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LETTERS
TO THE EDITOR

Redox Reaction of Red Phosphorus with Hydrosulfide Anions in DMSO

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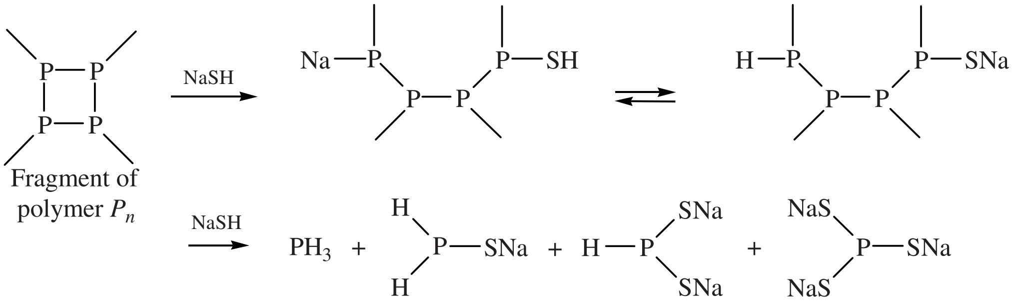
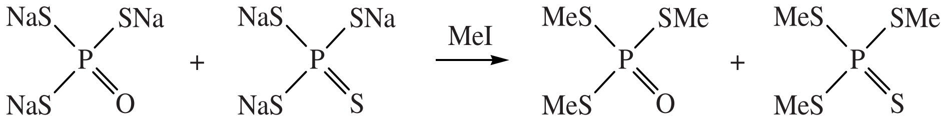
Recently red phosphorus came into wide use as the starting reagent for one-pot synthesis of phosphines and phosphine oxides in three-component reactions with an alkali metal hydroxide and electrophiles in superbasic media and under phase-transfer catalysis conditions [1–3]. Therewith, hydroxide anions participate in the redox reaction with elemental phosphorus by cleaving the P–P bond and generating polyphosphide and polyphosphinite anions which are further scavenged by an electrophile present in the system (organyl halides [1–4], electrophilic alkenes [1, 2, 5], acetylenes [1, 6], or oxiranes [2]). It could be anticipated that the reaction of red phosphorus (polymer P_n) with hydrosulfide anion would proceed in a similar way, that is, via redox P–P bond cleavage with intermediate formation of compounds with P–H and P–S bonds, and finally leading to phosphine and trisodium phosphorotrithioite:

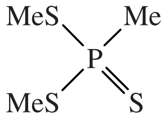


Trisodium phosphorotrithioite should be readily oxidized with air oxygen and elemental sulfur to form *S,S,S*-trisodium phosphorotrithioate (**I**) and trisodium phosphorotetrathiate (**II**), respectively. Actually, upon heating (100–116°C, 4.5 h) of red phosphorus in a solution of NaSH in DMSO (prepared by the procedure described in [7, 8]), evolution of phosphine (slow stream) and hydrogen sulfide (qualitative reactions with aqueous $CuSO_4$ and $Cd(AcO)_2$, respectively) was observed, as well as formation of elemental sulfur and dimethyl sulfide. After the reaction mixture was cooled to room temperature and treated with methyl iodide, a ~1:1 mixture of *S,S,S*-trimethyl phosphorotrithioate (**III**) and trimethyl phosphorotetrathiate (**IV**) was obtained in a total yield of 10% (nonoptimized).



I **II** **III** **IV**

In some cases, ~3% of methylphosphonotrithioate **V** was identified in the crude product (^{1}H and ^{31}P NMR, GC–MS).



V

Thus, the discovered reaction contributes a principally new basic knowledge into the chemistry of phosphorus and sulfur and opens new possibilities for synthesis of phosphorus- and sulfur-containing compounds on the basis of elemental phosphorus in its most stable and handy red modification.

***S*,*S*,*S*-Trimethyl phosphorotrithioate (III) and trimethyl phosphorotetrathioate (IV).** To 63 ml of a 0.64 M solution of NaSH in DMSO, 0.77 g of red phosphorus was added, the reaction mixture stirred at 100–116°C for 4.5 h, and cooled to 20–22°C. Methyl iodide, 7.8 ml, was then added dropwise over the course of 15 min (exothermic effect, self-heating to 45°C). The mixture was stirred at 50–55°C for another 2 h and then diluted by half with water and extracted with ether (3×30 ml). The ethereal extract was washed with water, dried over potassium carbonate, the ether was removed, and the residue was dried in a vacuum to give 0.22 g of the product. According to the ^{31}P NMR spectrum, it contained compounds **III** and **IV** in ~1:1 ratio (total yield 10% per taken NaSH).

Compound **III**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 d (9H, Me, $^3J_{HP}$ 15.9 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 69.8. Mass spectrum, *m/z* (I_{rel}, %): 188 (12) $[M]^{+\cdot}$, 142 (19) $[M - CH_2S]^{+\cdot}$, 141 (53) $[M - MeS]^+$, 95 (16) $[MeSPOH]^+$, 94 (45) $[MeSPO]^{+\cdot}$, 79 (17) $[MeSPH]^+$, 77 (6) $[CH_2SP]^+$, 63 (8) $[SP]^+$, 51 (25), 49 (75), 47 (100) $[SMe]^+$, 46 (35) $[CH_2S]^{+\cdot}$, 45 (58) $[HCS]^+$, 44 (22) $[CHP]^+$, 43 (16).

Compound **IV**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 d (9H, Me, $^3J_{HP}$ 17.7 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 100.2. Mass spectrum, *m/z* (I_{rel}, %): 204 (25) $[M]^{+\cdot}$, 157 (45) $[M - MeS]^+$, 125 (26) $[(MeS)_2P]^+$, 111 (11) $[MeSPSH]^{+\cdot}$, 110 (8) $[MeSPS]^{+\cdot}$, 94 (11), 79 (13) $[MeSPH]^+$, 78 (5) $[MeSP]^+$, 77 (11) $[CH_2SP]^+$, 63 (100) $[SP]^+$, 47 (29) $[SMe]^+$, 45 (35) $[HCS]^+$. Found, %: C 18.96; H 4.79; P 15.32; S 57.32. $C_3H_9OPS_3$ (**III**) : $C_3H_9PS_4$ (**IV**) = 1 : 1. Calculated, %: C 18.35; H 4.62; P 15.78; S 57.17.

Dimethyl methylphosphonotrithioate (V). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 d (3H, MeP, $^3J_{HP}$ 13.0 Hz), 2.35 d (6H, MeS, $^3J_{HP}$ 15.9 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 83.1. Mass spectrum, *m/z* (I_{rel}, %): 172 (68) $[M]^{+\cdot}$, 140 (8) $[M - S]^{+\cdot}$, 125 (76) $[M - SMe]^+$, 111 (11) $[MeSPSH]^+$, 93 (48) $[MeSPMe]^+$, 79 (51) $[MeSPH]^+$, 78 (29) $[MeSP]^+$, 77 (40) $[CH_2SP]^+$, 65 (42) $[H_2SP]^+$, 63 (100) $[SP]^+$, 51 (15), 49 (64), 48 (21), 47 (44) $[SMe]^+$, 46 (28), 45 (84) $[HCS]^+$, 44 (36) $[CHP]^+$, 43 (8).

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 and 161.98 MHz, respectively), internal standard HMDS, external standard 85% H_3PO_4. The electron impact mass spectra (70 eV) were obtained on a GCMS-QP5050A instrument (quadrupole mass analyzer, mass range 34–450, SPB–5 capillary column).

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