The Reaction of Some Amine Salts of Heterocyclic Compounds with Acetone

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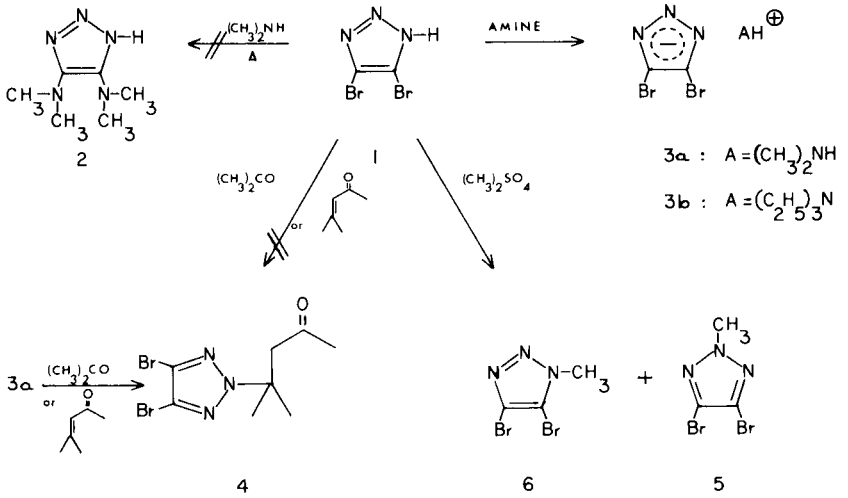
In our continuing search for new insect chemosterilants (1) we desired to synthesize a series of bis(dimethylamino) heterocyclic compounds including the 1,2,3-triazole **2**. One approach to **2** was an attempted displacement of bromide from the known (2) 4,5-dibromo-1,2,3-triazole (**1**) by dimethylamine. We were unable to effect this displacement; the single hydrogen of **1** proved to be rather acidic and **1** instantly formed the salt **3a** when treated with dimethylamine. No further reaction occurred even when **1** and excess dimethylamine were heated together in a sealed tube at 260° for 140 hours (3).

The dimethylamine salt **3a** was most conveniently prepared by adding a slight excess of anhydrous dimethylamine to a solution of **1** in methanol and evaporating to dryness. It was soluble in water and many organic solvents (more soluble in many cases than **1**) and could be recrystallized from benzene-hexane, m.p. 95-96°.

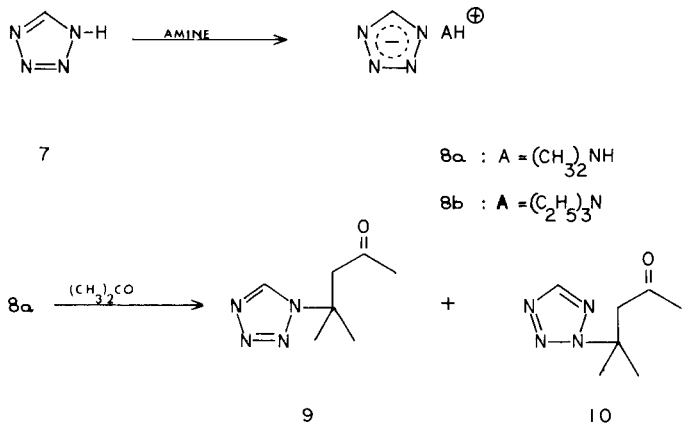
When an acetone solution of **3a** that had been allowed to stand at room temperature four days was evaporated, only a trace of **3a** could be detected; the major product was a clear oil that could be purified by distillation (0.2 mm., bath temperature 70°) or by preparative gas chromatography. The infrared spectrum contained a carbonyl band at 1720 cm^{-1} and the NMR spectrum consisted of three singlets at δ = 1.73 (6H), 2.10 (3H), and 3.16 (2H). The sample analyzed correctly for $C_8H_{11}Br_2N_3O$, and its mass spectrum confirmed a molecular weight of 325; this corresponds to the combination of **1** and two molecules of acetone with the loss of water. A peak in the mass spectrum at m/e = 98 (mesityl oxide (4-methyl-3-penten-2-one)) further supported this conclusion, and indeed, the same product, **4**, was obtained by reacting **3a** with mesityl oxide in tetrahydrofuran. In contrast, **1** reacted with neither acetone nor mesityl oxide under comparable conditions.

The spectral data and the formation of a semicarbazone (Experimental) clearly indicate that **4** is a 1-4 adduct of 4,5-dibromo-1,2,3-triazole and meistyl oxide. Only one of the two possible isomeric adducts was isolated, and we have tentatively assigned to **4** the structure of 4-(4,5-dibromo-2*H*-1,2,3-triazol-2-yl)-4-methyl-2-pentanone, rather than that of the 1*H*-isomer, from the following considerations. We synthesized the known (4) 4,5-dibromo-2-methyl-2*H*-1,2,3-triazole (**5**) and the previously unreported 4,5-dibromo-1-methyl-1*H*-1,2,3-triazole (**6**), and compared their ultraviolet and infrared spectra to those of **4**. Both **4** and **5** had λ max 238 mμ (ϵ 11,530 and 8,840, respectively) whereas **6** had λ max 232 mμ

Scheme I



Scheme II



(ε, 4,820). We have no basis for making specific assignments in the infrared spectra of the dibromotriazoles, but some noteworthy similarities are found in the spectra of **4** and **5** while the spectra of **4** and **6**, or even of **5** and **6**, contain almost no bands in common. The infrared absorptions of the three compounds are listed in Table I in the Experimental. Gold (5) and Wiley, *et al.* (6) have observed 1,4-additions of 1,2,3-triazole, but their studies are of little help with respect to our structural assignment. 1,2,3-Triazole reacts with acrylonitrile at the 2-position, but with nitroethylene at the 1-position (5). Wiley and coworkers assigned the triazole adducts with some unsaturated ketones as the 1-isomers, but their only reason was by analogy to the reactions of benzotriazole (6). Finally, the stability of **4** to distillation and gas chromatography is consistent with the generalization that 2-substituted 1,2,3-triazoles are significantly lower boiling than the corresponding 1-isomers (5).

We similarly converted tetrazole (**7**) to its dimethylamine salt (**8a**). Salt **8a**swas nearly insoluble in acetone at room temperature but dissolved at reflux temperature. A sample of **8a** was refluxed in acetone 40 hours; evaporation of the acetone provided an oil that consisted of a little mesityl oxide plus two ketones identified by their infrared and NMR spectra (and subsequently by elemental analysis of their semicarbazones) as the isomeric adducts **9** and **10** (6). These compounds were less thermally stable than **4** and gas chromatography resulted in decomposition; however, they were readily separated by column chromatography on silica gel, and by this technique pure 4-methyl-4-(1*H*-tetrazol-1-yl)-2-pentanone (**9**) and 4-methyl-4-(2*H*-tetrazol-2-yl)-2-pentanone (**10**) were isolated in yields of 35% and 44%, respectively. Their NMR spectra (**9**: δ = 1.83 (S, 6), 2.10 (S, 3), 3.24 (S, 2), and 8.84 (S, 1); **10**: δ = 1.85 (S, 6), 2.12 (S, 3), 3.32 (S, 2), and 8.55 (S, 1)) confirmed their analogy to **4** and also provided the basis for assigning the site of substitution on the tetrazole ring since the hydrogen on a tetrazole ring appears at lower field in 1-substituted tetrazoles than in 2-substituted tetrazoles (7). This assignment is also supported by the order of elution during chromatography (**10** before **9**; 1-substituted tetrazoles reportedly have

TABLE I

Infrared Absorptions (a) of **4**, **5**, and **6**,

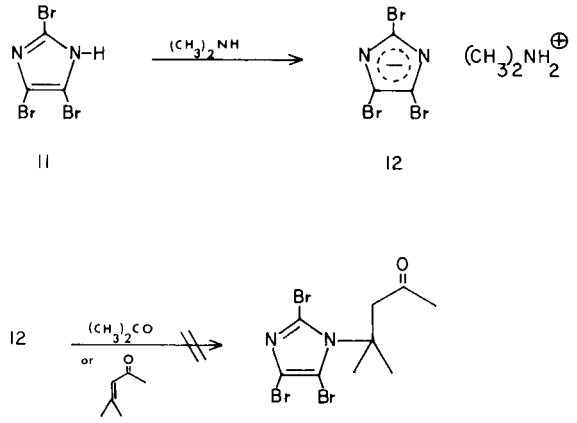
Compound	Absorptions, cm^{-1}
4	2985 (m), 2940 (w), 1720 (s), *1388 (s)*, 1355 (m) 1335 (w), 1318 (w), *1300 (w)*, 1130 (m), *1041* (s), 979 (s)
5	*2950 (w)*, 1413 (w), *1387 (s)*, *1300 (w)*, *1039 (s)*, *988 (w)*,
6	*2950 (w)*, 1478 (m), 1438 (w), 1072 (s) 1202 (m), 1098 (m), 1020 (m), *989 (m)*

(a) Recorded as 1% solutions in carbon tetrachloride. Italicized figures designate absorptions common to two spectra.

larger dipole moments than their 2-substituted isomers (8)).

As one further test of the generality of the reaction we converted another acidic heterocyclic compound, 2,4,5-tribromoimidazole **11** (9), to its dimethylamine salt (**12**). In contrast to the previous examples, when **12** was heated in refluxing acetone for three days, or allowed to stand in acetone for seven days, no ketone corresponding to **4** could be found. A white solid was recovered in high

Scheme III



yield that was identified by its infrared spectrum as the starting salt **12** along with a little of the free imidazole **11**. A small amount of mesityl oxide could be detected by gas chromatography, however, and we subsequently found that **12** was recovered unchanged after treatment with mesityl oxide at room temperature for 72 hours.

Triethylamine salts of **1** and **7** were similarly prepared (**3b** and **8b**, respectively) and were heated in refluxing acetone 56 hours and 69 hours, respectively. In each case unchanged triethylamine salt was recovered in high yield, and only traces (< 5%) of ketonic products could be detected by infrared spectroscopy. The triethylamine salt **3b** did react smoothly with mesityl oxide in refluxing tetrahydrofuran, however, to yield **4**.

The formation of ketones **4**, **9**, and **10** can be explained by the self-condensation of acetone to mesityl oxide and subsequent 1,4-addition of dibromotriazole and tetrazole, respectively, present as relatively nucleophilic anions, to the mesityl oxide. The absence of an adduct from **12** and mesityl oxide has at least three possible explanations: low nucleophilicity of the rather stable tribromoimidazole anion (10), excessive steric requirements of the bromine atoms on either side of the nitrogens, or a reversible addition with the equilibrium lying completely on the side of the reactants.

Aldol condensations catalyzed by secondary amines are known, and in some cases an equivalent of a weak acid such as acetic acid facilitates the reaction (11). Tertiary amines are much less effective aldol catalysts; this is consistent with the low reactivity of our triethylamine salts. Dimethylamine itself does catalyze the condensation of acetone to mesityl oxide (see Experimental); both this reaction and the reaction of **3a** and **8a** with acetone are relatively slow, and it is doubtful whether the amine-heterocyclic salts are more effective catalysts than the amine itself. The unique features of **3a** and **8a** seem to be that they contain a catalyst for both the aldol condensation and subsequent dehydration, and a nucleophile capable of forming a stable adduct with the aldol product.

EXPERIMENTAL (12)

Melting points were obtained on a Büchi apparatus and are uncorrected. Nuclear magnetic resonance spectra (deuteriochloroform) were recorded on a Varian Model T-60 spectrophotometer, and ultraviolet spectra on a Beckman DK-2 recording spectrophotometer. Infrared spectra were routinely obtained on a Perkin Elmer Model 137 sodium chloride prism spectrophotometer; the spectra in Table I were recorded on a Perkin Elmer Model 521 Grating Infrared Spectrophotometer.

Gas Chromatographic conditions were: (**A**) a MicroTek Model 220 gas chromatograph with a flame ionization detector and an 8 ft. x ¼ in. glass column packed with 6% DEGS on 80/100 Chromosorb W; (**B**) a Barber-Colemen Model 5320 gas chromatograph with a flame ionization detector and a 10 ft. x 1/8 in. stainless steel column packed with 10% silicone rubber on 60/80 Diatoport S.

Magnesium sulfate was employed as a drying agent. Tetrazole was purchased from Raylo Chemicals, Ltd., Edmonton, Alberta. Acetone was refluxed several hours over potassium permanganate, dried over potassium carbonate, and distilled. It was examined by gas chromatography (**A**, 75°) for mesityl oxide. None could be detected (in standard samples we were able to detect one part of mesityl oxide in 10^5 parts of acetone). Mesityl oxide was distilled and a center fraction, b.p. 128°, was retained.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Amine Salts of Acidic Heterocyclic Compounds.

An equivalent or slight excess of anhydrous dimethylamine or triethylamine was added to a solution of the heterocyclic compound in methanol at room temperature. The solution was evaporated to dryness and the residue was recrystallized. The dimethylamine salts were generally higher melting and more stable than the corresponding triethylamine salts; the latter tended to lose triethylamine if heated *in vacuo*.

4,5-Dibromo-1,2,3-triazole Dimethylamine Salt (**3a**).

This compound was obtained in 78% yield after recrystallization from hexane-benzene, m.p. 95-96°.

Anal. Calcd. for $C_4H_8Br_2N_4$: C, 17.67; H, 2.96; N, 20.60. Found: C, 17.42; H, 2.75; N, 20.47.

4,5-Dibromo-1,2,3-triazole Triethylamine Salt (**3b**).

This compound was obtained in 86% yield after recrystal-

lization from ether, m.p. 62-65° dec.

Anal. Calcd. for $C_8H_{16}Br_2N_4$: C, 29.29; H, 4.92; N, 17.08. Found: C, 29.21; H, 4.94; N, 16.96.

Tetrazole Dimethylamine Salt (**8a**).

This compound was obtained in 74% yield after recrystallization from tetrahydrofuran-ethanol, m.p. 89-90.5°. It was rather hygroscopic, and further recrystallizations tended to lower the melting point.

Anal. Calcd. for $C_3H_9N_5$: C, 31.29; H, 7.88; N, 60.83. Found: C, 31.22; H, 7.99; N, 60.77.

Tetrazole Triethylamine Salt (**8b**).

This compound was an oil (obtained in essentially quantitative yield upon evaporation of solvent) that crystallized in large prisms upon cooling and melted very near room temperature. It was used without further purification, and no elemental analyses were attempted.

2,4,5-Tribromoimidazole Dimethylamine Salt (**12**).

This compound was obtained in 64% yield after recrystallization from tetrahydrofuran-ethanol, m.p. 157-159° dec.

Anal. Calcd. for $C_5H_8Br_3N_3$: C, 17.17; H, 2.30; N, 12.01. Found: C, 17.13; H, 2.02; N, 11.89.

Reaction of 4,5-Dibromotriazole Dimethylamine Salt (**3a**) with Acetone.

A solution of **3a** (0.500 g., 1.84 mmoles) in acetone (2 ml.) was allowed to stand at room temperature 96 hours. Evaporation of the solvent at reduced pressure left an oil that was purified by chromatography on neutral alumina. Elution with benzene provided 4-(4,5-dibromo-2*H*-1,2,3-triazol-2-yl)-4-methyl-2-pentanone (**4**) as a colorless oil (0.434 g., 73%). An analytical sample was prepared by distillation through a micromolecular still (0.2 mm., bath temperature 70°). The pure sample had: n_D^{25} 1.5277; ν (neat) 1720 cm^{-1}; δ 1.73 (S, 6), 2.10 (S, 3), 3.16 (S, 2); λ max (95% ethanol) 238 mμ (ϵ 11,530).

Anal. Calcd. for $C_8H_{11}Br_2N_3O$: C, 29.56; H, 3.41; N, 12.93. Found: C, 29.51; H, 3.25; N, 13.29.

The semicarbazone of **4** had m.p. 190-191° dec.

Anal. Calcd. for $C_9H_{14}Br_2N_6O$: C, 28.29; H, 3.69; N, 22.00. Found: C, 28.41; H, 3.60; N, 22.24.

Reaction of **3a** with Mesityl Oxide.

A solution of **3a** (0.554 g., 2.0 mmoles) and mesityl oxide (0.196 g., 2.0 mmoles) in tetrahydrofuran (10 ml.) was refluxed 24 hours. Evaporation of thessolvent and chromatography on alumina yielded **4** (0.576 g., 89%), identical in all respects to the sample desdribed previously.

Attempted Reaction of 4,5-Dibromo-1,2,3-triazole (**1**) with Acetone.

A solution of **1** (0.227 g.) in acetone (5 ml.) was heated at reflux 24 hours. Removal of the solvent left 0.225 g. (99%) of unchanged **1**, m.p. 190° dec., whose infrared spectrum was identical to that of the pure starting material.

Attempted Reaction of **1** with Mesityl Oxide.

A solution of **1** (0.227 g., 1.0 mmole) and mesityl oxide (0.098 g., 1.0 mmole) in tetrahydrofuran (5 ml.) was refluxed 41 hours. The solvent was stripped *in vacuo* and unchanged **1** was recovered as a white solid (0.220 g., 97%, m.p. 190° dec.).

Preparation of 4,5-Dibromo-1-methyl-1*H*-1,2,3-triazole (**6**) and 4,5-Dibromo-2-methyl-2*H*-1,2,3-triazole (**5**).

Dimethyl sulfate (1.0 g., 7.9 mmoles) was added dropwise to a vigorously stirred solution of 4,5-dibromo-1,2,3-triazole (**1**, 1.0 g., 4.4 mmoles) in 1 *N* sodium hydroxide (10 ml.). The mixture was stirred at room temperature 0.5 hour, then chilled, and the white solid (0.82 g., 78%) was collected by filtration. Separation of the isomers was accomplished by chromatography on silica gel.

Elution with 1:1 petroleum ether (30-60°)-benzene yielded 0.31 g. (29%) of **5**; recrystallization from pentane afforded the pure compound, m.p. 66.5-67.5° (lit (4) m.p. 66.5-67.5°); δ 4.20; λ max (95% ethanol) 238 mμ (ϵ, 8,840).

Elution with benzene gave 0.31 g. (29%) of **6**; it was recrystallized from toluene-pentane to give 0.28 g., m.p. 116.5-117.5°; δ 4.10; λ max (95% ethanol) 232 mμ (ϵ, 4,820).

Anal. Calcd. for $C_3H_3Br_2N_3$: C, 14.96; H, 1.26; N, 17.44. Found: C, 15.09; H, 1.14; N, 17.61.

Reaction of Tetrazole Dimethylamine Salt (**8a**) with Acetone.

A solution of **8a** (0.50 g., 4.5 mmoles) in acetone (18 ml.) was heated at reflux 40 hours and then the solvent was evaporated at reduced pressure. A clear oil (1.16 g.) was obtained that smelled of mesityl oxide; the sample was stored in a desiccator evacuated to 0.2 mm. for 1 hour to remove mesityl oxide and any other volatile products; then it was chromatographed on silica gel. Elution with benzene provided 4-methyl-4-(2*H*-tetrazol-2-yl)-2-pentanone (**10**) as a clear oil (0.33 g., 44%); 4-methyl-4-(1*H*-tetrazol-1-yl)-2-pentanone (**9**, 0.25 g., 35%) was eluted as ether was gradually added to the benzene.

Physical constants for **9** and **10** are: **9**: n_D^{20} 1.4746; ν (neat) 1720, 1370, 1097, 683 cm^{-1}; δ 1.83 (S, 6), 2.10 (S, 3), 3.24 (S, 2), 8.84 (S, 1). The semicarbazone of **9** had m.p. 185°.

Anal. (**9**-semicarbazone) Calcd. for $C_8H_{15}N_7O$: C, 42.65; H. 6.71; N, 43.53. Found: C, 42.74; H, 6.74; N, 43.64.

10: n^{20} 1.4610; ν (neat) 1720, 1370, 1023, 700 cm^{-1}; δ 1.85 (S, 6), 2.12 (S, 3), 3.32 (S, 2), 8.55 (S, 1). The semicarbazone of **10** had m.p. 161-162°.

Anal. (**10**-semicarbazone) Calcd. for $C_8H_{16}N_7O$: C, 42.65; H, 6.71; N, 43.53. Found: C, 42.70; H, 6.67; N, 43.36.

Reaction of 2,4,5-Tribromoimidazole Dimethylamine Salt (**12**) with Acetone.

At Room Temperature.

A mixture of **12** (0.659 g.) and acetone (15 ml.) was allowed to stand at room temperature. This salt was relatively insoluble in acetone and never completely dissolved. After 7 days undissolved **12** was removed by filtration (0.343 g., m.p. 161-164° dec.), the filtrate was concentrated to *ca.* 1 ml., and ether was added to precipitate a second crop of unreacted **12** (0.228 g., m.p. 161° dec.). The filtrate was carefully concentrated (20°, 150 mm.) to a yellow oil (*ca.* 0.1 g.). Gas chromatographic analysis (**B**, 100°) indicated the presence of traces of ether (0.5 minutes), acetone (0.75 minutes), and mesitul oxide (1.5 minutes) plus two unidentified minor components (1.1 and 1.75 minutes). Mesityl oxide constituted only about 5% of the total mixture.

At Reflux Temperature.

A mixture of **12** (0.591 g.) and acetone (15 ml.) was heated at reflux 17 hours (about 1 hour was required for complete dissolution of **12**); then the solvent was stripped and unchanged **12** was recovered as a white solid (0.557 g., m.p. 148-153° dec.) whose infrared spectrum was identical to that of the pure starting material. Another portion of acetone (20 ml.) was added and the solution was refluxed another 49 hours; this time a slightly

oily yellow solid (0.538 g.) was recovered whose infrared spectrum indicated unchanged **12** plus a considerable amount of tribromoimidazole, **11** (1393, 980 cm^{-1}).

Attempted Reaction of **12** with Mesityl Oxide.

A solution of **12** (0.492 g., 1.4 mmoles) and mesityl oxide (0.148 g., 1.5 mmoles) in ethanol (10 ml.) and methanol (5 ml.) was allowed to stand at room temperature 66 hours. The solvent was stripped and the residue was dried at 0.1 mm. (room temperature) to remove traces of mesityl oxide. A yellowish solid (0.491 g., m.p. 159° dec.) was recovered whose infrared spectrum was identical to that of pure **12**.

Reaction of 4,5-Dibromo-1,2,3-triazole Triethylamine Salt (**3b**) with Acetone.

A solution of **3b** (0.656 g.) in acetone (5 ml.) was refluxed 56 hours and then the solvent was stripped and ether was added to the oily residue. Most of the material was insoluble, and the ether was decanted leaving 0.603 g. (92% recovery) of a material whose infrared spectrum was identical to that of starting **3b**. The ether solution was examined by gas chromatography (**B**, 181°); a trace of the dibromotriazole-mesityl oxide adduct **4** was detected (6.1 minutes).

Reaction of **3b** with Mesityl Oxide.

A solution of **3b** (0.328 g., 1.0 mmole) and mesityl oxide (0.098 g., 1.0 mmole) in tetrahydrofuran (10 ml.) was refluxed 24 hours. Evaporation of the solvent left an oily residue (0.286 g.) that was chromatographed on neutral alumina to provide 0.247 g. (76%) of 4-(4,5-dibromo-2*H*-1,2,3-triazol-2-yl)-4-methyl-2-pentanone (**4**).

Reaction of Tetrazole Triethylamine Salt (**8b**) with Acetone.

Impure **8b** (0.488 g.) was refluxed in acetone (15 ml.) 69 hours; then the clear solution was dried, filtered, and evaporated. A clear oil (0.472 g.) was obtained whose infrared spectrum was essentially identical to that of the starting salt. However, a very weak band at 1720 cm^{-1} suggested a trace of ketonic product(s).

Reaction of Dimethylamine with Acetone.

A solution of anhydrous dimethylamine (0.3 ml.) in acetone (10 ml.) was allowed to stand at room temperature 72 hours. The slightly yellow solution was carefully concentrated to *ca.* 1 ml., taken up in ether and dried, and again concentrated (20°, 100 mm.) to near dryness. The residue was a yellow oil (0.090 g.) whose composition was judged by infrared spectroscopy and gas chromatography (**B**, 90°) to be >80% mesityl oxide (1.8 minutes) along with traces of ether and acetone (0.5 minutes and 0.7 minutes, respectively, *ca.* 10% total) and an unidentified component (2.3 minutes, *ca.* 5%).

Attempted Displacement of Bromide from **1** with Dimethylamine.

A solution of 4,5-dibromo-1,2,3-triazole (0.227 g., 1.0 mmole, m.p. 192° dec.) in 40% aqueous dimethylamine (1 ml.) was heated at 260° in a sealed tube for 140 hours. The solvent was evaporated at reduced pressure to yield a semisolid residue that was chromatographed on silica gel. Elution with chloroform yielded a white solid (0.186 g., 82%, m.p. 191° dec.) whose infrared spectrum was identical to that of **1** (the salt **3a** loses dimethylamine upon chromatography).

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