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REACTIONS OF P(III) THIOBENZYL ESTERS WITH METHYL IODIDE

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The reactions of S-benzyl diphenylthiophosphinite and 2-benzylthio-4,5-benzol,3-dioxaphospholane with methyl iodide have been examined. In contrast to the oxygen analogs, the reaction occurs under mild conditions, and does not give Arbuzov reaction products.

We have previously reported the preparation of some novel thiobenzyl esters of P(III) acids [1, 2]. Benzyl diphenylphosphinite has been reported to react with methyl iodide at 70°C to give methyldiphenylphosphine oxide [3]. It was of interest to examine the behavior of thiobenzyl esters of P(III) acids in the analogous reaction. S-Benzyl diphenylthiophosphinite reacts in 1 h at ~20°C with methyl iodide, but methyldiphenylphosphine thiooxide is not formed. When the reaction was complete, a crystalline solid separated from the reaction mixture (CD_2Cl_2 , δP 35.5 ppm), ¹H NMR spectrum 2.2811 d (SCH_3 , ³J_{PH} = 13.78), 3.9629 d (CH_2Ph , ²J_{PH} = 11.78), which on recrystallization and storage underwent conversion into benzyldiphenylphosphine sulfide (δP 44 ppm).



2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane also reacts with methyl iodide under mild conditions. The reaction required 1 day at ~20°C, with the formation of 2-benzyl-2-thiooxo-4,5-benzo-1,3,2-dioxaphospholane (δP 118 ppm).



There have been no reports of the reaction of the corresponding oxygen analog with methyl iodide. We have prepared 2-benzyloxy-4,5-benzo-1,3,2-dioxaphospholane, which reacts with methyl iodide only on heating at 160°C for 10 h, giving a mixture of methyl- (δP 55 ppm) and benzylphosphonates (δP 48 ppm).

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The anomalous behavior of S-benzyl diphenylthiophosphinite and 2-benzylthio-4,5-benzo-1,3,2-dioxaphospholane in their reactions with methyl iodide can be rationalized by assuming the reaction center in the P-S system to be the sulfur atom.

EXPERIMENTAL

 31 P NMR spectra were recorded on a nonstandard KGU-4 NMR spparatus (10.2 MHz), with 85% H₃PO₄ as external standard. ¹H NMR spectra were obtained on a Varian T-60 spectrometer, internal standard TMS.

<u>Reaction of S-Benzyl Diphenylthiophosphinite with Methyl Iodide.</u> To S-benzyl diphenylthiophosphinite, obtained as in [1] from 2 g (0.009 mole) of diphenylchlorophosphine and 1.78 g (0.009 mole) of trimethylsilyl benzyl sulfide under argon, was added (after removal of trimethylchlorosilane) 1.29 g (0.009 mole) of methyl iodide. After 1 h, a crystalline yellow solid separated from the mixture (δ P 35.5 ppm). Recrystallization from 2-propanol gave 2.44 g (88%) of benzyldiphenylphosphine sulfide, mp 162°C. ¹H NMR spectrum (δ , ppm, DMSOd₆): 4.1 d (-P-CH₂-, ²J_{PH} 14 Hz), 7.05 s (C₆H₅P), 7.45 m (C₆H₅CH₂). ³¹P NMR spectrum (DMF): δ P 44 ppm. Found, %: C 73.72, H 5.54, P 9.99, S 9.41. C₁₉H₁₇PS. Calculated, %: C 74.03, H 5.52, P 10.06, S 10.34.

Reaction of 2-Benzylthio-4,5-benzo-1,3,2-dioxaphosphorane with Methyl Iodide. To 2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane, obtained as in [1] from 5.235 g (0.03 mole) of pyrocatechol chlorophosphite and 5.88 g (0.03 mole) of trimethylsilyl benzyl sulfide, was added 4.26 g (0.03 mole) of methyl iodide. All operations were carried out under dry argon. The mixture was kept for 1 day at ~20°C, and fractionated under an oil pump vacuum to give 5.9 g (75%) of 2-benzyl-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane, bp 139-145°C (0.03 mm), mp 62°C. ¹H NMR spectrum (δ , ppm, CCl₄): 3.80 d (-P-CH₂, ²J_{PH} 17 Hz), 6.97 s (C₆H₄), 7.30 s (C₆H₅). ³¹P NMR spectrum: δ P 118 ppm. Found, %% C 59.26, H 4.23, P 11.83. C₁₃H₁₁-O₂PS. Calculated, %: C 59.54, H 4.20, P 11.83.

<u>2-Benzyloxy-4,5-benzo-1,3,2-dioxaphospholane</u> was obtained from 7.1 g (0.04 mole) of pyrocatechol chlorophosphite, 4.4 g (0.04 mole) of benzyl alcohol, and 6.05 g (0.04 mole) of N,N-diethylaniline in benzene for 3 h at ~20°C. The solid was filtered off, and the filtrate evaporated under a water pump vacuum and the residue fractionated to give 8 g (80%) of 2-benzyloxy-4,5-benzo-1,3,2-dioxaphospholane, bp 112-115°C (0.02 mm), $n_D^{2^0}$ 1.5750, $d_4^{2^0}$ 1.2371. ¹H NMR spectrum in capillary (δ , ppm): 4.40 d (-POCH₂, ³J_{PH} 7 Hz), 6.83 m (C₆H₄), 7.00 s (C₆H₅). ^{3 1}P NMR spectrum, δ P 129 ppm. Found, %: C 63.09, H 4.41, P 12.15. C₁₃H₁₁-O₃P. Calculated, %: C 63.41, H 4.47, P 12.60.

<u>Reaction of 2-Benzyloxy-4,5-benzo-1,3,2-dioxaphospholane with Methyl Iodide.</u> A mixture of 3.75 g (0.015 mole) of pyrocatechol chlorophosphite and 2.16 g (0.015 mole) of methyl iodide was kept for 12 h, then heated at 160°C for 10 h in a sealed ampul. The progress of the reaction was followed by ³¹P NMR: δP 48 ppm (2-methyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane), δP 55 ppm (2-benzyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane). ¹H NMR spectrum in capillary (δ , ppm): 1.98 d (-PCH₃, ³J_{PH} 18 Hz), 3.70 d (-PCH₂Ph, ²J_{PH} 21 Hz), 4.52 s (ICH₂Ph), 7.00 s (C_{6H₄}), 7.08 m (C_{6H₅}CH₂).

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