Reactions of sterically hindered phenols with P_2S_5

N. F. Dzhanibekov, E. I. Markova, M. Kh. Mamedov, and S. R. Rafieva*

Institute of Petrochemical Processes, Academy of Sciences of Azerbaijan, 30 ul. N. Rafieva, 370025 Baku, Azerbaijan. Fax: +7 (892 2) 98 8169

The direction of the reaction of 2,6-disubstituted phenols with P_2S_5 leading to bis(hydroxyaryl)dithiophosphinic acids or O,O-bis(aryl) dithiophosphates is determined by the degree of shielding of the OH group.

Key words: sterically hindered phenols, phenolic alcohols, dithiophosphoric and dithiophosphinic acids, phosphorus pentasulfide.

It is known that phenols react fairly easily with P_2S_5 to give either O, O-bis(aryl) dithiophosphates¹⁻³ or diaryldithiophosphinic acids.⁴

In this work, we studied reactions of P_2S_5 with 2,6di-R-phenols (R = Me, Bu^t, Ph) and 4-HO(CH₂)_nsubstituted 2,6-di-*tert*-butylphenols (n = 0, 1, 3).

We showed that 2,6-di-R-phenols (R = Me, Bu¹) gave only the corresponding bis(hydroxyaryl)dithiophosphinic acids (1a,b) because of strong shielding of the OH group with *tert*-butyl or phenyl groups, whereas 2,6-dimethylphenol whose OH group is slightly shielded reacts with P₂S₅ to give O,O-bis(2,6-dimethylphenyl) dithiophosphates (2). 2,6-Di-*tert*-butylhydroquinone and 4-hydroxyalkyl-2,6-di-*tert*-butylphenols react with P₂S₅ involving the unshielded OH group.



1: $R = Bu^{t}$ (a), Ph (b). 2: R = Me. 3: n = 0 (a), 1 (b), 3 (c) The composition and the structures of the synthesized compounds were confirmed by elemental analysis and ¹H NMR and IR spectral data.

In the IR spectra of compounds 1–3, bands assigned to stretching vibrations of S–H, P–S, and P=S groups are observed in the regions 2550 to 2500, 560 to 530, and 670 to 645 cm⁻¹, respectively. In the IR spectra of acids 2 and 3a, a band at 1215 to 1160 cm⁻¹ assigned to vibrations of the P–O–C arom. group is present, which is absent in the spectra of acids 1a and 1b. The IR spectra of acids 1a,b contain bands of stretching vibrations of the P–C arom. group in the region 1450 to 1350 cm⁻¹.

The signal of the OH proton at δ 4.98 is observed in the ¹H NMR spectrum of the initial 2,6-dimethylphenol, whereas the spectrum of product 2 contains only the signal of S—H proton at δ 3.75. In the ¹H NMR spectrum of the initial 2,6-di-*tert*-butyl-4-hydroquinone, the signals of 1- and 4-OH groups are observed at δ 5.97 and 4.87, respectively, and the former signal is preserved in the spectrum of product **3a**. Instead of the latter signal, a new signal appears at δ 3.51 assigned to the SH group. In the case of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol, the signals of the phenolic and alcohol OH groups are observed at δ 6.98 and 5.15, respectively. The spectrum of product **3b** contains the shifted signal of the former OH group at δ 6.20, but instead of the latter signal, a signal of the S—H group at δ 3.05 appears.

Experimental

Reactions with P_2S_5 were carried out both in the melt at a temperature 10–15 °C higher than the melting point of phenol and in a solution by refluxing. When the reaction was completed, the reaction mixture was either evacuated (680–700 Torr) or flushed with an inert gas to remove completely the H_2S that liberated. IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets. ¹H NMR spectra were recorded on a Tesla BS-487 (80 MHz) spectrometer. The purity of products was monitored using TLC on Al₂O₃ (activity

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 7, pp. 1442-1444, July, 1998. 1066-5285/98/4707-1403 \$20.00 © 1998 Plenum Publishing Corporation 111); an isooctane — toluene (1:1) mixture was used as the eluent.

Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)dithiophosphinic acid (1a). The reactants were heated at 120–130 °C for 4–4.5 h to give acid 1a as an oil in 96.7% yield. Found (%): C, 66.20; H, 8.36; P, 6.00; S, 12.57. $C_{28}H_{43}O_2PS_2$. Calculated (%): C, 66.40; H, 8.50; P, 6.13; S, 12.65. 1R, v/cm⁻¹: 3600 (OH); 2520 (S–H); 1450 (P–C arom.); 1230 (Bu¹); 660 (P=S); 560 (P–S). ¹H NMR (CCl₄), 8: 1.67–1.72 (36 H, Bu¹); 3.48 (1 H, S–H); 5.98 (2 H, 4-OH); 6.70–7.10 (4 H, C₆H₂).

0,0-Bis(3,5-di-terr-butyl-4-hydroxyphenyl) dithiophosphate (3a). The reaction was carried out in toluene at 100–110 °C for 2.0–2.5 h. After the toluene was distilled off, the residue crystallized. The crystals were filtered off and washed with isooctane. Yield 96.4%. M.p. 160 °C. Found (%): C, 62.30; H, 7.88; P, 5.58; S, 11.76. $C_{28}H_{43}O_4PS_2$. Found (%): C, 62.45; H, 7.99; P, 5.76; S, 11.90. IR, v/cm⁻¹: 3597 (OH); 2500 (S–H); 1210 ((P–O–C arom.); 670 (P=S); 560 (P–S). ¹H NMR (CCl₄), δ : 1.63–1.73 (36 H, Bu⁴); 3.51 (1 H, S–H); 5.25 (2 H, 4–OH); 7.38 (4 H, C₆H₂).

0,0-Bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) dithiophosphate (3b). The reactants were heated at 140–145 °C for 5.0–6.0 h. After the reaction was completed, nitrogen was passed through to remove H₂S. Yield 97.1%. M.p. 125 °C. Found (%): C, 63.72; H, 8.21; P, 5.61; S, 11.13. $C_{30}H_{47}O_4PS_2$. Calculated (%): C. 63.60; H, 8.30; P, 5.48; S, 11.31. 1R, v/cm⁻¹: 3650 (OH); 2530 (S–H); 1160 (P–O–C arom.); 670 (P=S); 530 (P–S). ¹H NMR (CCl₄), 8: 1.65 (36 H, Bu^t); 3.05 (1 H, S– H); 4.07 (4 H, –-CH₂O); 6.20 (2 H, 4-OH); 7.10–7.30 (4 H, C₆H₂).

 \bar{O} , O-Bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl] dithiophosphate (3c). The reaction was carried out in toluene at 110 °C for 2.0--2.5 h. The reaction mixture crystallized when it was chilled. The product was separated by filtration and washed with isooctane. Yield 96.3%. M.p. 95 °C. Found (%): C, 65.66; H, 8.69; P, 5.12; S, 10.11. C₃₄H₅₅O₄PS₂. Calculated (%): C, 65.59; H, 8.84; P, 4.98; S, 10.29. IR, v/cm^{-1} : 3615 (OH); 2520 (S-H); 1180 (P-O-C arom.); 655 (P=S); 530 (P-S). ¹H (CCl₄), δ : 1.54–1.60 (36 H, Bu¹); 3.25 (1 H, S-H); 3.90 (6 H, -(CH₂)₃--); 6.10 (2 H, 4-OH); 6.90-7.15 (4 H, C₆H₂).

Bis(4-hydroxy-3,5-diphenyl)dithiophosphinic acid (1b). The reaction was carried out in toluene at 110 °C for 4.0 h. The toluene was distilled off and the material that crystallized was separated by filtration and washed with cold isooctane. Yield 96.6%. M.p. 104 °C. Found (%): C, 73.55; H, 4.54; P, 5.12; S, 10.83. $C_{36}H_{27}O_2PS_2$. Calculated (%): C, 73.72; H, 4.61; P, 5.29; S, 10.92. IR, v/cm⁻¹: 3610 (max. OH); 2500 (S-H); 1380 (P-C arom.); 655 (P=S); 550 (P-S).

0,0-Bis(3,5-dimethylphenyl) dithiophosphate (2). The reaction was carried out in toluene at 100-110 °C for 2.0-2.5 h. After the reaction mixture was chilled, the resulting crystals were filtered off and washed with cooled isooctane. Yield 97.3%. M.p. 106 °C. Found (%): C, 56.89; H, 5.60; P, 9.21; S, 19.00. $C_{16}H_{19}O_2PS_2$. Calculated (%): C, 56.80; H, 5.62; P, 9.17; S, 18.93. IR, v/cm⁻¹: 2500 (S-H); 1190 (P-O-C arom.); 660 (P=S); 560 (P-S). ¹H NMR (CCl₄), δ : 2.70 (12 H, Me); 3.75 (1 H, S-H); 7.10-7.25 (4 H, C₆H₂).

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