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Unexpected formation of 1,4-diphenylbutylphosphinic acid from 1,4-diphenylbuta-1,3-diene and elemental phosphorus *via* the Trofimov–Gusarova reaction

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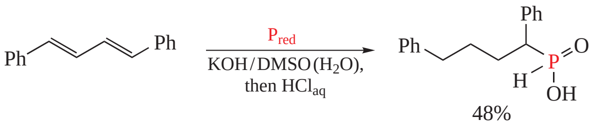
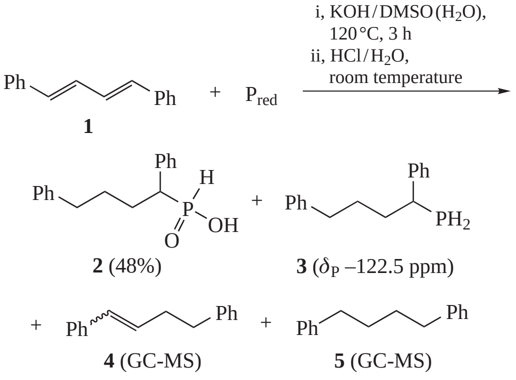
***trans*,*trans*-1,4-Diphenylbuta-1,3-diene reacts with elemental (red) phosphorus in the superbasic KOH/DMSO(H_2O) system (120 °C, 3 h) to give, after acidic work-up, 1,4-diphenylbutylphosphinic acid in 48% yield.**



The synthesis of organophosphorus compounds from elemental phosphorus attracts a significant attention as a straightforward and environmentally benign approach to C–P bond formation.[1] Nowadays, several efficient methods have been developed for the activation of elemental phosphorus (mainly, its white modification). Among these are the reaction of P_4 with organic substrates in highly basic heterogeneous media,[2] as well as under electrochemical,[3] metal-mediated[4] and photochemical[5] conditions. As for low-reactive but non-hazardous red phosphorus, its activation most successfully occurs in the reactions with diverse C-electrophiles under the action of highly basic systems such as KOH/DMSO (or HMPA) or KOH_{aq}/organic solvent/phase-transfer catalyst.[2] This methodology, now referred to the Trofimov–Gusarova reaction,[6] allowed one to prepare phosphines, phosphine oxides and/or phosphinic acids[2] from alkynes (het)arylalkenes, as well as organic halides and elemental phosphorus. Meanwhile, dienes still remained unexplored in this reaction, although this may be a promising way to access new or unavailable organophosphorus compounds.

Herein, we have implemented the direct phosphorylation of *trans*,*trans*-1,4-diphenylbuta-1,3-diene **1** with red phosphorus in a superbase system KOH/DMSO(H_2O). The reaction was found to occur effectively under vigorous stirring of the reactants at 100–130 °C to afford unexpected 1,4-diphenylbutylphosphinic acid **2** which was isolated after the acidic work-up of the reaction mixture (Scheme 1).[†] Under the best conditions (120 °C, 3 h, a molar ratio **1**/P/KOH·0.5H_2O/H_2O of 1 : 6.9 : 8.5 : 3.8) the preparative yield of acid **2** was 48%. In addition, as by-products, primary phosphine **3**, 1,4-diphenylbut-1-ene **4**, and 1,4-diphenylbutane **5** were also identified by ^{31}P NMR and GC-MS techniques.



Scheme 1

Acid **2** represents air-stable crystals, well soluble in the common organic solvents. Its structure was established by NMR (^1H, ^{13}C, ^{31}P, COSY, HSQC and HMBC ^1H–^{31}P), EI-MS and FT-IR data.[‡]

To gain a primary insight into the reaction pathway, we have carried out the control experiment. We have found that diene **1**, when heated in the superbase KOH/DMSO(H_2O) suspension

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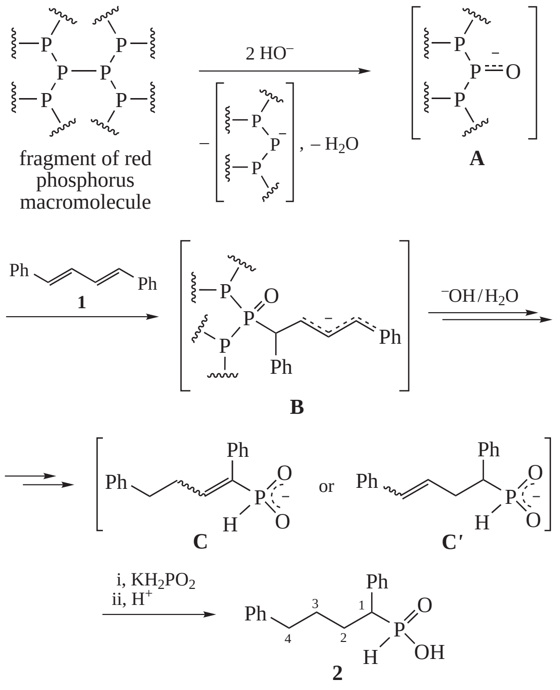
[†] *Reaction of diene* **1** *with red phosphorus in the KOH/DMSO system.* **Caution!** Phosphine PH_3 is released during the reaction, so it should be carried out only in a hood. A mixture of red phosphorus (3.10 g, 100 mmol), *trans*,*trans*-1,4-diphenylbuta-1,3-diene **1** (3.000 g, 14.5 mmol), KOH·0.5H_2O (8.00 g, 123 mmol), DMSO (35 ml) and water (1.0 ml) was stirred at 120 °C for 3 h, then cooled to room temperature and analyzed. The ^{31}P NMR spectrum revealed the presence of potassium salt of acid **2** [δ_P 26.0 (d, $^1J_{PH}$ 466 Hz)], KH_2PO_2 [δ_P –2.3 (t, $^1J_{PH}$ 469 Hz)] and primary phosphine **3** [δ_P –122.5 (t, $^1J_{PH}$ 193 Hz)] in about 21 : 12 : 1 molar ratio (Figure S1). The mixture was diluted with water (60 ml) and extracted with $CHCl_3$ (3 × 30 ml). The aqueous layer was filtered through Büchner funnel, acidified with aqueous HCl (10 M, up to pH ~ 1) and extracted with $CHCl_3$ (2 × 30 ml). The extract was washed with water (3 × 20 ml) and dried over Na_2SO_4. The solvent was distilled off and the residue was dried under vacuum to give phosphinic acid **2** (1.90 g, 48%) as colorless oil, whose crystallization from hexane furnished colorless crystals. The organic extract containing compounds **3**, **4** and **5** was washed with water (3 × 20 ml), the solvent was removed and the residue obtained (*ca.* 0.8 g) was redissolved in acetone (20 ml). To the resulting solution, aqueous H_2O_2 (30%, 1 ml) and KOH·0.5H_2O (1 g in 5 ml H_2O) were added. The mixture was stirred at room temperature for 5 min, diluted with water (30 ml) and extracted with $CHCl_3$ (2 × 20 ml). The extract was dried with K_2CO_3 and the solvent was removed to give 0.52 g of the mixture of 1,4-diphenylbutane **5** and 1,4-diphenylbut-1-ene **4** in a ~1 : 1 ratio (GC-MS data, Figure S3).

(100 °C, 3 h), remains almost unchanged (for more details, see Online Supplementary Materials). Thus, the formation of compounds **4** and **5** as by-products of the reaction is likely due to the side reduction of **1** with potassium hypophosphite, which is formed in the reaction mixture. Importantly, the ^{13}C NMR spectrum of aqueous layer of the diluted reaction mixture contains signals of the potassium salt of acid **2** and no peaks of the olefinic carbons (Figure S2). This clearly indicates that this acid is originated directly from the reaction of red phosphorus with **1**, rather than through H_3PO_2-assisted hydrogenation of possible initial unsaturated species, *e.g.* (1,4-diphenylbut-3-en-1-yl)- or (1,4-diphenylbut-2-en-1-yl)phosphinic acids.

Basing on these results, we propose that the process is triggered by the cleavage of P–P bonds of red phosphorus network by hydroxide anions furnishing highly nucleophilic polynuclear species, phosphide, $[P_m]^-$, and phosphinite, $[P_n–O]^-$ (**A**), anions (Scheme 2). Further addition of the phosphinite anion to diene **1** produces resonance-stabilized carbanion **B**, in which the C–P bond is attached to the phosphorus cluster. Subsequent cleavage of the remaining P–P bonds within **B** by HO^- anions eventually gives the salt of (1,4-diphenylbut-3-en-1-yl)phosphinic (**C**) or/and (1,4-diphenylbut-2-en-1-yl)phosphinic (**C′**) acids. Finally, their KH_2PO_2 reduction leads to the salt of acid **2**, whose acidification delivers free acid **2**. The primary phosphine **3** is probably formed either from phosphide anions $[P_m]^-$ in a similar way or through superbase-catalyzed monoaddition of PH_3 to diene **1**. Phosphine PH_3 is a common by-product of reactions between red phosphorus and alkali.



Scheme 2

In summary, the one-pot transformation of 1,4-diphenylbuta-1,3-diene to 1,4-diphenylbutylphosphinic acid, which represents the first example of the straightforward phosphorylation of dienes with the triad P/KOH/DMSO, has been implemented. The results obtained extend the scope of the organophosphorus synthesis based on the Trofimov–Gusarova reaction.[2]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.03.009.

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[‡] *1,4-Diphenylbutylphosphinic acid* **2**. White crystals, mp 55–58 °C (hexane). ^{1}H NMR ($CDCl_3$) δ: 10.25 (br. s, 1H, OH), 7.25–7.01 (m, 10H, Ph), 6.97 (d, 1H, PH, $^1J_{PH}$ 543.8 Hz), 3.06 (td, 1H, C^2H_2, $^2J_{HH}$ 13.6 Hz, $^3J_{HH}$ 5.6 Hz), 2.78–2.62 (m, 3H, C^2H_2 and C^4H_2), 2.09–1.95 (m, 2H, C^1H and C^3H_2), 1.83–1.70 (m, 1H, C^3H_2). ^{13}C NMR ($CDCl_3$) δ: 141.1 (*i*-C, PhC^4), 138.4 (d, *i*-C, PhC^1, $^2J_{CP}$ 12.6 Hz), 129.1 (*o*-C, PhC^1), 128.6 (*o*-C, PhC^4), 128.4 (*m*-C, PhC^4 and PhC^1), 126.0 (*p*-C, PhC^4), 38.8 (d, C^1, $^1J_{CP}$ 95.2 Hz), 33.4 (d, C^2, $^2J_{CP}$ 7.3 Hz), 33.1 (C^4), 27.8 (C^3). ^{31}P NMR ($CDCl_3$) δ: 41.52 (dd, $^1J_{PH}$ 543.7 Hz, $^2J_{PH}$ 14 Hz). EI-MS, *m*/*z*: 274 $[M]^+$. FT-IR (KBr, ν/cm^{-1}): 2382 (m, $\nu_{P–H}$), 1637 (br., $\nu_{O–H}$), 1172 (s, $\nu_{P=O}$), 967 (s, $\nu_{P–O}$). Found (%): C, 69.91; H, 6.93; P, 11.04. Calc. for $C_{16}H_{19}O_2P$ (%): C, 70.06; H, 6.98; P, 11.29.