moisture to be analyzed, they were characterized as their derivatives.

Experimental Section

p-**Toluoyl Isocyanate.**—Oxalyl chloride (31.7 g., 0.25 mole) in ethylene dichloride was added to *p*-toluamide (24.3 g., 0.18 mole) in ethylene dichloride at 0°. The solution was allowed to warm to room temperature, then refluxed with stirring for *ca.* 24 hr. The solvent was evaporated *in vacuo*, and the residue was distilled under reduced pressure to give *p*-toluoyl isocyanate (23.0 g., 0.14 mole, 79%), b.p. 61–67° (0.75 mm.).

The other acyl isocyanates were prepared similarly, except methylene chloride was used as the solvent for the preparation of the low-boiling isocyanates (propionyl and carbomethoxy).

2-Chloroallyl-N-(*p*-toluoyl) Carbamate.—2-Chloro-2-propen-1-ol (2.3 g., 0.025 mole) in methylene chloride was added to *p*-toluoyl isocyanate (4.06 g., 0.025 mole) in methylene chloride, and the resulting solution was heated and concentrated. The addition of hexane and cooling gave 2-chloroallyl-N-(*p*-toluoyl) carbamate which was recrystallized from methylene chloride–hexane (4.0 g., 0.016 mole, 63%), m.p. 93–95°. The derivatives of other acyl isocyanates were prepared similarly.

Reaction of Cyclopropanecarboxamide and Oxalyl Chloride.—Oxalyl chloride (20.3 g., 0.16 mole) in methylene chloride was added to cyclopropanecarboxamide (11.9 g., 0.14 mole) in methylene chloride at 0°. The solution was allowed to warm to room temperature and stirred for 2.5 hr., and the solvent was removed *in vacuo*. The residue was distilled to give γ-chlorobutyroyl isocyanate (18.0 g., 0.08 mole, 0.12 *M*, 87%), b.p. 78–80° (15 mm.).

The Preparation of the Inner Salts of Two Aminophosphonates

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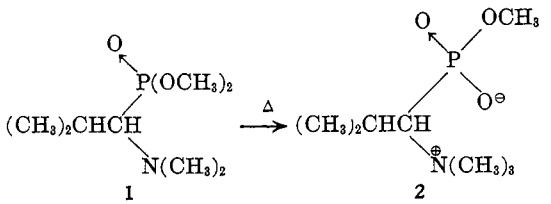
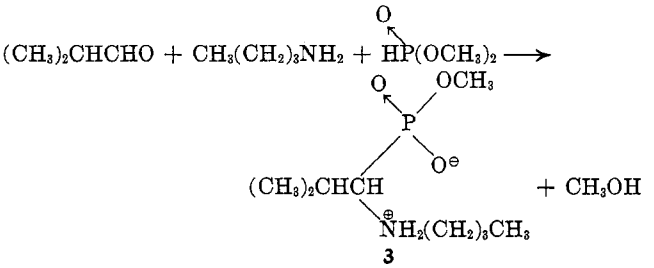
Received May 17, 1965

Aminophosphonates are well-known and readily available compounds.[1,2] The conversion of two aminophosphonates to the corresponding inner salts has been encountered in these laboratories. Their structural assignments were based on elemental analyses and n.m.r. spectra. When dimethyl 1-(dimethylamino)-2-methylpropylphosphonate (**1**), prepared[2] by the addition of dimethyl hydrogen phosphite to N,N-dimethylisobutenylamine, was heated, a crystalline hygroscopic solid resulted. This solid was insoluble in common organic solvents but quite soluble in water. It was assigned the structure of the inner salt of trimethyl-[2-methyl-1-(methylphosphono)propyl]ammonium hydroxide (**2**).



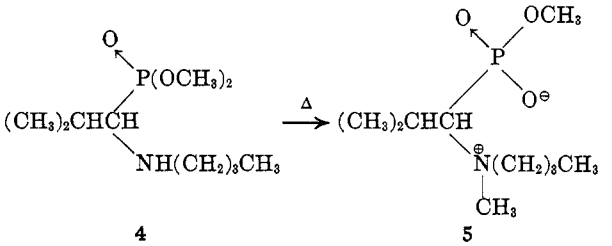
1 **2**

In an attempt to prepare dimethyl 1-(butylamino)-2-methylpropylphosphonate (**4**) by allowing isobutyraldehyde to react with a mixture of dimethyl hydrogen phosphite and butylamine,[1] we obtained, instead, the inner salt of butyl-[2-methyl-1-(methylphosphono)-propyl]ammonium hydroxide (**3**). This compound may have arisen from partial hydrolysis of the intermediate aminophosphonate **4** under the conditions of its formation.



3

Compound **4** was obtained by addition of dimethyl hydrogen phosphite to N-(2-methylpropylidene)butylamine. A small amount of solid from the distillation residue proved to be the inner salt **3**. When **4** was heated, the inner salt of butylmethyl-[2-methyl-1-(methylphosphono)propyl]ammonium hydroxide (**5**) was formed as an impure oil.



4 **5**

Diethyl 1-(dimethylamino)-2-methylpropylphosphonate, dimethyl 1-(dibutylamino)-2-methylpropylphosphonate, and dimethyl 1-(dimethylamino)butylphosphonate gave yields of intractable unidentified oily mixtures when heated. Dibutyl 1-(dimethylamino)-2-methylpropylphosphonate and dimethyl 1-(dimethylamino)cyclohexylphosphonate decomposed to starting materials when heated.

Experimental Section[3]

Dimethyl 1-(Dimethylamino)-2-methylpropylphosphonate (**1**).—The method described by Opitz[2] was utilized in the preparation of this compound. It was obtained in 78% yield: b.p. 64–66° (*ca.* 0.3–0.4 mm.); $n^{20}D$ 1.4452; infrared absorptions (neat) 8.06, 8.45, and 9.7 μ; n.m.r. spectrum (neat) pair of doublets with chemical shifts of 3.65 and 3.67 p.p.m. and J = 10.4 c.p.s. with a combined area equivalent to 6 protons [$(-OCH_3)_2$], doublet with spacing of 2.7 c.p.s. centered at 2.42 [$-N(CH_3)_2$], pair of doublets with splittings of 9.0 and 14.5 c.p.s. centered at 2.45 (>N–CH–P<, one of the peaks is obscured by the >N–CH_3 peak), multiplet at 2.02, and pair of doublets at 1.00 [$-CH(CH_3)_2$] p.p.m.

Anal. Calcd. for $C_8H_{20}NO_3P$: N, 6.7. Found: N, 6.6.

Inner Salt of Trimethyl-[2-methyl-1-(methylphosphono)propyl]ammonium Hydroxide (**2**).—The crude reaction mixture from the reaction of N,N-dimethylisobutenylamine (99 g., 1 mole) and dimethyl hydrogen phosphite (110 g., 1 mole) was refluxed at atmospheric pressure. The temperature of this mixture rose from 160 to 170° during the 1-hr. reflux period. No loss of weight occurred. The resulting viscous syrup crystallized on standing. The mixture, on trituration with acetone, gave an 85-g. (50%) yield of **2**. The filtrate was distilled to give a 40-g. yield of the aminophosphonate **1**. A sample of **2** was recrystallized from acetonitrile, m.p. 233–235° dec. This material proved

(1) E. K. Fields, *J. Am. Chem. Soc.*, **74**, 1528 (1952).

(2) G. Opitz, A. Griesinger, and H. Schubert, *Ann. Chem.*, **665**, 91 (1963).

(3) The boiling and melting points are uncorrected. The melting points were determined on a Fischer-Johns melting point block. N.m.r. spectra were measured at 60 Mc. on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. The infrared spectra were determined on Baird AB-2 and MK-1A spectrophotometers.

to be very hygroscopic and consistent elemental analyses were not obtained: infrared absorptions (KBr) 8.0–8.2, 9.19, 9.3, 9.5, 11.29, and 13.1 μ; n.m.r. spectrum (D_2O) doublet with J = 10.9 c.p.s. centered at 3.66 with an area equivalent to 3 protons ($-OCH_3$), single peak at 3.32 with an area equivalent to 9 protons [$-\overset{\oplus}{N}(CH_3)_3$], peaks due to (>N–CH–P<) were overlapped by one of the ($-OCH_3$) and the (>N–CH_3) peaks, broad peak at 2.5, and pair of doublets at 1.32 [$-CH(CH_3)_2$] p.p.m.

Anal. Calcd. for $C_8H_{20}NO_3P$: C, 45.9; H, 9.6; N, 6.7; P, 14.8; mol. wt., 209. Found: C, 44.1; H, 10.1; N, 7.1; P, 13.3; mol. wt. (ebullioscopic in ethyl alcohol), 202.

When the reaction was carried out in the presence of 0.1 g. of *p*-toluenesulfonic acid, essentially the same results were obtained.

Inner Salt of Butyl-[2-methyl-1-(methylphosphono)propyl]-ammonium Hydroxide (3).—Isobutyraldehyde (36 g., 0.5 mole) was added to a refluxing mixture of dimethyl hydrogen phosphite (55 g., 0.5 mole) and butylamine (36 g., 0.5 mole). The temperature of the mixture rose to 120°. Sodium sulfate was added to the mixture after it had cooled to room temperature. After standing for 72 hr. the mixture was filtered and the filtrate was distilled to a base temperature of 130° (2 mm.). The residue crystallized to a gummy solid which, on trituration with cold acetone, gave a 28-g. (25%) yield of the inner salt **3**: m.p. 181–185°; infrared absorptions (KBr) 8.2 (wide), 9.2–9.5, 13.2, and 14.15 μ; n.m.r. spectrum (D_2O) doublet at 3.69 with an area equivalent to 3 protons and J = 10.9 c.p.s. ($-OCH_3$), peaks centered at 3.23 [>CH–$\overset{\oplus}{N}(CH_2)$<], broad peak at 2.34 (tertiary proton of the isopropyl group), broad peak at 1.58 (>$\overset{\oplus}{N}$–CH_2–), and two doublets with an overlapping triplet centered at 1.07 (methyl groups) p.p.m.

Anal. Calcd. for $C_9H_{22}NO_3P$: C, 48.4; H, 9.93; N, 6.3; P, 13.9; mol. wt., 223. Found: C, 48.4; H, 9.96; N, 6.4; P, 13.6; mol. wt. (ebullioscopic in ethyl alcohol), 231.

Dimethyl 1-(Butylamino)-2-methylpropylphosphonate (4).—The method described by Fields[1] was utilized in the preparation of this compound. It was obtained in 71% yield: b.p. 96–98° (*ca.* 0.25 mm.); $n^{20}D$ 1.4418; n.m.r. spectrum (neat) pair of doublets with an area equivalent to 6 protons and with chemical shifts of 3.76 and 3.79 p.p.m. and J = 10.0 c.p.s. [($^-OCH_3$)$_2$], peaks centered at 2.70 ($-CH_2-\overset{|}{N}-CH$<), broad peak centered at 2.03 (tertiary proton of the isopropyl group), broad peak at 1.40 ($-CH_2CH_2CH_2-N$<), and three peaks, probably two doublets with an overlapping triplet at 1.00 (methyl groups) p.p.m.

Anal. Calcd. for $C_{10}H_{24}NO_3P$: C, 50.6; H, 10.2; N, 5.9; P, 13.1. Found: C, 50.6; H, 10.3; N, 5.7; P, 13.1.

The residue from the distillation of **4** gave a 2-g. yield of solid which was identical with **3**.

Inner Salt of Butylmethyl-[2-methyl-1-(methylphosphono)-propyl]ammonium Hydroxide (5).—Dimethyl 1-(butylamino)-2-methylpropylphosphonate (20 g., 0.08 mole) was heated to 190° over a period of 0.5 hr. A viscous oil resulted which did not give a yield of solid on treatment with various solvents. This oil appeared by n.m.r. spectroscopy to be impure **5**: n.m.r. spectrum (D_2O) doublet at 3.65 with J = 11.0 c.p.s. and an area equivalent to 3 protons ($-OCH_3$), single sharp peak at 3.19 [>$\overset{\oplus}{N}$–CH_3 which overlapped peaks for the $-CH_2-\overset{\oplus}{N}(CH-)$<] with total area equivalent to 6 protons, broad band from 1.2 to 2.2 (tertiary proton of the isopropyl group and methylene protons of the butyl group), and three peaks centered at 1.08 (methyl groups) p.p.m.

Reaction of Benzoyl Azide with Aldimines and Ketimines

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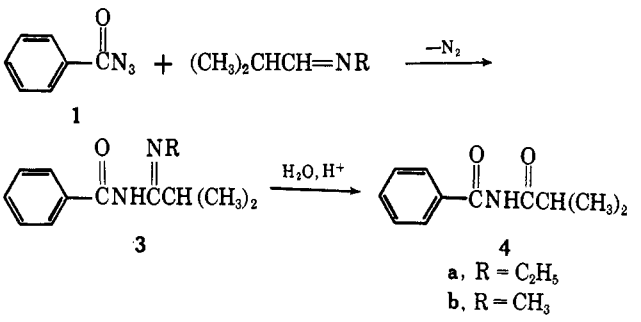
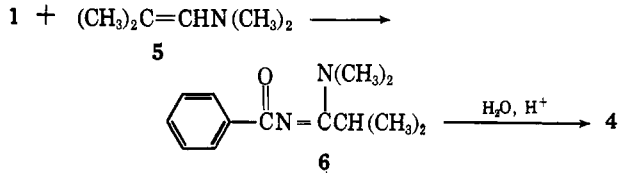
Received May 17, 1965

Papers dealing with reactions of azides and other 1,3-dipolar compounds with enamines have appeared recently.[1-5] Similar reactions were carried out in these laboratories and the results were found to be in agreement with those reported. The reaction of azidobenzene with alicyclic ketone anils to give triazoles was reported by Alder and Stein.[6]

We made a brief study of the reactions of benzoyl azide (**1**) with selected aldimines and ketimines. When **1** was allowed to react with N-alkylisobutylideneamines **2a** and **2b**, spontaneous loss of nitrogen occurred and the benzamide derivatives **3a** and **3b** resulted. Acidic hydrolysis of **3a** and **3b** gave N-isobutyrylbenzamide (**4**).



N-Isobutyrylbenzamide (**4**) was also prepared by allowing **1** to react with N,N-dimethyl-2-methylpropenylamine (**5**) and hydrolyzing the product.



The structural assignments of **3b** and **6** were based on their n.m.r. spectra and on their hydrolysis to **4**. Structure **3b** rather than its tautomer was chosen because of the absence of splitting of the N-methyl peak in its n.m.r. spectrum and the low-field position of the NH resonance (11.61 p.p.m.). The assignment of **3b** is also supported by n.m.r. spectra of similar compounds and by analogy with spectra of amides and imides, in which the imides give the lower NH peak position.

With N-cyclohexylideneisopropylamine (**7**), **1** gave a product **8** which resulted from contraction of the cyclohexane ring. A similar ring contraction was observed in the reaction of a sulfonyl azide with an alicyclic enamine.[3] Hydrolysis of **8** gave N-(cyclopentylcarbonyl)benzamide (**9**) which was also obtained from the reaction of **1** and 4-(1-cyclohexen-1-yl)morpholine (**10**). In the structural assignment of **8**, its tautomer was ruled out on the basis of the NH peak position in its n.m.r. spectrum.

(1) M. E. Kuehne, S. J. Weaver, and P. Franz, *J. Org. Chem.*, **29**, 1582 (1964).

(2) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).

(3) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963).

(4) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Gazz. chim. ital.*, **91**, 849, 933 (1961); **92**, 1040 (1962).

(5) While this paper was in preparation, G. Bianchetti, P. D. Croce, and D. Pocar [*Tetrahedron Letters*, **No. 25**, 2043 (1965)] published similar work on the reactions of various Schiff bases with *p*-toluenesulfonyl azide and 1-azido-4-nitrobenzene.

(6) K. Alder and G. Stein, *Ann. Chem.*, **501**, 1 (1933).