

librium between dissolved B and BH<sup>+</sup>, with  $pK_a \approx 8.9$  to 9.6. If the previous conductivity data have been interpreted correctly, we are once more brought to the approximation of the micelle as an ideal mixture; for D and DH<sup>+</sup>, the range of Z is moreover much wider than it was for lauric acid.

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## Preparation of Di-*p*-nitrobenzyl-phosphoryl chloride via the Corresponding Phosphite

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The very promising phosphorylating reagents recently introduced by Leonidas Zerwas and collaborators, *e. g.* di-*p*-nitrobenzylphosphoryl chloride, were originally synthesized by procedures involving silver salt esterifications<sup>1</sup>. For preparation of these reagents in large batches it seems to be preferable to use the phosphite route<sup>2,3</sup>. In connection with syntheses of phosphopeptides<sup>4</sup> we have obtained di-*p*-nitrobenzyl phosphite in good yield from

*p*-nitrobenzyl alcohol and phosphorus trichloride. This phosphite gives, as expected, the desired phosphoryl chloride quantitatively by chlorination with sulphuryl chloride.

### *Experimental. Di-p-nitrobenzyl phosphite.*

To a vigorously stirred solution of 27.6 g phosphorus trichloride (1 mole) in 600 ml dry benzene of room temperature a warm solution of 61.2 g *p*-nitrobenzyl alcohol (2 moles) and 48.4 g dimethylanilin (2 moles) in 200 ml benzene was added in small portions within one hour. After an additional hour of stirring, 30.6 g *p*-nitrobenzyl alcohol (1 mole) in 200 ml benzene was added within 20 minutes. The mixture was stirred for a further two hours and then left overnight. The benzene solution was washed with water (3 × 200 ml), 5 N ammonia (2 × 200 ml), water (2 × 200 ml) and dried over anhydrous sodium sulphate. By addition of light petroleum, di-*p*-nitrobenzyl phosphite separated as white crystals. The yield was 43.5 g (62 % of the theoretical). The phosphite was recrystallized from ethanol or chloroform-cyclohexane. M. p. 75°. (Found: C 47.70; H 3.70; N 7.91; P 9.00. Calc. for C<sub>14</sub>H<sub>13</sub>O<sub>7</sub>N<sub>2</sub>P: C 47.70; H 3.72; N 7.96; P 8.81).

*Chlorination.* To a suspension of 35.3 g phosphite in 250 ml carbon tetrachloride 8 ml sulphuryl chloride was added dropwise with shaking. Dry nitrogen was slowly bubbled through the mixture and the temperature was held under 20°. After 20 minutes the solvent was removed *in vacuo* and the solid dissolved in chloroform. Addition of light petroleum gave white crystals of di-*p*-nitrobenzylphosphoryl chloride (36.0 g = 93 %) with the m. p. 107–108°. The mixed melting point with phosphoryl chloride prepared according to Zerwas<sup>1</sup> showed no depression. (Found: P 7.91; Cl 8.89. Calc. for C<sub>14</sub>H<sub>12</sub>O<sub>7</sub>N<sub>2</sub>PCl: P 8.00; Cl 9.16).

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