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LETTERS TO THE EDITOR

Microwave Activation of the Reaction of Red Phosphorus with Alkanethiolate Anions

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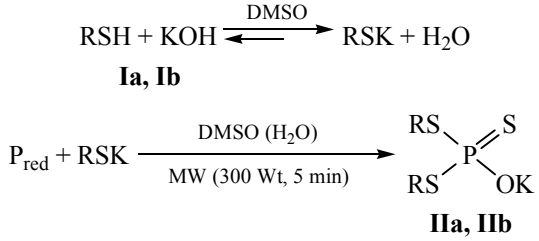
The direct phosphorylation of organic compounds with elemental phosphorus and, first of all, with non-combustible and non-toxic red phosphorus, is a convenient method of the C–P bond formation, which has advantages over the methods of synthesis of organophosphorus compounds based on the use of toxic, aggressive and less available phosphorus halides. Nowadays, to activate red phosphorus, superbasic media [1] like alkali metal hydroxide–polar nonhydroxylic solvent (DMSO, HMPTA) or aqueous solution of alkali metal hydroxide–organic solvent–phase transfer catalyst [2–4] are widely used. Polyphosphide and polyphosphinite ions generated in these media by successive rupture of the P–P bonds in macromolecules of red phosphorus under the action of hydroxide anion react with versatile electrophiles (electrophilic alkenes, acetylenes, organyl halides, oxiranes) to form organic phosphines and phosphine oxides [1–7]. Recently, short communications appeared reporting the splitting of the macromolecule of red phosphorus in the presence of sulfur-centered nucleophiles (sodium hydrosulfide [8] or alkanethiolate anions [9]). In particular, the reaction of red phosphorus with alkanethiolate anions (generated *in situ* from alkanethiols in the system KOH–DMSO) proceeds upon heating (125–128°C) and leads in 4 h to the earlier unknown *O*-potassium *S*,*S*-dialkyl trithiophosphates in 13–15% yield.

In the present communication we report the results of activation of this new reaction under the conditions of microwave irradiation. It turned out that microwave irradiation (Samsung M181DNR, 300 Wt) of the mixture of red phosphorus and potassium alkanethiolates generated from alkanethiols **Ia, Ib** and KOH in DMSO resulted in the reduction of the time of the reaction to 5 min (that is, almost 50-fold) and in the formation of potassium dialkyl trithiophosphates in 19–20% yield [the yield was calculated with respect to the reacted alkanethiol **Ia, Ib** whose conversion was 98–99%].



R = Bu (**a**), C_7H_{15} (**b**).

Possible routes of formation of salts **IIa, IIb** were discussed in [9].

In the reaction mixture were identified the corresponding trialkyltetrathiophosphates (^{31}P NMR) as well as dialkyldisulfides (the products of oxidation of alkanethiols) and alkyl methyl sulfides (the GLC and mass spectrometry data). The sulfides appear as a result of the reaction of thiols with the system KOH–DMSO [10].

Therefore, we have proved the effect of microwave activation of the new reaction of splitting the three-dimensional macromolecule of red phosphorus under the action of sulfur-centered nucleophiles (alkanethiolate anions) leading to the formation of the P–S bonds and *O*-potassium *S*,*S*-dialkyl trithiophosphates,

promising precursors for preparation of *S,S,S*-trialkylthiophosphates [9].

***O*-Potassium *S,S*-dibutyltrithiophosphate (IIa)**. The mixture of 2.13 g (32.7 mmol) of the ground $KOH·0.5H_2O$ and 2.95 g (32.7 mmol) of BuSH in 35 ml of DMSO was heated (60°C) at stirring to full homogenization. The obtained solution was cooled to 40°C, 0.63 g (20.3 mmol) of red phosphorus was added, the reaction mixture was irradiated in a domestic microwave oven (Samsung M181DNR, 300 Wt power) during 5 min, cooled, filtered, the precipitate was washed successively with DMSO (10 ml), H_2O (10 ml), acetone (10 ml), ether (10 ml), and dried in a vacuum to obtain 0.22 g of red phosphorus (conversion 65%). The filtrate was combined with the DMSO and water washing solutions and analyzed (NMR, GLC). In the ^{31}P NMR spectrum (δ_P, ppm) the signals were observed at 3.4 t ($^1J_{PH}$ 464 Hz), 73.6, and 98.1 ppm in the ratio of 3:9:1, belonging, respectively, to KH_2PO_2, $Bu_2P(S)OK$ **IIb**, and $Bu_3P(S)$. According to the GLC data (xylene as a standard, temperature of column 50°C, of injector 200°C), the filtrate also contains 0.01 g of Me_2S, 0.03 g of BuSH (conversion 99%), and 0.39 g of BuSMe (12%, hereinafter the yield is calculated with due regard to the conversion of the thiol) (all compounds were identified by com-parison with authentic samples). The filtrate was diluted with water (1 : 1), extracted with ether (3×30 ml), the extract was washed with water (3×30 ml), dried over K_2CO_3, ether was removed at the atmospheric pressure, BuSH and BuSMe, at 2 mm Hg (for BuSMe *m/z* = 104 $[M]^{+\cdot}$), the residue in the flask was dibutyldisulfide, 0.87 g (30%) (its spectra were identical to those of the authentic sample). Found, %: C 53.59; H 9.95; S 35.49. $C_8H_{18}S_2$. Calculated, %: C 53.87; H 10.17; S 35.96. The aqueous solution after the extraction with ether was combined with washings of the ether extract, 5% aqueous solution of HCl was added to pH 4, the water solution was extracted with ether (3×30 ml), the extract was washed with water (3×30 ml), and dried over K_2CO_3. Ether was removed at the atmospheric pressure, the residue was dried in a vacuum, and washed with hexane to obtain 0.64 g (20%) of *O*-potassium *S,S*-dibutyl trithiophosphate (**IIa**), white crystals, mp 98–100°C (hexane). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (6H, Me, $^3J_{HH}$ 7.29 Hz), 1.42 m (4H, CH_2Me), 1.67 m (4H, CH_2Et), 2.90 m (4H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.42 (Me), 21.85 (CH_2), 31.69 d (CH_2, J_{CP} 5.53 Hz), 35.24 d (CH_2, J_{CP} 2.58 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 85.6. IR spectrum (KBr, cm^{-1}): 645 (P=S). Found, %: C 32.28, H 6.40, P 9.95, S 32.17. $C_8H_{18}KOPS_3$. Calculated, %: C 32.41, H 6.12, P 10.45, S 32.44.

***O*-Potassium *S,S*-diheptyltrithiophosphate (IIb)** was prepared similarly to salt (**IIa**) at the microwave irradiation (300 Wt, 5 min) of 36.6 mmol of potassium heptanethiolate and 0.71 g (22.9 mmol) of red phosphorus in 50 ml of DMSO. Yield 0.87 g (19% at 98% conversion of heptanethiol), white crystals, mp 114–116°C (hexane). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (6H, Me, $^3J_{HH}$ 6.72 Hz), 1.20–1.45 m (16H, CH_2), 1.68 m (4H, CH_2CH_2S), 2.88 m (4H, CH_2S). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 86.5. IR spectrum (KBr, cm^{-1}): 635 (P=S). Found, %: C 44.45, H 7.89, P 7.51, S 24.81. $C_{14}H_{30}KOPS_3$. Calculated, %: C 44.17, H 7.94, P 8.14, S 25.27. Conversion of red phosphorus was 55%, yield of $C_7H_{15}SMe$ 21%, yield of diheptyldisulfide 27%.

^1H, ^{13}C, and ^{31}P NMR spectra were registered on a Bruker 400 DPX spectrometer (at 400.13, 100.69, and 161.98 MHz, respectively), internal standard HMDS, external standard 85% H_3PO_4. IR spectra were recorded on a Bruker ISF 25 instrument. Electron impact (70 eV) mass spectra were obtained on a GCMS-QP5050A SHIMADZU instrument (quadruple mass analyzer, the range of detected masses 34–450 D, capillary column, stationary phase SPB-5). GLC analysis was performed on an LKhM 8MD instrument (column 1.2 m×3 mm, 1% of PEG 20000 on NaCl, carrier gas helium, 2 l h^{-1}).

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