A Case of Slow Nitrogen Inversion due to Intramolecular Hydrogen Bonding. Study of Slow Nitrogen Inversion in Diethyl 2-Aziridinylphosphonate from the Paramagnetic Induced Shifts in the Proton Magnetic Resonance Spectra Using Tris(dipivalomethanato)europium(III), and Solvent Shifts

S. RENGARAJU[1] AND K. DARRELL BERLIN*[2]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

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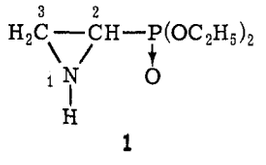
Retardation of pyramidal inversion of nitrogen was observed in diethyl 2-aziridinylphosphonate due to intramolecular hydrogen bonding. The presence of two invertomers has been shown by the nuclear magnetic resonance (nmr) studies using the paramagnetic shift reagent tris(dipivalomethanato)europium(III) [Eu(DPM)$_3$] and benzene solvent shift studies.

High barriers to pyramidal inversion of the nitrogen atom in aziridines has been proposed as early as 1939,[3] due to the strain in the three-membered ring. Since then several attempts have been made to resolve various substituted aziridines, without success.[3,4] However, the rates of nitrogen inversion in many derivatives of aziridine are measurable on the nmr time scale.[5] The temperature dependence of the nmr spectra of these aziridines have been used to calculate the activation parameters for nitrogen inversion.[5] Recently, diastereoisomeric forms of 1-chloro-2-methylaziridine have been separated by gas–liquid chromatography.[6] Similarly, separation of diastereoisomers of *N*-chlorocyclohexenimine by column chromatography has also been reported.[7] These reports suggest that some 1-haloaziridines will prove resolvable at room temperature. The slow inversion in *N*-haloaziridines has been attributed, besides the strain of the three-membered ring, to higher s character of the nitrogen lone pair due to the high electronegativity of the halogen substituent.[6,7] Conjugative destabilization by the repulsion between the nonbonding electron pairs of nitrogen and the halogen atom may also contribute to the enhancement of the barrier to inversion.[8] Synthesis of *N*-amino-[9] and *N*-methoxyaziridines[10a] and detection of very slow nitrogen inversion even at higher temperatures suggests that the presence of an adjacent heteroatom will decrease the rate of nitrogen inversion. So far the few examples of slow nitrogen inversion reported are in 1-substituted aziridines.[10b] Slow nitrogen inversion in aziridines without a substituent on nitrogen appears to have been reported in only one case.[10c]

This paper deals with the synthesis and nmr investigation of the aziridine **1**. Aziridine **1** has no substituent on nitrogen but has a structural feature which can contribute to the slow nitrogen inversion. This is the phosphoryl group at C-2, which can form an internal hydrogen bond with the hydrogen on nitrogen. This internal hydrogen bonding can be expected to be strong because it involves a five-membered ring as depicted in **2**. Evidence for the internal hydrogen bonding in



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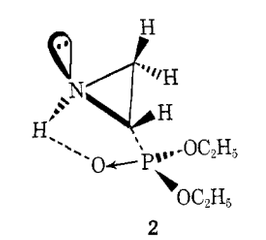

2

1 was obtained from ir studies. The ir spectrum of **1** in neat film showed two N–H stretching frequencies at 3450 and 3240 cm^{-1}. The peak at longer wavelength was attributed to the hydrogen-bonded N–H group. In the case of ethylenimine where no internal hydrogen bonding is possible, only one peak for N–H stretching is observed.[11] That the peak at 3240 cm^{-1} belongs to the internally bonded N–H was confirmed by ir dilution studies. The position of the band at 3240 cm^{-1} was found to be independent of concentration changes. Roberts and coworkers[4e,f] have shown that hydroxylic solvents decrease the rate of nitrogen inversion in the derivatives of aziridine. If that is the case, intramolecular hydrogen bonding, which will be stronger than a solvent–solute type hydrogen bonding, might decrease the rate of nitrogen inversion in the aziridine **1**.

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(2) The senior author gratefully acknowledges support of this work by the Public Health Service, Cancer Institute, Grant CA 07202-09. This paper was presented in part at the 163rd National Meeting of The American Chemical Society, Boston, Mass., April 1972.

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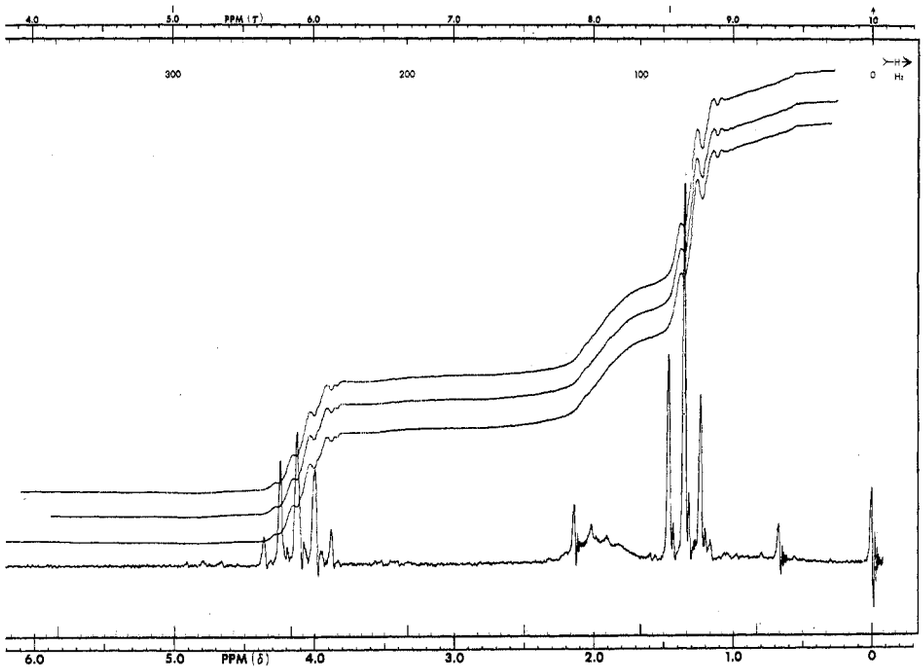
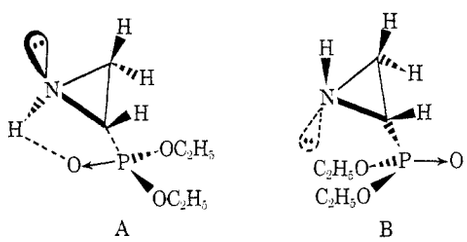


Figure 1.—60-MHz spectrum of diethyl 2-aziridinylphosphonate in $DCCl_3$.

The nmr spectrum of the aziridine **1** at 60 MHz in $DCCl_3$ (Figure 1) showed the aziridine ring protons as an envelope of unresolved peaks between δ 1.5–2.3. Analysis at 100 MHz also did not resolve the ring protons. In the 60-MHz spectrum methylene protons of the $P(O)(OC_2H_5)_2$ group displayed a quintet (due to common overlap of the two quartets arising from P–O–C–H coupling) at δ 4.12 (J = 7 Hz). The methyl protons absorbed at δ 1.35 as a triplet (J = 7 Hz). The presence of a smaller triplet at δ 1.33 indicated the presence of both invertomers of aziridine **1**. Further proof was obtained by the study of nmr spectra in $DCCl_3$ in the presence of paramagnetic shift reagent tris(dipivalomethanato)europium(III) [Eu(DPM)$_3$].

Eu(DPM)$_3$ has been used to effect paramagnetic induced shifts in the nmr spectra of alcohols.[12] Recently we have used this reagent in the study of syn–anti isomerism in oximes.[13] It was shown that the coordination of the Eu(DPM)$_3$ takes place on the oxime nitrogen lone pair and there is a steric effect in the coordination. This steric effect was useful in the analysis of syn–anti isomerism in oximes since the steric environments of the lone pair of electrons differs in the syn–anti forms of the oximes studied. Since syn–anti isomerism in oximes is due to an extreme case of high barrier to inversion of nitrogen lone pair, it is logical to expect similar paramagnetic induced shifts in the case of a slowly inverting aziridine.

In the case of aziridine **1**, the two invertomers can be represented as A and B. Intramolecular hydrogen bonding can take place between the N–H band P→O groups in invertomer A owing to the favorable cis arrangement of these groups. This will stabilize this form. In the invertomer B, unfavorable trans arrangement of N–H and P→O groups for intramolecular hydrogen bonding and the repulsion between the nitrogen lone pair and P→O group could make this invertomer less stable compared to A.



The nmr spectrum of the aziridine **1** in $DCCl_3$ (89 mg in 0.4 ml) containing 20 mg of Eu(DPM)$_3$ showed peaks corresponding to two invertomers A and B (Figure 2). A triplet at δ 1.37 (J = 7 Hz, OCH_2CH_3), unresolved multiplets approximately between 1.8 and 2.6 (aziridine ring protons), and a quintet (an overlap of two quartets due to P–O–C–H coupling in O←P-OCH_2) at 4.21 (J = 7 Hz, O←$POCH_2CH_3$) were attributed to the invertomer B. Corresponding peaks for the invertomer A are two triplets at δ 1.65 and 1.68 (J = 7 Hz, O←$POCH_2CH_3$), four partially resolved multiplets between 3.1 and 3.9 (aziridine ring protons), and two partly overlapping quintets at 4.8 and 4.87 (J = 7 Hz, O←$POCH_2CH_3$). The doubling of the signals for the methyl protons (δ 1.65 and 1.68) and methylene protons (4.8 and 4.87) of the OC_2H_5 group is attributed to the nonequivalence of the ethoxy groups due to restricted rotation of the C–P bond and the presence of the asymmetric center in invertomer A.

By increasing the concentration of the shift reagent Eu(DPM)$_3$, further downfield shifts of all the peaks of the invertomer A were observed as expected (Figure 3). However, overlap of ring methylene proton signals of invertomer A and the ethoxy methylene proton signals of the invertomer B occurs. The optimum concentration of Eu(DPM)$_3$ to observe all the peaks

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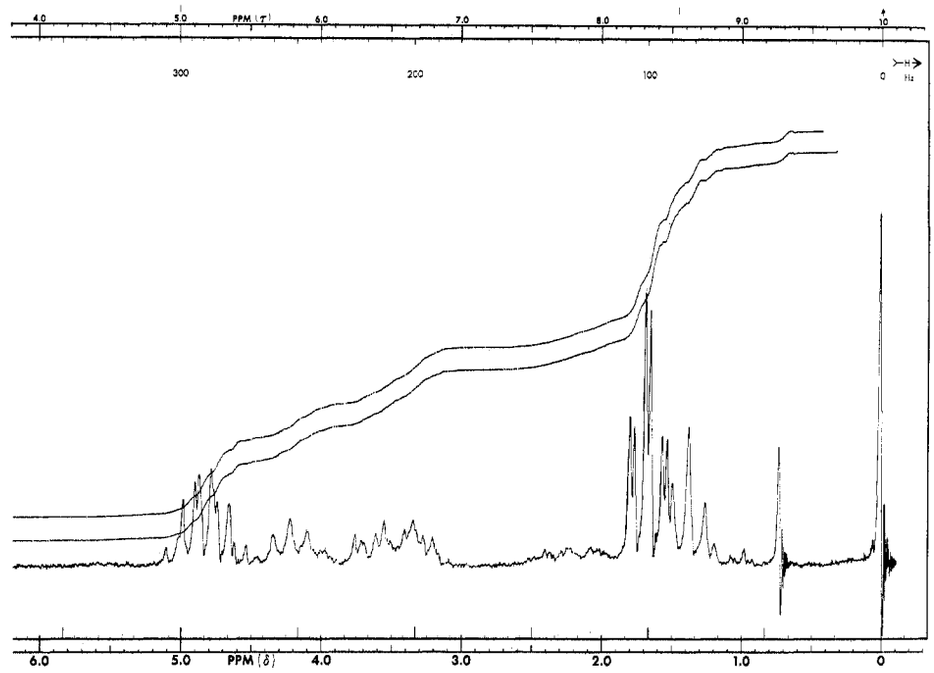


Figure 2.—60-MHz spectrum of diethyl 2-aziridinylphosphonate (0.0005 mol) in 0.4 ml of $DCCl_3$ containing 20 mg of $Eu(DPM)_3$.

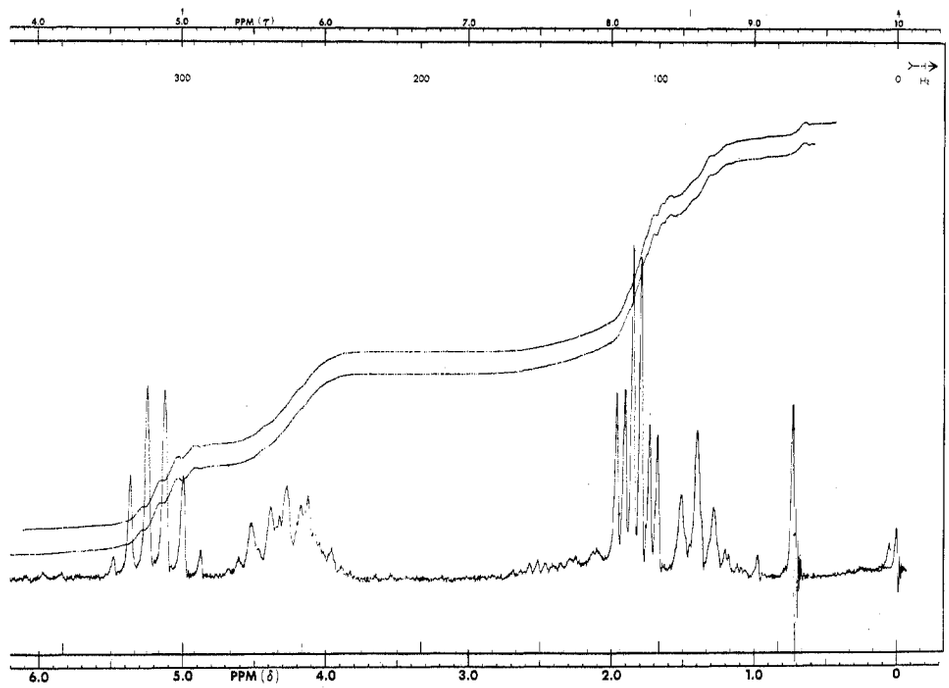
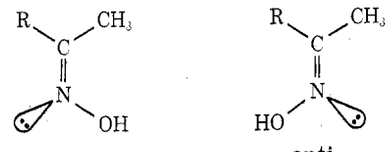


Figure 3.—60-MHz spectrum of diethyl 2-aziridinylphosphonate (0.0005 mol) in 0.4 ml of $DCCl_3$ containing 30 mg of $Eu(DPM)_3$.

of both invertomers was found to be 20 mg in a solution of 89 mg of **1** in 0.4 ml of $DCCl_3$.

One significant observation is that peaks of the invertomer B (compare Figures 1–3) did not significantly shift on addition of 20 or 30 mg of $Eu(DPM)_3$. This can be explained on the basis that there is little coordination of $Eu(DPM)_3$ with the nitrogen lone pair in the invertomer B due to steric hindrance of the bulky $O\leftarrow P(OC_2H_5)_2$ group. Similar steric interference to coordination was observed in our study of syn–anti isomerism in oximes.[13] In the syn form of the oximes studied, coordination with the lone pair was not so effective as in the anti form owing to steric hindrance from the bulky alkyl groups (R). From the ratio of the corresponding peaks for both invertomers A and B, the invertomer ratio was calculated as 3:1 (A:B).



syn anti

$R = C_2H_5$, $CH_3(CH_2)_2$, $CH_3(CH_2)_4$, $CH_3(CH_2)_5$, $(CH_3)_2CH$, $(CH_3)_2CHCH_2$

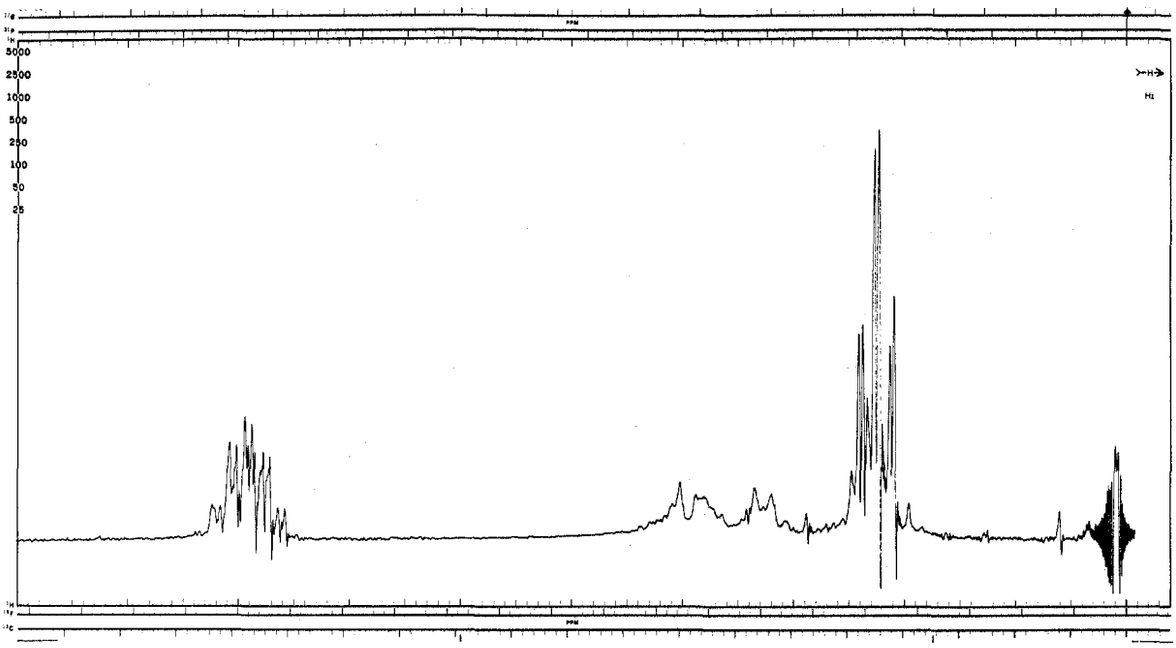


Figure 4.—100-MHz spectrum of diethyl 2-aziridinylphosphonate in benzene.

In the invertomer A the value of paramagnetic induced shift [$\Delta\delta$, $\Delta\delta = \delta$ with $Eu(DPM)_3 - \delta$ without $Eu(DPM)_3$] decreased in the order aziridine ring protons > methylene protons of $P(O)(OEt_2)$ > methyl protons of $P(O)(OEt)_2$, in all the three concentrations studied (Table I). This order suggests that the coordination of europium takes place with the nitrogen lone pair on the basis that shifts for protons close to the point of association are larger than those protons further removed.[12] A comparison of the $Eu(DPM)_3$-induced shifts for aziridines and related (but open chain) phosphonates shows that the shifts are very high in the case of aziridines (Table II). This may be attributed to the high basicity of the nitrogen lone pair in aziridines. It is known that $Eu(DPM)_3$-induced shifts are higher for amines compared to alcohols and ethers.[12c] $Eu(DPM)_3$-induced shifts for the phosphonates **6–10** can be explained on the basis of coordination of europium with P→O group. In the phosphonates **8–10**, since protons nearer to the P→O group are more shifted on addition of $Eu(DPM)_3$ than the protons nearer to the nitrogen atom, coordination of europium may occur with the P→O group. The coordination at the nitrogen lone pair in the phosphonates **8** and **10** may be less favorable owing to the probable lowered basicity of the nitrogen in view of its bonding to more electronegative elements. In **9** a steric effect around the nitrogen atom may reduce its complexing ability. The observation that europium coordinates with the P→O group in the phosphonates **6–10** suggests a possible bidendate arrangement of europium with the aziridine nitrogen and P→O group in **1**. This could also explain the high induced shifts in **1**.

TABLE I

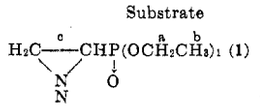
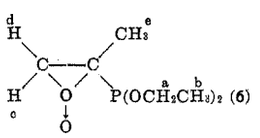
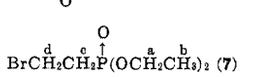
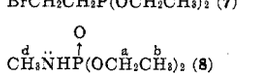
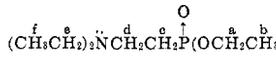
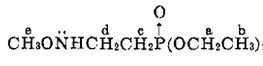
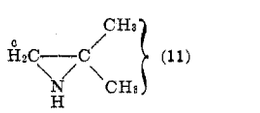
$\Delta\delta$ VALUES FOR THE INVERTOMER A

Wt of $Eu(DPM)_3$,[a] mg	$\Delta\delta_{CH_3}$	$\Delta\delta_{CH_2}$	$\Delta\delta$ ring protons
10	0.16	0.35	0.78
20	0.34	0.70	1.55
30	0.5	1.05	2.3

[a] In a solution of 89 mg of aziridine 1 in 0.4 ml of $DCCl_3$.

TABLE II

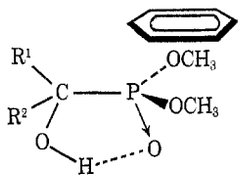
PARAMAGNETIC SHIFTS[a]

Substrate	$\Delta\nu^a$	$\Delta\nu^b$	$\Delta\nu^c$	$\Delta\nu$ (other protons)
 (1)	42	20	~90	
 (6)	19	7	21	9 (d), 12.5 (e)
 (7)	26	11	25	14 (d)
 (8)	25	12		13 (d)
 (9)	24	9	~20	~13 (d), 3.5 (e), 2 (f)
 (10)	24.5	9.5	22	27 (d), 4 (e)
 (11)			73	55 (e)

[a] $\Delta\nu$ (Hz), observed with 20 mg of $Eu(DMP)_3$ in a solution of 0.005 mol of substrate in 0.4 ml of $DCCl_3$.

The pmr spectrum of **1** in benzene (10% solution w/v) (Figure 4, 100 MHz spectrum) showed an interesting solvent effect. For example, in $DCCl_3$ the CH_3 of $P(O)(OCH_2CH_3)_2$ gave a triplet centered at δ 1.35 corresponding to the invertomer A and a smaller triplet at 1.33 corresponding to the invertomer B. However, in benzene as solvent an upfield shift of both the triplets occurs. In addition doubling of the triplet corresponding to the invertomer A was also observed (Figure 4).

The solvent shifts in an anisotropic solvent like benzene for different type of compounds have been explained on the basis of equilibrium formation of collision complexes between the benzene molecule and a polar functional group in the solute.[14] Benzene-induced shifts for two slowly inverting aziridines have been suggested in the literature.[15] It was observed that the upfield shift is more sensitive to the protons trans to the oriented nitrogen lone pair than to those which are cis oriented. Thus a model for the collision complex was proposed in which the benzene-solvent molecule occupies a position as far away as possible at the opposite side of the nitrogen lone pair.[15] In the present case, the benzene-induced shifts (going from $DCCl_3$ to C_6H_6, $\Delta = \delta_{DCCl_3} - \delta_{C_6H_6}$) for the methyl group in invertomer A and B are 0.27 (measured from the center of the two triplet for invertomer A at δ 1.09 and 1.075) and 0.21 ppm, respectively. The higher shift in invertomer A can be explained because of the trans arrangement of the nitrogen lone pair and the $P(O)(OCH_2CH_3)_2$ group. In the invertomer B, the arrangement is cis. The doubling of the triplet in invertomer A occurs because of the presence of an asymmetric center in the molecule and restricted rotation around the C–P bond owing to internal hydrogen bonding. Benzene-induced upfield shifts have also been reported in the case of several dimethyl alkylphosphonates.[16] In these phosphonates, where the $P(O)(OCH_3)_2$ group is attached to an asymmetric center, a different solvent shift was noted for the two methyl groups resulting in a peak doubling. A model for the benzene substrate complex as shown in **12** has been proposed where a benzene molecule occupies a position perpendicular to the P→O group and as far away from the negative end of the P→O dipole.



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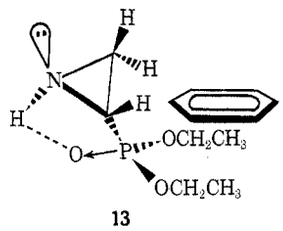
In the present system **1**, we propose a model for the complex in which the benzene molecule occupies a similar position as in **12** but as far away from the nitrogen lone pair as shown in **13** (representation for invertomer A). This model explains the higher upfield shift (0.27 ppm) for invertomer A due to the trans stereochemistry of the nitrogen lone pair and the $P(O)(OCH_2CH_3)_2$ group, compared to the invertomer B (0.21 ppm) where the stereochemistry is cis.



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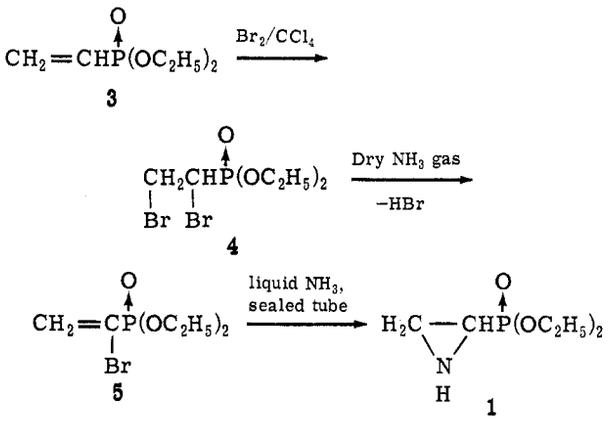
To observe the effect of heating on the invertomer ratio of aziridine **1**, variable high temperature nmr spectra was recorded up to 110° with neat sample of **1**, where only a slight increase in the amount of invertomer B was observed.

The synthesis of aziridine **1** was carried out according to the following scheme. While the synthesis was in progress in our laboratories, a patent[17] on the



synthesis of **1** appeared in the literature. Bromination of diethyl vinylphosphonate (**3**) using bromine in CCl_4 gave the crude dibromo compound **4** in theoretical yield. The crude product was at least 95% pure as shown by nmr. However, distillation of **5** results in partial decomposition. It was found convenient to purify the vinyl bromide **5**, which was obtained by passing dry ammonia gas through the dibromo compound **4**. The yield of pure vinyl bromide from crude **4** was 86–88% depending upon the purity of **4**. Reaction of vinyl bromide **5** with liquid ammonia in a sealed tube at room temperature gave the aziridine **1** in varying yields of 56–62%. In the case of aziridine **1** also partial polymerization was observed upon distillation. However, preliminary purification of the crude aziridine **1** by chromatography over neutral alumina before distillation reduced the degree of polymerization.

Owing to the difference in the hydrogen bonding in the two invertomers A and B, some solubility difference in solvents might be expected for the two forms. Thus, repeated extraction of aziridine **1** with hexane gave a hexane-soluble portion which contained more of invertomer B (ratio of A:B decreased from 3:1 to 3:2) compared to the starting mixture (Figure 5; *cf.* with Figure 2). However, a complete separation of the two forms could not be affected by all standard techniques attempted. Although invertomers A and B behave like rather special geometric isomers, the similarity in adsorption ability on substrates for chromatography and in solubility undoubtedly contributes to the separation problem. Work is continuing in the area.

Experimental Section

General and Spectra.—Infrared spectra of thin films were recorded on a Beckman IR-5A. Dilution studies to detect intramolecular hydrogen bonding in **1** were carried out in CCl_4 solutions using a Beckman IR-7 instrument. Nmr spectra were

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(15) T. Yonezawa, I. Morishima, and K. Fukuta, *Bull. Chem. Soc. Jap.*, **41**, 2297 (1968).

(16) C. Benezra and G. Ourisson, *Bull. Soc. Chim. Fr.*, 2270, (1966).

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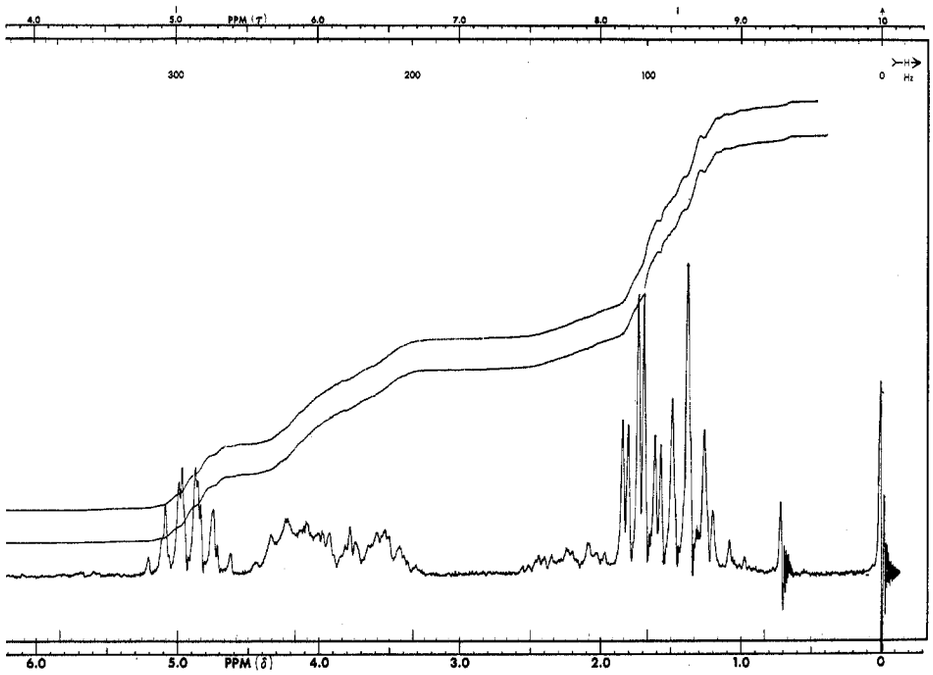

Figure 5.—60-MHz spectrum of diethyl 2-aziridinylphosphonate (hexane-soluble portion) (0.0005 mol) in 0.4 ml of $DCCl_3$ containing 20 mg of $Eu(DPM)_3$.

obtained on a Varian A-60 spectrometer, with TMS as internal standard while 100-MHz spectra were run on a Varian XL-100 spectrometer with TMS as internal standard. The shift reagent tris(dipivalomethanato)europium(III) was purchased from Norell Chemical Co., Inc. Diethyl vinylphosphonate (**3**) and diethyl 2-diethylaminoethylphosphonate (**9**) were prepared by the method of Kosolapoff.[18] 2,2-Dimethylaziridine (**11**) was prepared according to the known procedure.[19]

Diethyl 1,2-Dibromoethylphosphonate (**4**).—To a solution of diethyl vinylphosphonate (**3**, 16.4 g, 0.1 mol) in dry carbon tetrachloride (100 ml), dry bromine (19.2 g, 0.12 mol) in CCl_4 (100 ml) was added at 50° in the course of 90 min. After the addition was over, the reaction mixture was maintained at 60° for 8 hr. Evaporation of CCl_4 gave 32.3 g (theoretical) of **4**. The nmr spectrum of crude **4** did not show any impurities. An analytical sample was prepared by distillation under vacuum: bp 128–129° (2 mm); $n^{29}D$ 1.4861 [lit.[20] bp 123–125° (3 mm), $n^{20}D$ 1.4943]; ir (film) 1260 cm^{-1} (P→O); nmr (CCl_4) δ 1.35 (t, 6, J = 7 Hz, CH_3) and 4.17 [m, $P(O)OCH_2$] and the multiplets of C-1, C-2 hydrogens appeared as overlapping peaks with the $P(O)OCH_2$ methylene hydrogen. The area under these multiplets corresponded to seven hydrogens.

Diethyl 1-Bromovinylphosphonate (**5**).—A slow stream of dry ammonia gas was passed through **4** (32.4 g, 0.1 mol) with cooling in ice water until no more ammonium bromide precipitated out (about 45 min). The ammonium bromide was filtered off, and it was washed with 300 ml of benzene. The filtrate and washings were rinsed and washed with water and dried ($MgSO_4$). Evaporation of benzene gave 24 g of crude **6**, which was distilled under reduced pressure to give a single fraction of pure **5** (21.4 g, 88%): bp 65–66° (0.1 mm); $n^{28}D$ 1.4579 [lit.[19] bp 88–90° (3 mm); $n^{20}D$ 1.4681]; ir (film) 1585 (C=C), 1257 cm^{-1} (P→O); nmr (neat) δ 1.32 (t, J = 7 Hz, CH_3), 4.08 [m, $P(O)CH_2$], 6.45 [2 m, 1, J_{PH} = 37 Hz, vinyl proton trans to $P(O)(C_2H_5)_2$ group], and 6.8 [2 m, 1, J_{PH} = 14 Hz, vinyl proton cis to $P(O)(C_2H_5)_2$ group].

Diethyl 2-Aziridinylphosphonate (**1**).—A mixture of diethyl 1-bromovinylphosphonate (**5**, 12.15 g 0.05 mol) and 15 ml of liquid ammonia was allowed to react at room temperature in a sealed tube for 18 hr. The sealed tube was opened and the ammonia was evaporated off. The aziridine **1** was then dissolved in 100 ml of chloroform and the ammonium bromide filtered off. The chloroform solution, on evaporation, gave 8.84 g of crude reaction product. Extensive polymerization took place if distillation was attempted. Initial purification by passing the crude aziridine **1** (8.84 g) in chloroform through a column of neutral alumina (200 g, activity I) gave 6.8 g of aziridine **1**, which was further purified by vacuum distillation: bp 72° (0.15 mm); yield 5.55 g (62%); $n^{28}D$ 1.4451; ir (film) 3450 (NH free), 3240 (intramolecularly hydrogen bonded NH), and 1240 cm^{-1} (P→O); nmr ($DCCl_3$) δ 1.35 (t, 6, J = 7 Hz, CH_3), unresolved multiplets between δ ~1.5 and 2.3 (4, aziridine ring protons), and 4.12 [m, 4, J = 7 Hz, $P(O)OCH_2$].

Anal. Calcd for $C_6H_{14}O_3PN$: N, 7.82; P, 17.32. Found: N, 7.68; P, 17.12.

Diethyl 1-Methylepoxyethylphosphonate (**6**).—A solution of diethyl phosphite (27.6 g; 0.2 mol) in 50 ml of dry dimethylformamide was added very slowly to avoid frothing to a suspension of sodium hydride (5.3 g; 0.22 mol) in 300 ml of dimethylformamide with mechanical stirring and cooling in ice cold water under N_2. After the addition was completed, the mixture was heated at a water bath for 30 min when the evolution of hydrogen stopped. To this sodium salt of diethyl phosphite, α-chloroacetone (18.5 g; 0.2 mol) was added in the course of 45 min with mechanical stirring. After the addition, the reaction mixture was heated on a water bath for 3 hr. About 200 ml of DMF was removed under aspirator and the residue was diluted with 1.2 l. of water. The water solution was extracted with chloroform (1.5 l.) and the $HCCl_3$ extract was washed with water and dried ($MgSO_4$). Evaporation of $HCCl_3$ gave 31 g of crude reaction product, which upon distillation (using a 10 in. Vigreux column), gave **6**: bp 69–70° (0.1 mm) (19.5 g, 50%); $n^{23}D$ 1.4306; ir (film) 1260 (P→O), 850 cm^{-1} (oxirane ring); nmr (neat) δ 1.28 (t, 6, J = 7 Hz, CH_3CH_2O), 4.07 (m, 4, J = 7 Hz, CH_3CH_2O), 1.4 (d, 3, J = 10.5 Hz, CH_3 on the epoxide ring).

Anal. Calcd for $C_7H_{15}O_4P$: C, 43.30; H, 7.73. Found: C, 42.99; H, 7.57.

Diethyl 2-Aminomethoxyethylphosphonate (**10**).—To an alcoholic solution of methoxyamine [generated by treating methoxyamine hydrochloride (5.01 g; 0.06 mol) with alcoholic KOH (3.65 g, 0.065 mol in 25 ml of C_2H_5OH) and filtering off the KCl], diethyl vinylphosphonate (**3**, 3.28 g, 0.02 mol) was added, and the mixture was heated at 50–60° for 4 days. Alcohol was removed under aspirator vacuum and the residue was diluted with 100 ml of water. The aqueous solution was then extracted with $HCCl_3$ (3 × 50 ml) and the $HCCl_3$ extract was washed (H_2O) and dried ($MgSO_4$). Evaporation of solvent gave crude **10**, which was

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distilled to give a single fraction: bp 79° (0.05 mm) (2.11 g, 50%); $n^{23}D$ 1.4361; ir (film) 3220 and 3450 (NH), and 1240 cm^{-1} (P→O); nmr ($DCCl_3$) δ 1.32 (OCH_2CH_3), two triplets at 1.85 and 2.15 (CH_2 adjacent to P→O, J_{HH} = 7 Hz and J_{PCH} = 18 Hz), two triplets at 3.04 and 3.13 (CH_2 adjacent to NH, J_{HH} = 7 Hz and J_{PCCH} = 13 Hz), 3.47 (s, $NHOCH_3$), and 4.08 (m, J = 7 Hz, OCH_2CH_3).

Anal. Calcd for $C_7H_{18}NO_4P$: P, 14.70; N, 6.63. Found: P, 14.61; N, 6.46.

Registry No.—**1**, 35212-68-1; **6**, 1445-84-7; **7**, 5324-30-1; **8**, 6326-73-4; **9**, 3958-23-4; **10**, 35212-72-7; **11**, 2658-24-4; tris(dipivalomethanato)europium(III), 15522-71-1.

Anisyl Neighboring-Group Participation in Carbonium Ion Formation in Antimony Pentafluoride and Sulfur Dioxide

BRIAN G. RAMSEY,*[1,2] JAMES A. COOK, JR.,[3] AND JAMES A. MANNER[3]

Departments of Chemistry, University of Akron, Akron, Ohio 44304, and California State University, San Francisco, California 94132

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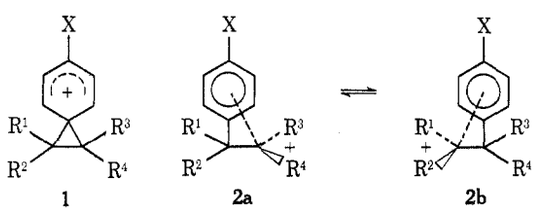
A study by nmr spectroscopy of the carbonium ions formed in $SbF_5 \cdot SO_2$ at −60° from p-$CH_3OC_6H_4CR_2CR_2X$, p-$CH_3OC_6H_4CR_2(CH_2)_3X$, and o-$CH_3OC_6H_4CH_2CH_2X$ was carried out where each R was varied systematically from H to methyl and X was halogen, mesylate, or OH. Except for p-$CH_3OC_6H_4CH_2CH_2X$, only benzylic ion formation was observed. Where X left from a primary carbon at −60° anisyl migration occurred prior to benzylic ion formation. Where OH_2^+ (or $^+OHSbF_5^-$) leaves from a secondary carbon, D or CD_3 labeling established that less than 60% of the product ion formed could be derived from β-anisyl migration from a secondary or tertiary origin. It was suggested that β-anisylcarbonium ions formed without specific solvation at the carbonium ion center or anisyl participation probably rearrange to benzylic ions much faster than anisyl migration occurs. The activation energy (6 kcal/mol) for equilibration of all alkyl methyl groups in p-$CH_3OC_6H_4CMeCMe_3^+$ was determined. The o-anisylethyl chloride forms the corresponding oxonium ion in $SbF_5 \cdot SO_2$ rather than an ortho anisonium or benzylic ion. There is no evidence of anisyl participation in the formation of benzylic ions from p-$CH_3OC_6H_4(CH_2)_4X$ or p-$CH_3OC_6H_4CMe_2(CH_2)_3X$ in $SbF_5 \cdot SO_2$ at −60°.

Because of our previous success[5] in generating and studying simple alkoxycarbonium ions in strong acid solutions, we became interested in another group of alkoxy-stabilized carbonium ions more commonly known as anisonium ions, or methoxy-stabilized phenonium ions, **1** (X = OCH_3). Phenonium ions have been



1 **2a** **2b**

regarded[6] by many, though not all, as being intermediates in the normal solvolysis reactions of β-arylalkyl primary and secondary halides, tosylates, etc. The well-established[5,7] thermodynamic stability of alkoxycarbonium ions and ability of the p-anisyl group to enhance the solvolysis rates[6b,8] even in systems where anchimeric assistance by other β-aryl groups was contended, seemed when this work was initiated to make the anisyl system ideal for observing phenonium ions directly by spectroscopic means.

Further, it has been demonstrated[9] that apparent discrepancies between observed product ratios and titrimetric rates in β-arylalkyl solvolysis reactions disappear if the reaction rate is treated as a sum of the rates of a neighboring aryl-assisted reaction proceeding through a phenonium ion intermediate (rate constant k_Δ) and either a solvent-assisted rate (k_s) or alternatively[9d] simply unassisted ionization in secondary derivatives as originally proposed by Winstein. The observed rate constants then are k_Δ, corrected by a factor (F) for internal return, plus k_s, *i.e.*, $k_{tit} = Fk_\Delta + k_s$. The success of this treatment does not necessarily mean that k_Δ leads to a phenonium ion intermediate or transition state; a π complex ion (transition state), or ion pair, can yield the same rate expression.

Schleyer[10] argues that in the solvolysis of secondary alkyl tosylates, etc., participation by solvent in the ionization must be very strong and there is no "leakage" or conversion between phenonium ion and the solvent-complexed classical ion. This mechanism accounts for the much larger rate enhancements by β-aryl groups of solvolysis reactions in trifluoroacetic acid, a relatively weak nucleophilic solvent. *Extrapolating this solvent effect model to $SbF_5 \cdot SO_2$ would lead to the expectation that the process characterized by k_Δ would be the only significant ionization process in this solvent system.* Further, in $SbF_5 \cdot SO_2$ we can expect carbonium

(1) Department of Chemistry, California State University, San Francisco, Calif. 94132.

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(3) (a) Taken in part from the Ph.D. theses of James A. Cook, Jr., and James A. Manner. (b) PPG Industries Fellows.

(4) Manuscript originally received by *J. Amer. Chem. Soc.*, Aug 1970.

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(10) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297, 4300 (1969).