

MgSO<sub>4</sub>, and evaporated on a rotary evaporator. The residue (2.9 g) was heated for 0.5 h at 150-160°C (100-120 mm) and distilled, collecting the fraction with bp 148-150°C (13 mm). The product yield was 1.33 g (65%).

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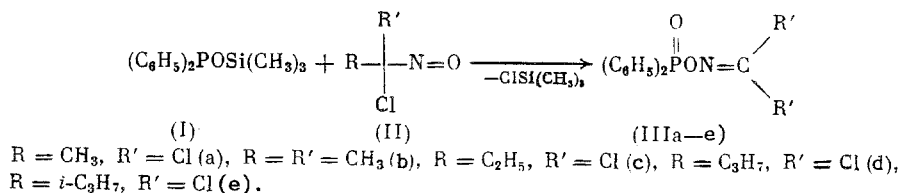
#### REACTION OF $\alpha$ -CHLORONITROSOALKANES WITH THE TRIMETHYLSILYL ESTER OF DIPHENYLPHOSPHONOUS ACID

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*The reaction of  $\alpha$ -chloronitrosoalkanes with the trimethylsilyl ester of diphenylphosphonous acid leads to the formation of products of the Allen reaction, namely, phosphorylated oximes.*

The reactions of  $\alpha$ -halonitroso compounds with the esters of P(III) acids (Allen reaction) have been studied rather extensively [1, 2]. On the other hand, the question of the use of silyl esters of P(III) acids as the phosphorus-containing reagent in these reactions has remained open. In the case of the trimethylsilyl ester of diphenylphosphonous acid (I), we have demonstrated the use of silyl esters of P(III) acids in the Allen reaction. Ester (I) reacts exothermally with  $\alpha$ -chloronitrosoalkanes (II) at 10-15°C to give the corresponding phosphorylated oximes (IIIa)-(IIIe) in 37-44% yield.



Phosphorylated oximes (IIIa)-(IIIe) are white crystalline compounds whose composition and structure were demonstrated by elemental analysis and IR and NMR spectroscopy.

#### EXPERIMENTAL

The PMR and <sup>31</sup>P NMR spectra were taken on a Bruker CXP-200 spectrometer in CDCl<sub>3</sub> relative to TMS (<sup>1</sup>H NMR) and 85% H<sub>3</sub>PO<sub>4</sub> (external standard for the <sup>31</sup>P NMR spectra).

**O-Methylchloroformiminodiphenylphosphonate (IIIa).** A sample of 1.3 g (0.01 mole) 1,1-dichloro-1-nitrosoethane was added with stirring in an argon stream to a solution of the

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trimethylsilyl ester of diphenylphosphonous acid, obtained according to Chauzov et al. [3] from 2.0 g (0.01 mole) diphenylphosphonous acid, 1.1 g (0.01 mole) trimethylchlorosilane, and 1.0 g (0.01 mole) triethylamine in 50 ml benzene, at 10-15°C. The reaction mixture was brought to 20°C and stirred for 1 h. Benzene was distilled off and the residue was recrystallized from hexane to give 1.2 g (42.3%) phosphonate (IIIa), mp 89-90°C. Found: C, 57.73; H, 4.91; N, 4.81, P, 10.32%. Calculated for  $C_{14}H_{13}ClNO_2P$ : C, 57.26; H, 4.46; N, 4.77; P, 10.55%. PMR spectrum ( $\delta$ , ppm): 2.28 s (3H,  $CH_3$ ), 7.54 (3H + 3H, 3CH + 3CH), 7.90 m (2H + 2H, 2CH + 2CH).  $^{31}P$  NMR spectrum:  $\delta$  34.60 ppm.

O-Dimethylformiminodiphenylphosphonate (IIIb) was obtained by analogy to (IIIa) from 2.0 g diphenylphosphonous acid, 1.1 g trimethylchlorosilane, 1.0 g triethylamine, and 1.1 g 2-chloro-2-nitrosopropane. The yield of (IIIb) was 1.0 g (37.0%), mp 110°C (from hexane). Found: C, 65.52; H, 6.28; N, 5.31; P, 11.57%. Calculated for  $C_{15}H_{16}NO_2P$ : C, 65.93; H, 5.90; N, 5.13; P, 11.33%. PMR spectrum ( $\delta$ , ppm): 1.95 s (3H,  $CH_3$ ), 2.1 s (3H,  $CH_3$ ), 7.3 m (3H + 3H, 3CH + 3CH), 7.85 m (2H + 2H, 2CH + 2CH).  $^{31}P$  NMR spectrum:  $\delta$  32.13 ppm.

O-Ethylchloroformiminodiphenylphosphonate (IIIc) was obtained by analogy from 2.0 g dimethylchlorosilane, 1.0 g triethylamine, and 1.42 g 1,1-dichloro-1-nitrosopropane. The yield of (IIIc) was 1.2 g (39.1%), mp 75-77°C (from hexane). Found: C, 58.26; H, 4.77; N, 4.59; P, 9.69%. Calculated for  $C_{15}H_{15}ClNO_2P$ : C, 58.55; H, 4.91; N, 4.55; P, 10.07%. PMR spectrum ( $\delta$ , ppm): 1.05 t (3H,  $CH_3$ ), 2.55 q (2H,  $CH_2$ ), 7.55 m (3H + 3H, 3CH + 3CH), 7.90 m (2H + 2H, 2CH + 2CH).  $^{31}P$  NMR spectrum:  $\delta$  34.72 ppm.

O-Propylchloroformiminodiphenylphosphonate (IIId) was obtained by analogy to (IIIa) from 2.0 g diphenylphosphonous acid, 1.1 g trimethylchlorosilane, 1.0 g triethylamine, and 1.56 g 1,1-dichloro-1-nitrosobutane. The yield of (IIId) was 1.3 g (40.5%), mp 77-78°C (from hexane). Found: C, 59.44; H, 5.50; N, 4.22; P, 9.37%. Calculated for  $C_{16}H_{17}ClNO_2P$ : C, 59.73; H, 5.33; N, 4.35; P, 9.63%. PMR spectrum in  $CDCl_3$  ( $\delta$ , ppm): 0.75 t (3H,  $CH_3$ ), 1.60 q (2H,  $CH_2$ ), 2.50 t (2H,  $CH_2$ ), 7.60 m (3H + 3H, 3CH + 3CH), 7.95 m (2H + 2H, 2CH + 2CH).  $^{31}P$  NMR spectrum:  $\delta$  34.57 ppm.

O-Isopropylchloroformiminodiphenylphosphonate (IIIe) was obtained by analogy to (IIIa) from 2.0 g diphenylphosphonous acid, 1.1 g  $(CH_3)_3SiCl$ , 1.0 g  $(C_2H_5)_3N$ , and 1.56 g 1,1-dichloro-1-nitrosobutane. The yield of (IIIe) was 1.4 g (43.6%), mp 69-70°C (from hexane). Found: C, 59.41; H, 4.91; N, 4.20; P, 9.54%. Calculated for  $C_{16}H_{17}ClNO_2P$ : C, 59.73; H, 5.33; N, 4.35; P, 9.63%. PMR spectrum in  $CDCl_3$  ( $\delta$ , ppm): 1.10 d (6H, 2 $CH_3$ ,  $J = 7$  Hz), 2.84 m (H, CH), 7.58 m (3H + 3H, 3CH + 3CH), 7.92 m (2H + 2H, 2CH + 2CH).  $^{31}P$  NMR spectrum:  $\delta$  34.75 ppm.

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