Tetrahedron Letters No.9, pp. 699-702, 1971. Pergamon Press. Printed in Great Britain.

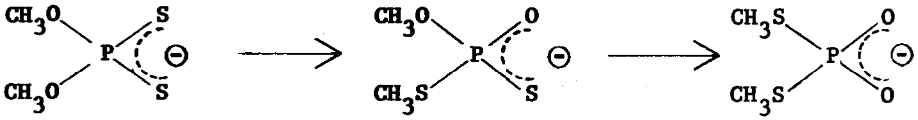
STUDIES OF SODIUM O,O-DIMETHYLPHOSPHORODITHIOATE AND ITS ISOMERS

C. K. Tseng and James H.-H. Chan
Stauffer Chemical Company, Western Research Center,
Richmond, California 94804

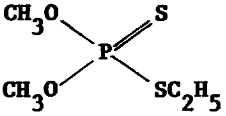
(Received in USA 22 January 1971; received in UK for publication 15 February 1971)

Previous studies by Kabachnik and co-workers[1] have shown, by the use of the Hammett relationship, that phosphorothioic acids exist as the thione and thiol forms. Discrepancies in structural assignments as to whether the product was a thionate or thiolate from the reaction of potassium O,O-diethylphosphorothioate with methyl chloroformate, were also reported[2,3].

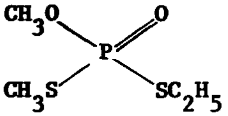
We have observed that an aqueous solution of sodium O,O-dimethylphosphorodithioate (1) isomerizes under mild heating (60°C) to sodium O,S-dimethylphosphorodithioate (2) and sodium S,S-dimethylphosphorodithioate (3). When a mixture of 1, 2 and 3 was allowed to react with ethyl iodide, O,O-dimethyl-S-ethylphosphorodithioate (4) and O,S-dimethyl-S-ethylphosphorodithioate (5) were formed. No O,S-dimethyl-O-ethylphosphorodithioate, the O-ethylated product, was detected. Analysis of the solution showed that it contained only unreacted sodium salt 3. Under forcing conditions (heating at 90-95°C under autogenous pressure), 3 was found to react with ethyl iodide to give S,S-dimethyl-O-ethylphosphorodithioate (6). The reaction products were isolated by preparative gas chromatography and characterized by NMR and infrared spectrometric methods.



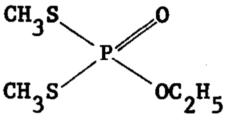
1 2 3



4



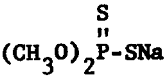
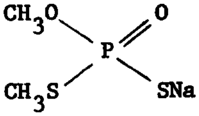
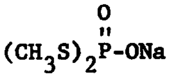
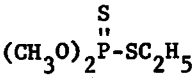
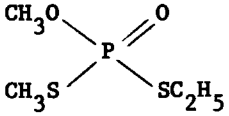
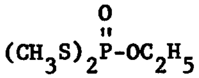
5



6

Since no O,S-dimethyl-O-ethylphosphorodithioate was detected, it is evident that the sulfur atom, rather than the oxygen atom, reacts preferentially with ethyl iodide. The relative reactivity of 1 and 3 further supports this result. The NMR chemical shifts and coupling constants of the respective sodium salts and their esters are listed in the table below.

Table: NMR Data of the Various Dithiophosphates and Their Salts*

Compd. No.	Compound	δ_{CH_3S}[c] (J_{HCSP})[d]	δ_{CH_3O}[c] (J_{HCOP})[d]	δ_{CH_3C}[c] (J_{HCCH})[d]	δ_{CH_2S}[c] (J_{HCSP})[d]	δ_{CH_2O}[c] (J_{HCOP})[d]
1[a]	 $(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SNa$	-	3.58 (14.4)	-	-	-
2[a]		2.13 (13.5)	3.57 (14.7)	-	-	-
3[a]	 $(CH_3S)_2\overset{O}{\overset{\|}{P}}\text{-}ONa$	2.18 (14.3)	-	-	-	-
4[b]	 $(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}SC_2H_5$	-	3.75 (15.1)	1.29 (7.3)	2.82 (16.6)	-
5[b]		2.32 (16.2)	3.82 (13.6)	1.36 (7.3)	2.91 (15.6)	-
6[b]	 $(CH_3S)_2\overset{O}{\overset{\|}{P}}\text{-}OC_2H_5$	2.32 (16.0)	-	1.35 (7.0)	-	4.23 (9.8)

* The spectra were obtained from a Varian HA-60-IL spectrometer using TMS as an internal reference.

a. Solvent CD_3OD.

b. Solvent $CDCl_3$.

c. Expressed in ppm.

d. Expressed in Hz.

The relative rate of reaction[4] of sodium O,O- (1) and sodium O,S-dimethylphosphorodithioate (2) (determined by allowing a mixture of the two sodium salts to compete for a deficiency of methyl iodide-d_3) was determined by NMR spectrometric methods. The reaction was carried out at room temperature with deuterated methanol as solvent. It was found that 1 reacted 6.4 ± 0.3 times faster than 2 (i.e. $k_{\underline{1}}/k_{\underline{2}} = 6.4 \pm 0.3$).

References

1. M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov and T. A. Melentyeva, Tetrahedron, 9, 10 (1960).
2. J. I. G. Cadogan, J. Chem. Soc., 3067 (1961).
3. A. N. Nesmeyanov and M. I. Kabachnik, Experimentia, Suppl. II, 67 (1955).
4. B. Rickborn and J. H.-H. Chan, J. Org. Chem., 32, 3576 (1967).