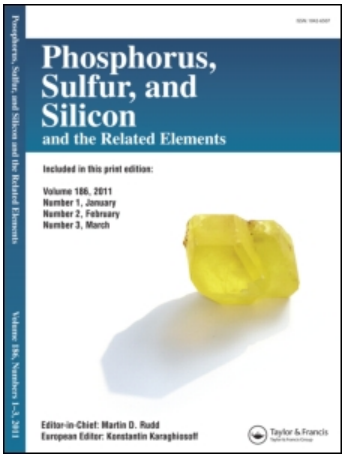

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Dealkylation of Phosphorus-Containing Alkylammonium Salts Formed by the Interaction of Phosphonic, Methanephosphonic and Phosphoric Acid Esters with Diamines

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DEALKYLATION OF PHOSPHORUS-CONTAINING ALKYLAMMONIUM SALTS FORMED BY THE INTERACTION OF PHOSPHONIC, METHANEPHOSPHONIC AND PHOSPHORIC ACID ESTERS WITH DIAMINES

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Primary diamines have been alkylated by esters of phosphonic, methanephosphonic and phosphoric acids, and the reaction products characterized by a combination of ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. The diamines undergo either single or multiple alkylations in their reactions with phosphoryl esters, depending on the mole ratio of the reactants. These alkylation products then undergo further dealkylation under the reaction conditions. Methylalkylammonium salts undergo dealkylation more readily than do the corresponding ethylalkylammonium salts.

Key words: Dialkyl phosphonate, dialkyl alkylphosphonate, trialkyl phosphate, alkylation.

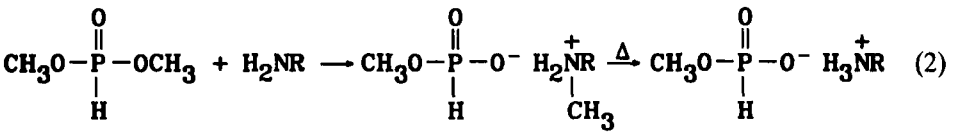
INTRODUCTION

It has been previously established that the alkyl esters of phosphonic,[1–5] methanephosphonic[3,6] and phosphoric acids[3] readily alkylate various types of amines as shown in Equation 1. An interesting observation that has been made earlier

$$(RO)_2P(O)A + NR'_3 \longrightarrow RO-\underset{\underset{A}{|}}{\overset{\overset{O}{\|}}{P}}-O^- \; \overset{+}{\underset{\underset{R}{|}}{NR'_3}} \qquad (1)$$

$$(A = H, Me, OMe)$$

indicates, however, that when a vinylamine-vinylpyrollidone copolymer is alkylated with methyl esters of phosphonic, methanephosphonic or phosphoric acid, the corresponding ^{1}H NMR spectra of the products do not contain anticipated signals for the NCH_3 protons of the transferred methyl group.[7] Further studies of the stabilities of different salts obtained *via* the alkylation of primary and tertiary amines with dimethyl phosphonate have demonstrated that the alkylation products of the primary amines are unstable at ambient temperature, and readily decompose to the corresponding ammonium salts, presumably by a carbene cleavage reaction (Equation 2).[8] Because of these observations,[7,8] we have decided to further extend our studies to alkylammonium salts that have been obtained from primary diamines and esters of phosphonic, methanephosphonic and phosphoric acids. Our interest



in this study, in addition to questions related to the stabilities of the expected salts of the alkyl transfer reactions, has also been motivated by the possibility that alkylation of the second amine group may also occur. A previous study of amine salts of methanephosphonic acid indicates the formation of dicationic products, although insufficient spectroscopic data have been presented to justify the reported structures.[6]

EXPERIMENTAL

The diamines and the phosphorus containing esters used were purchased from Aldrich or Fluka and distilled under argon prior to use. The dimethyl ester of the cyclohexylidene vinylphosphonic acid was provided by prof. Angelov, Shumen University and used as supplied. Methanol was distilled over magnesium turnings under an atmosphere of dry argon. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on either a Bruker WP 250 or an Omega GE 400 NMR spectrometers. Melting points were determined on a Kofler hot-stage microscope and are uncorrected. All experiments were carried out under a dry argon atmosphere in order to prevent hydrolysis of the corresponding esters.

A. Reactions of Dialkyl Phosphonates with Diamines

Ethylenediamine dialkylammonium salt of monomethyl phosphonate **1**. A solution of ethylenediamine 3.0 g (0.05 moles) in 5 ml of methanol was added droppwise at 40°C to a stirred solution of dimethyl phosphonate 22.0 g (0.2 moles) in 15 ml of methanol. The mixture was stirred for 2 hrs at 50°C. The methanol was removed by distillation at room temperature under reduced pressure, followed by removal of the excess dimethyl phosphonate under high vacuum conditions (0.2 mm Hg) to give the compound as a viscous oil. Yield 7.3 g (94%). ^{1}H NMR (DMSO): δ 3.05 (s, 4H, CH_2N); δ 3.55 (d, 6H, $POCH_3$, $^{3}J(PH)$ = 11.8 Hz); δ 6.53 (d, 2H, PH, $^{1}J(PH)$ = 592.5 Hz); δ 8.70 (brs, 6H, NH_3).

Ethylenediamine monoalkylammonium salt of monomethyl phosphonate **2**. This compound was synthesized by the published procedure.[8] The following spectral data characterize the compound: ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 2H, CH_2); δ 2.78 (s, 2H, CH_2); δ 3.31 (d, 3H, $POCH_3$, $^{3}J(PH)$ = 11.8 Hz); δ 6.03 (brs, 3H, NH_3); δ 6.49 (d, 1H, PH, $^{1}J(PH)$ = 587.4 Hz). $^{13}C\{^{1}H\}$ NMR (DMSO): δ 41.46, (s, CH_2N); δ 53.30 (d, $^{2}J(PC)$ = 3.1 Hz, OCH_3). ^{31}P NMR (DMSO): δ 7.64 (dq, $^{1}J(PH)$ = 618.8 Hz, $^{3}J(PH)$ = 11.5 Hz).

1,3-Propanediamine monoalkylammonium salt of monomethyl phosphonate **3**. A solution of 1,3-propanediamine 14.0 g (0.2 moles) in 5 ml of methanol was added droppwise at 40°C to a stirred solution of dimethyl phosphonate 5.5 g (0.05 moles) in 15 ml of methanol. The mixture was then stirred for 2 hrs at 50°C. The methanol was removed by distillation at room temperature under reduced pressure, followed by removal of the excess 1,3-propanediamine under high vacuum conditions (0.2 mm Hg) to give the compound as a viscous oil. Yield 7.4 g. ^{1}H NMR (D_2O): δ 1.78 (m, 2H, $CH_2CH_2CH_2$); δ 2.97 (t, 4H, NCH_2, $^{3}J(HH)$ = 7.4 Hz); δ 3.55 (d, 3H, $POCH_3$, $^{3}J(PH)$ = 12.8 Hz); δ 6.49 (d, 1H, PH, $^{1}J(PH)$ = 587.40 Hz). $^{13}C\{^{1}H\}$ NMR (D_2O): δ 29.94 (s, $CH_2CH_2CH_2$); δ 39.59 (s, CH_2N); δ 53.24 (d, $POCH_3$, $^{2}J(PC)$ = 3.1 Hz). ^{31}P NMR (D_2O); δ 9.24 (dq, $^{1}J(PH)$ = 645.0 Hz, $^{3}J(PH)$ = 11.0 Hz).

1,6-Hexanediamine monoethylalkylammonium salt of monoethyl phosphonate **4**. 13.8 g (0.1 moles) diethyl phosphonate and 11.6 g (0.1 moles) 1,6 hexanediamine were heated together at 130°C for two hours. The product was obtained as a viscous oil after removal of the volatiles under high vacuum conditions. Yield 25.1 g (99%). ^{1}H NMR ($CDCl_3$): δ 1.33 (m, 14H, CH_3CH_2O, CH_3CH_2N and $CH_2(CH_2)_4CH_2$); δ 2.80 (m, 6H, CH_2N and CH_2N^+); δ 3.93 (qu, 2H, $POCH_2$, $^{3}J(PH)$ + $^{3}J(HH)$ = 8.0 Hz); δ 5.8 (s, 4H, NH); δ 7.31 (d, 1H, PH, $^{1}J(PH)$ = 562.0 Hz).

1,6-Hexanediammonium salt of phosphonic acid **5**. The salt **4** deposits, after remaining at room temperature for several months, small amounts of **5** as a crystalline solid (approximately 10% by weight).

This solid was filtered off and washed with ethanol. ^{1}H NMR (D_2O): δ 1.26 (m, 4H, CH_2); δ 1.50 (m, 4H, CH_2); δ 2.83 (t, 4H, NCH_2, ^3J(HH) = 7.6 Hz); δ 6.56 (d, 1H, PH, ^1J(PH) = 566.1 Hz). ^{31}P NMR (D_2O): δ 3.77 (d, ^1J(PH) = 566.7 Hz).

B. Reactions of Dimethyl Methylphosphonate with Ethylene Diamine

Ethylenediamine monoalkylammonium salt of monomethyl methylphosphonate **6**. A solution of ethylenediamine 12.0 g (0.2 moles) in 5 ml of methanol was added droppwise at 40°C to a stirred solution of dimethyl methylphosphonate 6.2 g (0.05 moles) in 15 ml of methanol. The mixture was stirred for 4 hrs at 70°C. The methanol was removed by distillation at room temperature under reduced pressure, followed by removal of the excess ethylenediamine under high vacuum conditions (0.2 mm Hg) at 50°C to give the compound as a viscous oil. Yield 6.9 g (80%). ^{1}H NMR (D_2O): δ 1.30 (d, 3H, PCH_3, ^2J(PH) = 15.8 Hz); δ 3.30 (s, 4H, CH_2N); δ 3.57 (d, 3H, $POCH_3$, ^3J(PH) = 10.8 Hz).

Ethylenediamine dialkylammonium salt of monomethyl methylphosphonate **7**. A solution of ethylenediamine 3.0 g (0.05 moles) in 5 ml of methanol was added droppwise at 40°C to a stirred solution of dimethyl methylphosphonate 12.4 g (0.1 moles) in 15 ml of methanol. The mixture was stirred for 2 hrs at 140°C. The methanol was removed by distillation at room temperature under reduced pressure to give a colorless viscous liquid, which deposits **7** as colorless crystals upon standing. These crystals were filtered off and recrystallized from methanol. Yield 11.6 g (91%), m.p. 161–165°C. ^{1}H NMR (DMSO): δ 1.05, (d, 6H, PCH_3, ^2J(PH) = 16.0 Hz); δ 3.03 (s, 4H, NCH_2); δ 3.37 (d, 6H, $POCH_3$, ^3J(PH) = 10.4 Hz); δ 3.39 (s, 6H, NH_3). ^{31}P NMR (D_2O): δ 29.10 (m). ^{13}C{^{1}H} NMR (D_2O): δ 10.53 (d, PCH_3, ^2J(PC) = 135.7 Hz); δ 36.68 (s, NCH_2); δ 51.39 (d, $POCH_3$, ^3J(PC) = 4.8 Hz).

C. Reaction of Trimethyl Phosphate with Ethylenediamine

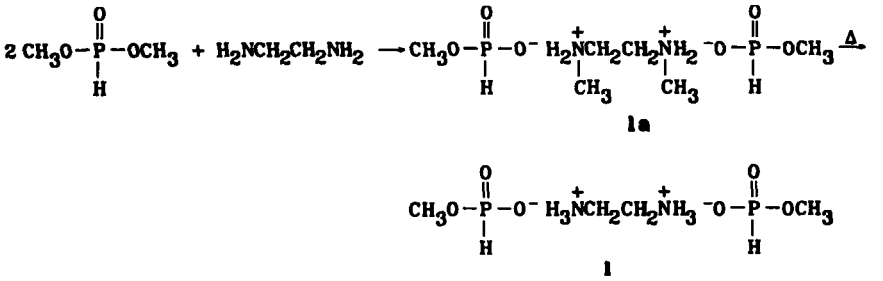
Ethylenediamine monoalkylammonium salt of dimethyl phosphate **8**. A solution of ethylenediamine 12.0 g (0.2 moles) in 5 ml of methanol was added droppwise at 40°C to a stirred solution of trimethyl phosphate 7.0 g (0.05 moles) in 15 ml of methanol. The mixture was stirred for 4 hrs at 70°C. The methanol was removed by distillation at room temperature under reduced pressure, followed by removal of the excess ethylenediamine under high vacuum conditions (0.2 mm Hg) at 50°C to give the compound as a viscous oil. Yield 8.5 g (91%). ^{1}H NMR (DMSO): δ 2.71 (s, 4H, NCH_2); δ 3.30 (d, 6H, $POCH_3$, ^3J(PH) = 10.3 Hz); δ 3.50 (br, s, 5H, NH). ^{31}P{^{1}H} NMR (D_2O): δ 3.80. ^{13}C{^{1}H} NMR (D_2O): δ 39.97 (s, NCH_2); δ 55.87 (d, $POCH_3$, ^2J(PC) = 5.2 Hz).

D. Reaction of the Dimethyl Cyclohexylidenevinylphosphonate with N,N-dimethylethanolamine

A solution of N,N-dimethylethanolamine 1.96 g (0.022 moles) in 2 ml of benzene was added droppwise to a stirred solution of dimethyl cyclohexylidene vinylphosphonate 4.3 g (0.02 moles) in 8 ml of benzene. The mixture was stirred for 5 hrs at 75°C. The solvent and the excess of the amine were removed under vacuo at 120°C, yielding the corresponding alkylated product **9** as a viscous oil. Upon cooling this oil crystallized. Yield 6.0 g (98%). ^{1}H NMR (D_2O): δ 1.58 (m, 6H, CH_2); δ 2.19 (m, 4H, CH_2); δ 3.20 (s, 9H, NCH_3); δ 3.52 (t, 2H, CH_2OH, ^3J(HH) = 8.8 Hz); δ 3.56 (d, 3H, $POCH_3$, ^3J(PH) = 10.6 Hz); δ 4.06 (m, 2H, NCH_2); δ 5.11 (m, 1H, PCH). ^{31}P{^{1}H} NMR (D_2O): δ 15.07.

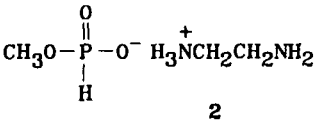
RESULTS AND DISCUSSION

An analysis of the NMR data for the reaction product **1** that is obtained by treatment of ethylenediamine with a fourfold excess of dimethyl phosphonate as shown in Equation 3 indicates that it has the structure shown. Compound **1** is therefore the methyl phosphonate salt of the doubly protonated ethylene diamine dication. This salt results from a reaction sequence that involves the initial dialkylation of the diamine by dimethyl phosphonate to give the salt **1a**, followed by dealkylation of both methylammonium groups. The ^{1}H NMR spectrum of **1** does not contain any resonances due to the $\overset{+}{N}CH_3$ group. The intensity of the resonances in this ^{1}H NMR spectrum indicates the presence of two monomethylphosphonate anions. The resonance for the PH group at δ 6.53 has a ^1J(PH) coupling constant 592.5



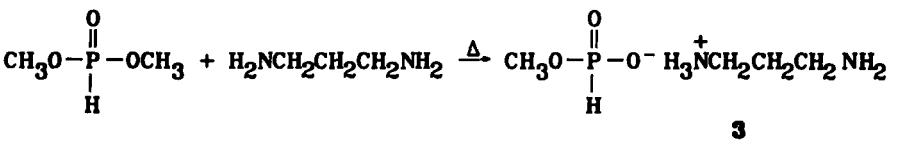
(3)

Hz, which is characteristic of a phosphonate structure having a delocalized negative charge.[9] Although the intermediate **1a** has not been detected in this case, in a previous study[8] we have demonstrated that this type of intermediate can be isolated when the reaction is carried out at lower temperatures. The use of elevated temperatures or reduced pressures facilitates the cleavage of the carbon-nitrogen bonds. This result demonstrates that depending on the mole ratio of the diamine and the dimethyl phosphonate we can isolate either of two products using these reaction conditions. The monoalkylammonium salt **2** is formed when the diamine is in



excess,[8] and the diammonium salt **1** is formed when the dimethyl phosphonate is in excess. Even with ethylenediamine where the two nitrogens are separated by two methylene groups, the charge delocalization of the positive charge in the monocation does not inhibit the second amino group from participating in the alkylation reaction with a second molecule of dimethyl phosphonate. This situation is not the case, however, for dialkyl phosphonates, where it has been established that the second alkoxy group cannot be dealkylated by amines due to the delocalization of the negative charge in the monoanion.[10]

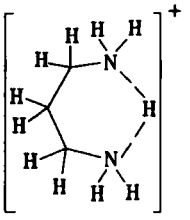
The reaction between dimethyl phosphonate and 1,3-propanediamine has also been carried out using a 1:4 mole ratio of reactants (Equation 4). By analogy with the preceding reaction with ethylenediamine, the corresponding monoammonium salt **3** is formed. The structure of **3** has been verified by NMR spectroscopy. A



(4)

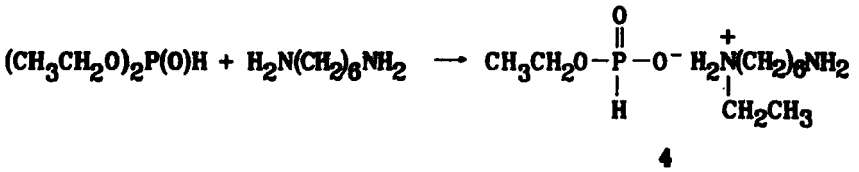
characteristic feature of both the ^{1}H and ^{13}C NMR spectra of **3** is the symmetric arrangement of both the proton and carbon signals of the methylene groups of the monoammonium cation. This symmetric arrangement leads to the observation of two resonances in the ^{1}H NMR spectrum of **3** at δ 1.78 and δ 2.97 along with two resonances in the ^{13}C NMR spectrum at δ 29.94 and δ 39.59. These observations imply the presence of a rapid proton exchange, taking place either in the framework

of the cyclic cationic structure **A** shown, or facilitated by exchange with the D_2O solvent.



A

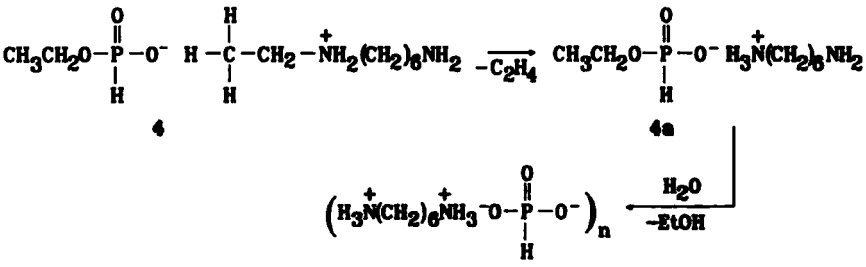
Diethyl phosphonate alkylates 1,6-hexanediamine when the two reagents are added in a 1:1 mole ratio forming the corresponding monoethylalkylammonium salt **4** (Equation 5). The relative stability of the salt **4** with respect to the subsequent



(5)

4

dealkylation of the cation under the reaction conditions (130°C) implies a decrease in the acidity of the CH_3 protons in the $\overset{+}{N}$Et group as compared to those in the $\overset{+}{N}$Me group in the preceding reactions. The Hoffman elimination of ethylene does, however, eventually takes place, although this is a reaction that occurs at a very low rate. This transformation is supported by the isolation of the salt **5**, which is formed by a sequence involving an initial Hoffman elimination reaction, followed by subsequent hydrolysis of the intermediate phosphonate ester **4a** (Equation 6).



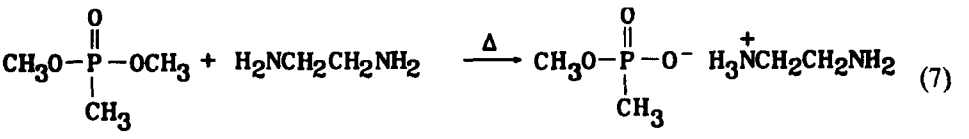
(6)

4 **4a** **5**

The ^1H NMR spectrum of **5** contains resonances due only to CH_2 (δ 1.26, δ 1.50, δ 2.83) and P*H* (δ 6.56) protons, and does not give any indication of the presence of POEt or NEt groups. The ^{31}P NMR spectrum of **5** indicates a typical phosphonate structure with a delocalized charge, giving rise to a doublet at δ 3.77 with $^1J(PH)$ = 566.7 Hz.

The reaction between dimethyl methylphosphonate and ethylenediamine has been studied with the reactants present in two different mole ratios. When a fourfold excess of ethylenediamine is used in the reaction the product is the salt **6**. This compound is formed by the alkylation of one of the amine groups by dimethyl

methylphosphonate, followed by cleavage of the $\overset{+}{N}Me$ bond under the high temperature (70°C) of the reaction (Equation 7). An apparent symmetry of the signals

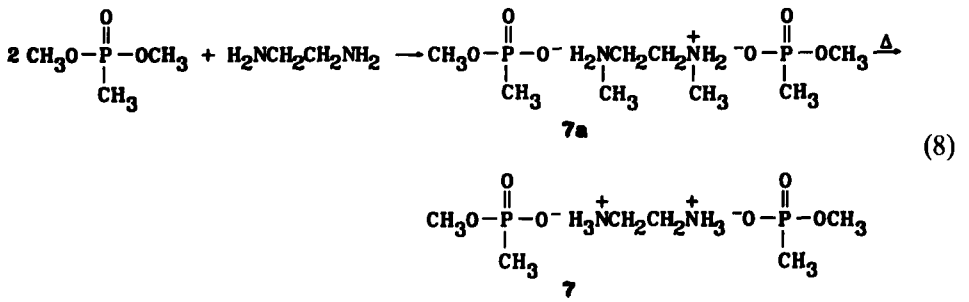


(7)

6

for the four methylene protons of the alkylammonium cation due to proton exchange is also observed in the ^1H NMR spectrum of this compound. This exchange process results in the observation of a single resonance at δ 3.03 corresponding to the four methylenic protons. This spectrum does not show any resonances for the presence of any $\overset{+}{N}CH_3$ groups. The monomethylphosphonate anion shows a resonance due to the PCH_3 group at δ 1.30 (^2J(PH) = 16.0 Hz), and a resonance due to the $POCH_3$ group at δ 3.57 (^3J(PH) = 10.8 Hz).

When this reaction between dimethyl methylphosphonate and ethylenediamine is carried out with a twofold excess of dimethyl methylphosphonate for two hours at 140°C, the second amino group of ethylenediamine is also methylated, and then subsequently demethylated in the course of the reaction to give **7** (Equation 8).



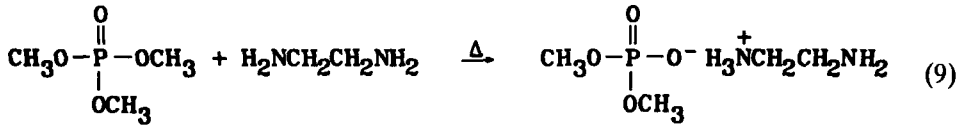
(8)

7a

7

This final dialkylammonium salt **7** contains no resonances in the either the ^1H, ^{31}P or ^{13}C NMR spectra that correspond to $\overset{+}{N}CH_3$ groups. This result contrasts with a previously reported one where the same reaction was been carried out for six hours at the same temperature, and the dimethylated ethylenediammonium intermediate **7a** was reported to be the only reaction product.[6]

Trimethyl phosphate reacts with a fourfold excess of ethylenediamine to give the corresponding alkylammonium salt **8**. Again, by analogy with the reaction products **2** and **6**, the salt **8** results from an alkylation of one amino group of ethylenediamine, followed by cleavage of the N-methyl bond (Equation 9). The ^1H NMR spectrum of **8** contains only two resonances, a singlet at δ 2.70 and a

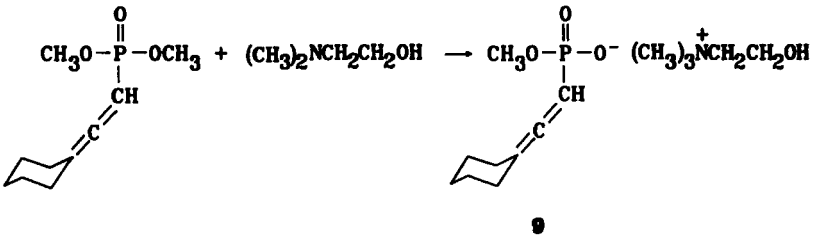


(9)

8

doublet at δ 3.30 with $^3J(PH)$ = 10.3 Hz. These signals with an intensity ratio 2:3 correspond to the NCH_2 and $POCH_3$ protons respectively. The $^{31}P\{^1H\}$ NMR spectrum of **8** shows a single resonance at δ 3.80 characteristic for the dimethyl phosphate anion.

Using similar reaction conditions N,N-dimethyl ethanolamine can be alkylated using the dimethyl ester of cyclohexylidenevinylphosphonic acid to yield the stable quaternary ammonium salt **9** (Equation 10). The structure of this product **9** has



(10)

9

again been characterized by a combination of ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectrum shows a resonance (9H) at δ 3.20 characteristic of the $\overset{+}{N}(CH_3)_3$ group. This result correlates with our previous observation that the presence of additional alkyl substituents on the nitrogen atom stabilizes the cationic methylalkylammonium group with respect to the N-methyl cleavage reaction.[8]

The results of this study demonstrate that diamines undergo either single or multiple alkylations in their reactions with phosphoryl esters, depending on the mole ratios of the reactants. We also find that the alkylation products of primary amines are unstable with respect to dealkylation, and that methylalkylammonium salts undergo dealkylation more easily than do the corresponding ethylammonium salts.

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