higher hydroxide ion concentrations, a brown precipitate of $Tl(OH)_3$ was formed.

The reaction described by eq 1 was found to be reversible in 50% aqueous acetic acid containing 1.0 *M* sodium acetate. The Tl(III)–isobutylene adduct decomposed at approximately equal rates to Tl(III) and Tl(I) ($t_{1/2} \sim 18$ min).

Since the Tl(III)–propylene adduct could not be isolated, it was prepared *in situ* at a concentration of about 1 *M* in a solvent consisting of 10% water, 10% acetic acid, and 80% THF. This solution (1 ml) was dissolved in 100 ml of 0.1 *M* aqueous $LiClO_4$ solution (pH 7.18). Under these conditions the decomposition of the propylene adduct was several times slower than for I, $t_{1/2}$ was 93 min.

The results of our kinetic experiments show that with increasing H^+ concentration, Tl(I) becomes a better leaving group, presumably because of increased positive charge on the Tl(III) due to protonation or exchange of anions in the labile first coordination sphere. A similar dependence on acid concentration was obtained by Jensen and Ouellette[9] for solvolysis reactions of alkylmercuric ions. This mode of adduct decomposition must even outweigh intramolecular displacement of Tl(III) by the adduct alkoxide ion as observed in the conversion of chlorohydrin to epoxides. Such a pathway might have been expected because of the increased acidity of the adduct hydroxyl group.

The slower rate of decomposition and the formation of acetone from the propylene adduct show the sensitivity of this reaction to methyl substitution on the β carbon, similar to the chlorohydrin case.[10] The acetone could arise from the β hydrogen participating as a neighboring group. However, under strongly acidic conditions where substantial formation of glycolic products does occur, this reaction may proceed exclusively through an epoxide intermediate. This possibility could only be tested by $H_2{}^{18}O$ tracer experiments, similar to the ones Long and Pritchard[11] performed in their study on the hydrolysis of substituted ethylene oxides.

Experimental Section

The nmr data were obtained with a Varian Associates HR-60 spectrometer, ir spectra with a Perkin-Elmer 237B grating spectrophotometer, and polarographic data with a modular Heath polarograph. The olefins were Phillips CP grade reagents. Thallium triacetate was prepared according to the literature.[12]

Epoxidation of Isobutylene and Propylene.—A 0.65 *M* slurry of thallic acetate (6 ml) in a solvent consisting of 70% (v/v) tetrahydrofuran, 20% water, and 10% acetic acid were placed in a capped pressure tube.[13] The slurry was stirred and isobutylene was introduced under a pressure of about 1.8 atm at room temperature. After the solids dissolved, the reactor tube was placed in a water bath at 70° and connected by means of 2-mm diameter stainless steel tubing to cooled traps made of capped pressure tubes. The reaction mixture was then sparged with isobutylene at a rate of about 40 ml/min. Most of the solvent, isobutylene oxide, and isobutyraldehyde were collected in the first trap held at 0°, and unreacted isobutylene in the second one held at −78°. Within 30 min, 90% of the thallic acetate was reduced to thallous acetate as determined by iodometric titration. The distillates and reaction mixture were quantitatively analyzed by glc (F & M Model 700, 12-ft column, Carbowax 20M). The oxidation products consisted of isobutylene oxide (82%), 1-acetoxy-2-methyl-2-propanol (15%) (left in reactor), and isobutyraldehyde (3%).

In a similar experiment, the reaction mixture was kept under 2 atm of propylene for 30 min at room temperature and then sparged 15 min at 70°; 60% of the thallium triacetate was reduced. The oxidation product consisted of 72% propylene oxide and 16% acetone; the remainder was 1-acetoxy-2-propanol.

Preparation of Hydroxythallation Adduct.—In the case of isobutylene, I was isolated at 0° in 40% yield from a solvent mixture of 80% THF, 10% acetic acid, and 10% water and excess isobutylene as a white crystalline product which could be recrystallized from methanol. The experimental details are the same as in the previous paragraph. I melted and decomposed slowly at 70° to isobutylene and isobutylene oxide in about equal amounts. The elemental analysis indicated one water of crystallization. *Anal.* Calcd for $C_8H_{17}O_6Tl$: C, 23.22; H, 4.11; Tl, 49.44. Found: C, 23.16; H, 3.72; Tl, 49.87.

The infrared spectrum of a mineral oil mull of I showed a broad OH band at 3250 cm^{-1} which is an indication of internal hydrogen bonding. In dry, deuterated dimethyl sulfoxide the peak shifted to 3450 cm^{-1}, indicating the displacement of complexed water by dimethyl sulfoxide. The characteristic absorption bands assignable to ν_{sym} (COO) in the solid state were observed at 1608 (vs) and 1555 cm^{-1} (vs); the ν_{sym} (COO) bands were found at 1375 (vs) and 1337 cm^{-1} (vs) indicating that the acetate was coordinated in two different ways, one probably a bridged structure.[14] The bands at 500 (m) and 455 cm^{-1} (m) were probably due to the ρ_r (COO) modes. Although the origin of the poorly resolved band at 505 cm^{-1} (w) is uncertain, it may be associated with the Tl-C stretching vibrations. The remaining bands at 412 (m) and 350 cm^{-1} (w) have not been assigned. The spectra were obtained in either Nujol (700–4000 cm^{-1}) or in hexachlorobutadienes (250–700 cm^{-1}) mulls.

In the proton nmr spectrum of I in deuterated dimethyl sulfoxide, a doublet with the expected large spin–spin coupling constant for the geminal protons appeared.[15] Each of the peaks in this doublet had in itself a doublet character. This character is due to the slightly different coupling of the ^{203}Tl and ^{205}Tl isotopes to the methylene protons ($J_{^{203}Tl-CH_2}$ = 864 Hz, $J_{^{205}Tl-CH_2}$ = 871.5 Hz). The isotopic difference in the long range Tl–CH_3 coupling is not resolved although the peaks show broadening (J_{Tl-CH_3} = 101 Hz). The chemical shifts of the protons are δ 2.70 and 1.38 ppm, respectively.

Registry No.—I, 27621-79-0; thallium triacetate, 2570-63-0; isobutylene, 115-11-7; propylene, 115-07-1.

Acknowledgment.—The authors thank Dr. P. M. Henry and Dr. H. G. Tennent for helpful discussions, Dr. G. H. Lee for the nmr data, and Mr. D. S. Rice for technical assistance.

(9) F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **83**, 4478 (1961).
(10) A. A. Frost and R. G. Pearson, "Kinetic and Mechanism," Wiley, New York, N. Y., 1961, p 350.
(11) F. L. Long and J. G. Pritchard, *J. Amer. Chem. Soc.*, **78**, 2663 (1956).
(12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1150.
(13) D. F. Shriver, "The Manipulation of Air-sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 157.
(14) N. Kurosawa and R. Okawasa, *J. Organometal. Chem.*, **19**, 253 (1969).
(15) F. A. L. Anet, *Tetrahedron Lett.*, 3399 (1964); J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 637 (1965).

Amidrazones. I. The Methylation of Some Amidrazones and Hydrazide Imides

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The inner salt 1 has been jointly proposed by Professor M. S. Gibson and us[2] as an intermediate to ac-

(1) American Chemical Society Petroleum Research Fund Scholar.
(2) M. S. Gibson, R. F. Smith, P. D. Callaghan, A. C. Bates, J. R. Davidson, and A. J. Battisti, *J. Chem. Soc. C*, 2577 (1967).

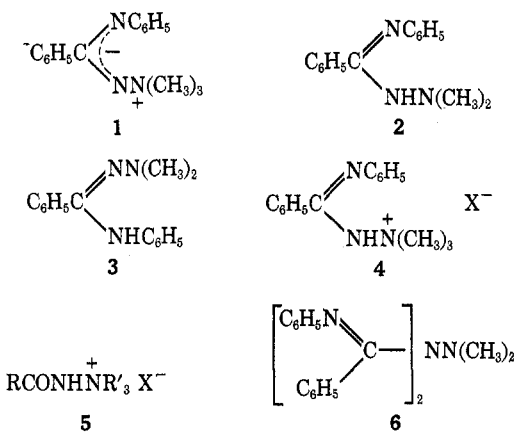
count for the formation of three minor products (2-phenylbenzimidazole,[3] benzanilide, and 1,3-diphenylurea) which are formed during the thermolysis of 1,1,1-trimethyl-2-benzoylhydrazinium hydroxide inner salt.

This note reports some novel aspects of amidrazone chemistry[4] which were encountered during unsuccessful attempts to synthesize **1**.

Our initial approach to **1** was based on the assumption that the hydrazide imide **2** (tautomeric with the amidrazone **3**) would undergo selective methylation on the dimethylamino group to give **4**. Neutralization of **4** with base should give **1** because of its resemblance to quaternary hydrazides **5** which give amine imides on neutralization.[5]

The hydrazide imide **2** was synthesized in excellent yield by reaction of *N*-phenylbenzimidoyl chloride with excess 1,1-dimethylhydrazine. Attempts to prepare **2** by reaction of the imidoyl chloride with 2 mol of 1,1-dimethylhydrazine in benzene resulted in a mixture of **2** and the diimidoylated product **6**[6] (Chart I).

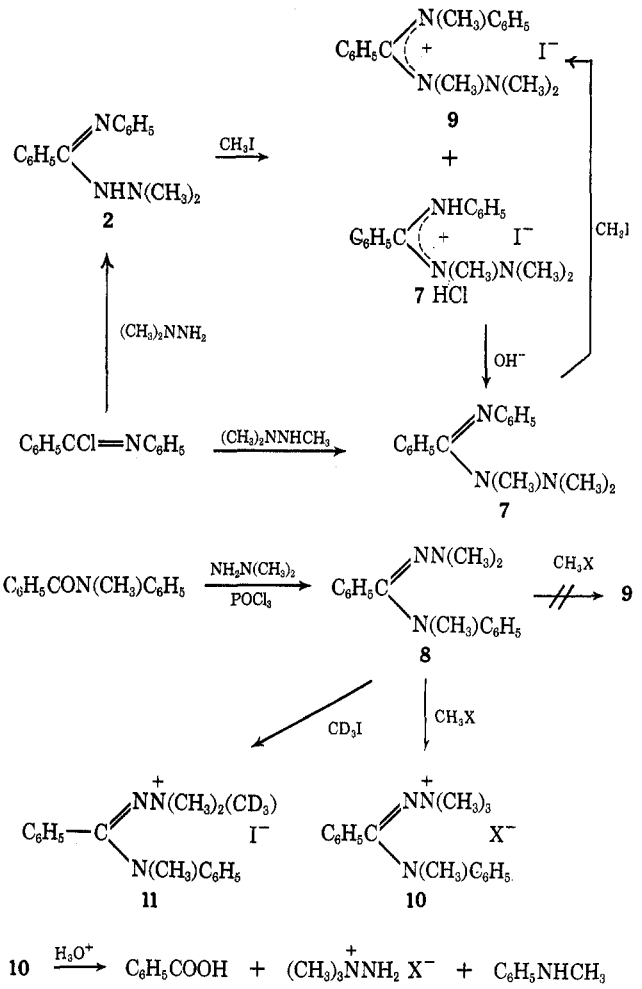
CHART I



The nmr spectrum of **2** did not indicate the presence of a tautomeric mixture. The assignment of the hydrazide imide structure is based on a comparison of the ultraviolet spectrum of **2** with N-methylated model compounds which were available from the synthetic work described below. The ultraviolet spectrum of **2** is virtually identical with that of the model hydrazide imide [1,1,2-trimethyl-2-(*N*-phenylbenzimidoyl)hydrazine (**7**)] and differs markedly from that of the model amidrazone [*N*-methylbenzanilide dimethylhydrazone (**8**)]. Compounds **2** and **7** exhibited broad absorption bands with shoulders at 253 mμ (log ε 4.26 and 4.28 for **2** and **7**, respectively) and 282 mμ (log ε 3.84 and 3.78 for **2** and **7**, respectively), while the amidrazone **8** exhibited maxima at 244 mμ (log ε 3.83) and 296 (3.53).

Reaction of **2** with methyl iodide gave a mixture of salts which was separated into two components by fractional crystallization. The major and minor components analyzed for the introduction of one- and two-methyl groups, respectively. However, the nmr spectrum of the major product was incompatible with structure **4**. The spectra of the salt (a hydriodide) and its free base exhibited two upfield methyl singlets that integrated 6 H:3 H thus indicating structure **7** or **8** for the free base. Treatment of the free base with hydriodic acid gave the same salt that was obtained from the methylation reaction. Both of these isomers were synthesized by unambiguous routes (see Scheme I), and **7**

SCHEME I



was shown to be identical with the product obtained by methylation of **2**.

The nmr spectrum of the minor product from the methylation reaction was compatible with its assignment of the amidinium-type[7] structure **9**. Reaction of **7** with methyl iodide gave **9** in excellent yield. The latter reaction was observed to be appreciably slower than reaction of **2** with methyl iodide.

In contrast to the behavior of the hydrazide imides, the amidrazone **8**, when treated with methyl iodide or methyl tosylate, undergoes methylation on the dimethylamino group to give the amidrazonium salt **10**. Salts of structure **10** were of interest since on thermolysis they could conceivably give a benzimidazole in a manner analogous to that postulated for **1**. The structure of **10** was established by hydrolytic degradation of the tosylate salt to give benzoic acid, *N*-methylaniline

(3) For similar conversions of 2-arylamidoximes to 2-substituted benzimidazoles, see J. H. Boyer and P. J. A. Frints, *J. Org. Chem.*, **35**, 2449 (1970), and references cited therein.

(4) For a discussion of amidrazone chemistry, see D. G. Neilson, R. Roger, J. W. M. Heattie, and L. R. Newlands, *Chem. Rev.*, **70**, 151 (1970).

(5) R. L. Hinman, *J. Org. Chem.*, **24**, 660 (1959).

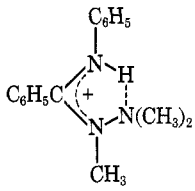
(6) Reaction of 1,1-dimethylhydrazine with benzoyl chloride in benzene solution has been observed to give mixtures of mono- and dibenzoylated products: R. L. Hinman, *J. Amer. Chem. Soc.*, **78**, 1645 (1956).

(7) For a discussion of amidinium salts, see P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, p 181.

(as its benzenesulfonyl derivative), and 1,1,1-trimethylhydrazinium tosylate. Nmr could not be used to establish the structure because of the magnetic equivalence of the chemically nonequivalent methyl groups. The possibility that the magnetic equivalence of the methyl groups may be due to unprecedented methyl exchange between nitrogen atoms was ruled out by labeling experiments. Reaction of **8** with CD_3I gave **11**, which on acid hydrolysis gave deuterium-free *N*-methylaniline (as its benzenesulfonyl derivative).

Thermolysis of the fluoroborate salt of **10** at 220° afforded resinous material and no detectable volatile bases.

The alkylation sites in **2**, **7**, and **8** warrant comment. The ultraviolet spectra of the amidinium-type salt **9** and the hydriodide of **7** are virtually superimposable. These spectra showed a broad absorption band which exhibited a shoulder at approximately 260 mμ (log ε 3.88 and 3.85 for **7** HI and **9**, respectively), rising to a maximum at 219 mμ (log ε 4.44 and 4.40 for **7** HI and **9**, respectively). Correction for absorption by the iodide ion removed the 219-mμ maximum. On the basis of the absorption spectra, it is proposed that the methylation of **2** results in the formation of a resonance stabilized amidinium-type ion, **7** HI, formed *via* N → N proton transfer either prior to or accompanying the methylation. Since a planar geometry has been demonstrated[8] for amidinium ions, a likely configuration for **7** HI is **12** in which the highly deshielded proton [δ 10.58 (CH_3CN)] is hydrogen bonded to the dimethylamino group.



12

As shown above, the site of alkylation in amidrazone **8** is at the dimethylamino group rather than the imino nitrogen which would give **9**. When compared with **12**, ion **9** is less stable because of (1) lack of opportunity for hydrogen bonding and (2) increased steric crowding which is caused by the presence of a methyl group in place of hydrogen. Accordingly, we propose that alkylation of **8** takes place at the dimethylamino group because the amidrazonium salt **10**, although lacking the charge delocalization of an amidinium-type ion, does not have the steric crowding inherent in **9**.

The slow conversion of **7** to **9** is best explained by simple steric considerations. When compared with **2**, the nucleophilicity of the nitrogen atoms in the hydrazinic moiety in **7** is decreased by the presence of the third methyl group. Thus the imino nitrogen of **7** becomes the most nucleophilic and the "crowded" cation **9** is preferentially formed.

We have also attempted the synthesis of **4**[9] by reaction of *N*-phenylbenzimidoyl chloride with 1,1,1-trimethylhydrazinium chloride and **1** by the reaction of methyl *N*-phenylbenzimidate with 1,1,1-trimethylhydrazinium chloride or tosylate in the presence of methoxide ion. The latter experiments were conducted in both methanol and tetrahydrofuran and are an extension of the amine imide synthesis of McKillip and Slagel.[10] These procedures yielded complex mixtures, and the only products isolated were those derived from starting materials.

(8) R. C. Newman, Jr., G. S. Hammond, and T. J. Dougherty, *J. Amer. Chem. Soc.*, **84**, 1506 (1962).

(9) The reaction of 1,1,1-trimethyl-2-benzoylhydrazinium chloride with aniline in the presence of PCl_5 also failed to give **4**: M. S. Gibson and P. D. Callaghan, personal communication.

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. Nmr spectra were determined with a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane or H_2O (for D_2O spectra) as the internal standard. Integrated intensity ratios supported all chemical shift assignments. Ultraviolet spectra were determined in 95% ethanol utilizing a Bausch and Lomb Spectronic 505 instrument (for data reported on the structure of **2**) and a Cary 14 instrument (for data on **7** HI and **9**). Analyses are by Mr. K. Fleischer of the Sterling-Winthrop Research Institute.

1,1-Dimethyl-2-(*N*-phenylbenzimidoyl)hydrazine (2).—*N*-Phenylbenzimidoyl chloride[11] (100 g) was added with stirring to 250 ml of 1,1-dimethylhydrazine at a rate sufficient to maintain the temperature below 65°. The reaction mixture was refrigerated. After 5 days 66.8 g of product, mp 69–71°, was filtered off. A second crop, 45.0 g, mp 69–72°, was filtered after refrigeration of the filtrate for several weeks. Recrystallization from petroleum ether gave white crystals: mp 71–72.5°; nmr (CH_3CN) δ 8.03 (broad s, NH), 2.45 [s, $(CH_3)_2N$], and 6.3–7.4 (m, $2C_6H_5$).

Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.3; H, 7.2; N, 17.6. Found: C, 75.1; H, 7.2; N, 17.4.

The **picrate** was recrystallized from ethanol, mp 206–207° dec.

Anal. Calcd for $C_{21}H_{20}N_6O_7$: C, 53.8; H, 4.2; N, 17.9. Found: C, 53.8; H, 4.3; N, 17.9.

The **hydriodide** was prepared in ethanol and precipitated with ether. Recrystallization from ethanol–ether gave white crystals, mp 251–252°.

Anal. Calcd for $C_{15}H_{18}IN_3$: C, 49.1; H, 4.9; N, 11.4; I, 34.6. Found: C, 49.4; H, 4.7; N, 11.2; I, 34.6.

Reaction of *N*-Phenylbenzimidoyl Chloride with 1,1-Dimethylhydrazine in Benzene.—A solution containing 5.0 g of the imino chloride and 3 ml of 1,1-dimethylhydrazine in 50 ml of dry benzene was kept at room temperature for 4 hr. The benzene solution was decanted from insoluble material and evaporated to an oil that partially crystallized on standing. The crude material was crystallized from aqueous ethanol to give 0.60 g of crude 1,1-dimethyl-2,2-di(*N*-phenylbenzimidoyl)hydrazine (**6**), mp 123–125°. Recrystallization from ethanol gave yellow crystals: mp 131–133°; nmr ($CDCl_3$) δ 2.65 [s, $N(CH_3)_2$] and 6.4–7.9 (m, $4C_6H_5$).

Anal. Calcd for $C_{28}H_{26}N_4$: C, 80.3; H, 6.3; N, 13.4. Found: C, 80.2; H, 6.5; N, 13.2.

The mother liquors from the isolation of **6** gave **2** picrate, mp and mmp 206–207°.

Reaction of 1,1-Dimethyl-2-(*N*-phenylbenzimidoyl)hydrazine with Methyl Iodide.—The hydrazide imide (10 g) was dissolved in 30 ml of methyl iodide. After an initial exothermic reaction, the reaction mixture was allowed to stand at room temperature for 48 hr. The solid was filtered off and washed with ether to give 15.4 g of crude material, mp 189–225°. One recrystallization from ethanol afforded 6.5 g of 1,1,2-trimethyl-2-(*N*-phenylbenzimidoyl)hydrazine hydriodide (**7** HI), mp 227–229°. Dilution of the mother liquors with an equal volume of dry ether afforded an additional 1.2 g of crude hydriodide, mp 200–220°. Recrystallization from ethanol gave white crystals: mp 228–229°; nmr (CH_3CN) δ 10.58 (broad s, NH), 2.79 [s, $N(CH_3)_2$], 2.99 (s, NCH_3), 7.11 (s, C_6H_5), and 7.43 (s, C_6H_5).

Anal. Calcd for $C_{16}H_{20}IN_3$: C, 50.4; H, 5.3; N, 11.0. Found: C, 50.6; H, 5.1; N, 11.1.

The hydriodide was also obtained by treatment of an ethanolic solution of the free base with 40% HI, mp and mmp 228–229°.

Treatment of the hydriodide (1.0 g) with 10 ml of 6 *N* NaOH followed by extraction with chloroform gave, after evaporation of the dried solution, the **free base 7**, 0.4 g, mp 97–100°. Recrystallization from petroleum ether gave white crystals: mp 100–

(10) W. J. McKillip and R. S. Slagel, *Can. J. Chem.*, **45**, 2619 (1967).

(11) J. von Braun and W. Pinkernelle, *Ber.*, **67B**, 1218 (1934).

101°; nmr ($CDCl_3$) δ 2.35 [s, $N(CH_3)_2$], 2.98 (s, NCH_3), and 6.4–7.2 (m, $2C_6H_5$).

Anal. Calcd for $C_{16}H_{19}N_3$: C, 75.9; H, 7.6; N, 16.6. Found: C, 76.1; H, 7.7; N, 16.4.

The ethanol–ether filtrate remaining after isolation of the hydriodide was diluted with a large volume of ether to give 5.0 g of solid material, mp 179–190°. Three recrystallizations from water gave 0.40 g of N^1,N^1,N^2,N^3-tetramethyl-N^3-phenylbenzamidrazonium iodide (**9**),[12] mp 243–244°. The infrared spectrum of this product was identical with that of the amidrazonium salt prepared by the following procedure.

A solution containing 2.0 g of 1,1,2-trimethyl-2-(*N*-phenylbenzimodoyl)hydrazine (**7**) in 5 ml of methyl iodide was allowed to stand for 24 hr. Dilution with ether gave 1.1 g of crude product, mp 230–235°. An additional 2 ml of methyl iodide was added to the evaporated filtrate and a second crop, 1.6 g, mp 238–242°, was collected after 5 days. Recrystallization from ethanol gave white crystals: mp 245–246°: nmr (D_2O, 85°) δ 2.91 [s, $N(CH_3)_2$], 3.41 (s, NCH_3), 3.91 (s, NCH_3), 7.92 (s, C_6H_5), and 8.10 (s, C_6H_5).

Anal Calcd for $C_{17}H_{22}IN_3$: C, 51.7; H, 5.6; N, 10.6; I, 32.1. Found: C, 51.3; H, 5.8; N, 10.6; I, 32.1.

1,1,2-Trimethyl-2-(*N*-phenylbenzimidoyl)hydrazine (7).—*N*-Phenylbenzimidoyl chloride (14.0 g) was added to a solution of 10.0 g of 1,1,2-trimethylhydrazine[14] in 30 ml of dry benzene. After 6 days at room temperature, the reaction mixture was evaporated to give a solid residue from which the product (10.5 g, mp 99–100°) was extracted with boiling petroleum ether. The nmr spectrum of the product was identical with that of the product obtained by the methylation of **2**.

Preparation of *N*-Methylbenzanilide Dimethylhydrazone Hydriodide (8 HI).—Condensation of *N*-methylbenzanilide with 1,1-dimethylhydrazine was carried out by the procedure of Rapoport and Bonner[13] on a 0.1-mol scale utilizing a 12-hr reflux period. The oily product was dissolved in 40 ml of ethanol and treated with 15 ml of 57% hydriodic acid. Dilution with ether gave 7.2 g (19%) of the **hydriodide**, mp 233–236°. Recrystallization from ethanol gave white crystals: mp 245–246°; nmr (D_2O, 85°) δ 3.18 [s, $N(CH_3)_2$], 3.95 (s, NCH_3), 7.8–8.1 (m, $2C_6H_5$).

Anal. Calcd for $C_{16}H_{20}IN_3$: C, 50.4; H, 5.3; N, 11.0; I, 33.3. Found: C, 50.6; H, 5.3; N, 11.1; I, 33.3.

The **free base 8** was obtained by extraction of a solution containing 7.2 g of the hydriodide in 250 ml of 6 *N* NaOH with three 100-ml portions of chloroform. Evaporation of the dried solution gave 4.0 g of the oily amidrazone: nmr ($CDCl_3$) δ 2.70 [s, $N(CH_3)_2$], 3.22 (s, NCH_3), and 6.6–7.8 (m, $2C_6H_5$).

N^1,N^1,N^1,N^3-Tetramethyl-N^3-phenylbenzamidrazonium Salts (10).—The **iodide** was prepared by treating the free base (from 2.4 g of the hydriodide) with 3 ml of methyl iodide. After 24 hr, dilution with ether gave the crude product as an oil which after trituration with ether gave 1.7 g of white solid, mp 162–165°. Recrystallization from ethanol gave white crystals: mp 166–167°; nmr (DMSO-d_6) δ 3.31 [s, $N^+(CH_3)_3$ and NCH_3] and 7.2–7.7 (m, $2C_6H_5$).

Anal. Calcd for $C_{17}H_{22}IN_3$: C, 51.7; H, 5.6; N, 10.6; I, 32.1. Found: C, 51.9; H, 5.3; N, 10.6; I, 32.5.

Reaction of the amidrazone with CD_3I gave the deuterated salt **11**, mp 157–160°. The nmr spectrum (DMSO-d_6) showed the correct (10:9) aromatic:methyl integration.

The **fluoroborate** was obtained by treatment of a saturated aqueous solution of the iodide with 1 equiv of sodium fluoroborate and recrystallized from ethanol–ether as white crystals, mp 138–139°. The nmr spectrum was identical with that of the iodide.

Anal. Calcd for $C_{17}H_{22}BF_4N_3$: C, 57.2; H, 6.2; N, 11.8. Found: C, 57.2; H, 6.2; N, 11.7.

The **tosylate** was obtained by heating 2.0 g of the amidrazone and 2 ml of methyl tosylate on the steam bath for 2 hr. The oily salt was precipitated with ether, washed with ether several times, and dried *in vacuo* at 100°: nmr (DMSO-d_6) δ 3.22 [s, $(CH_3)_3N^+$ and CH_3N], 2.22 (s, $CH_3C_6H_4SO_3^-$), and 7.1–8.0 (m, aromatic). The nmr spectrum showed the salt to be contaminated with methyl tosylate: δ 2.31 (s, CCH_3) and 3.68 (s, OCH_3).

Hydrolysis of N^1,N^1,N^1,N^3-Tetramethyl-N^3-phenylbenzamidrazonium Salts (10).—A solution of the iodide (0.9 g) in 25 ml of 6 *N* HCl was heated under reflux for 2 days. Iodide sublimed in the condenser. On cooling, 0.10 g of benzoic acid (mp and mmp 118–120°) crystallized and was filtered off. The filtrate was made basic with sodium carbonate and extracted with chloroform. Evaporation of the dried solution gave an oil which was suspended in 10 ml of 6 *N* NaOH and shaken with 0.5 ml of benzenesulfonyl chloride giving crude *N*-methyl-*N*-phenylbenzenesulfonamide, 0.15 g, mp 69–75°. One recrystallization from aqueous ethanol gave mp 72–74° (*lit.*[15] 79°). Identity was established by ir and nmr ($CDCl_3$) δ 3.08 (s, NCH_3) and 6.9–7.7 (m, $2C_6H_5$).

When the deuterated iodide **11** was hydrolyzed as described above, the nmr spectrum of the *N*-methyl-*N*-phenylbenzenesulfonamide showed integrated methyl:aromatic intensity ratios (3:10) that indicated complete absence of NCD_3.

The **tosylate salt** (1.0 g) was hydrolyzed as described above. After filtration of the benzoic acid, the filtrate was divided in half. One-half was treated as before to give the benzenesulfonyl derivative, mp 69–75°. The other half was evaporated, *in vacuo*, to an oil which was dissolved in ethanol, filtered from insoluble material, and reprecipitated twice from ether. The crude product partially solidified on standing. Its nmr spectrum (D_2O) exhibited all of the characteristics of authentic 1,1,1-trimethylhydrazinium tosylate plus contamination by ethanol and minor impurities at δ 7.25 (s) and 2.25 (m).

1,1,1-Trimethylhydrazinium Tosylate.—The salt was obtained in quantitative yield by slowly adding methyl tosylate to an ice-cooled solution of 1,1-dimethylhydrazine in ether. The product was recrystallized from ethanol as white crystals: mp 220–222°; nmr (D_2O) δ 1.98 (s, CH_3C), 3.05 [s, $(CH_3)_3N^+$], and 7.05, 7.58 (d, J = 7 Hz, aromatic AB).

Anal. Calcd for $C_{10}H_{18}N_2O_3S$: C, 48.8; H, 7.4; N, 11.4. Found: C, 49.0; H, 7.8; N, 11.5.

Registry No.—**2**, 27808-65-7; **2** picrate, 27808-66-8; **2** HI, 27808-67-9; **6**, 27808-68-0; **7**, 27873-63-8; **7** HI, 27928-68-3; **7** MeI, 27808-69-1; **8**, 27808-70-4; **8** HI, 27808-71-5; **10** iodide, 27808-72-6; **10** fluoroborate, 27808-73-7; **10** tosylate, 27808-74-8; **10** benzenesulfonyl derivative, 27808-75-9; **11**, 27808-76-0; 1,1,1-trimethylhydrazinium tosylate, 27808-77-1.

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(12) Completely substituted amidrazonium salts have apparently not been previously prepared. We have adopted the nomenclature proposed by Rapoport and Bonner (ref 13) and recommended in ref 4 for naming these salts.

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Quinoxaline Studies. XVIII.[1] Unequivocal Syntheses of 2-Amino-6- and -7-chloroquinoxalines

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Discussion

2-Amino-6- (or 7-) chloroquinoxalines have two known biomedical utilities: as a sulfaquinoxaline[2] and

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