α-Phosphorylsulphoxides. I.[1] Synthesis

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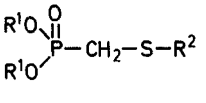
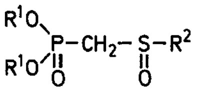
Recently, there has been widespread interest in chemistry and stereochemistry of α-substituted and α,β-unsaturated sulphoxides[2,3,4]. This prompted us to report a facile synthesis of α-phosphorylsulphoxides (**2**) which can be used under Horner-Wittig reaction conditions as a reagents for the preparation of α,β-unsaturated sulphoxides. It is to be point out that, in contrast to the well-known α-phosphorylsulphides (**1**)[5-9] and α-phosphorylsulphones (**3**)[10-12], the title compounds have hitherto not been obtained and characterized.



1



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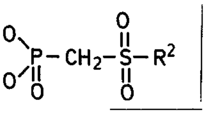

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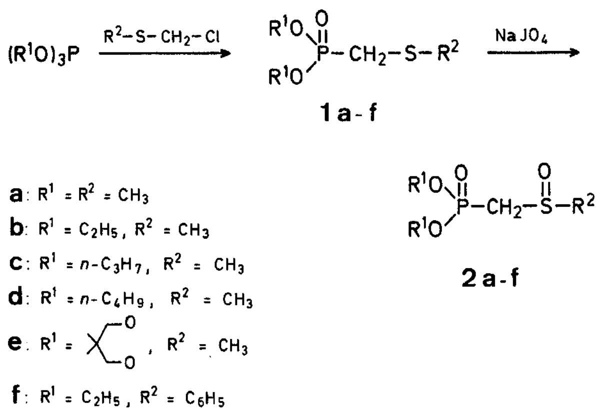
α-Phosphorylsulphoxides (**2**) have been prepared in this work according to the following reaction scheme:



We have found that full conversion of **1** to **2** can be achieved using the acetone-water solution of sodium metaperiodate which is known to oxidise sulphides selectively to sulphoxides[13]. The crude compounds **2** (100% yield) were pure according to the ^{1}H- and ^{31}P-N.M.R. spectra and may be used directly for further transformations. The traces of the unreacted sulphides (**1**) and the corresponding sulphones (**3**) could only be detected by T.L.C. This is important since the sulphoxides (**2**) are thermally unstable and cannot be purified by distillation. They disproportionate at ~100° affording a mixture of **1** and **3**. Analytically pure sulphoxides (**2**) free of contaminations by sulphide (**1**) and sulphone (**3**) were obtained by column chromatography on silifica gel. Their physical properties, elemental analyses and ^{1}H-N.M.R. data are summarized in Table 2. The ^{31}P-N.M.R. chemical shifts of the α-phosphoryl-sulphides (**1**) -sulphoxides (**2**) and -sulphones (**3**) are collected in Table 3.

Finally, we would like to comment on the recent paper by Almog and Weissman[14] who suggested the formation of the sulphoxide (**2b**) in the reaction between diethyl phosphorochloridate and the methylsulphinyl carbanion. Our own findings do not confirm this assumption. In the ^{31}P-N.M.R. spectrum of the reaction mixture we observed two signals at $\delta = +1.4$ ppm and $\delta = +13.0$ ppm corresponding to diethylphosphoric acid and tetraethyl pyrophosphate. No signal of the sulphoxide (**2b**) ($\delta = -17.6$, dimethyl sulfoxide solution) was found. This result is indicative of *O*- and not *C*-phosphorylation of the methyl-

Table 1. Preparation of Compounds **1**

Compound	Reactions conditions		Yield (%)	b.p.°/torr (m.p. solv.)	n_D^{20}	Formula m.w.	Elemental Analysis				Ref.
	Temperature	Time (hr)									
1a	115–125°	6	39	53–55/0.02	1.4780	$C_4H_{11}O_3PS$ 170.17	calc. found	C 28.23 28.08	H 6.52 6.72	P 18.20 18.16	7
1b	120–130°	16	49	67/0.01	1.4650	$C_6H_{15}O_3PS$ 198.22	calc. found	C 36.41 36.05	H 7.62 7.55	P 15.63 15.71	5, 6
1c	130–145°	16	46	88–90/0.01	1.4622	$C_8H_{19}O_3PS$ 226.28	calc. found	C 42.46 42.30	H 8.46 8.50	P 13.69 13.67	
1d	130–160°	18	39	108–110/0.03	1.4612	$C_{10}H_{23}O_3PS$ 254.33	calc. found	C 47.23 47.52	H 9.12 9.40	P 12.18 12.00	
1e	115–125°	4	61	(54–55, benzene: ether)		$C_7H_{15}O_3PS$ 210.23	calc. found	C 39.99 39.97	H 7.19 7.10	P 14.73 14.62	
1f	120–140°	16	70	120–122/0.2	1.5326	$C_{11}H_{17}O_3PS$ 260.29	calc. found	C 50.76 50.61	H 6.58 6.71	P 11.90 12.00	6

Table 2. Preparation of α-Phosphorylsulphoxides (**2**)

Compound	Yield of the anal. pure **2** (%)	Eluent[a]	n_D^{20} (m. p., solvent)	Formula M. W.	Elemental analysis	^{1}H-N. M. R. (80 MHz) data (CDCl$_3$)[c] δ, (ppm) *J*, (Hz)
2a	96	B/M 10:1	(52–4°, A/P)	$C_4H_{11}O_4PS$ 186.17	calc. C 25.81 H 5.96 P 16.64 found 26.10 5.74 16.70	2.83 (s, 3H, $\underline{CH}_3$—SO—), 3.38 (d, 2H, —$\underline{CH}_2$—P—, *J* = 16.0), 3.80 (d, 6H, $\underline{CH}_3$—O—P, *J* = 11.0).
2b	96.5	B/A/M 9:1:1	1.4766	$C_6H_{15}O_4PS$ 214.22	calc. C 33.64 H 7.06 P 14.46 found 33.56 7.14 13.88	1.30 (t, 6H, $\underline{CH}_3$—CH_2—), 2.77 (s, 3H, $\underline{CH}_3$—SO—), 3.46 (d, 2H, $\underline{CH}_2$—P, *J* = 16.0) 4.10 (qt, 4H, CH_3—$\underline{CH}_2$—).
2c	42	B/A/M 18:3:1	1.4674	$C_8H_{19}O_4PS$ 242.28	calc. C 39.66 H 7.90 P 12.78 found 39.53 8.05 12.73	0.97 (t, 6H, CH_3—CH_2—CH_2—O—), 1.72 (sx, 4H, CH_3—$\underline{CH}_2$—CH_2—O), 2.83 (s, 3H, $\underline{CH}_3$—SO—), 3.36 (d, 2H, $\underline{CH}_2$—P, *J* = 15.7), 4.05 (q, 4H, CH_3—CH_2—$\underline{CH}_2$—O).
2d	12.5[b]	B/A/M 18:3:1	1.4684	$C_{10}H_{23}O_4PS$ 270.33	calc. C 44.43 H 8.58 P 11.46 found 44.37 9.16 11.52	0.95 (t_d, 6H, $\underline{C}H_3$—$(CH_2)_2$—CH_2—O), 1.39 (m, 8H, CH_3—$(CH_2)_2$—CH_2—O—), 2.81 (s, 3H, $\underline{CH}_3$SO—), 3.40 (d, 2H, $C\underline{H}_2$—P, *J* = 16.0), 4.10 (m, 4 H, CH_3—$(CH_2)_2$—$\underline{CH}_2$—O)
2e	92	B/A/M 27:3:2	(118–20°, B/A)	$C_7H_{15}O_4PS$ 226.23	calc. C 37.21 H 6.68 P 13.69 found 37.22 6.68 13.72	1.02 and 1.19 (two s, 6H, $CH_{3\,ring}$). 1.74 (s, 3H, $\underline{CH}_3$—SO—), 3.58 (d, 2H, $\underline{CH}_2$—P, *J* = 15.2), 4.11 (m, 4H, $CH_{2\,ring}$).
2f	85	B/C/E 4:3:3	1.5236	$C_{11}H_{17}O_4PS$ 276.29	calc. C 47.82 H 6.20 P 11.21 found 48.00 6.33 11.23	1.26 (t, 6H, $\underline{CH}_3$—CH_2—O), 3.41 (d, 2H, $\underline{CH}_2$—P, *J* = 15.0), 4.11 (m, 4H, CH_3—$\underline{CH}_2$—O), 7.60 (m, 5 H_{arom}).

[a] B-benzene, A-acetone, M-methanol, E-ethyl acetate, P-petroleum ether.
[b] No attempt has been made to improve the yield by changing the eluting system.
[c] s-singlet, d-doublet, t-triplet, q-quartet, qt-quintet, sx-sextet, t_d-degenerate triplet.

sulphinyl carbanion. Therefore, the synthesis of α,β-unsaturated sulphoxides reported by the above mentioned authors must take place by a different reaction sequence. This point is under current study.

General Remarks:

N.M.R. spectra were run on a Tesla BS-487C and Jeol C-60H spectrometers using TMS as an internal standard in ^{1}H-N.M.R. measurements and 85% phosphoric acid as an external standard in ^{31}P-N.M.R. measurements. Heteronuclear spin decoupler INH-SD-HC was used for precise ^{31}P chemical shift determinations.

Melting and boiling points are uncorrected.

Preparation of α-Phosphorylsulphides (1):

Compounds **1** were obtained according to Ref.[6] by the Arbuzov reaction of trialkyl phosphites with α-chlorosulphides and isolated by fractional distillation or crystallization. All products were identified and checked for purity by ^{1}H- and ^{31}P-N.M.R. spectra and G.L.C. The results and analytical data for **1** are given in Table 1.

Preparation of α-Phosphorylsulphoxides (2); General Procedure:

A solution of sodium metaperiodate (0.021 mol) in water (75 ml) was dropwise added to a well-stirred and cooled (−5–0°) solution of the sulphide **1** (0.02 mol) in acetone (20 ml) and water (10 ml) during the course of 45 min. After being stirred for further 4hr at 0°, the precipitated sodium iodate was filtered off and solvent evaporated. The second portion of sodium iodate was isolated from the residue and washed with acetone (20 ml). Total yield of sodium iodate obtained varied between 94 and 100%. Evaporation of acetone and drying of the residue over phosphorus pentoxide afforded the crude sulphoxide **2** in quantitative yield. Analytical sample was obtained by column chromatography on silica gel (100–200 mesh). The yield and eluent are given in the Table 2.

Table 3. ^{31}P-N.M.R. Chemical Shifts of **1**, **2**, and **3**

Compound	$\delta_{^{31}P}$, ppm **1**[a]	**2**[b]	**3**[c]
a	−26.7	−21.3	−15.8
b	−23.4	−17.6	−12.8
c	−24.0	−17.7	−13.0
d	−23.8	−17.8	−13.5
e	−17.3	−10.3	−5.6
f	−22.0	−16.5	−11.6

[a] Measured as neat liquids.
[b] Measured as neat liquids with the exception of **2a** and **2e** spectra of which were taken in chloroform solution.
[c] Measured in dimethylsulfoxide solution.

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