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Reactions of Triphenylsilyl Azide with Tetraphenyldiphosphine and Diphenylphosphine

KAY L. PACIOREK[1] AND REINHOLD H. KRATZER[1]

U. S. Naval Ordnance Laboratory, Corona, California,
and
MHD Research, Inc., Newport Beach, California

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Triphenylsilyl azide reacts readily with triphenylphosphine to give the phosphinimine.[2,3] With chlorophosphines exchange of the azido and chloro groups occurs concurrently with nitrogen evolution resulting in the formation of phosphonitriles and quantitative recovery of the alkyl- or arylsilyl moiety in the form of the chloride.[4] The reaction of phosphine with phenyl azide investigated by Staudinger and Hauser[5] is the only case in which the behavior of a P–H bond during the interaction with an azide could be studied. Although the authors seem to have failed in the isolation of a pure material, they point out that the initial reaction product is probably susceptible to rearrangement.

$$C_6H_5N_3 + PH_3 \longrightarrow \{C_6H_5N{=}PH_3\} + N_2 \longrightarrow C_6H_5NH{-}PH_2$$
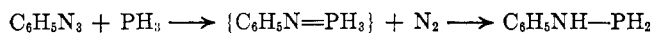
No results have as yet been published on the reactivity of azides toward diphosphines, which are known to be prone to rearrangements originating in the breaking of the phosphorus–phosphorus bond.[6]

The present work was thus undertaken to investigate the behavior of the two different types of phosphines toward triphenylsilyl azide.
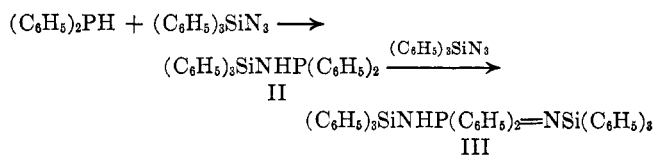
Tetraphenyldiphosphine was prepared following the procedure of Kuchen and Buchwald;[7] however, the product exhibited a somewhat different infrared spectrum from that reported by the above-mentioned authors. Of special significance is the weakness of the absorption in our spectrum at 1180 cm^{-1}, where a strong band was observed by Kuchen and Buchwald. We attribute the absorption at 1180 cm^{-1} to the presence of the oxide.[8,9] Since other analytical data given by these authors show their material to be pure, we believe that oxidation evidenced in their infrared spectrum occurred during either sample preparation or the actual recording of the spectrum.

Interaction of tetraphenyldiphosphine with triphenylsilyl azide afforded the desired doubly oxidized

$$(C_6H_5)_3SiN{=}P(C_6H_5)_2P(C_6H_5)_2{=}NSi(C_6H_5)_3$$
$$I$$
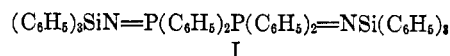
product I. No other material was isolated from the reaction mixture.

The reaction of diphenylphosphine with triphenylsilyl azide did not proceed very readily. From the equimolar reaction mixture two products were isolated with Si:P ratios of 1:1 and 2:1. The reaction sequence can be best explained by the equation depicted below, wherein the monoadduct II reacts with an additional mole of silyl azide to give compound III, which now

$$(C_6H_5)_2PH + (C_6H_5)_3SiN_3 \longrightarrow$$
$$(C_6H_5)_3SiNHP(C_6H_5)_2 \xrightarrow{(C_6H_5)_3SiN_3}$$
$$II$$
$$(C_6H_5)_3SiNHP(C_6H_5)_2{=}NSi(C_6H_5)_3$$
$$III$$

contains the phosphorus in a pentavalent state. The second step appears to proceed more readily than the first step, since even though equimolar quantities of triphenylsilyl azide and diphenylphosphine were employed a 45% yield of the disubstituted material was isolated together with unreacted diphenylphosphine. If the reaction is conducted using an excess of triphenylsilyl azide only the diadduct is obtained. The proposed structures of compounds II and III are based on their infrared and P^{31} nmr spectra. The presence in compound II of a weak but sharp absorption at 3315 cm^{-1} in conjunction with a strong absorption at 905 cm^{-1} [10,11] points to the presence of the P–NH moiety. This is further supported by the absence of characteristic P–H absorption at 2440–2350 cm^{-1} and the lack of splitting in P^{31} nmr, which would be expected from a P–H group. The formation of $(C_6H_5)_3SiNHP(C_6H_5)_2{=}NSi(C_6H_5)_3$ is an additional proof of the proposed structure for compound II, since in $(C_6H_5)_3SiN{=}P(H)(C_6H_5)_2$ the phosphorus is already in a pentavalent state. The postulated structure of the diadduct III is again in agreement with its infrared and P^{31} nmr spectra (sharp band at 3315 cm^{-1}, strong absorption at 935 cm^{-1}, no absorption at 2440–2350 cm^{-1}, and lack of splitting in the nmr).

Reactions of other types of azido compounds with diphenylphosphine and other secondary phosphines are currently being investigated in order to elucidate the mechanism which leads to the formation of $(C_6H_5)_3SiNHP(C_6H_5)_2$ (II). This reaction is probably an exchange process with a peculiar mechanism due to the electronegativities involved, or a complex oxidation-reduction reaction involving more diphenylphosphine than stoichiometrically required.

Experimental Section

The reactions were conducted either in a vacuum system or in a nitrogen atmosphere with rigid exclusion of moisture and oxygen. All chemicals were purified by applicable methods. Triphenylsilyl azide, mp 84.5–85.5°, was prepared in 83% yield following the procedure of Wiberg, *et al.*;[3] diphenylphosphine, bp 163–163.5° (14.8 mm), was obtained by the method of Kuchen and Buchwald[7] in 51% yield. Melting points were determined in sealed capillaries and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer double-beam (Model 21) infrared

(1) MHD Research, Inc., Newport Beach, Calif. 92663.
(2) R. West and J. S. Thayer, *J. Am. Chem. Soc.*, **84**, 1763 (1962).
(3) N. Wiberg, F. Raschig, and R. Sustmann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 551 (1962).
(4) R. H. Kratzer and K. L. Paciorek, *Inorg. Chem.*, **4**, 1767 (1965).
(5) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).
(6) R. S. Hayter and L. F. Williams, *Inorg. Chem.*, **3**, 717 (1964), and references cited therein.
(7) W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2871 (1958).
(8) The infrared spectrum of $(C_6H_5)_2P(O)P(O)(C_6H_5)_2$, given by Kuchen and Buchwald,[7] exhibits a very strong band at 1180 cm^{-1}.
(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p 312, reports absorption in the vicinity of 1200 cm^{-1} for phosphine oxides.

(10) $(C_6H_5)_2P(O)NH_2$ exhibits a strong absorption at 910 cm^{-1}: K. L. Paciorek and R. H. Kratzer, unreported results.
(11) E. Steger, *Chem. Ber.*, **94**, 266 (1961).

spectrophotometer. The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation of Tetraphenyldiphosphine.—Following the procedure of Kuchen and Buchwald[7] a 70% yield of tetraphenyldiphosphine was obtained, mp 126–127°. The infrared spectrum (Nujol oil mull, 1430–670-cm^{-1} region) exhibited the following bands: 1430 m, 1380 m, 1325 w, 1300 w, 1183 vw, 1088 vw, 1065 m, 1020 m, 997 m, 919 w, 905 w, 744 m, 734 s, and 692 s cm^{-1}.

Anal. Calcd for $C_{24}H_{20}P_2$: C, 77.83; H, 5.44; P, 16.73; mol wt, 370.37. Found: C, 77.59; H, 5.60; P, 16.89; mol wt, 355 (cryoscopic in benzene).

Preparation of $(C_6H_5)_3SiN=P(C_6H_5)_2P(C_6H_5)_2=NSi(C_6H_5)_3$.—In a capsule was sealed *in vacuo* triphenylsilyl azide (6.02 g, 20 mmoles), benzene (50 ml), and tetraphenyldiphosphine (3.70 g, 10 mmoles). The mixture was heated at 80–115° (gradually raising the temperature) over the period of 14 days. On opening to a vacuum system only 17.13% of nitrogen was collected. Subsequently, benzene was removed *in vacuo* at room temperature, and the residue was heated at 140° for 3 days (until no additional increase in pressure was observed). Total amount of nitrogen collected was 18.57 mmoles (93% yield). The product was crystallized from benzene–heptane mixture followed by boiling with acetonitrile. This material was then dried overnight at 70° *in vacuo*, mp 236–238°. The infrared spectrum (Nujol mull, 1430–670-cm^{-1} region) exhibited the following bands: 1430 w, 1370 m, 1300 m, 1250 w, 1100 m, 740 w, 722 m, and 700 s cm^{-1}.

Anal. Calcd for $C_{60}H_{50}P_2Si_2N_2$: C, 78.56; H, 5.50; P, 6.76; Si, 6.13; N, 3.06; mol wt, 916.61. Found: C, 78.70; H, 5.59; P, 6.96; Si, 6.41; N, 3.18; mol wt, 847 (in chloroform, using a Mechrolab osmometer).

Treatment of $(C_6H_5)_2PH$ with $(C_6H_5)_3SiN_3$. A. Using Equimolar Quantities.—In a nitrogen atmosphere $(C_6H_5)_3SiN_3$ (9.04 g, 0.03 mole) in ether (90 ml) was treated with $(C_6H_5)_2PH$ (5.5 g, 0.03 mole) in ether (10 ml); the solution was then refluxed overnight. Subsequently, the ether was removed *in vacuo* and the residue was heated to 100° for 10 days. On cooling a solid mass was obtained. This material failed to show in its spectrum any absorption in the vicinity of 2130 cm^{-1}, indicating an absence of azido moieties. Repeated crystallization from heptane gave 4.67 g (45% yield, based on triphenylsilyl azide employed) of $(C_6H_5)_3SiNHP(C_6H_5)_2=NSi(C_6H_5)_3$: mp 161–162°; P^{31} nmr, a single peak at −43 ppm (in benzene solution, referenced to 85% H_3PO_4). The infrared spectrum (Nujol oil) exhibited the following bands: 3315 w (N–H), 2900 s, 2858 w (Nujol), 1587 w (C=C), 1460 s (Nujol), 1430 s (PC$_6$H$_5$), 1375 s (Nujol), 1290 s, 1250 s, 1180 m, 1155 w, 1105 s, 1025 m, 997 m, 935 s (PNH), 791 m, 744 s, 735 s, and 694 s cm^{-1}.

Anal. Calcd for $C_{48}H_{41}PSi_2N_2$: C, 78.65; H, 5.64; P, 4.23; Si, 7.41; N, 3.55; mol wt, 733.03. Found: C, 78.26; H, 5.72; P, 4.25; Si, 7.41; N, 3.55; mol wt, 670 (in benzene, using a Mechrolab osmometer).

The compound $(C_6H_5)_3SiNHP(C_6H_5)_2=NSi(C_6H_5)_3$ was heated in air above its melting point; no change resulted.

The mother liquors, from the recrystallization of $(C_6H_5)_3SiN$-HP$(C_6H_5)_2=NSi(C_6H_5)_3$, were freed from solvent on the vacuum line. Unreacted $(C_6H_5)_2PH$ was removed *in vacuo* at ca. 95°; subsequent sublimation at 135° afforded $(C_6H_5)_3SiNHP(C_6H_5)_2$ (2.14 g, 19% yield). This sublimate was recrystallized from heptane: mp 148–149°; P^{31} nmr, a single peak at −26.6 ppm (in benzene solution, referenced to 85% H_3PO_4). The infrared spectrum (Nujol oil mull) exhibited the following bands: 3320 w (N–H), 2900 s, 2855 s (Nujol), 1460 s (Nujol), 1430 (PC$_6$H$_5$), 1380 m (Nujol), 1307 w, 1220 m, 1212 m, 1190 w, 1117 s, 1030 w, 1000 w, 905 s (P–NH), 741 s (shoulder), 733 s, and 698 s cm^{-1}.

Anal. Calcd for $C_{30}H_{26}PSiN$: C, 78.40; H, 5.70; P, 6.74; Si, 6.11; N, 3.05; mol wt, 459.61. Found: C, 78.62; H, 5.83; P, 6.63; Si, 5.75; N, 2.92; mol wt, 455 (in benzene, using a Mechrolab osmometer).

B. Excess $(C_6H_5)_3SiN_3$.—In a sealed, evacuated ampoule $(C_6H_5)_2PH$ (582.0 mg, 3.126 mmoles) was heated with $(C_6H_5)_3SiN_3$ (2.541 g, 8.430 mmoles) at 110–115° for 90 hr. On opening to the vacuum system, nitrogen (6.349 mmoles) was obtained, thus $N_2:(C_6H_5)_2PH = 2.03:1$, showing that only the diadduct $(C_6H_5)_3SiNHP(C_6H_5)_2=NSi(C_6H_5)_3$ was formed. The reaction mixture on washing with ether, followed by crystallization of the ether-insoluble material from heptane, afforded 1.62 g (71% of the diadduct, mp 161–162°). Additional quantities of the product remained in ether and heptane mother liquors admixed with the excess of $(C_6H_5)_3SiN_3$.

The Synthesis of 19-Oxygenated Cardenolides. I. A Convenient Preparation of 19-Hydroxydesoxycorticosterone

R. DEGHENGHI

Ayerst Research Laboratories, Montreal, Canada

In the recently described total synthesis of periplogenin[1] we took advantage, as an alternative and practical shortcut, of the microbiological hydroxylation in 14α of desoxycorticosterone as a means of introducing the 14,15 double bond and subsequently, by a sequence of steps well known in the steroid literature,[2] the 14β-hydroxyl group characteristic of this class of cardioactive substances.

It seemed attractive therefore to prepare by an efficient method 19-hydroxydesoxycorticosterone as a substrate for 14α-hydroxylation. By applying essentially the already disclosed synthetic sequence used for periplogenin,[1] 19-hydroxy-DOC could be considered a starting material for the synthesis of strophanthidol and related 19-oxygenated cardenolides.

It is of interest that 19-hydroxy-DOC was first obtained by degradation of strophanthidin itself.[12]

The commercially available 21-hydroxypregnenolone diacetate I was converted to the chlorohydrin II in 70% yield by allowing it to react with freshly prepared and chlorine-free hypochlorite solution in acetone. The 6,19-oxide III was obtained in 70% yield from chlorohydrin II by the iodine–lead tetraacetate reaction[13] and saponified to the diol IV with KHCO$_3$ in aqueous methanol in about 90% yield.

(1) R. Deghenghi, A. Philipp, and R. Gaudry, *Tetrahedron Letters*, 2045 (1963).

(2) A recent statement[3] claiming priority over a number of steps well documented in the previous literature (*e.g.*, for the addition of HOBr to a 14,15 double bond followed by Raney nickel debromination, *cf.* Ringold, *et al.*;[4] followed by β-epoxide formation, *cf.* Meister,[5] Bloom, *et al.*,[6] and Reichstein;[7] *cf.* also Meyer[8] and Bernstein;[9] for the hydride reduction of a 14,15β epoxide without epimerization of the 17β chain, *cf.* Meyer[10] and ref 5; also Kondo[11] and references cited therein), deserves little comment.

(3) C. R. Engel and G. Bach, *Steroids*, **3**, 593 (1964).

(4) H. J. Ringold, F. Sondheimer, and G. Rosenkrantz, U. S. Patent 2,889,346 (June 2, 1959; priority Dec 23, 1953).

(5) P. D. Meister, U. S. Patent 2,930,791 (March 29, 1960; applied June 7, 1955).

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(7) A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **45**, 943 (1962).

(8) P. Hofer, H. Linde, and K. Meyer, *ibid.*, **45**, 1041 (1962).

(9) M. Heller, F. J. McEvoy, and S. Bernstein, *Steroids*, **3**, 193 (1964).

(10) H. Linde and K. Meyer, *Helv. Chim. Acta*, **42**, 807 (1959).

(11) H. Kondo, U. S. Patent 3,134,772 (May 26, 1964; priority May 1, 1961).

(12) G. W. Barber and M. Ehrenstein, *J. Org. Chem.*, **19**, 1758 (1954).

(13) J. Kalvoda, K. Heusler, G. Anner, and A. Wettstein, *Helv. Chim. Acta*, **46**, 1017 (1963).