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Synthesis of Tris(*N*,*N*-dimethyl-2-carbamoylethyl)phosphine Oxide

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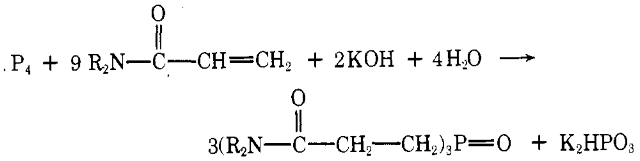
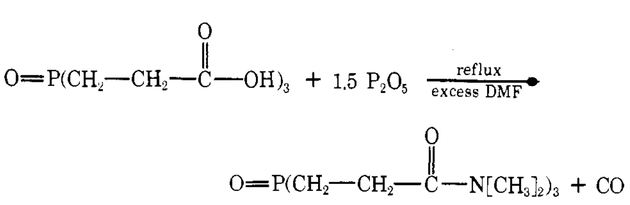
Tris(*N*,*N*-dimethyl-2-carbamoylethyl)phosphine oxide was prepared by reacting phosphorus pentoxide with tris(2-carboxyethyl)phosphine oxide in excess *N*,*N*-dimethylformamide. The compound was very hygroscopic and could only be recrystallized from a cold DMF–ethyl acetate–petroleum ether mixture.

Preparation of tris(*N*,*N*-dialkyl - 2 - carbamoylethyl)-phosphine oxides have been reported in the patent literature but their physical properties, yields, and general characteristics of identification have not been described (*5*). These compounds were prepared by the following reaction (*3*):



$$P_4 + 9\,R_2N-\overset{\overset{O}{\|}}{C}-CH=CH_2 + 2KOH + 4H_2O \longrightarrow 3(R_2N-\overset{\overset{O}{\|}}{C}-CH_2-CH_2)_3P=O + K_2HPO_3$$

The authors have prepared one of these compounds, tris(*N*,*N*-dimethyl-2-carbamoylethyl)phosphine oxide in quantitative yield by the Schindlbauer reaction, as shown by the following equation (*6*):



$$O=P(CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH)_3 + 1.5\,P_2O_5 \xrightarrow[\text{excess DMF}]{\text{reflux}} O=P(CH_2-CH_2-\overset{\overset{O}{\|}}{C}-N[CH_3]_2)_3 + CO$$

(Because carbon monoxide is a side product, this reaction should be performed under a well-ventilated hood.)

The crude material isolated was hygroscopic. Because of this latter property and its solubility (soluble in polar solvents and insoluble in nonpolar solvents), the compound was difficult to purify. Initial purification involved dissolving the dark brown crystals in ethanol and adding petroleum ether until a dark brown oil separated. The clear solution was decanted from the impure dark oil and evaporated to give light yellow crystals. Recrystallization was achieved by dissolving the yellow crystals in a minimum amount of *N*,*N*-dimethylformamide and adding a 2:1 by volume mixture of petroleum ether–ethyl acetate. The cloudy solution was refrigerated. The white needles were isolated the next day by filtering the solution under an argon atmosphere.

An ir spectrum of a chloroform solution of the compound showed the carbonyl absorption band at 5.93 μ (Vs) and the P=O absorption band at 8.6 μ (m). The proton nmr spectrum (Varian A-60A spectrometer) of a deuteriochloroform solution at 60 MHz showed a multiplet centered at δ 2.5 and two singlets, one at δ 3.03, the other at δ 3.13. The ratio of the multiplet to the methyl groups singlets was 3:2. The chemical shift between the methyl groups was due to their different environments in the planar structure (*1*, *2*).

Experimental

Tris(N,N-dimethyl-2-carbamoylethyl)phosphine oxide (I). Tris-(2-carboxyethyl)phosphine oxide (8.6 grams, 0.0323 mole) (*4*) was refluxed with phosphorus pentoxide (7.2 grams, 0.05 mole) in 125 ml of *N*,*N*-dimethylformamide for 15 hr under a well-ventilated hood. The resulting solution was cooled and the *N*,*N*-dimethylformamide (DMF–petroleum ether–ethyl acetate). *Anal:* Calcd for vacuum to give an oil which slowly crystallized. These dark crystals were dissolved in ethanol and enough petroleum ether added to separate a dark brown oil. The clear solution, after decantation and evaporation under vacuum, yielded 8.5 grams (76%). Mp 100–102°C (DMF–petroleum ether–ethyl acetate). Anal. Calcd for $C_{15}H_{30}O_4N_3P$: C, 51.85; H, 8.70; N, 12.09; P, 8.91. Found: C, 51.61; H, 8.81; N, 11.89; P, 8.84.

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