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Letters to the Editor

A novel method for synthesizing diorganylphosphinous acids from red phosphorus and arylalkenes

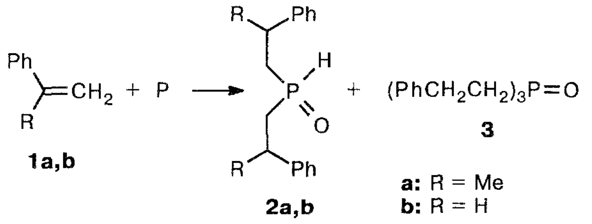
N. K. Gusarova,★ B. A. Trofimov, T. N. Rakhmatulina, S. F. Malysheva, S. N. Arbuzova, S. I. Shaikhudinova, and A. I. Albanov

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395) 246 2952

The reaction of styrene and α-methylstyrene with P in aprotic polar solvents in the presence of KOH affords diorganylphosphinous acids.

Key words: diorganylphosphinous acids, synthesis; red phosphorus; styrene; α-methylstyrene.

α-Methylstyrene (**1a**) reacts with red phosphorus (molar ratio of reagents 1:2) when heated (65—75 °C, 4 h) in a polar aprotic solvent (DMSO, HMPA) containing an alkali metal hydroxide to give the previously unknown bis(2-methyl-2-phenylethyl)phosphinous acid (**2a**). Under the same conditions styrene (**1b**) gives a small amount of tris(2-phenylethyl)phosphine oxide (**3**) along with bis(2-phenylethyl)phosphinous acid (**2b**).



Compounds **2a,b** were isolated from the reaction mixture in the usual manner (dilution with water, extraction with ether) and purified by preparative TLC (Al_2O_3, eluent — ether); yields up to 20 % (not optimized).

Thus, the reaction of red phosphorus with arylalkene in the presence of a strong base offers a new convenient approach to the synthesis of diorganylphosphinous acids.

Bis(2-methyl-2-phenylethyl)phosphinous acid (2a) is a viscous substance, which cannot be distilled. ^{1}H NMR, δ: 7.23 (m, 10 H, Ph); 6.42 (d, 1 H, PH); 3.11 (m, 2 H, CH); 1.88 (m, 4 H, CH_2); 1.3 (d, 6 H, CH_3). ^{31}P NMR, δ: 32.1, 29.2, 27.1, 25.9 (ratio of relative intensities is 10:26:42:22, $J_{P,H}$ = 485 Hz). The four signals in the ^{31}P NMR spectra may be explained by the presence of two asymmetric centers in compound **2a**. IR, ν/cm^{-1}: 2310 (P—H); 1140 (P=O). Found (%): C, 74.97; H, 8.23; P, 11.06. $C_{18}H_{23}OP$. Calculated (%): C, 75.52; H, 8.05; P, 10.83.

Bis(2-phenylethyl)phosphinous acid (2b) , m.p. 57—58 °C (*cf.* Ref. 1: m.p. 69—71 °C). ^{1}H NMR, δ: 7.11 (s, 10 H, Ph); 6.83 (d, 1 H, PH); 2.88 (m, 4 H, CH_2Ph); 2.03 (m, 4 H,

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CH_2P). ^{31}P NMR, δ: 31.1 ($J_{P,H}$ = 453 Hz). IR, ν/cm^{-1}: 2290 (P—H); 1140 (P=O). Found (%): C, 74.49; H, 7.48; P, 11.60. $C_{16}H_{19}OP$. Calculated (%): C, 74.40; H, 7.41; P, 11.99.

References

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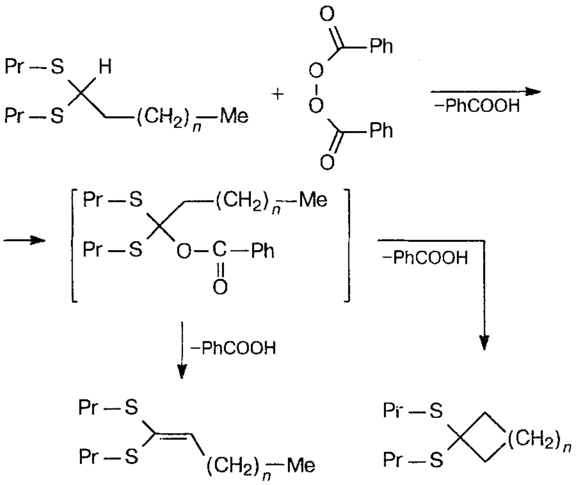
Formation of cyclic compounds in the reaction of benzoyl peroxide with thioacetals

Yu. I. Puzin* and G. V. Leplyanin

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347) 234 2914

Previously[1] we have reported that the reactions of benzoyl peroxide with thioacetals do not afford products of the oxidation of the S atoms. In the case of formaldehyde thioacetal, the methylene group is mostly transformed,[2] while the reaction of acetaldehyde thioacetal predominantly involves dehydrogenation to give a ketene thioacetal.[3]

We showed that the reactions of *n*-pentanal or *n*-hexanal dipropyldithioacetals with benzoyl peroxide occur *via* α,β- or α,ω-dehydrogenation, probably by the scheme presented below: dipropyldithioacetals of cyclopentanone and cyclohexanone are formed in addition to 1,1-bis(alkylthio)-1-alkenes.



n = 2, 3

The reaction was carried out according to the known procedure;[1] the products were isolated and purified chromatographically (silica gel, hexane—chloroform as the eluent). NMR spectra were recorded in $CDCl_3$.

Cyclopentanone dipropyldithioacetal. Yield 60 %. Found (%): C, 58.98; H, 10.75; S, 30.12. $C_{11}H_{22}S_2$. Calculated (%): C, 60.55; H, 10.09; S, 29.36. ^1H NMR, δ: 0.85 (t, 6 H, Me); 1.4—1.5 (m, 8 H, $-CH_2-$); 1.3 (m, 4 H, $-CH_2-$); 2.45 (t, 4 H, $-CH_2S-$). ^{13}C NMR, δ: 13.95 (q, Me, *J* = 124.42 Hz); 22.76 (t, $-CH_2-$, *J* = 122.89 Hz); 32.78 (t, $-CH_2S-$, *J* = 136.8 Hz); 65.71 (s, C(1)); 41.74 (t, α-*cyclo*-CH_2, *J* = 132.91 Hz); 24.27 (t, β-*cyclo*-CH_2, *J* = 131.82 Hz). MS, *m/z*: 218 $[M]^+$.

1,1-Bis(propylthio)-1-pentene. Yield 30 %. Found (%): C, 59.70; H, 9.97; S, 30.06. $C_{11}H_{22}S_2$. Calculated (%): C, 60.55; H, 10.09; S, 29.36. ^1H NMR, δ: 0.7—0.9 (m, 9 H, Me); 1.32 (m, 2 H, $-CH_2-$); 2.4 (t, 4 H, $-CH_2S-$); 4.0 (m, 2 H, $-CH_2CH=$); 6.0 (t, 1 H, $-CH=$). IR (CCl_4), ν/cm^{-1}: 1685 (C=C). ^{13}C NMR, δ: 13.12 (Me); 22.17 (CH_2); 35.28 (CH_2S); 112.38 (=CH); 107.6 (C(1)).

Cyclohexanone dipropyldithioacetal. Yield 47 %. Found (%): C, 61.98; H, 10.55; S, 27.12. $C_{12}H_{24}S_2$. Calculated (%): C, 62.07; H, 10.34; S, 27.59. ^1H NMR, δ: 0.85 (t, 6 H, Me); 1.4—1.5 (m, 10 H, $-CH_2-$); 1.25 (m, 4 H, $-CH_2-$); 2.45 (t, 4 H, $-CH_2S-$). ^{13}C NMR, δ: 13.98 (q, Me, *J* = 124.30 Hz); 22.91 (t, $-CH_2-$, *J* = 124.6 Hz); 30.58 (t, $-CH_2S-$, *J* = 138.3 Hz); 61.58 (s, C(1)); 38.32 (t, α-*cyclo*-CH_2, *J* = 129.2 Hz); 22.59 (t, β-*cyclo*-CH_2, *J* = 127.8 Hz); 26.08 (t, γ-*cyclo*-CH_2, *J* = 126.4 Hz). MS, *m/z*: 232 $[M]^+$.

1,1-Bis(propylthio)-1-hexene. Yield 39 %. Found (%): C, 62.97; H, 9.95; S, 28.01. $C_{12}H_{24}S_2$. Calculated (%): C, 62.07; H, 10.34; S, 27.59. ^1H NMR, δ: 0.7—0.9 (m, 9 H, Me); 1.32 (m, 2 H, $-CH_2-$); 2.4 (t, 4 H, $-CH_2S-$);

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