

Small Charged Rings. XIV.
Dimer Formation through 2-Arylaziridinium Salts (1,2)

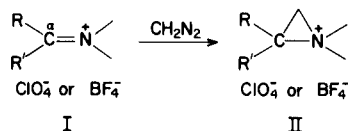
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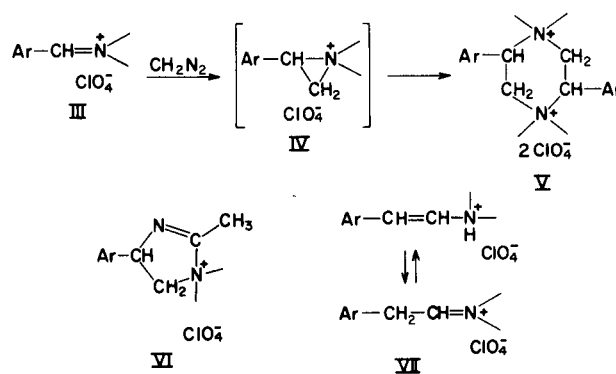
2,5-Diaryl-substituted *N,N,N',N'*-tetramethylpiperazinium diperchlorates have been synthesized in two steps: condensation of an aromatic aldehyde with dimethylamine perchlorate to give the corresponding *N,N*-dimethylaralkylideneiminium perchlorate, followed by reaction with diazomethane. Nmr evidence was obtained for the intermediate in the second step being the corresponding 2-aryl-1,1-dimethylaziridinium perchlorate.

In earlier studies we have concentrated on the formation of aziridinium salts (II) from alkylideneiminium salts (I) (3) by treatment with diazomethane and on the reactions of these unsymmetrically substituted aziridinium salts (4-9). The isolation of several 2-acyl-3-aryl-substituted aziridinium salts *via* another synthetic route has been reported (10), but the preparation of simple 2-aryl-substituted aziridinium salts from aralkylideneiminium salts and diazomethane has not been described.



A pilot reaction of diazomethane in ether with *N,N*-dimethylbenzylideneiminium perchlorate (IIIa) in ethylene dichloride at 0° led to immediate evolution of nitrogen. The nmr spectrum of the reaction mixture had an upfield signal diagnostic of aziridinium methylene protons (9), indicating the formation of 1,1-dimethyl-2-phenylaziridinium perchlorate (IVa) as an intermediate. An attempt to obtain complete reaction with diazomethane under continuation of the same conditions led to the isolation of products other than the aziridinium salt. That the major product isolated, m.p. > 300°, was dimeric, *i.e.*, probably 2,5-diphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate (Va), was suggested by earlier work of Bartlett (11-13) and in this Laboratory (9) and was indicated by microanalyses, correct for C₁₀H₁₄ClNO₄ (or C₂₀H₂₈Cl₂N₂O₈); infrared spectrum, showing the lack of the C=N⁺ moiety; ultraviolet spectrum, showing the lack of conjugation with phenyl; lack of reaction with aqueous sodium thiosulfate, indicating that an aziridinium ring was not present; and

osmometric molecular weight, consistent with the dimeric structure. Whereas the intermediate IVa, if formed in acetonitrile, might have been trapped as 5-phenyl-2,3,3-trimethylimidazolinium perchlorate (VIa), since we have found that aziridinium salts undergo ring expansion with acetonitrile (1,7,9), the lack of infrared absorption in the range 1630-1800 cm⁻¹ in the crude product obtained at 0° ruled out this possibility, and the same bis-piperazinium salt, Va, was isolated.

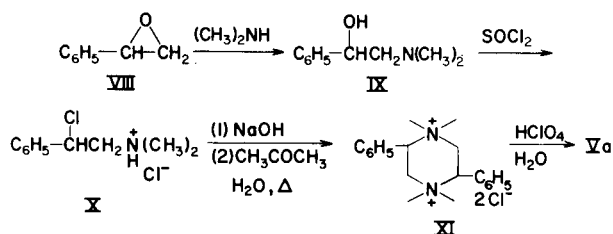


a, Ar = C₆H₅; b, Ar = *p*-CH₃OC₆H₄; c, Ar = *p*-CH₃C₆H₄

One possibility originally considered for a C₁₀H₁₄ClNO₄ product of reaction of diazomethane with IIIa was *N,N*-dimethylstyrylamine perchlorate (VIIa), since this might result from thermal rearrangement of IVa as an intermediate, even at the low temperature employed (4,9). However, the properties of the product isolated, as described above, eliminated this possibility. This conclusion was sustained by the independent synthesis of *N,N*-di-

methylstyrylamine and its conversion to perchlorate salt. Treatment of *N,N*-dimethylstyrylamine in methylene chloride with ethereal perchloric acid caused the precipitation of a white solid, m.p. 65°, with elemental analysis consistent with *N,N*-dimethylstyrylamine perchlorate. The salt exhibited unusual nmr spectral characteristics in that they were a function of solvent (see Experimental), indicating that it can exist *N*-protonated or *C*-protonated (VII). The phenomenon of *N*- vs. *C*-protonation of certain enamines has been observed previously (14).

The elimination of IV, VII, and VI (in acetonitrile) as possibilities for one of the reaction products of diazomethane with IIIa under the conditions cited left only the bis-piperazinium salts in consideration. One of the dimeric structures, Va, was synthesized independently by the following scheme (VIII → IX → X → XI → Va):



A similar sequence examined by Chapman (15) did not give the bis-piperazinium salt, XI, when X was neutralized and treated with aqueous acetone. Apparently concentrated solutions favor piperazinium salt formation. The 2,5-diphenyl-1,1,4,4-tetramethylpiperazinium dichloride (XI) was prepared under the same conditions that Bartlett and his coworkers used in their study of aziridinium intermediates leading to dimeric structures (11-13). Treatment of XI with 70% perchloric acid in water gave 2,5-diphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate (Va) in nearly quantitative yield. This product and the purified material isolated from the reaction of diazomethane with IIIa had identical nmr and infrared spectral characteristics. The crude diazomethane product also contained at least one other component isomeric with Va, on the basis of identical analysis and similar nmr difference spectrum (spectrum of crude product minus spectrum of Va obtained from XI) (16).

The method of conversion of an aromatic aldehyde *via* III and diazomethane treatment to a diaryl-substituted *N,N,N',N'*-tetramethylpiperazinium diperchlorate (V) appears to be general as judged by the formation of 2,5-di-*p*-methoxyphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate (Vb) from *N,N*-dimethyl-*p*-methoxybenzylideneiminium perchlorate (IIIb) and of 2,5-di-*p*-methylphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate (Vc) from *N,N*-dimethyl-*p*-methylbenzylideneiminium perchlorate (IIIc). Reactions of diazomethane in ethylene or methylene

dichloride-ether with iminium salts having additional functionality, as represented by *N,N*-dimethyl- α -methoxyethylideneiminium fluoborate, *N,N,N',N'*-tetramethylacetamidinium chloride, *O*-ethyl-*N*-nitrosodimethylamine fluoborate, and *N*-methyl-*N*-phenylisopropylideneiminium fluoborate or perchlorate, were unsuccessful.

EXPERIMENTAL (17)

N,N-Dimethylstyrylamine.

Following the general method of Blanchard (18) for the preparation of *N,N*-dimethyl- and *N,N*-diethyl-enamines, a solution of 24 g. (0.2 mole) of phenylacetaldehyde, 45 g. of 8-mesh calcium chloride, 16 g. (0.5 mole) of dimethylamine, and 400 ml. of ether was stirred for 64 hours followed by filtration, concentration, and distillation to yield 21.9 g. (75%) of light yellow liquid, b.p. 100-102° (0.5 mm.) (reported, 105-110° (20-22 mm.) (19), 75-78° (1 mm.) (20), 116-117° (19 mm.) (21), 90-91° (1 mm.) (22)); nmr (in deuteriochloroform): δ from TMS 2.63 (6H, s, N(CH₃)₂), 5.11 (1H, d, *J* = 13.9 Hz, C=CH-N), 6.55 (1H, d, *J* = 13.9 Hz, Ph-CH=C), 7.1 ppm (5H, m, C₆H₅).

Dimethylstyrylamine Perchlorate (VII).

To a solution of 0.50 g. (3.44 mmoles) of *N,N*-dimethylstyrylamine in 50 ml. of ether and 50 ml. of methylene dichloride was added 50 ml. (3.59 meq.) of ethereal perchloric acid. After cooling to 5° the solid product was collected and dried, yield 0.82 g. (94%), m.p. 65°; major nmr signals (10% in DMSO-*d*₆): δ 2.25-2.8 (6H,

overlapping doublets, NH (CH₃)₂⁺, 6.72-7.62 (7H, m, C₆H₅, CH=CH), 8.0-8.4 (1H, br m, ⁺NH); (5% in TFA): δ 3.62-3.83 (6H, m, ⁺N(CH₃)₂), 3.83-4.14 (2H, br d, C₆H₅CH₂), 7.10-7.36 (5H, s, C₆H₅), 8.06-8.40 (1H, br m, HC=N⁺); (20% in deuterioacetonitrile): δ 3.42-3.70 (6H, m, ⁺N(CH₃)₂), 3.81-4.10 (2H, br d, C₆H₅CH₂), 7.13 (5H, s, C₆H₅), 8.03-8.28 (1H, br m, HC=N⁺); λ max (acetonitrile) 302 m μ (ϵ , 5380), 232 (3360).

Anal. Calcd. for C₁₀H₁₄ClNO₄: C, 48.49; H, 5.70; N, 5.65. Found: C, 48.39; H, 5.77; N, 5.51.

N,N-Dimethyl-2-phenethanolamine (IX).

This compound was prepared by the method of Emerson (23). A mixture of 120 g. (1 mole) of styrene oxide (VIII) and 458 g. of 40% aqueous dimethylamine solution was heated in a glass-lined high-pressure bomb at 125° for 12 hours with rocking. The resulting solution was concentrated under reduced pressure and distilled, yield 102.6 g. (62%), b.p. 62-65° (0.12 mm.) (reported (24), 132-133° (15 mm.)); nmr (in deuteriochloroform): δ 2.28 (6H, s, N(CH₃)₂), 2.32 (2H, m, CH₂), 3.92 (1H, s, OH), 4.68 (1H, d of d, CH), 7.3 (5H, m, C₆H₅); ν max (chloroform) 3400, 2940, 2820, 2780, 1450, 860 and 690 cm⁻¹.

2-Chloro-*N,N*-dimethylphenethylamine Hydrochloride (X).

A 31-g. (0.2 mole) sample of *N,N*-dimethyl-2-phenethanolamine (IX) was allowed to react with 33.4 g. (20.4 ml., 0.28 mole) of thionyl chloride in chloroform solution. Recrystallization from 2-butanone, ethanol, water (10:20:1) yielded 19.2 g. (49%) of colorless plates, m.p. 206° dec. (reported, 202-203° (21), 202-205° (22)); nmr (in 10% deuterium oxide, external TMS) δ 3.39 (6H, s, (CH₃)₂), 4.08 (2H, m, CH₂), 5.85 (1H, d of d, CH), 7.88 (5H, s, C₆H₅); ν max (potassium bromide) 2960, 2660, 1620, 1440, 1345, 690 and 650 cm⁻¹.

2,5-Diphenyl-1,1,4,4-tetramethylpiperazinium Diperchlorate (Va) from 2-Chloro-*N,N*-dimethylphenethylamine.

To a solution of 11.0 g. (0.05 mole) of 2-chloro-*N,N*-dimethylphenethylamine hydrochloride (X) in 25 ml. of water overlaid with 50 ml. of ether was added 50 ml. of 1*N* sodium hydroxide solution (0.05 eq.) at ice-bath temperature with magnetic stirring. The ether was decanted and the aqueous solution was extracted with three 50 ml. portions of ether. The ether was dried over potassium carbonate and concentrated to give 6.18 g. (68%) of colorless oil. The oil was dissolved in 150 ml. of 2:1 acetone-water solution and stirred at ambient temperature for 52 hours. The solution was concentrated and the white solid was collected and recrystallized from ethyl acetate, ethanol, and heptane to give 3.40 g. (55%) of colorless needles of XI, m.p. 309-310° dec.

To 1.0 g. (2.73 mmoles) of 2,5-diphenyl-1,1,4,4-tetramethylpiperazinium dichloride (XI) in 20 ml. of water was added 70% perchloric acid until there was no further precipitation. The white solid was collected, washed with water and dried, yield 1.25 g. (92%) m.p. > 300°. A sample was recrystallized from acetonitrile, acetone, and heptane, m.p. > 325°; nmr (in TFA): δ 3.7-3.0 (12H, broad pseudotriplet, CH₃'s), 3.9-5.6 (6H, m, CH₂CH's), 7.62 (10H, s, C₆H₅); ν max (potassium bromide) 3000, 1620, 1580, 1470, 1140, 770, 710 and 615 cm⁻¹.

Anal. Calcd. for C₂₀H₂₈Cl₂N₂O₈: C, 48.49; H, 5.70; N, 5.66. Found: C, 48.79; H, 5.88; N, 5.39.

N,N-Dimethylbenzylideneiminium Perchlorate (IIIa).

A solution containing 21.25 g. (0.2 mole) of benzaldehyde, 14.5 g. (0.1 mole) of dimethylamine perchlorate, and 5 drops of diisopropylethylamine in 200 ml. of ethylene dichloride was heated for 24 hours under reflux so that the condensed solvent passed through a soxhlet thimble containing molecular sieves (Linde 4A). The solution was cooled and concentrated to a yellow oil which was triturated with ether until crystalline. The light yellow solid, crude yield 87%, was recrystallized from 2-butanone-ether as colorless needles, m.p. 80-81°, yield 61%; nmr (20% in TFA): δ 3.93 (6H, unresolved singlets, ⁺N(CH₃)₂), 7.6-8.0 (5H, m, C₆H₅), 8.8 (1H, s, CH=N⁺).

Anal. Calcd. for C₉H₁₂ClNO₄: C, 46.11; H, 5.50; N, 5.97. Found: C, 46.42; H, 5.55; N, 5.89.

N,N-Dimethyl-*p*-methoxybenzylideneiminium Perchlorate (IIIb).

This compound was prepared from *p*-anisaldehyde by the method employed for IIIa, colorless needles from acetonitrile-ether, m.p. 129-131°, yield 85%; nmr (in TFA): δ 3.4 (6H, unresolved singlets, ⁺N(CH₃)₂), 3.55 (3H, s, OCH₃), 6.6-6.9 (2H, d, C₆H₄), 7.3-7.6 (2H, d, C₆H₄), 8.15 (1H, s, CH=N⁺).

Anal. Calcd. for C₁₀H₁₄ClNO₅: C, 45.55; H, 5.35; N, 5.31. Found: C, 45.85; H, 5.38; N, 5.38.

N,N-Dimethyl-*p*-methylbenzylideneiminium Perchlorate (IIIc).

This compound was prepared in a similar manner from *p*-tolualdehyde, colorless needles from acetone-acetonitrile-ether, m.p. 100-101°, yield 87%, nmr (20% in acetone-*d*₆): δ 2.50 (3H, s, CH₃-Ar), 3.9 (6H, unresolved singlets, ⁺N(CH₃)₂), 7.4-8.1 (4H, m, C₆H₄), 8.11 (1H, s, CH=N⁺).

Anal. Calcd. for C₁₀H₁₄ClNO₄: C, 48.49; H, 5.70; N, 5.66. Found: C, 48.64; H, 5.79; N, 5.94.

N,N-Dimethyl-2-furfurylideneiminium Perchlorate.

The same procedure was used with furfural. The crude solid was treated twice with charcoal in acetone, and the resulting solid was recrystallized from acetone-ether as tan needles, m.p. 67-68°, yield 62%; nmr (15% in deuterioacetonitrile): δ 3.73 and 3.82

(3H each, singlets, ⁺N(CH₃)₂), 6.87 (1H, m, 4-H), 7.75 (1H, m, 3-H), 8.18 (1H, m, 5-H), 8.60 (1H, m, CH=N).

Anal. Calcd. for C₇H₁₀ClNO₅: C, 37.60; H, 4.51; N, 6.26. Found: C, 37.49; H, 4.60; N, 6.24.

Reaction of *N,N*-Dimethylbenzylideneiminium Perchlorate (IIIa) with Diazomethane.

To 1.0 g. (4.38 mmoles) of *N,N*-dimethylbenzylideneiminium perchlorate (IIIa) in 150 ml. of ethylene dichloride (distilled from Linde 4A sieves) was added 19 ml. (4.7 mmoles) of ethereal diazomethane solution at 0°. Upon addition of the diazomethane, there was immediate gas evolution. The colorless solution was stirred for 1 hour and then concentrated under anhydrous conditions to give a yellow oil which exhibited the following nmr signals (deuterioacetonitrile): δ 2.60 (3H, s, ⁺NCH₃), 3.30 (3H, s, ⁺NCH₃), 3.60 (2H, q, ⁺NCH₂C), 4.60 (1H, br t, ArCH), 7.60 (5H, s, C₆H₅) which can be assigned to the intermediary 1,1-dimethyl-2-phenylaziridinium perchlorate (IVa). There were also signals assignable to *N,N*-dimethylbenzylideneiminium perchlorate. The lack of nmr signals in the region δ 5.0 to δ 6.0 indicated that very little piperazinium dimer formation had occurred at this stage. The presence of starting iminium salt was confirmed by infrared spectroscopy. The oil was treated with additional ethereal diazomethane (1.2 mmoles) at 0° in 100 ml. of ethylene dichloride and then reconcentrated to a yellow oil. This oil was dissolved in 50 ml. of ethylene dichloride at ambient temperature for 8 hours, during which time a white solid precipitated, 0.841 g. (79%). The white solid was recrystallized from acetonitrile, 2-propanol, ether to give colorless needles, m.p. > 300°. Analysis of the nmr spectrum of the crude solid indicated that the bis-piperazinium salts were the only products, with 2,5-diphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate (Va) accounting for approximately 75% of the mixture. The other 25% was possibly the isomeric 2,6-diphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate. This analysis was based upon differences in nmr signal areas calculated using the DuPont 310 curve resolver. The elemental analyses of both the crude and the recrystallized material are consistent with dimer formation. However, recrystallization tends to enrich the concentration of the less soluble dimer Va. After three recrystallizations the nmr spectrum of the product was identical with that of independently synthesized material (see above). The major component had the following nmr (20% in TFA): δ 3.1-3.7 (12H, multiplet consisting of three broad signals, ⁺N(CH₃)₂), 4.0-5.8 (6H, series of multiplets, ring protons), 7.85 (10H, s, C₆H₅); nmr of crude material (20% in TFA): δ 3.0-3.8 (12H, multiplet consisting of four broad signals, ⁺N(CH₃)₂), 4.0-5.8 (6H, series of multiplets, ring protons), 7.7 (10H, s, C₆H₅). The final product did not react with aqueous sodium thiosulfate under conditions amenable to reaction with 5-azoniadispiro-[4.0.5.1]dodecane perchlorate (9).

Anal. Calcd. for C₂₀H₂₈Cl₂N₂O₈: C, 48.49; H, 5.70; N, 5.66; mol. wt., 495. Found: C, 48.35; H, 5.85; N, 5.67; mol. wt., 523 (osmometric in acetonitrile).

Reaction of *N,N*-Dimethyl-*p*-methylbenzylideneiminium Perchlorate (IIIc) with Diazomethane.

To 1.0 g. (4.05 mmoles) of *N,N*-dimethyl-*p*-methylbenzylideneiminium perchlorate (IIIc) was added with stirring 4.2 mmoles of ethereal diazomethane solution at 0°. After being stirred for 1 hour, the solution was concentrated under anhydrous conditions to give a yellow solid which was triturated with ether to yield yellow needles, 0.985 g. (93%); ν max (Nujol) 1090 (ClO₄⁻), 625 cm⁻¹ (C₆H₅), lack of absorption in 1610-1800 cm⁻¹ region; nmr on the portion of the yellow needles soluble in deuterioacetonitrile indicated the presence of 1,1-dimethyl-2-*p*-methylphenylaziridinium

perchlorate with δ 2.38 (3H, s, C₆H₄-CH₃), 2.51 (3H, s, ⁺N-CH₃), 3.2 (3H, s, ⁺N-CH₃), 3.45 (2H, q, ⁺NCH₂C), 4.35 (1H, m, C₆H₄CH), 7.4 (4H, m, C₆H₄); nmr of yellow needles (20% in TFA): δ 2.41 and 2.51 (6H, s, C₆H₄-CH₃), 3.05-3.71 (12H, multiplet consisting of 3 broad signals, ⁺N(CH₃)₂), 3.97-5.74 (6H, series of multiplets, ring protons), 7.55 (8H, s, C₆H₄). These signals are consistent with the piperazinium dimers, 2,5-di-*p*-methylphenyl-1,1,4,4-tetramethylpiperazinium diperchlorate (Vc) and its 2,6-di-*p*-methylphenyl isomer. The two signals for the methyl substituent on the phenyl ring indicate that both structural dimers are present. Recrystallization of the yellow needles from acetone afforded colorless needles (72% recovery), m.p. > 290°, nmr (10% in TFA), same as the nmr spectrum above.

Anal. Calcd. for C₂₂H₃₂Cl₂N₂O₈: C, 50.49; H, 6.16; N, 5.35. Found: C, 50.60; H, 6.16; N, 5.50.

Reaction of *N,N*-Dimethyl-*p*-methoxybenzylideneiminium Perchlorate (IIIb) with Diazomethane.

The reaction of *N,N*-dimethyl-*p*-methoxybenzylideneiminium perchlorate (IIIb) with diazomethane was carried out in a manner similar to the reaction of *N,N*-Dimethylbenzylideneiminium perchlorate to give colorless needles (80%) of Vb from 2-butanone, 2-propanol, m.p. > 300°; nmr (10% in TFA): δ 2.91-3.72 (12H, multiplet consisting of 3 broad signals, ⁺N(CH₃)₂), 4.0 (6H, s, OCH₃), 4.0-5.6 (6H, series of multiplets, ring protons), 7.09-7.77 (8H, q, C₆H₄).

Anal. Calcd. for C₂₂H₃₂Cl₂N₂O₁₀: C, 47.58; H, 5.81; N, 5.04. Found: C, 47.36; H, 5.81; N, 5.04.

N,N-Dimethyl- α -Methoxyethylideneiminium Fluoborate.

This compound was prepared by the method of Lee (25). To a solution containing 11.62 g. (0.06 mole) of silver fluoborate and 5.65 ml. (0.06 mole) of freshly distilled dimethylacetamide in 65 ml. of ethylene dichloride at -78° was added 8.8 ml. (20 g., 0.141 mole) of freshly distilled methyl iodide by injection below the surface of the liquid. The mixture was stirred at ambient temperature for 2 hours, filtered, and the filtrate was concentrated to half volume under reduced pressure. Addition of ether yielded a colorless solid, 96% crude yield, which was recrystallized from 2-butanone to give colorless needles, m.p. 142-143° (reported 143-145°) (25), yield 76%; nmr (20% in TFA) δ 2.62 (3H, s, CCH₃), 3.39 (3H, s, ⁺NCH₃), 3.50 (3H, s, ⁺NCH₃), 4.35 (3H, s, OCH₃): ν max (Nujol) 1680 (C=N); 1100-1000 cm⁻¹ (BF₄⁻).

Anal. Calcd. for C₅H₁₂BF₄NO: C, 31.78; H, 6.40; N, 7.41. Found: C, 31.80; H, 6.50; N, 6.94.

Attempted reaction with ethereal diazomethane in ethylene dichloride led to a 95% recovery of *N,N*-dimethyl- α -methoxyethylideneiminium fluoborate. The spectral characteristics of the residual oil indicated that the C=N⁺ functionality was still present.

N,N,N',N'-Tetramethylacetamidinium Chloride.

This compound was prepared in 35% yield using the procedure of Arnold (26), m.p. 120° (reported 121°); nmr (10% in deuteriochloroform): δ 3.35 (12H, s, CH₃), 7.56 (1H, s, CH=N⁺). Attempted reaction of *N,N,N',N'*-tetramethylacetamidinium chloride with diazomethane in methylene chloride led to a colorless oil that had the same infrared spectral characteristics as the starting material. The lack of reaction was confirmed by comparison of the nmr spectra of the final oil and of the original in deuteriochloroform.

O-Ethyl-*N*-nitrosodimethylamine Fluoborate.

This compound was made in 74% yield according to the procedure of Hüinig *et al.* (27) m.p. 38-40° (reported 40-41.5°); nmr

(10% deuteriochloroform): δ 1.62 (3H, t, CCH₃), 4.20 and 3.90 (6H, s, s, ⁺N(CH₃)₂), 5.20 (2H, q, CH₂). Attempts to cause this compound to react with diazomethane in methylene chloride led to oils that had the same spectral characteristics as the starting material, *O*-ethyl-*N*-nitrosodimethylamine fluoborate.

N-Methylanilinium Fluoborate.

To 107 g. (1.0 mole) of freshly distilled *N*-methylaniline was added 160 ml. of 50% fluoboric acid solution with external ice-bath cooling. Additional *N*-methylaniline was added until the solution was basic to Congo red paper. After concentration under reduced pressure and dissolution in methylene chloride, 2-propanol (3:1), bluish-white plates were precipitated with ether, heptane (1:1), yield 70%, m.p. 68-69°. The solid was recrystallized from 1,2-dichloroethane, carbon tetrachloride as silvery plates, m.p. 73-74°; nmr (20% in TFA): δ 3.32 (3H, t, CH₃), 7.61 (5H, s, C₆H₅).

Anal. Calcd. for C₇H₁₀BF₄N: C, 43.12; H, 5.17. Found: C, 43.41; H, 5.31.

N-Methyl-*N*-Phenylisopropylideneiminium Fluoborate.

To a solution of 9.7 g. (0.05 mole) of *N*-methylanilinium fluoborate and 5.8 g. (0.1 mole) of acetone was added two drops of diisopropylethylamine. The solution was heated at reflux for 10 minutes and cooled to give colorless needles which were recrystallized from acetone-ether, m.p. 144-146°, yield 78%; nmr (10% in deuteriochloroform): δ 2.37 (3H, s, CCH₃), 2.82 (3H, s, CCH₃), 3.92 (3H, s, ⁺NCH₃), 7.60 (5H, s, C₆H₅).

Anal. Calcd. for C₁₀H₁₄BF₄N: C, 51.11; H, 6.01; N, 5.96. Found: C, 51.20; H, 5.97; N, 6.20.

N-Methylanilinium Perchlorate.

This amine perchlorate was made in the same manner as the fluoborate salt to give colorless prisms from ethylene dichloride, ether, m.p. 79°.

Anal. Calcd. for C₇H₁₀ClNO₄: C, 40.49; H, 4.86; N, 6.75. Found: C, 40.19; H, 4.66; N, 6.64.

N-Methyl-*N*-Phenylisopropylideneiminium Perchlorate.

This compound was prepared in a similar manner, colorless needles from acetone, ether in 71% yield, m.p. 134-134.5°.

Anal. Calcd. for C₁₀H₁₄ClNO₄: C, 48.48; H, 5.70; N, 5.65. Found: C, 48.40; H, 5.61; N, 5.84.

The reaction of either the iminium perchlorate or fluoborate with diazomethane at 0° led to a very complex mixture of products.

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