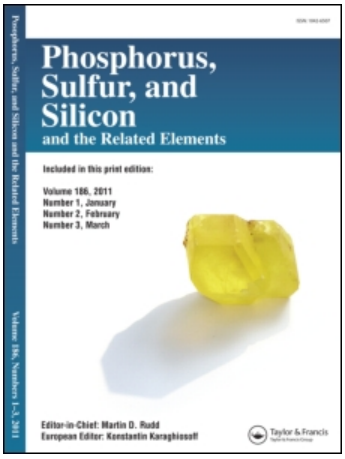

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTIVITY OF MANGANESE DIETHYLAMIDE WITH PHOSPHATE TRIESTERS

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To cite this Article Fester, V. D. , Vather, S. M. and Modro, T. A.(1987) 'THE REACTIVITY OF MANGANESE DIETHYLAMIDE WITH PHOSPHATE TRIESTERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 31: 3, 281 — 283
To link to this Article: DOI: 10.1080/03086648708080646
URL: http://dx.doi.org/10.1080/03086648708080646

Phosphorus and Sulfur, 1987, Vol. 31, pp. 281–283
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THE REACTIVITY OF MANGANESE DIETHYLAMIDE WITH PHOSPHATE TRIESTERS

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(Received May 30, 1986; in final form September 26, 1986)

Manganese bis-(diethylamide) reacts with phosphoric triesters with a selective displacement of single ester function by the diethylamide group. In the reaction of the manganese reagent with dialkyl phosphites products of both, mono- and disubstitution were observed.

Stimulated by the recent interest[1] in the use of titanium tetrakis (diethylamide) (**1**) as chemoselective protecting agents for carbonyl groups, we investigate the reactions between aminoderivatives of transition elements and esters of phosphorus oxyacids. In the previous paper[2] we reported that while treatment of phosphorous diesters, $(RO)_2P(O)H$, with (**1**) resulted in a displacement of both ester functions by the diethylamine groups, phosphoric triesters, $(RO)_3PO$, were inert to the titanium reagent. Since it was reported[1] that manganese dialkylamido derivatives, e.g. $Mn(NEt_2)_2$ (**2**), react smoothly and selectively with aldehydes and ketones, we decided to investigate the reactivity of (**2**)[3] towards triesters of phosphoric acid. In contrast to the behaviour of the titanium reagent, (**1**) towards phosphate triesters, addition of (**2**) to triesters $(RO)_3PO$ at 0°C resulted in an exothermic reaction. After aqueous work-up and extraction with dichloromethane the products were purified by distillation and identified as dialkyl (or diaryl) *N,N*-diethylphosphoroamidates (**3**)

$$\underset{\mathbf{2}}{(RO)_3PO} + Mn(NEt_2)_2 \rightarrow \underset{\mathbf{3}}{(RO)_2P(O)NEt_2} \qquad (1)$$

Table I summarises the results of reactions of (**2**) with phosphoric derivatives.

Reaction of triethyl phosphate with 0.5 mol-equivalent of **2** was slow, but after sufficiently long time (48 h) 76% yield of the product could be attained. This result indicates that reagent (**2**) is capable of donating both diethylamino groups (as it does with respect to carbonyl substrates) in the reaction with phosphate esters. The displacement, however, involves only one ester group of a phosphate; treatment of of $(EtO)_3PO$ with 3 mol-equivalents of **2** resulted in the isolation of **3b** as the only phosphorus-containing product, with no indication of the formation of the monoester diamide or triamide derivatives. In agreement with this, **3b** proved inert towards reagent **2**. When the mixed ester, diethylphenyl phosphate, was used as a substrate, only the product corresponding to the displacement of the phenoxy group was obtained. This result indicates that the selectivity in the product-determining step is governed by the usual leaving group abilities of the substituents at phosphorus. The reaction shown in Equation (**1**) to our knowledge

TABLE I

Reactions of phosphates with **2**; O°C

Substrate	Mol-equiv of **2**	Reaction time	Product	Yield (%)
$(MeO)_3PO$	1.2	30 min	**3a**(R = Me)	28
$(EtO)_3PO$	0.5	30 min	**3b**(R = Et)	24
$(EtO)_3PO$	0.5	48 h	**3b**(R = Et)	76
$(EtO)_3PO$	1.2	1.5 h	**3b**(R = Et)	86
$(EtO)_3PO$	3	18 h	**3b**(R = Et)	83
$(PhO)_3PO$	1.2	30 min	**3c**(R = Ph)	65
$(EtO)_2(PhO)PO$	1.2	30 min	**3b**	63
3 (R = Et)	1.2	15 h	no reaction	

represents the first example of the direct displacement of an acyclic phosphate ester function by an amino group. The fact that this reaction is rigorously restricted to the exchange of only one ester group and probably shows high regioselectivity opens up the possibility of its application to the synthesis of phosphoric diester derivatives *via* the triester substrates.

With respect to dialkyl phosphites, **2** shows greater selectivity than the titanium analogue **1**. Treatment of $(RO)_2P(O)H$ with **1** at −40°C resulted in displacement of both ester functions by the NEt_2 groups, yielding $(Et_2N)_2P(O)H$, (**4**) with no evidence of the intermediate amidoester $(Et_2N)(RO)P(O)H$ (**5**). In contrast, treatment of $(EtO)_2P(O)H$ with **2** at room temperature for 18 h gave (in addition to some unreacted phosphite) a mixture of **5** and **4** in a 3.8:1 ratio.

$$\underset{\mathbf{2}}{(EtO)_2P(O)H} + Mn(NEt_2)_2 \rightarrow \underset{\mathbf{5}}{(Et_2N)(EtO)P(O)H} + \underset{\mathbf{4}}{(Et_2N)_2P(O)H} \qquad (2)$$

The mechanisms of the above reactions are currently being investigated in our laboratory.

EXPERIMENTAL SECTION

^1H NMR spectra were recorded on a Bruker WH 90 spectrometer with TMS as internal standard. Diethylphenyl phosphate was prepared from diethyl phosphorochloridate and phenol in the presence of triethylamine in benzene. Bp 110–115°C (0.1 mm): ^1H NMR ($CDCl_3$). δ 1.30 (t, 6H, J 6.3 Hz, $2 \times CH_3$); 4.20 (q, 4H, J 6.3 Hz, $2 \times CH_2$); 6.7–7.5 (m, 5H, Ph). M^+ 230.

Reactions of phosphates with **2**

Phosphoric triester was added to **2** at 0°C (exothermic effect) and the mixture was incubated for a period indicated in Table I. The mixture was then quenched with water, filtered and extracted with CH_2Cl_2. After drying and evaporating the solvent, the product was purified by distillation or column chromatography (c.c) **3a**: purified by c.c. (silica gel, CH_2Cl_2/benzene). ^1H NMR ($CDCl_3$). δ 1.12 (t, 6H, J 7.2 Hz, $2 \times \beta$-CH_3); 3.00 (d of q, 4H, J 7.2 Hz, 13.5 Hx; $2 \times CH_2$); 3.64 (d, 6H, J 11.7 Hz, $2 \times OCH_3$). MS, 181 (M^+). Calc. for $C_6H_{16}NO_3P$: C, 39.8; H, 8.8; N, 7.7%. Found: C, 40.15; H, 8.8; N, 7.5%.

3b: bp 90°C (0.3 mm). ^1H NMR ($CDCl_3$). δ 1.1 (t, 6H, J 7.2 Hz, $2 \times CH_3$); 1.3 (t, 6H, J 7.2 Hz, $2 \times CH_3$); 3.10 (d of q, 4H, J 7.2 and 11.7 Hz, $2 \times CH_2N$); 4.02 (d of q, 4H, J 8.1 and 9.9 Hz, $2 \times CH_2O$). MS, 209 (M^+). Calc. for $C_8H_{20}NO_3P$: C, 45.9; H, 9.6; N, 6.7%. Found: C, 45.6; H, 9.5; N, 6.4%.

3c: purified by c.c. (silica gel, CH_2Cl_2/benzene). ^1H NMR ($CDCl_3$). δ 1.06 (t, 6H, J 7.2 Hz, $2 \times CH_3$); 3.22 (d of q, 4H, J 7.2 and 11.7 Hz, $2 \times CH_2$); 6.72 – 7.80 (m, 10H, $2 \times$ Ph). MS, 305 (M^+). The product was identical to the compound prepared independently from $(PhO)_2P(O)Cl$ and Et_2NH.

Reaction between diethylphenyl phosphate and **2**

After the aqueous work-up, extraction and evaporation, the reaction product was distilled under reduced pressure; bp 100–115°C (0.1 mm). ^{1}H NMR of the distillate indicated that it consisted of *ca.* 1:1 mixture of **3b** and phenol. These two products were separated by G.C. (3% Silicone OV 17 on chromo WH, 80/100 mesh) and identified by addition of authentic samples.

Reaction between diethyl phosphite and **2**

Diethyl phosphite was added to **2** (1.2 molar equivalents) at 0° and the mixture was allowed to stir at room temperature for 18 h. The mixture was quenched with water and extracted with CH_2Cl_2 which was dried and evaporated *in vacuo*. ^{1}H NMR spectrum showed three distinct products which were identified by comparison with the P-H signals of authentic samples of $(EtO)_2P(O)H$ and **4**: $(EtO)_2P(O)H$, δ ($CDCl_3$) 7.12 (J_{PH} 695 Hz), $(EtO)(Et_2N)P(O)H$, δ 7.29 (J_{PH} 544 Hz) and $(Et_2N)_2P(O)H$, δ 6.76 (J_{PH} 570 Hz).

ACKNOWLEDGEMENTS

Financial assistance from the University of Cape Town and from the C.S.I.R. is gratefully acknowledged. We thank Miss C. Steyn for help with GC determination.

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2. S. M. Vather and T. A. Modro, *Phosphorus and Sulfur*, 1986, **26**, 383.
3. We are grateful to Professor M. T. Reetz for kindly providing us with the unpublished procedure for the preparation of (**2**). In our slightly modified procedure, butyl lithium (6.24 ml of a 15% solution in hexane, 10 mmol) was added slowly to diethylamine (0.74 g, 10 mmol) at −20°C. The mixture was stirred for 1 h, anh. $MnCl_2$ (0.63 g, 5 mmol) was added quickly under nitrogen and the mixture was stirred for 15 min. The resultant pink solution was allowed to warm up to 0°C and reacted immediately with the organophosphorus substrate.