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ANCHIMERIC ASSISTANCE AND SELECTIVITY IN DIETHYLAMINO GROUP TRANSFER FROM METALS TO PHOSPHORYL CENTRES

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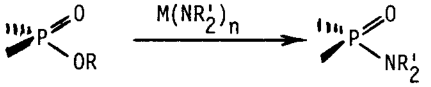
Summary: Diethylamides of Ti(IV), Mn(II), Sn(II) and Sn(IV) are inert towards diethyl benzylphosphonate, but react easily with diethyl α-hydroxybenzylphosphonate with the exchange of one or two EtO groups at phosphorus for diethylamino groups.

We have recently found that dialkylamides of elements such as Ti(IV),[1] Mn(II),[2] and Sn(II) or Sn(IV)[3] are capable of displacing the alkoxy (or aryloxy) substituents at the phosphoryl centre by a dialkylamino group (eq. 1).



(1)

R = alkyl, aryl; R' = alkyl; M = Ti(IV), Mn(II), Sn(II), Sn(IV)

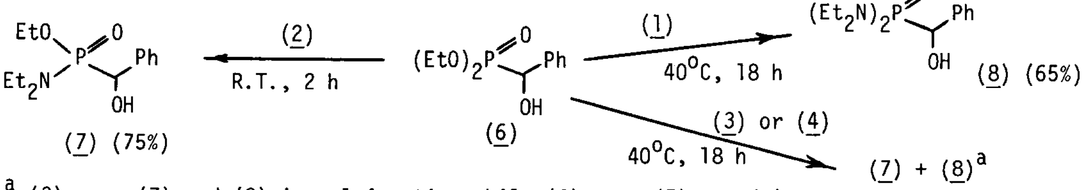
Reaction (1) proceeds with various degrees of selectivity, depending on the nature of the aminating reagent, $M(NR'_2)_n$ and the substituents in the phosphoryl substrate.

We have found that diethylamides of all three elements, i.e. $Ti(NEt_2)_4$, (1),[1] $Mn(NEt_2)_2$, (2),[2] $Sn(NEt_2)_2$, (3)[4] and $Sn(NEt_2)_4$, (4)[5] are completely unreactive towards dialkyl phosphonic esters, such as diethyl benzylphosphonate (5), even after 16 h at 50°C.

$$\underset{(5)}{PhCH_2P(O)(OEt)_2} \xrightarrow{(1)\ -\ (4)} \text{no reaction} \qquad (2)$$

In contrast, diethyl α-hydroxybenzylphosphonate (6)[7] reacts easily with reagents (1) - (4) giving, depending on the reagent, the product of the exchange of one (product 7[8]) or two (product 8[9]) ethoxy groups in (6) for the diethylamino group(s). The results of these reactions are summarised in the Scheme.

Scheme



[a] (3) gave (7) and (8) in a 1:4 ratio, while (4) gave (7) and (8) in a 4:1 ratio. These ratios were unchanged in the presence of the excess of Sn reagent.

In view of the inertness of a simple phosphonic ester such as (5) (eq. 2) it is obvious that the α-hydroxy group in (6) promotes the exchange of an ester for an amino group at phosphorus. The mechanism of this anchimeric assistance is currently under study in our lab.

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References and Notes

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2. V. D. Fester, S. M. Vather and T. A. Modro, Phosphorus and Sulfur, in press.
3. M. Froneman, S. M. Vather and T. A. Modro, in preparation.
4. I. Foley and M. Feldin, Inorg. Chem., 1975, 14, 2264.
5. (4) was prepared[6] by adding $SnCl_4$ to a solution of four mole-equivalents of Et_2NH and four mole-equivalents of BuLi in hexane. After filtration and evaporation of solvent the product was distilled (bp 110°/0.5 mm) and stored in darkness at 0°C. Yield 73%. Anal. Calc. for $C_{16}H_{40}N_4Sn$: C, 47.2; H, 9.8; N, 13.8. Found: C, 48.0; H, 9.5; N, 13.4%.
6. I. M. Thomas, Can. J. Chem., 1961, 39, 1386.
7. (6) was prepared by refluxing the mixture of benzaldehyde (10.5 mL), diethyl phosphite (12.3 mL), triethylamine (12.3 mL) and benzene (30 mL) for 1.5 h. After evaporation of volatile products under reduced pressure (6) was purified by crystallisation (benzene/pet. ether), mp 64-65°C. Yield 94%. δ($CDCl_3$): 1.23 (6H, t, J 5Hz, $OCH_2\underline{CH_3}$); 4.04 (4H, q, J 5Hz, $O\underline{CH_2}CH_3$); 5.00 (1H, d, J 10Hz, $PhC\underline{H}$); 7.44 (5H, m, Ph). Anal. Calc. for $C_{11}H_{17}O_4P$: C, 54.1; H, 7.0. Found: C, 53.7; H, 7.0%. M.S. m/e 244(M^+).
8. Product (7) was too unstable to be purified by distillation or column chromatography. δ ($CDCl_3$): 0.80 - 1.35 (9H, m, $OCH_2\underline{CH_3}$, $NCH_2\underline{CH_3}$); 2.65 - 3.20 (4H, m, $N\underline{CH_2}CH_3$); 4.00 (2H, m, $O\underline{CH_2}CH_3$); 4.92 (1H, d, J 9Hz, $PhC\underline{H}$); 7.00 - 7.40 (5H, m, Ph). Anal. Calc. for $C_{13}H_{22}O_3NP$: C, 57.4; H, 8.1; N, 5.2. Found: C, 58.3; H, 8.4; N, 5.0%. M.S. m/e 271(M^+).
9. After the aqueous work-up of the reaction mixture (8) was purified by filtering through a layer of silica gel. δ($CDCl_3$): 0.80 - 1.40 (12H, m, $NCH_2\underline{CH_3}$); 2.60 - 3.20 (4H, m, $N\underline{CH_2}CH_3$); 4.87 (1H, d, J 9Hz, $PhC\underline{H}$); 7.10 - 7.70 (5H, m, Ph). Anal. Calc. for $C_{15}H_{27}N_2O_2P$: C, 59.7; H, 9.1; N, 9.3. Found: C,59.9; H, 9.1; N, 8.5%. M.S. m/e 298(M^+).

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