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Novel alkyl (1,2,4,5-tetrahydro-3*H*-2,4,3-benzodiazaphosphepin-3-yl)carbamate-*P*-oxides (**7**) were synthesized by cyclization of the corresponding dichlorophosphinylcarbamates (**5**) with α,α' -diamino-*o*-xylene (**6**). A steric limitation in the synthesis of analogs is discussed.

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Numerous examples of five and six membered ring diazaphosphorous heterocycles can be found in the literature. Far fewer references can be found to smaller or larger ring systems containing two nitrogens and a phosphorous atom. Quast and Heuschmann (1) reported a three membered diazaphosphiridine and Bermann and van Wazer (2) reported several 1,3,2-diazaphosphetidines. One 1,3,2-diazaphosphepine (**1**) was reported by Russian workers (3) and a nine membered ring 1,3,2-diazaphosphonine was reported by Lampin (4) in 1975. Even fewer examples of benzodiazaphosphorous compounds can be found. Naidu and Reddy (5) reported the synthesis of 2-phenoxy-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole

2-oxide (**2**) and Ludeman and Zon (6) have synthesized *N,N*-bis(2-chloroethyl)-3,4-dihydro-1,3,2-benzodiazaphosphorin-2-(1*H*)amine 2-oxide (**3**). To our knowledge nothing

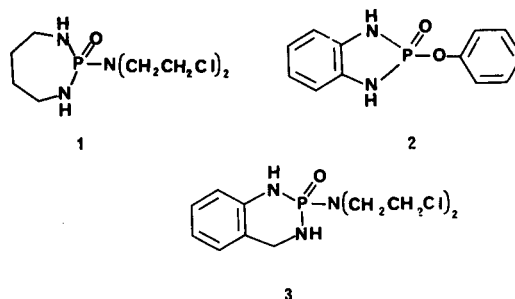
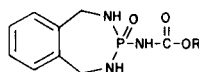





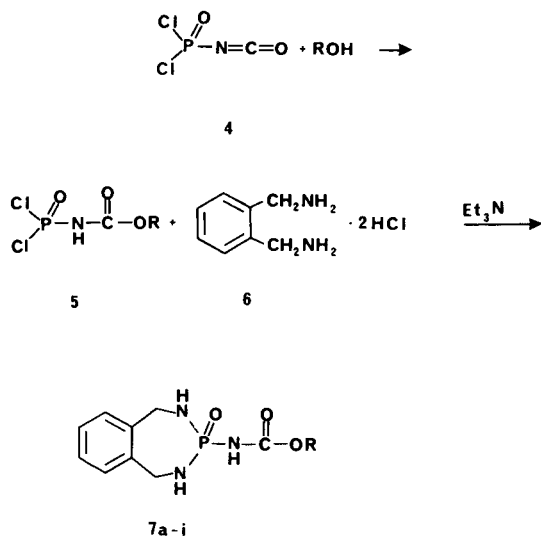
Table 1



Compound No.	R	M.p., °C	Yield, % (solvent)			Analysis		
			Toluene	Methylene Chloride	Molecular Formula	Calcd. C	(Found) H	N
7a	CH ₃ -	197-200 dec. (a,d)	15	42	C ₁₀ H ₁₄ N ₃ O ₃ P	47.06 (46.83)	5.53 (5.55)	16.46 (16.54)
7b	C ₂ H ₅ -	190-192 dec. (a)	37	22	C ₁₁ H ₁₆ N ₃ O ₃ P	49.07 (49.20)	5.99 (6.04)	15.61 (15.62)
7c	CH ₃ CH ₂ CH ₂ -	190-192 dec. (a)	24	---	C ₁₂ H ₁₈ N ₃ O ₃ P	50.88 (50.72)	6.40 (6.38)	14.83 (14.94)
7d	CH ₃ (CH ₂) ₃ -	187-188 dec. (b)		39	C ₁₃ H ₂₀ N ₃ O ₃ P	52.52 (52.36)	6.78 (6.76)	14.13 (14.20)
7e	C ₆ H ₅ -CH ₂ -	197-198 dec. (b)		36	C ₁₆ H ₁₈ N ₃ O ₃ P	58.00 (57.92)	5.48 (5.49)	12.68 (12.73)
7f	(CH ₃) ₂ CH-	176-177 dec. (a)		38	C ₁₂ H ₁₆ N ₃ O ₃ P	50.88 (50.90)	6.40 (6.44)	14.83 (14.83)
7g		187-187.5 dec. (c)		19	C ₁₄ H ₂₀ N ₃ O ₃ P	54.36 (54.32)	6.52 (6.53)	13.58 (13.57)
7h		173-175 dec. (a)	18	24	C ₁₅ H ₂₂ N ₃ O ₃ P	55.72 (55.64)	6.86 (6.89)	13.00 (12.96)
7i		117 dec. (a)		4	C ₁₉ H ₂₆ N ₃ O ₃ P · 1/2 C ₂ H ₅ OH	60.28 (60.00)	7.34 (7.35)	10.54 (10.39)
7j	(CH ₃) ₃ C-			0				

(a) Recrystallized from 100% ethanol. (b) Recrystallized from 95% ethanol. (c) Recrystallized from ethanol-water. (d) Recrystallized from water.

has been published on benzodiazaphosphepine. We wish to report our synthesis of alkyl (1,2,4,5-tetrahydro-3H-2,4,3-benzodiazaphosphepin-3-yl)carbamate *P*-oxide (7). To prepare this novel heterocycle we made use of the highly reactive isocyanate 4 first synthesized by Kirsanov (7-8) and modified by Papanastassiou and Bardos (9). This isocyanate reacts with a variety of alcohols to yield the dichlorophosphinylcarbamates (5), which upon condensation with the diamine 6 gives rise to compounds 7a-i (9-10). The yields were generally in the range of 30-40% for the two step conversion of the dichloroisocyanatophosphine oxide to the final products (Table I). Two solvents were used, toluene and methylene chloride. In general methylene chloride proved to be the superior solvent both in yield and ease of handling. While primary and secondary alcohols reacted readily with the isocyanate to give their respective carbamates it should be noted that like simple carbon substituted isocyanates which do not react with tertiary alcohol, tertiary butyl alcohol did not give the expected carbamate 5. The less sterically crowded adamantanol did react with 4 to give a carbonate which gave 7i in an overall yield of 4%. It is interesting that the benzodiazaphosphepines (7) are relatively nonreactive. Attempts to convert 7 to a urea derivative by heating with various secondary amines have proved unsuccessful.



EXPERIMENTAL

Melting points were determined on a Thomas-Hoover Capillary melting point apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer while nuclear magnetic resonance spectra were determined on a Varian EM 360 spectrometer in DMSO-*d*₆. Chemical shifts are quoted in parts per million.

General Synthetic Method. Benzyl (1,2,4,5-tetrahydro-3H-2,4,3-benzodiazaphosphepin-3-yl)carbamate *P*-oxide (7e).

To a solution of 1.59 g. (0.01 mole) of dichloroisocyanatophosphine oxide (4) in 25 ml. of redistilled methylene chloride, was added 1.08 g. (0.01 mole) of benzyl alcohol in 10 ml. of methylene chloride. The addition was done while maintaining a temperature of 0-10° and with stirring. After the addition was complete the solution was allowed to stir without cooling for 1 hour. An ir of the reaction mixture characteristically exhibits absorption at 1740-1760 cm⁻¹ and lacks the 2270 cm⁻¹ shown for the isocyanate. The reaction mixture was transferred to a dropping funnel and added dropwise to a mixture of 2.09 g. (0.01 mole) of α,α-diamino-*o*-xylene dihydrochloride (6) and 4.04 g. (0.04 mole) of triethylamine in 25 ml. of methylene chloride maintained at 0-10°. Following the addition the reaction mixture was stirred at 25° for 48 hours, heated under reflux for 2 hours, cooled in an ice bath, and filtered. The solid white filtrate was washed with cold water and the residue was recrystallized from 95% ethanol. A total of 1.2 g. of 7e was recovered; ir (potassium bromide): 1710, 1200, 1240, 1250 cm⁻¹; nmr: δ 8.83 (d, 1, J = 8 Hz, exchangeable), 7.5 (s, 5), 7.25 (s, 4), 5.22 (s, 2) 5.0-5.5 (m, 2, exchangeable), 3.8-4.5 (m, 4).

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