Synthesis and Reactivity of the First Spectroscopically Observed 1*H*-Diazirine

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Abstract: *C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphino]nitrilimine (**1**) reacts at −50 °C with tetrachloro-*o*-benzoquinone (TCBQ) leading to *C*-thioxophosphoranyl-*N*-phosphoranyldiazirine **3**, which rearranges above −30 °C into heterocycle **4** (84% yield). 1*H*-Diazirine **3**, which has been characterized by ^{31}P and ^{13}C NMR spectroscopy, reacts with triisopropylsilyl trifluoromethanesulfonate and trimethylphosphine, affording *N*-phosphonionitrilimine **5** and phosphorus ylide **6** in 51 and 95% yields, respectively. [Bis(diisopropylamino)-thioxophosphoranyl][bis(diisopropylamino)phosphino]diazomethane (**8**) also reacts with TCBQ leading to **4** (90% yield) via **3**. This result is rationalized by the formation of the (thioxophosphoranyl)(phosphoranyl)diazomethane **9**, which is in equilibrium with the ion pair thioxophoranyl diazo anion **21**/phosphonium **12**; attack of the nitrogen end of the diazo anion on the phosphorus cation **12** affords **3**. The transient formation of the ion pair **21**/**12** has been proved by trapping reactions with CH_3OD and $CDCl_3$ and by the reaction of the lithium salt of the [bis-(diisopropylamino)thioxophosphoranyl]diazomethane (**13**) with phosphonium salt **12**, which also leads to **3** and **4** (82% yield).

Introduction

Among the theoretical concepts that constitute the rational basis of modern chemistry there are some controversial constructs, but perhaps none to such a degree as those of aromaticity and antiaromaticity.[1] Nevertheless, one should admit that usually (4*n*+2)-π-electron ring systems are stable, while those with 4*n*-π-electrons are unstable. Only a few 4-π-electron four-membered-ring systems have been isolated,[2] and very little is known concerning 4-π-electron three-membered rings.[3]

For several years, we have been interested in the chemistry of diazo compounds and of their structural isomers.[4] Indeed, diazomethane **C** is unique among small molecules since it has six potentially accessible isomers.[5] Experimentally stable derivatives of all possible isomers are known, except for the antiaromatic 1*H*-diazirine **G**.[6] Theoretical studies on the relative stabilities of compounds **A**−**G** have been done.[7] Interestingly, the antiaromatic isomer **G** was found to be only slightly higher in energy than the nitrilimine **F** by 14.2 kcal·mol^{-1} at the HF/6-31G level,[7c] 8.4 kcal·mol^{-1} at the HF/3-21G* level (with electron correlation),[7b] and only 1.1 kcal·mol^{-1} at the G2(MP2) level[7d] (Scheme 1).

There is some experimental evidence for the rearrangement of nitrilimines **F** into carbodiimides **B**.[8] It has been postulated that this isomerization proceeds through a 1*H*-diazirine intermediate **G**, although ab initio calculations predicted a high energy barrier for the ring closure of **F** to **G**.[7b,d] In the same way, a few examples of the rearrangement of nitrilimines **F** into diazo derivatives **C** have been described,[8c,9] although here also the energy barrier for the 1,3-hydrogen shift has been calculated to be high.[7b,d] Considering the thermodynamics, these two isomerizations are not surprising since carbodiimides **B** and diazo derivatives **C** are supposed to be some 50 and 25 kcal·mol^{-1}, respectively, lower in energy than **F**[7] (Scheme 1).

Here, we report spectroscopic and chemical evidence for the formation of a relatively stable 1*H*-diazirine from a nitrilimine as well as from a diazo derivative. The possibility of the unprecedented rearrangement of a diazo derivative into a nitrilimine is also discussed.

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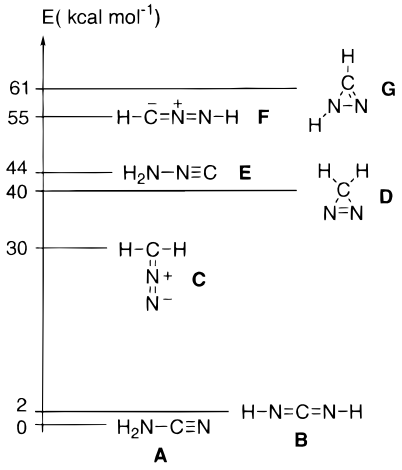
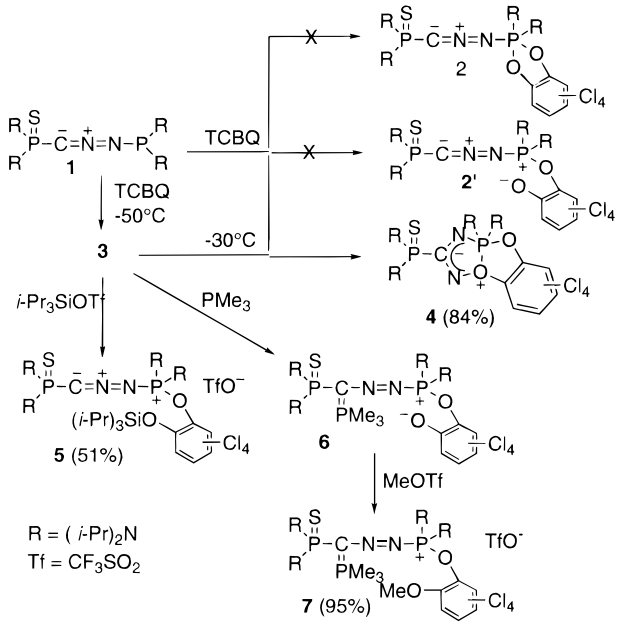
Scheme 1



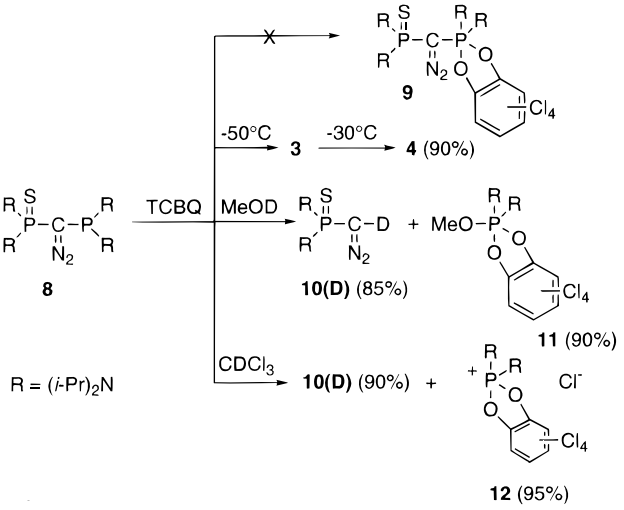
Scheme 2



Results

Preliminary studies on the reactivity of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphino]nitrilimine (**1**)[10] with tetrachloro-*o*-benzoquinone (TCBQ) have shown some striking results.[11] Indeed, although quinones are known to react with phosphines to give, depending on the nature of the phosphorus substituents, either the corresponding neutral phosphoranes or alternatively the open zwitterionic compounds,[12] none of the expected nitrilimines **2** or **2′** were formed; instead the bicyclic compound **4** was obtained in 84% yield (Scheme 2).[11] Just after the addition of TCBQ to a solution of **1** at −50 °C, a green color appeared, which faded on warming to −30 °C. When the reaction was monitored at −50 °C by ^{31}P and ^{13}C NMR spectroscopy, an intermediate **3** was detected. This compound **3** is stable for several months in solution at −50 °C, but readily rearranges into **4** at −30 °C. Because of its instability and its high solubility in most of the classical solvents, all attempts to obtain crystals suitable for an X-ray diffraction study failed. The structure of **3** will be commented upon in the Discussion.

Scheme 3



Compound **3** cleanly reacted at −40 °C with triisopropylsilyl triflate, affording the *N*-phosphonio-substituted nitrilimine **5**, which was isolated in 51% yield (Scheme 2). This compound has been fully characterized by spectroscopic methods. Typical for the nitrilimine skeleton[4a] are the strong infrared absorption at 2181 cm^{-1}, the high-field chemical shift of the thioxophosphoranyl phosphorus atom (+27.3, J_{PP} = 7.1 Hz), and the signal of the CNN carbon at 70.4 (J_{PC} = 89.9 and 13.9 Hz).

A clean reaction also occurred upon addition of trimethylphosphine to a THF solution of **3** at −40 °C leading directly to phosphorus ylide **6**. The structure of **6** was readily apparent from the ^{31}P NMR (PS, +64, J_{PP} = 107.0 and 3.6 Hz; PO, +31, J_{PP} = 5.5 and 3.6 Hz; MeP, +1.7, J_{PP} = 107.0 and 5.5 Hz;) and the ^{13}C NMR spectra (CNN, 126, J_{PC} = 163 and 29 Hz). To confirm the zwitterionic structure of **6**, alkylation of the phenoxide group was carried out with methyl triflate, affording **7**, which was isolated in 95% yield (Scheme 2).

Regitz *et al.* have recently reported that a variety of α-diazophosphines react with TCBQ, affording the corresponding (diazoalkyl)phosphoranes.[13] Very surprisingly, it appeared that the addition of TCBQ to a dichloromethane or THF solution of the diazo isomer of nitrilimine **1**, namely, the [bis(diisopropylamino)thioxophosphoranyl][bis(diisopropylamino)phosphino]-diazomethane (**8**), did not lead to the expected σ^5-phosphorus substituted diazo compound **9**, but gave rise to the bicyclic compound **4** (90% yield). Once again, when the reaction was monitored at −50 °C, the intermediate **3** was detected (Scheme 3).

When the reaction of diazo **8** with TCBQ is carried out at −78 °C in THF, in the presence of a large excess of deuterated methanol, after workup we isolated the *C*-deuterio diazo compound **10(D)** and the methoxyphosphorane **11**, which were isolated in 85 and 90% yields, respectively. The physical data for **10(D)** and for the corresponding nondeuterated diazo compound **10**[14] are quite comparable [IR 2092 (H) and 2093 (D) cm^{-1}] except for the ^{31}P NMR proton-coupled spectrum, which appeared as a quintet (J_{PH} = 18.7 Hz), instead of a doublet of quintets (J_{PH} = 10.5 and 18.6 Hz). Similarly, when **8** is reacted with TCBQ in deuterated chloroform, **10(D)** is

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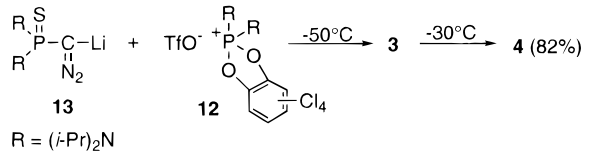
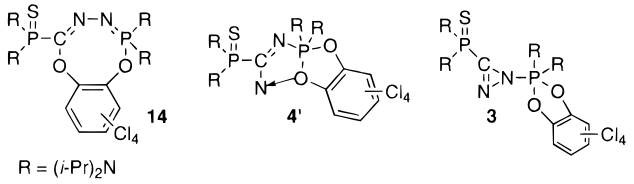
Scheme 4



Scheme 5



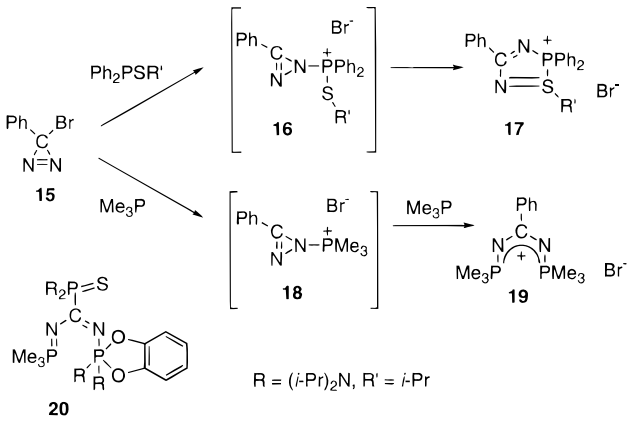
obtained in 90% yield along with the phosphonium salt **12(Cl⁻)**, which has been isolated as the trifluoromethanesulfonate salt **12(OTf⁻)** (95% yield) (Scheme 3). Salt **12(OTf⁻)** can also be prepared by addition of TCBQ to the bis(diisopropylamino)-phosphenium trifluoromethanesulfonate.

We have shown that, depending on the nature of the substituents, diazo lithium salts react with electrophiles, leading to either the corresponding nitrilimines or diazo derivatives.[4a] We therefore studied the reaction of the lithium salt of the [bis-(diisopropylamino)thioxophosphoranyl]diazomethane (**13**) with phosphonium salt **12**. Once again, a clean reaction occurred, not leading to the expected nitrilimine **2** or diazo compound **9**, but to **3**, which rearranged at −30 °C into bicyclic derivative **4** (Scheme 4).

Discussion

The first point to be discussed is the structure of the intermediate **3**. The ^{31}P NMR spectrum appeared as an AX system at +58.5 and +2.6 (J_{PP} = 13.0 Hz). The signal at low field is in agreement with the presence of a thioxophosphoranyl group which is not bonded to a nitrilimine skeleton (it would appear around +30).[4a] The high-field signal indicates the presence of a neutral phosphorane; the zwitterionic open form would give a signal around +30 ppm. Most interestingly, the signal for the quaternary carbon appears at 151.1 (dd, J_{PP} = 191.6 and 24.4 Hz). This chemical shift is well outside the range expected for a diazo or a nitrilimine fragment,[4a] but rather typical for an imine fragment; the large phosphorus−carbon coupling constant is characteristic of a carbon directly bonded to phosphorus, and thanks to a heteronuclear decoupling experiment, we can state that it is bonded to the thioxophosphoranyl phosphorus atom. Taking into account the reagents used (**1** and TCBQ) and all the structures one could imagine, the eight-membered heterocyclic structure **14** (Scheme 5) is the most consistent with the NMR data observed for **3**. However, it is difficult to rationalize the instability of such a product and especially its rearrangement to **4**. On the other hand, the final product **4** can be considered as an imidoylnitrene stabilized by a donor−acceptor interaction with an oxygen atom (**4′**) (Scheme 5). Note that the stabilization of nitrenes by coordination at nitrogen is well-known[15] and has also been postulated for oxygen.[16] Keeping this in mind, considering both the NMR data and the instability of compound **3**, and realizing that a potential precursor for an imidoylnitrene is the corresponding 1*H*-diazirine, we made the hypothesis that **3** was indeed such an antiaromatic compound.

Scheme 6



To rationalize the formation of 1*H*-diazirine **3**, the most reasonable hypothesis is to postulate the formation of transient nitrilimine **2** or **2′** (Scheme 2), which would undergo a ring closure. Then, a ring opening could lead to an imidoylnitrene, which would be trapped by the oxygen atom α to phosphorus, giving **4**. The whole process **2** → **3** → **4** corresponds in fact to the postulated mechanism of the rearrangement of nitrilimines into carbodiimides,[8] except that the imidoylnitrene is trapped instead of isomerizing into the carbodiimide. At that point, the main objection could be that it is highly debatable that the rearrangement of 1*H*-diazirines (or even oxirenes or oxazirenes) into the corresponding carbodiimides (ketenes or isocyanates) involved an imidoylnitrene (acylcarbene or acylnitrene): it could be concerted.[8ab,15,17] However, we have recently shown that bromophenyl-3*H*-diazirine (**15**)[18] reacts with diphenyl(isopropylthio)phosphine, affording five-membered heterocycle **17**.[19] In agreement with literature results,[20] we postulated that the observed product resulted from the addition of phosphine to a nitrogen atom of **15** via an S_N2' reaction, leading to a transient *N*-phosphoniodiazirine **16**. Then, the sulfur lone pair attacks at the second nitrogen of **16**, via an S_N2 reaction leading to the observed product **17** (Scheme 6). The similarities between the rearrangements of **16** to **17** and **3** to **4**, as well as between the structures of **17** and **4**, are really striking. Thus, it is clear that the transient formation of an imidoylnitrene is not necessary in the reaction process leading to **4**.

The reaction of **3** with triisopropylsilyl trifluoromethanesulfonate affording nitrilimine **5** confirms the nucleophilicity of the oxygen atom α to the phosphorus. It also demonstrates that, in **3**, the CNN skeleton is still present, in contrast with **4**, which features a NCN framework. The reaction of **3** with trimethylphosphine giving **6** confirms the presence of a CNN fragment in **3** (Scheme 2). However, the formation of **6** seems at first glance surprising. Indeed, since we have shown[19,21] that phosphines react with bromo-3*H*-diazirine **15** giving bis(adduct) **19** via *N*-phosphoniodiazirine **18**, one could imagine that adduct **20**, resulting from the attack at nitrogen, would be obtained

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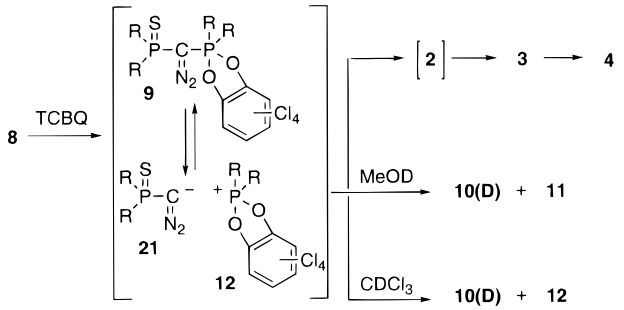
Scheme 7



(Scheme 6). In fact, literature results clearly show that the nature of the 1*H*-diazirine and of the nucleophile and the experimental conditions used have a considerable influence on the fate of the reaction.[20,22] Of course the phosphonio group in **18** has a strong electron-withdrawing effect while in **3** the phosphorus atom bonded to nitrogen is rather electron-rich.

Although the formation of the 1*H*-diazirine **3** seems reasonable from the reaction of nitrilimine **1** with TCBQ, it is much more surprising to observe the same three-membered heterocycle **3** starting from the isomeric diazo compound **8** (Scheme 3). The first step is probably the formation of the expected diazo-substituted phosphorane **9**. Then, since in **3** the pentacoordinate phosphorus atom is bonded to the nitrogen end of the CNN skeleton, we have to conclude that a diazo **9**−nitrilimine **2** rearrangement occurs. Such a rearrangement is not so surprising if we consider an equilibrium between **9** and the ion pair **21**/**12**, which is favored by the high stability of the phosphorus cation. Indeed, the formation of deuterated diazo compound **10(D)** and methoxyphosphorane **11** or phosphonium **12** in the presence of MeOD or $CDCl_3$, respectively, strongly argues for the ionization of **9** (Scheme 7). The definitive proof is given by the reaction of phosphonium **12** with lithium salt **13**, which also leads to **4**, via **3** (Scheme 4).

The unusual stability of 1*H*-diazirine **3** is probably due to the presence of a bulky electron-rich substituent which increases the pyramidalization of the nitrogen atom and hinders its inversion. The consequence is the nonparticipation of the nitrogen lone pair into the π-system, which therefore is not antiaromatic any more. The presence of the electron-rich phosphoranyl group bonded to the negatively charged nitrogen end of the nitrilimine **2** probably also decreases the energy barrier of the ring closure into **3**.

Conclusion

Several interconversions between structural isomers of diazo derivatives are known: cyanamide−carbodiimide,[23] diazo−3*H*-diazirine,[5] nitrilimine−diazo,[8c,9] and nitrilimine−carbodiimide.[8] In this paper, we have shown two new rearrangements: diazo−nitrilimine and nitrilimine−1*H*-diazirine.

In a recent paper,[21] we reported that *N*-phosphoniodiazirines have a sufficient lifetime to allow intermolecular versus intramolecular reactions. Their relative stability was explained by a possible back-donation of the nitrogen lone pair into the unoccupied σ^* orbitals of the phosphorus substituent bonds,[24] which reduces the antiaromatic character of the 1*H*-diazirine. The three-membered heterocycle **3** is probably also "poorly antiaromatic" because of a strong pyramidalization of the nitrogen atom, along with a high inversion barrier, which is induced by the presence of a bulky electron-rich phosphoranyl group.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points were obtained on a Electrothermal capillary apparatus and were not corrected. ^{1}H, ^{31}P, and ^{13}C spectra were recorded on Bruker AC80, AC200, WM250, or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1725X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

Addition of Tetrachloro-1,2-Benzoquinone to *C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[Bis(diisopropylamino)phosphino]-nitrilimine (1). To a dichloromethane solution (5 mL) of nitrilimine **1** (0.30 g, 0.56 mmol) was added at −78 °C a dichloromethane solution (5 mL) of TCBQ (0.15 g, 0.61 mmol). After warming to room temperature the solvent was removed under vacuum, and the residue was washed several times with pentane. Compound **4** was crystallized from THF at −20 °C as colorless crystals (0.37 g, 84% yield): mp >250 °C; ^{31}P NMR ($CDCl_3$) δ +56.5 (d, J(PP) = 2.6 Hz), −24.1 (d, J(PP) = 2.6 Hz); ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J(HH) = 6.7 Hz, 24 H, CH_3), 1.32 (d, J(HH) = 6.8 Hz, 12 H, CH_3), 1.37 (d, J(HH) = 6.8 Hz, 12 H, CH_3), 3.68 (sept d, J(HH) = 6.8 Hz, J(PH) = 21.9 Hz, 4 H, CH), 4.00 (sept d, J(HH) = 6.7 Hz, J(PH) = 16.0 Hz, 4 H, CH); ^{13}C NMR ($CDCl_3$) δ 22.6−23.9 (s, CH_3), 46.9 (d, J(PC) = 4.9 Hz, CH), 47.3 (d, J(PC) = 6.4 Hz, CH), 113.8 (d, J(PC) = 5.4 Hz, OC*C*), 114.0 (s, OC*C*), 123.2 (s, OCC*C*), 123.9 (s, OCC*C*), 126.1 (d, J(PC) = 32.8 Hz, OC), 140.4 (s, OC), 154.3 (dd, J(PC) = 183.3 and 6.1 Hz, C═N); mass spectrum (EI) *m/z* 778 (M^+). Anal. Calcd for $C_{31}H_{56}Cl_4N_6O_2P_2S$: C, 47.69; H, 7.18; N, 10.77. Found: C, 47.55; H, 7.22; N, 10.53.

Spectroscopic Characterization of 1*H*-Diazirine 3. To a CD_2Cl_2 solution (1.5 mL) of nitrilimine **1** (0.30 g, 0.56 mmol) was added at −78 °C a CD_2Cl_2 solution (1.5 mL) of TCBQ (0.15 g, 0.61 mmol). Monitoring the reaction by ^{31}P NMR spectroscopy at low temperature, we observed the formation of **3** at −50 °C, which is stable up to −30 °C. Isodiazirine **3** has been characterized in solution at −50 °C: ^{31}P NMR (CD_2Cl_2) δ +58.5 (d, J(PP) = 13.0 Hz), +2.6 (d, J(PP) =13.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 23.6 (m, CH_3), 47.4 (m, CH), 125.2 (d, J(PC) = 6.0 Hz, OC*C*), 126.5, 127.0 and 128.1 (s, OC*C* and OCC*C*), 138.1 (d, J(PC) = 5.1 Hz, O*C*), 147.5 (d, J(PC) = 3.4 Hz, O*C*), 151.1 (dd, J(PC) = 191.6 and 24.4 Hz, C═N).

Derivative **3** was also observed at −50 °C, both by adding TCBQ to diazo derivative **8** in dichloromethane solution and in reacting diazo lithium salt **13** with phosphonium salt **12** in THF solution.

Reactivity of 1*H*-Diazirine 3. To a dichloromethane solution (5 mL) of nitrilimine **1** (0.30 g, 0.56 mmol) was added at −78 °C a dichloromethane solution (5 mL) of TCBQ (0.15 g, 0.61 mmol). After warming to −40 °C, the formation of intermediate **3** was checked by ^{31}P NMR spectroscopy and a stoichiometric amount of iPr_3SiOTf (**5**) or Me_3P (**6**) was added to the reaction mixture. Then, the solution was warmed to room temperature, and the solvent was removed in vacuo.

5: yellow oil (0.31 g, 51% yield); ^{31}P NMR ($CDCl_3$) δ +34.1 (d, J(PP) = 7.1 Hz), +27.3 (d, J(PP) = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 12.0 (s, CH_3*C*HSi), 18.0 (s, *C*H_3CHSi), 22.5−24.0 (s, CH_3), 49.2 (d, J(PC) = 4.5 Hz, NCH), 51.5 (d, J(PC) = 4.2 Hz, NCH), 70.3 (dd, J(PC) = 89.9 and 13.8 Hz, CNN), 120.1 (q, J(FC) = 320.8 Hz, CF_3), 124.9 (s, POCC*C*), 125.9 (s, POCCC*C*), 130.6 (s, SiOC*C*), 138.1 (d, J(PC) = 10.1 Hz, POC), 138.9 (d, J(PC) = 5.4 Hz, POC*C*), 146.5 (d, J(PC) = 3.9 Hz, SiOC).

6. According to ^{31}P NMR spectroscopy, compound **6** was obtained in near quantitative yield as an orange oil and was characterized without any further purification: ^{31}P NMR ($CDCl_3$) δ +64.1 (dd, J(PP) = 107.0 and 3.6 Hz, PS), +31.2 (dd, J(PP) = 5.5 and 3.6 Hz, PO), +1.7 (dd,

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J(PP) = 107.0 and 5.5 Hz, PMe); ^{1}H NMR ($CDCl_3$) δ 1.14 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 1.22 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 1.29 (d, *J*(HH) = 6.8 Hz, 12 H, CH_3), 1.30 (d, *J*(HH) = 6.8 Hz, 12 H, CH_3), 2.19 (d, *J*(PH) = 13.6 Hz, 9 H, CH_3P), 3.95 (m, 4 H, NCH), 4.94 (m, 4 H, NCH); ^{13}C NMR ($CDCl_3$) δ 18.1 (d, *J*(PC) = 69.8 Hz, CH_3P), 23.5−25.1 (s, CH_3), 48.1 (d, *J*(PC) = 4.5 Hz, NCH), 48.4 (d, *J*(PC) = 5.7 Hz, NCH), 123.0 (s broad, C quinone), 126.1 (ddd, *J*(PC) = 162.9, 52.3 and 29.4 Hz, PCP).

7. To a dichloromethane solution (10 mL) of **6** (0.20g, 0.23 mmol) was added at −78 °C MeOTf (0.04 g, 0.23 mmol). After warming to room temperature, addition of pentane led to the precipitation of **7** as an orange powder (0.22 g, 95% yield): mp 104 °C; ^{31}P NMR ($CDCl_3$) δ +66.3 (dd, *J*(PP) = 98.9 and 4.3 Hz, PS), +32.5 (dd, *J*(PP) = 6.2 and 4.3 Hz, PO), +5.7 (dd, *J*(PP) = 98.9 and 6.2 Hz, PMe); ^{1}H NMR ($CDCl_3$) δ 1.08 (d, *J*(HH) = 6.7 Hz, 12 H, CH_3), 1.12 (d, *J*(HH) = 6.6 Hz, 12 H, CH_3), 1.20 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 1.26 (d, *J*(HH) = 6.4 Hz, 12 H, CH_3), 2.21 (d, *J*(PH) = 14.1 Hz, 9 H, CH_3P), 3.68 (s, 3 H, CH_3O), 3.87−4.06 (m, 8 H, NCH); ^{13}C NMR ($CDCl_3$) δ 12.3 (d, *J*(PC) = 53.5 Hz, CH_3P), 22.8−25.1 (s, CH_3), 48.4 (d, *J*(PC) = 3.4 Hz, NCH), 61.9 (s, CH_3O), 120.1 (q, *J*(FC) = 320.8 Hz, CF_3), 125.0 (s, POCC*C*), 125.8 (s, POCCC*C*), 128.7 (d, *J*(PC) = 5.8 Hz, POC*C*), 130.4 (s, CH_3OC*C*), 131.8 (ddd, *J*(PC) = 181.2, 53.5, and 26.1 Hz, PCP), 141.8 (d, *J*(PC) = 10.2 Hz, POC), 149.3 (d, *J*(PC) = 2.9 Hz, CH_3O*C*). Anal. Calcd for $C_{36}H_{68}Cl_4F_3N_6O_5P_3S_2$: C, 42.36; H, 6.71; N, 8.23. Found: C, 42.13; H, 6.60; N, 8.15.

Addition of Tetrachloro-1,2-Benzoquinone to Diazo Derivative 8. Procedure 1. To a dichloromethane solution (5 mL) of **8** (0.53 g, 1.00 mmol) was added at −78 °C a dichloromethane solution (5 mL) of TCBQ (0.25 g, 1.00 mmol). After warming to room temperature, the solvent was removed in vacuo. Compound **4** was purified as mentioned before (0.70 g, 90% yied).

Procedure 2. Using a similar experimental procedure, but in the presence of 2 equiv of CH_3OD, the formation of deuterated diazo compound **10(D)** and derivative **11** was observed. After the solvent and excess CH_3OD were removed in vacuo, the residue was washed with pentane (20 mL) affording **11** as a white powder, diazo derivative **10(D)** remaining in pentane solution.

10(D). This derivative was obtained as orange crystals by cooling the pentane solution at −20 °C (0.26 g, 85% yield): mp 79−81 °C; ^{31}P NMR ($CDCl_3$) δ +56.6; ^{1}H NMR ($CDCl_3$) δ 1.11 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 1.19 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 3.46 (sept d, *J*(HH) = 6.9 Hz, *J*(PH) = 18.6 Hz, 4 H, NCH); ^{13}C NMR ($CDCl_3$) δ 22.5, 22.6, 22.8, and 25.1 (s, CH_3), 46.4 (d, *J*(PC) = 5.6 Hz, NCH), CN was not observed; IR (pentane) 2093 cm^{-1} (CN_2). Anal. Calcd for $C_{13}H_{28}DN_4PS$: C, 51.12; H, 9.24; N, 18.34. Found: C, 51.01; H, 9.28; N, 18.22.

11. This phosphorane was crystallized from a toluene solution as colorless crystals (0.25 g, 90% yield): mp 98−99 °C; ^{31}P NMR ($CDCl_3$) δ −15.1; ^{1}H NMR ($CDCl_3$) δ 1.12 (d, *J*(HH) = 6.6 Hz, 12 H, CH_3), 1.14 (d, *J*(HH) = 6.6 Hz, 12 H, CH_3), 3.67 (d, *J*(PH) = 11.4 Hz, 3 H, CH_3O), 3.72 (sept d, *J*(HH) = 6.6 Hz, *J*(PH) = 22.6 Hz, 4 H, NCH); ^{13}C NMR ($CDCl_3$) δ 23.1 and 23.5 (s, CH_3), 47.2 (d, *J*(PC) = 5.8 Hz, NCH), 52.7 (s, CH_3O), 114.6 (d, *J*(PC) = 11.7 Hz, OC*C*), 128.1 (s, OCC*C*), 142.1 (s, OC). Anal. Calcd for $C_{19}H_{31}N_2Cl_4O_3P$: C, 44.90; H, 6.15; N, 5.51. Found: C, 44.83; H, 6.10; N, 5.64.

Procedure 3. Using similar experimental conditions, but in a $CDCl_3$ solution, the formation of deuterated diazo compound **10(D)** and phosphonium salt **12(Cl$^-$)** was observed. Compound **12(Cl$^-$)** precipitated as a white powder by addition of pentane. Anion exchange with $AgCF_3SO_3$ in acetonitrile led to **12(OTf$^-$)**, which was isolated in 90% yield. The spectroscopic and physical data of **12(OTf$^-$)** are similar to those of an original sample prepared as described below.

Synthesis of Phosphonium Salt 12. To a dichloromethane solution (5 mL) of bis(diisopropylamino)phosphenium trifluoromethanesulfonate[25] (0.44 g, 1.16 mmol) was added at −78 °C a dichloromethane solution (3 mL) of TCBQ (0.29 g, 1.16 mmol). After warming to room temperature, the solvent was removed under vacuum, and the residue was washed several times with pentane, leading to **12** as a white powder (0.62 g, 86% yield): mp 183−184 °C; ^{31}P NMR ($CDCl_3$) δ +50.9; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, *J*(HH) = 6.7 Hz, 24 H, CH_3), 3.97 (sept d, *J*(HH) = 6.8 Hz, *J*(PH) = 23.1 Hz, 4 H, NCH); ^{13}C NMR ($CDCl_3$) δ 22.1 (d, *J*(PC) = 2.2 Hz, CH_3), 51.5 (d, *J*(PC) = 3.8 Hz, NCH), 118.1 (d, *J*(PC) = 12.9 Hz, OC*C*), 120.9 (q, *J*(CF) = 320.8 Hz, CF_3), 130.7 (s, OCC*C*), 138.9 (d, *J*(PC) = 5.1 Hz, O*C*). Anal. Calcd for $C_{19}H_{28}Cl_4F_3N_2O_5PS$: C, 36.37; H, 4.49; N, 4.46. Found: C, 36.07; H, 4.77; N, 4.39.

Addition of Diazo Lithium Salt 13 to Phosphonium Salt 12. To a THF solution (5 mL) of diazo lithium salt **13**[10] (1 mmol) was added at −78 °C a THF solution (5 mL) of phosphonium salt **12** (0.62 g, 1 mmol). After warming to room temperature, the lithium salts were filtered, and the solvent was removed under vacuum. The residue was washed several times with pentane, and compound **4** was crystallized from THF at −20 °C as colorless crystals (0.64 g, 82% yield).

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