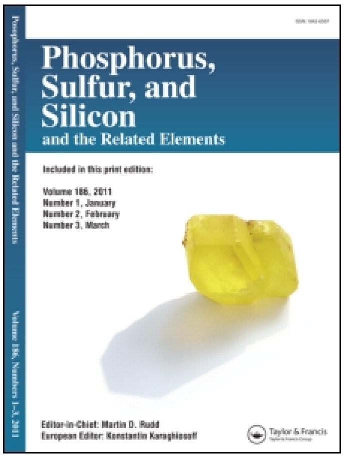

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# A DIRECT ROUTE TO ORTHO-HYDROXY PHENYL DITHIOPHOSPHINIC ACIDS

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# A DIRECT ROUTE TO ORTHO-HYDROXY PHENYL DITHIOPHOSPHINIC ACIDS

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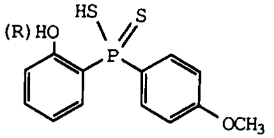
Through a direct and selective deprotection of 1 (R=methyl) with boron tribromide substituted o-hydroxy-dithiophosphinic acid 1 was prepared under mild conditions in excellent yield.

In the course of our work to design enzyme models,[1,2] we had occasion to synthesize a model with the structure:



1

FIGURE 1

Compound 1 is a dithiophosphinic acid with a hydroxy group ortho to the dithiophosphinic acid function on one of the aromatic rings. Molecules with structures related to 1 have potential interest as ligands for metals and pesticides.

Attempts to synthesize 1 by routes based on a conversion of a phosphinic acid to a dithiophosphinic acid as a last step were unsuccessful. However, the methyl derivative (R = Me) of 1, 2-methoxyphenyl-4-methoxylphenyl-dithiophosphinic acid, could be obtained easily through the reaction of a Grignard reagent prepared from 2-bromo anisol and Lawesson-reagent[3]. This intermediate was found to be selectively demethylated by reaction with boron tribromide[4] in 97% yield. After 15 seconds in methylene chloride at room temperature, followed by aqueous workup, only the methyl group on the ortho oxygen was removed.† Only after further reaction under the same reaction conditions for 8 hours was the second methyl group on the para oxygen also taken off.

H—NMR-spectra of the protected compound showed a remarkable chemical shift of the aromatic hydrogen ortho to the C—P bond, due to its fixed position above the other aromatic ring (ABCX; 8.45 ppm). With deprotection this signal shifts to 7.34 ppm, as the aromatic ring gains mobility. Crystal structure

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† Analytical Data; m.p. 169°C; $^1$H—NMR: ($CDCl_3$, ppm) 2.5 (broad, 1H, SH); 3.86 (3H, s, $-OCH_3$); 6.9–7.9 (8H, m, aromatic H); 9.1 (1 H, broad, OH); MS: (m/e)$M^+$, 296(65.3), 263(100.0), 155(51.3). EA: $C_{13}H_{13}O_2PS_2$ (calc.: C, 52.69; H, 4.42; found: C, 52.37; H, 4.46.)

confirmed selective demethylation and showed that the S hydrogen is oriented towards the free hydroxy group.‡

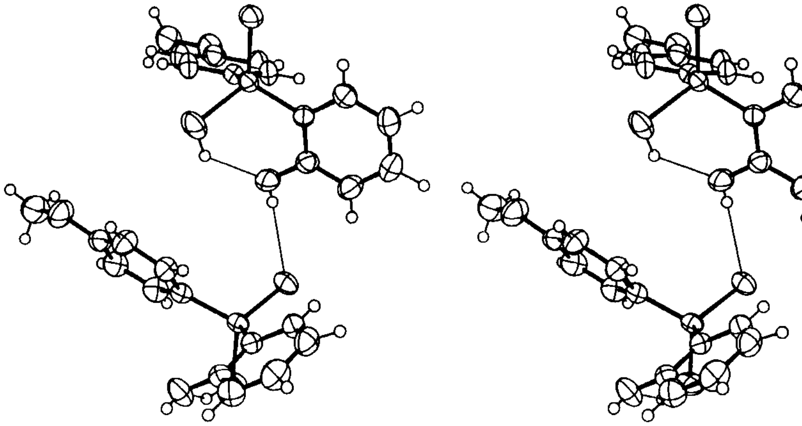

FIGURE 2 ORTEP [7] stereo drawing of two molecules of 1 showing the inter- and intramolecular hydrogen bonds. The vibration ellipsoids are at the 50% probability level.

The mechanistic origin of the surprisingly selective deprotection reaction is uncertain. A plausible first step involves the replacement of bromide of boron tribromide by the thiol function. Thereby the reagent is bonded to the region where further reaction occurs. Models based on known bond lengths in analogous compounds[8] and the data given by the crystal structure suggest that this intermediate is sterically well suited for reaction.

We examined other Lewis acids (aluminium trichloride, mercury dibromide and diiodide, zinc dichloride, dibromide and diiodide, cadmium dichloride) and also the reaction of boron tribromide with the sulfur analog in the 2 position. In no case was a selective demethylation observed. The simplest hypothesis is that altering the steric dimensions of groups in the cyclic complex makes methyl replacement much slower.

## ACKNOWLEDGEMENT

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‡ Crystal structure determination.

Crystal data: $C_{13}H_{13}O_2PS_2$, $M_r = 296.35\,g\,mol^{-1}$, monoclinic space group $P2_1/a$, $a = 12.484$, $b = 6.863$, $c = 16.957$ Å, $\beta = 102.70°$, $d_x = 1.39\,g\,cm^{-3}$, $Z = 4$. 3416 independent intensities were measured at 20°C on an Enraf Nonius CAD-4 four circle diffractometer (Graphite monochromator, $MoK_\alpha$ radiation, $\lambda = 0.71069$ Å) with $\theta < 28°$ of which 2194 with $I > 3\ \sigma(I)$ were considered significant. The structure was solved by direct methods with SHELX86 [5] and refined by full matrix least squares with SHELX76 [6]. The non-H atoms were refined anisotropically, the hydrogens isotropically. The refinement converged with $R = 0.034$. Atomic coordinates and atomic displacement parameters have been deposited with the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, England.

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