rightarrow R_5P^- \text{-} N^+R_3'$$

Scheme I



Scheme II



In the latter case they have the charge distribution of a zwitterion.[2,3] There is growing realization that hexacoordinate phosphorus species may play an important role in organophosphorus chemistry and biochemistry. Ramirez and his collaborators have postulated hexacoordinate intermediates from the observations of base catalysis in the hydrolysis of cyclic phosphoranes.[4]

Archie and Westheimer have provided strong support for the hypothesis that hydrolysis of some acyclic phosphoranes proceeds via hexacoordinate phosphorus intermediates or transition states.[5] There remains the intriguing problem of the extent to which the hexacoordinate compounds are involved as intermediates in the substitution at the pentacoordinate phosphorus atom.[6] We describe herein results which reveal that such hexacoordinate phosphorus complexes are indeed formed as observable species in the reaction between chlorophosphoranes containing single or double catechol bidentate ligands with benzyltri-*n*-butylammonium and trimethylsilyl azides.

The reactions of chlorophosphoranes **1** and **6** with trimethylsilyl or benzyltri-*n*-butylammonium azides were performed under the following conditions. To a solution of the chlorophosphorane in ethyl chloride or nitropropane was added the azide at the temperature of liquid nitrogen. The mixture was then warmed gradually and the changes in species present were observed by FT proton-decoupled ^{31}P NMR spectroscopy. The experimental results together with the structural assignments for intermediates and final products are given in Schemes I-III.

Reaction between bis(*O*-phenylene)chlorophosphorane **1** and 1 molar equiv of trimethylsilyl azide at −100 °C in ni-

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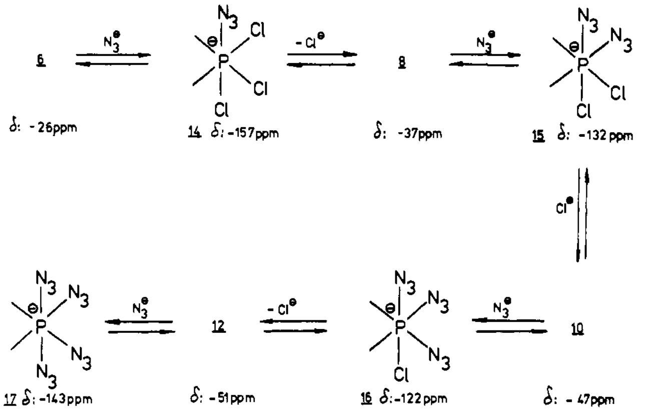
Scheme III



tropropane solution led to the adduct **2** as the major product, accompanied by some azidophosphorane **3**, unchanged chlorophosphorane **1**, and traces of compound **4**. A large increase in the amount of azidophosphorane **3**, formed by elimination of trimethylsilyl chloride, was observed on warming of the reaction mixture to −60 °C. At this temperature **3** became the major product while **2** and **4** were minor components and the chlorophosphorane **1** disappeared. Reaction with 2 equiv of trimethylsilyl azide afforded **4** as the main product, which in turn was transformed into **5** by the action of N_3^-. The azidophosphorane **3**, prepared in an independent way by nucleophilic displacement of the chloride group in **1** by the action of benzyltri-*n*-butyl ammonium azide at −80 °C in nitropropane, had the same ^{31}P NMR chemical shift and was transformed by the second equivalent of azide salt into the hexacoordinate salt **5**. The apparent equilibrium between **3** and **5** and between **3** and **4** was noted. These types of equilibria were observed by other investigators.[7] The chemical shifts related to 85% phosphoric acid of compounds **2**, **4**, and **5** are in the high-field range of −90 ppm to −114 ppm, which must be associated with hexacoordinate phosphorus derivatives. The proposed zwitterion structures of **2** and **4** are analogous to those accepted for adducts of phosphorane amines.[3]

Reaction between *O*-phenylenetrichlorophosphorane **6** and 3 equiv of trimethylsilyl azide in ethyl chloride solution led to the hexacoordinate adduct **7** and traces of the pentacoordinate dichloroazidophosphorane **8**. After slow warming to −90 °C, the amount of **7** determined by integration of the ^{31}P NMR signals decreased to 50% with parallel increase of the product **8** to 30%. Other components of the mixture were the diazide **10** (20%) and traces of the hexacoordinated diazide **9**. At −75 °C, **7** (15%), **8** (15%), **9** (8%), **10** (60%), and the triazide **11** (9%) were all seen. After slow warming to room temperature the spectrum indicated further the azides **12** (80%) and **13** (20%). The full picture of the above reaction is presented in Scheme II.

The structural assignments from ^{31}P NMR spectroscopy were supported by evidence from nucleophilic displacement reactions between **6** and benzyltri-*n*-butylammonium azide, described in Scheme III. The addition of trimethylsilyl chloride did not affect the reaction picture. Therefore, the elimination of trimethylsilyl chloride in reactions **7** → **8**, **9** → **10**, and **11** → **12** is most likely irreversible.

Treatment of **6** with 3 equiv of benzyltri-*n*-butylammonium azide in nitropropane solution at −100 °C results in the formation of the hexacoordinate phosphorus complex **14** (50%) accompanied by the hexacoordinate species **15** (20%) and **16** (10%) and phosphoranes **8** (10%) and **10** (10%). At −50 °C the concentration of the intermediate **14** decreases while **15** and **16** increase with parallel formation of the phosphorane **12**. At −20 °C the major product is **17**. Nucleophilic displacement of the chlorine atom by the azide anion in chlorophosphoranes thus proceeds via individually distinct hexacoordinate species.

The experiments describing the effect of added reagents and temperature and solvent, while qualitative, are indicative of the occurrence of various possible types of equilibria. No attempts have been made at this stage to define these equilibria rigorously. Similar observations of discrete hexacoordinate species in the reaction involving trimethylsilyl azide and azide anion were made in the case of other halogenophosphoranes.

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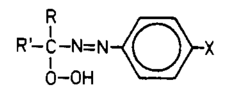
Hydroxylation of Benzene with α-Azohydroperoxide. A Novel Route for Generation of Hydroxyl Radical and Its Reaction in Anhydrous Media

Sir:

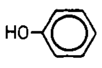
Recently the importance of hydroxyl radical as an intermediate in many chemical and biological processes has been documented, while the reactions of hydroxyl radical with organic compounds have been studied extensively.[1,2] In these cases, hydrogen peroxide or water is employed for a source of hydroxyl radical as demonstrated in the reactions with Fenton's reagent, radiation chemical techniques, and photochemical techniques,[1-4] which are, however, carried out usually under hydrous conditions. We now report that α-azohydroperoxide (**1**) can be another source of hydroxyl radical in anhydrous media, hydroxylating aromatic molecules to yield corre-



1a: R = Ph; R' = H; X = Br

1b: R = R' = CH_3; X = Br

1c: R = Ph; R' = H; X = CH_3



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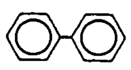

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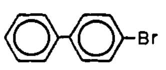

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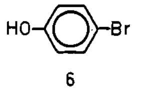

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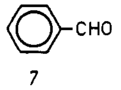

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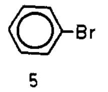

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