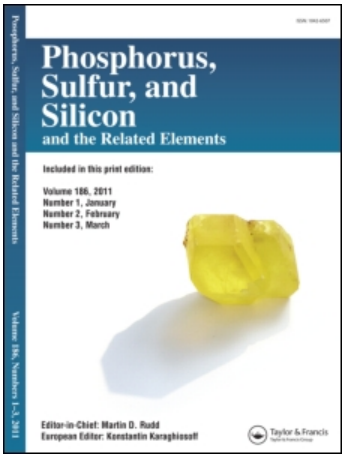

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

On the Reaction of Phosphorous Acid Esters with Nucleophiles in the Presence of Carbon Tetrachloride

Lothar Riesel[a]; Eckhard Herrmann[a]; Jörg Steinbach[a]
[a] Sektion Chemie, Humboldt-Universität Berlin und Technische Universität Dresden, G.D.R.

To cite this Article Riesel, Lothar , Herrmann, Eckhard and Steinbach, Jörg(1983) 'On the Reaction of Phosphorous Acid Esters with Nucleophiles in the Presence of Carbon Tetrachloride', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 253 — 256
To link to this Article: DOI: 10.1080/03086648308076014
URL: http://dx.doi.org/10.1080/03086648308076014

Phosphorus and Sulfur, 1983, Vol. 18 pp. 253-256
0308-664X/83/1801-0253/$18.50/0

ON THE REACTION OF PHOSPHOROUS ACID ESTERS WITH NUCLEOPHILES IN THE PRESENCE OF CARBON TETRACHLORIDE

LOTHAR RIESEL, ECKHARD HERRMANN AND JÖRG STEINBACH
Sektion Chemie, Humboldt-Universität Berlin und Technische Universität Dresden, G. D. R.

Abstract Esters of N-Phosphoryl phosphazenes are prepared by a modified Atherton-Todd reaction from di- and triesters of phosphorous acid, sodium azide, and carbon tetrachloride in high yields. The utilization of the two-component system trialkyl phosphite/ carbon tetrachloride for preparing phosphazenes, $(RO)_3P{=}NY$ (Y: $PO(OR)_2$, SO_2R, COR, CN), and dialkoxyphosphoryl compounds, $(RO)_2P(O)X$ (X: NHR, NR_2, OPh, CN, F, NCO), is presented.

In the presence of bases carbon tetrachloride is able to oxidize diesters of phosphorous acid (Atherton-Todd reaction) (Eq. (1)), whereas it reacts with triesters of phosphorous acid according to the Michaelis-Arbusov reaction[1] (Eq. (2)).

$$(RO)_2P(O)H + CCl_4 \xrightarrow{(b)} (RO)_2P(O)Cl + CHCl_3 \quad (1)$$

$$(RO)_3P + CCl_4 \longrightarrow (RO)_2P(O)CCl_3 + RCl \quad (2)$$

In Michaelis-Arbusov reactions as well as in systems consisting of CCl_4 and other tricoordinated phosphorus compounds tetracoordinated quasiphosphonium compounds are formed as reactive intermediates. For that reason such two-component systems exhibit a considerably synthetic potential, which has been shown in numerous instances for the systems PPh_3/CCl_4 and $P(NMe_2)_3/CCl_4$ by Appel[2] and for the system P_4/CCl_4 by Lehmann.[3] Contrary to these systems the system trialkyl phosphite / carbon tetrachloride has hardly been used for synthetic purposes. Only its reactions with alcohols, thioalcohols, and phenol are described.[1]

APPLICATION OF THE ATHERTON-TODD REACTION TO THE SYNTHESIS OF N-PHOSPHORYL PHOSPHAZENES[4]

Esters of N-phosphoryl phosphazenes, $(RO)_2P(O)-N=P(OR')_3$, I, are bioactive compounds. As their synthesis by the Staudinger reaction (Eq. (4)) requires manipulations with the highly toxic phosphoryl azides, $(RO)_2P(O)N_3$, we studied possibilities for their in situ formation by combining the Atherton-Todd reaction with the displacement of Cl^- by N_3^- and the Staudinger reaction (Eqs. (3)-(5)).

$$(RO)_2P(O)H + CCl_4 + N_3^- \xrightarrow{(b)} (RO)_2P(O)N_3 + Cl^- + CHCl_3 \quad (3)$$

$$(RO)_2P(O)N_3 + P(OR')_3 \longrightarrow \underline{I} + N_2 \quad (4)$$

$$(RO)_2P(O)H + CCl_4 + N_3^- + P(OR')_3 \longrightarrow \underline{I} + N_2 + Cl^- + CHCl_3 \quad (5)$$

Reaction (3) only takes place in the presence of a base (e.g. triethylamine), but even then it is not suited for preparing phosphorylazides on a preparative scale. In the presence of trialkyl phosphites, however, I are formed in nearly quantitative yield, even in the absence of an amine. Only by using phosphites containing aryl groups a base has to be added. In this way we succeeded in preparing about 40 different esters (R, R': Me, Et, Pr, n-Bu, i-Bu, Ph) by a "one-pot" synthesis in high yields.[4]

In our opinion dialkyl phosphite anions, $(RO)_2P(O)^-$, play a key role in the reaction mechanism. They can be formed either by the reaction of $(RO)_2P(O)H$ with a basic catalyst or with the charge transfer complex of $P(OR)_3$ with CCl_4. The anion reacts as a strong nucleophile with CCl_4 via a charge transfer complex to phosphoric acid ester chloride (Eq. (6)):

$$(RO)_2PO^- + CCl_4 \rightleftharpoons (RO)_2(O)P..Cl..CCl_3^- \rightleftharpoons (RO)_2P(O)Cl + CCl_3^-$$

The CT-complex as well as the very basic trichloromethanide anion should effect the deprotonation of additional dialkyl phosphite. Thus, the reaction proceeds automatically, if the equilibria are continuously disturbed by removing the reaction products. Such conditions are given in the system according to Eq. (5).

SYNTHESES WITH THE TWO-COMPONENT SYSTEM TRIALKYL PHOSPHITE / CARBON TETRACHLORIDE

The two-component system trialkyl phosphite / CCl_4 reacts with various nucleophiles containing protons. The type of reaction taking place depends on the number of protons and their acidity.

Amides of acids and cyanamide react with $(RO)_3P/CCl_4$ in the presence of bases forming phosphazenes (Eq. (7)).

$$(RO)_3P + H_2NY + CCl_4 \xrightarrow{(b)} (RO)_3P{=}N{-}Y + CHCl_3 + HCl \qquad (7)$$

(Y: $(RO)_2P(O)$, $PhSO_2$, $PhSO_2$, PhCO, NC)

In the case of cyanamide good yields (75 %) can only be achieved by using NaNHCN. On heating rearrangement of $(EtO)_3P{=}NCN$ occurs to give $(EtO)_2P(O){-}NEt{-}CN$. The preparation of $(EtO)_3P{=}NC(O)Ph$ requires the presence of an excess of amine as HCl-acceptor since HCl catalyzes its decomposition into PhCN and $(EtO)_3PO$.

For preparing I instead of $(RO)_2P(O)NH_2$ mixtures of di- and trialkyl phosphites and ammonia can be used (Eqs. (8) and (9)).

$$(RO)_2P(O)H + (RO)_3P + 2\ CCl_4 + 3\ NH_3 \longrightarrow \underline{I} + 2\ CHCl_3 + 2\ NH_4Cl \qquad (8)$$

$$2\ (RO)_3P + 2\ CCl_4 + 2\ NH_3 \longrightarrow \underline{I} + 2\ CHCl_3 + RCl + NH_4Cl \qquad (9)$$

However, in both cases phosphorylamides, $(RO)_2P(O)NH_2$, are formed as main products. I is only obtained in a 20 % yield.

Because of their higher basicity aliphatic amines react with the two-component system under the elimination of alkyl chloride forming phosphoryl amides in about 80 % yield (Eq. (10)).

$$(RO)_3P + H_2NR' + CCl_4 \longrightarrow (RO)_2P(O)NHR' + RCl + CHCl_3 \qquad (10)$$

(R: Et, Bu; R': n-Pr, n-Bu, $PhCH_2$, Ph)

Caused by ligand exchange reactions diamides $(RO)P(O)(NHR')_2$ are formed, too. The formation of phosphazenes (10 %) according to Eq. (7) could only be observed in the case of aniline. But in spite of its medium NH-acidity NEt_3 has to be added as HCl-acceptor. Otherwise only dialkoxyphosphoryl anilides (90 %) are obtained for the phosphazene is easily dealkylated by anilinium chloride (Eq. (11)).

$$PhN{=}P(OR)_3 + PhNH_3Cl \longrightarrow PhNH{-}P(O)(OR)_2 + PhNH_2 + RCl \quad (11)$$

In the case of sterically hindered amines the Michaelis-Arbusov reaction is favoured. So, secondary amines yield $(RO)_2P(O)NR'_2$ only to an extent of about 10 %. The main products are $Cl_3CPO(OR)_2$ (≈15 %) (Eq. (2)) and its dealkylation product $Cl_3C{-}P(O)(OR)O^-$ NR'_2RH^+ (≈50 %).

Weak acids possessing only one proton react with $P(OR)_3/CCl_4$ in the presence of catalytic amounts of NEt_3 forming acyl derivatives of phosphoric acid esters (Eq. (12)).

$$(RO)_3P + HX + CCl_4 \xrightarrow{(b)} (RO)_2P(O)X + CHCl_3 + RCl \quad (12)$$

(X = OPh (yield: 51 %; δ^{31}P: -7.1 ppm); CN (73 %; -21.7 ppm); NCO (25 %; -13.1 ppm); F (44 % - 13.3 ppm))

In all these reactions, initially, the formation of a CT-complex $(RO)_3P..Cl..CCl_3$ and its conversion into the quasiphosphonium salt $(RO)_3PCl^+ CCl_3^-$ can be supposed. Both compounds react with substances containing protons under the formation of chloroform and the displacement of chloride leading to the quasiphosphonium salts $(RO)_3PY^+ Cl^-$. On this stage ligand exchange reactions are possible. The route of stabilization of this intermediate depends on the electrophilic properties of the atoms and groups in the molecule. If the acidity of further H-atoms of Y is too small or in cases that no further H-atom exists alkyl chloride is eliminated yielding dialkoxyphosphoryl compounds. In the presence of acid H-atoms at Y, especially in basic medium, HCl-elimination takes place resulting in the formation of phosphazenes.

REFERENCES

1. H. Teichmann, Z. Chem., 14, 216 (1974).
2. R. Appel, Angew. Chem., 87, 863 (1975).
3. H.-A. Lehmann, Khim. i primen. fosfororg. soedin., Trudy Jubil. 6. Konf., Dec. 1977 Kiev (Naukova dumka, Kiev, 1981), p. 194. L. Riesel, Z. Chem., 19, 161 (1979).
4. L. Riesel, J. Steinbach and E. Herrmann, Z. anorg. allg. Chem., 502, 21 (1983).