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> SHORT COMMUNICATIONS

Reaction of 9-Bromoanthracene with Red Phosphorus in the System KOH–DMSO

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Organophosphorus compounds containing bulky anthracene fragments attract interest as ligands for metal complexes for various purposes [1-12], starting materials for the design of luminescent materials [12-16] (in particular, as components of molecular switches [13]), and nanoparticle stabilizers (used, e.g., in therapy of oncological diseases) [17].

Phosphorylation of anthracenes and their halogen derivatives is usually accomplished with the aid of phosphorus halides [5–7, 12, 18, 19], alkyl and aryl phosphites [3, 17, 20–22], or hypophosphites [23]. For example, anthracen-9-ylphosphinic acid was synthesized in two steps including reaction of phosphorus trihalide with anthrylmagnesium halide and subsequent hydrolysis of anthryl(dihalo)phosphine [1]. Kalek and Stawinski [23] described microwave-assisted synthesis of anthracen-9-ylphosphinic acid from 9-bromoan-thracene and anilinium phosphinite in the presence of $Pd_2(dba)_2$ ·CHCl₃–Xantphos–Et₃N as catalytic system.

One of the most convenient methods for the formation of P–C bond and synthesis of organophosphorus compounds is based on the direct reaction of elemental phosphorus with electrophiles in the presence of strong bases [24–31]. Herein, we report for the first time phosphorylation of 9-bromoanthracene (1) with red phosphorus. By heating (40–60°C, 3 h) bromide 1 with red phosphorus in the system KOH–DMSO containing a small amount of water we obtained anthracen-9ylphosphinic acid (2) in up to 10% yield (unoptimized). Under these conditions, 30% of anthracene 3 and 20% of 9,10-dihydroanthracene (4) were also formed (Scheme 1). The reaction mixture also contained traces of anthracen-9-ol (according to the GC/MS data).

No phosphorylation of 1 was observed in the absence of base, which confirms nucleophilic character of the C–P bond formation. In the first step, elemental phosphorus in superbasic medium generates phosphorus-containing nucleophilic species, polyphosphide (A) and polyphosphinite ions (B) [25, 26], which then react with bromide 1 to give acid 2 (Scheme 2).

Polyphosphide ions are most likely to be involved in concurrent one-electron transfer process with formation of unstable radical anion C which decomposes into bromide ion and anthryl radical D. The latter is capable of abstracting hydrogen from DMSO, yielding neutral anthracene (3). The subsequent electron transfer to molecule 3 from anion A or radical anion C leads to the formation of the reduction product, 9,10-dihydroanthracene (4) (Scheme 3).

This mechanism is consistent with published data for reactions of 9-bromoanthracene with sulfur and



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oxygen nucleophiles in superbasic medium, where the formation of anthracene was also detected [32–35]. The formation of 9,10-dihydroanthracene from anthracene was observed in the strong reducing system NiBr₂–NaBH₄ [36], under electrolysis conditions, or as a result of electron transfer [37, 38].

Thus, we were the first to accomplish phosphorylation of 9-bromoanthracene with red phosphorus in a superbasic system, which led to the formation of anthracen-9-ylphosphinic acid and reduction products (anthracene and 9,10-dihydroanthracene). Our results make a contribution to the methodology of $P-C_{sp2}$ bond formation by direct phosphorylation of weakly electrophilic aromatic halogen derivatives with elemental phosphorus and open the way to new organophosphorus compounds with bulky organic radicals. The latter are promising as ligands for the design of catalytically active metal complexes, precursors to medicines, luminophores, and building blocks for organic synthesis.

Reaction of red phosphorus with 9-bromoanthracene (1) in the system KOH–DMSO (H₂O). A solution of 1.00 g (3.9 mmol) of compound 1 in 5 mL of DMSO was heated to 60°C, 0.4 g (13 mmol) of red phosphorus, 1.25 g (19 mmol) of KOH \cdot 0.5H₂O, and 0.125 mL of water were added, and the mixture was stirred for 3 h at 60°C under argon. The mixture was cooled to room temperature and filtered from unreacted phosphorus (0.1 g) through a Schott filter, and the filtrate was diluted with water (20 mL) and extracted with methylene chloride $(3 \times 20 \text{ mL})$. The resulting emulsion was separated by centrifugation. The organic layer was washed with 10% aqueous potassium chloride $(3 \times 10 \text{ mL})$ and dried over Na₂SO₄. the solvent was distilled off, and the residue was dried under reduced pressure to obtain 0.337 g of a mixture

containing compounds **3** and **4** and anthracen-9-ol at a ratio of 60:39:1. Mass spectrum, $m/z: 178 [M]^+$ (**3**); $180 [M]^+$ (**4**); $193 [M]^+$ (anthracen-9-ol).

The alkaline aqueous layer was acidified with aqueous HCl to pH 4–5, acid **2** was extracted into chloroform (3×20 mL), the extract was dried over CaCl₂, the solvent was distilled off, and the residue was dried under reduced pressure. Yield 0.09 g (10%). The spectral parameters and analytical data for acid **2** (δ_P 13.5 ppm, ${}^1J_{PH}$ = 567 Hz; found, %: C 69.51; H 4.49. C₁₄H₁₁O₂P) were identical to those reported in [1, 23].

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.1 and 161.98 MHz for ¹H and ³¹P, respectively, using CDCl₃ as solvent and hexamethyldisiloxane (¹H) or 85% H₃PO₄ (³¹P) as reference. Gas chromatographic/mass spectrometric analyses were performed on an Agilent Technologies 6890N/5975C GC/MS system (HP-5MS column, 0.25 mm×30 m, film thickness 0.25 μ m; carrier gas helium; electron impact ionization, 70 eV). Elemental analyses were obtained on a Flash EA 1112 Series analyzer. Red phosphorus was commercial product (KSAN SIA, China). All operations were carried out under argon.

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