solution. The olefin was checked at this point and it was found that no isomerization had yet occurred (glc). The olefin (at 16°) was not able to dissolve the entire quantity of **3**. Both the amount of nitrogen released and the olefin composition were monitored during the photolysis. The photolysis was stopped after 75 ml of nitrogen had evolved, indicating that *ca.* three-fourths of **3** had decomposed. The olefin composition at this point was 92.6% *cis*- and 7.4% *trans*-4-methyl-2-pentene. The isolated material, having a total weight of 1.9 g, consisted of crystals (**3**) and an oil. Nmr analysis of the product mixture showed that both **6** (57%) and **7** (43%) were formed.

Irradiation of 6 in Cyclohexane.—A solution of **6** (50 mg) in cyclohexane was brought to 16° and irradiated for 8 hr. The excess cyclohexane was removed under reduced pressure and the remaining oil was analyzed by nmr. Compound **6** remained unchanged. **7** was not observed under these conditions.

Irradiation of 7 in Cyclohexane.—A solution of **7** (50 mg) in cyclohexane (50 ml) was brought to 16° in a Pyrex tube and irradiated for 1 hr. The excess solvent was stripped off, leaving an oil which was analyzed by nmr. Nearly complete isomerization to **6** was found. A small peak due to **7** was visible (<5%).

Irradiation of 7 in Cyclohexane Using Filtered Light.—A solution of **7** (0.15 g, 0.325 mmol) in 100 ml of cyclohexane was irradiated for 1 hr at 16° using filtered light. The filters employed were 5 cm of $CuSO_4 \cdot 5H_2O$ in H_2O (100 g/l.)[37] and 1 cm of 2,7-dimethyldiaza-3,6-cycloheptadiene-1,6-perchlorate in H_2O (0.1 g/100 ml).[37,38] These filters cut off all light below 350 nm. All of the apparatus which remained above the aqueous copper sulfate solution was covered with aluminum foil to prevent unfiltered light from striking the solution. Analysis of the product isolated showed that pure **7** was unchanged.

Photolysis of 3 in *cis*-4-Methyl-2-pentene Using Filtering Solutions.—*cis*-4-Methyl-2-pentene (50 ml) containing **3** (1.0 g, 2.45 mmol) was irradiated for 1 hr at 16° employing both filtering solutions as previously described. The starting olefin was stripped off and was found to be 94.7% *cis*- and 5.3% *trans*-4-methyl-2-pentene (glc). Analysis of the dark oil product showed that both **6** (55%) and **7** (45%) were present (nmr analysis using peak heights of the cyclopropyl methyl absorptions).

Photolysis of 3 in a Mixture of *cis*- and *trans*-4-Methyl-2-pentene.—A mixture of *cis*- and *trans*-4-methyl-2-pentene (*ca.* 60:40) containing **3** (0.5 g, 1.22 mmol) was irradiated at 16° for 1.5 hr using filtered light. Stripping off to the excess olefins left an oil in which **6** and **7** were observed in the ratio of 68:32, respectively.

Attempted Photosensitized Isomerization of 7 by 3.—A solution containing **3** (0.44 g, 1.08 mmol) and **7** (0.50 g, 1.08 mmol) in cyclohexane (100 ml) was photolyzed at 16° for 1 hr employing filtered light. After the cyclohexane was stripped off, nmr analysis of the product showed that **7** was unchanged by the conditions employed.

Photolysis of 3 in *cis*-4-Methyl-2-pentene Containing 90 Mol % 1,3-Butadiene.—*cis*-4-Methyl-2-pentene (3.46 g, 41.1 mmol) containing **3** (1.0 g, 2.45 mmol) and 1,3-butadiene (20.0 g, 270 mmol) was irradiated for 3 hr in a sealed ampoule using filtered light. The ampoule was opened, allowing the excess 1,3-butadiene to boil off. The excess cis olefin was stripped off, leaving a light yellow oil. Analysis of the mixture by nmr showed that both **6** and **7** were present. The trans product (**6**) was the major product (*ca.* 55%), but difficulties in analysis make this number less reliable than the others. It is probably good within 15%.

Registry No.—**1**, 14310-17-9; **2**, 38123-54-5; **3**, 38123-55-6; **4a**, 38123-56-7; **4b**, 38229-30-0; **4c**, 38123-57-8; **4d**, 38123-58-9; **4e**, 38123-59-0; **4f**, 38123-60-3; **4g**, 38123-61-4; **4h**, 38123-62-5; **6**, 38123-63-6; **7**, 38123-64-7.

Amidrazones. II.[1] Tautomerism and Alkylation Studies

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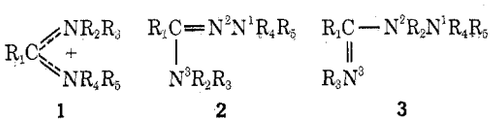
Amidrazone tautomers are exclusively formed from the reaction of *N*-methylbenzimidoyl chloride and 1,1-disubstituted hydrazines. A series of amidrazones and hydrazide imides have been prepared and their sites of alkylation with methyl iodide have been established. With the exception of the N^1,N^1-dimethyl substituted amidrazones **7**, **9**, and **11**, which undergo methylation at N^1, the other compounds displayed amidine-type behavior and afforded charge-delocalized cations resulting from substitution at either N^2 or N^3.

The reaction of amidines with alkyl halides results in alkylation of the imino nitrogen to give amidinium cations with the charge-delocalized structure **1**.[2] However, aside from the diverse results reported on three compounds in paper I[1] of this series, little is known of the site of alkylation in amidrazones (**2**) or hydrazide imides (**3**). The latter compounds possess three potential sites for alkylation and the position of alkylation could be expected to depend on a number of factors, including the nature of the substituents bonded to the nitrogen atoms and whether the compound reacting with the alkylating agent has structure **2** or **3**.



1 **2** **3**

This paper reports a study of structural effects on the site of alkylation of amidrazones and hydrazide imides with methyl iodide and some observations on amidrazone–hydrazide imide tautomerism. The recommended[3] method for numbering the nitrogen atoms in amidrazones and hydrazide imides is employed throughout and is illustrated in structures **2** and **3**.

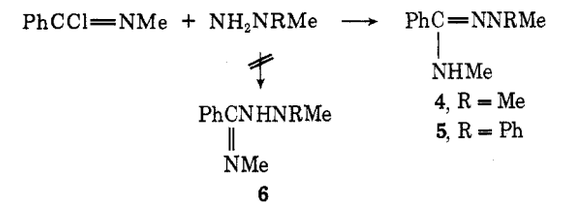
Tautomerism Studies.—Amidrazone–hydrazide imide tautomerism is possible with appropriately substituted compounds **2** and **3** (R_2 = H). In our earlier paper,[1] we established from spectroscopic data that compound **25** exists exclusively in the hydrazide imide form. However, we have found that, when the N^3-phenyl group is replaced by N^3-methyl, the amidrazone is apparently the exclusively formed tautomer. Reaction of *N*-methylbenzimidoyl chloride with 1,1-dimethylhydrazine and 1-methyl-1-phenylhydrazine gave *N*-methylbenzamide dimethylhydrazone (**4**) and *N*-methylbenzamide methylphenylhydrazone (**5**), respectively. The nmr spectrum of both **4** and **5** displayed N^3-methyl signals that are spin coupled to NH. The observed methyl doublets (J = 4 Hz) collapsed to singlets on deuterium exchange. These results are in-

(1) For paper I see R. F. Smith, D. S. Johnson, C. L. Hyde, T. C. Rosenthal, and A. C. Bates, *J. Org. Chem.*, **36**, 1155 (1971).

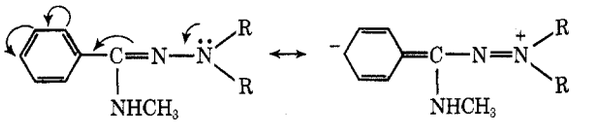
(2) For a discussion of amidinium salts, see P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, p 181.

(3) D. G. Nielsen, R. Roger, J. W. M. Heattie, and L. R. Newlands, *Chem. Rev.*, **70**, 151 (1970).

compatible with the structure of the hydrazide imide tautomer, **6**.

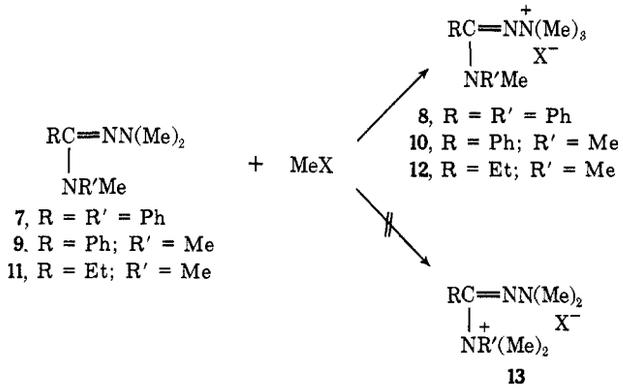


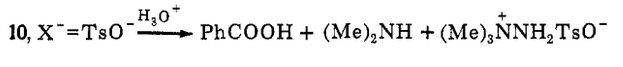
Simple resonance considerations most readily provide an explanation for the selective tautomerism described above. Conjugation of the N^3-phenyl group with the carbon–nitrogen double bond in **25** (and the currently reported **23**) provides enhanced stabilization to these compounds in their hydrazide imide forms. In **4** and **5**, hydrazone resonance[4] can be assumed to provide enhanced stabilization to the amidrazone forms of these compounds. Gol'din and coworkers[5] have



recently shown that N^3-unsubstituted compounds (**2**, $R_2 = R_3 = H$) exist exclusively in the amidrazone form.

Alkylation Studies.—*N*,*N*-Dimethylbenzamide dimethylhydrazone (**9**) and *N*,*N*-dimethylpropionamide dimethylhydrazone (**11**) were found to react with methyl iodide in a manner analogous to that previously reported for *N*-methylbenzanilide dimethylhydrazone (**7**); *i.e.*, alkylation occurred at N^1 providing the N^1-quaternized salts **10** and **12**, respectively. The nmr spectra of **10** and **12** [$-N(CH_3)_2$ and $-{}^+N(CH_3)_3$ singlets] did not permit distinction between their assigned structures and the unlikely structure **13**.





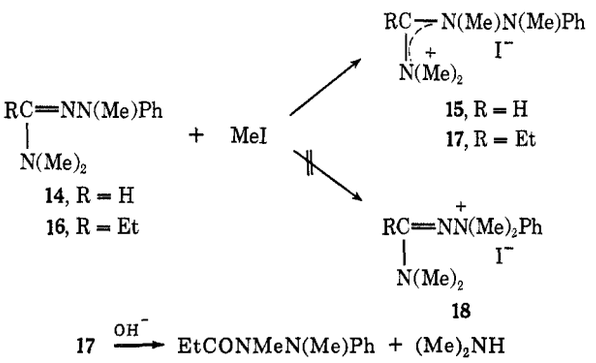
However, hydrolytic degradation provided confirmation of structure **10**. Acid hydrolysis of the latter compound (as its *p*-toluenesulfonate salt) gave benzoic acid, dimethylamine, and 1,1,1-trimethylhydrazinium *p*-toluenesulfonate. The structure of **8** has also been previously confirmed by hydrolytic degradation.[1]

(4) P. A. S. Smith and E. E. Most, Jr., *J. Org. Chem.*, **22**, 358 (1957).

(5) G. S. Gol'din, V. G. Poddubnyi, A. A. Simova, G. S. Shor, and E. A. Rybakov, *Zh. Org. Khim.*, **5** (8), 1440 (1969); *Chem. Abstr.*, **71**, 1123762 (1969).

Reaction of methyl iodide with the *N*,*N*-dimethylformamide methylphenylhydrazone (**14**)[6] and *N*,*N*-dimethylpropionamide methylphenylhydrazone (**16**)[7] resulted in alkylation at N^2, affording the charge-delocalized salts **15** and **17**, respectively. The nmr spectra of these salts show three upfield singlets with integrated intensity ratios of 6:3:3. Structure **18** is also compatible with the nmr spectra if nonequivalence of the two N^3-methyl groups is assumed due to restricted rotation.[8] However, structure **18** was eliminated from consideration by establishing that **17** affords 1,2-dimethyl-1-phenyl-2-propionylhydrazine on basic hydrolysis. Furthermore, no coalescence of the methyl signals in **17** was observed on heating to 140° in DMSO-d_6.

Assuming the planar geometry assigned to amidinium cations,[9a] models indicate some steric crowding in completely substituted salts of the type **15** and **17**. Hence, we conclude that, in the N^1-dimethylamidrazones **7**, **9**, and **11**, the factor which determines N^1 as the site of substitution is predominately steric in nature, since substitution at N^2 would result in the formation of sterically crowded cations. In **14** and **16** the nucleophilicity of N^1 is diminished by the electron-withdrawing resonance effect of the phenyl group and alkylation occurs at N^2 to give the resonance-stabilized (albeit crowded) salts **15** and **17**.



Reaction of amidrazones **4** and **5** with methyl iodide gave N^2-methylated salts to which we have assigned the charge-delocalized structures **19** and **20**, respectively. Neutralization of these salts afforded the hydrazide imides **21** and **22**. A plausible explanation for the alkylation of **4** at N^2 rather than N^1 (as found for the N^1,N^1-dimethylamidrazones **7**, **9**, and **11**) may be found by comparison of the cations obtained from these reactions. If an "inside" position for the strongly deshielded N^3 hydrogen is assumed for **19**, a likely structure for this cation is that shown. This structure is less sterically crowded than the analogous structures which would result from the N^2-methylation of **7**, **9**, or **11**, and it also may be considered to have enhanced stabilization owing to intramolecular hydrogen bonding.

(6) H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, **92**, 837 (1959).

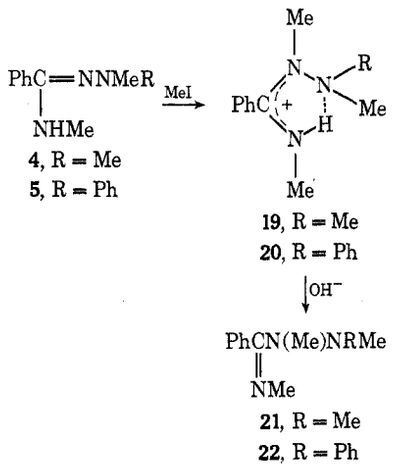
(7) H. Rapoport and R. M. Bonner, *J. Amer. Chem. Soc.*, **72**, 2783 (1950).

(8) For a recent review see C. G. McCarty in "The Chemistry of the Carbon–Nitrogen Double Bond," S. Patai, Ed., Interscience, London, 1969, p 363.

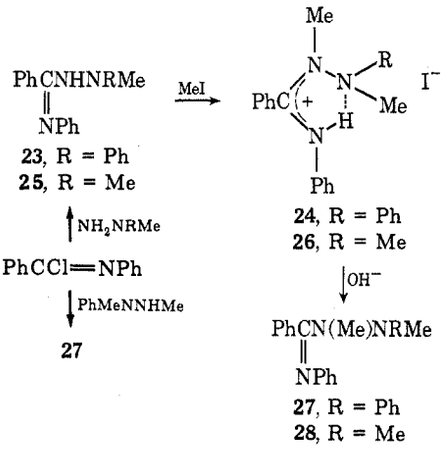
(9) (a) From nmr studies the rotational barrier in amidinium cations has been estimated to be in the same range as that reported for amides (7–18 kcal/mol): G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655 (1963). (b) The C–N rotational barrier in the tetramethylformamidinium cation has been determined as 17.5 ± 1.5 kcal/mol: J. Ranft and S. D. Dähne, *Helv. Chim. Acta*, **47**, 1160 (1964).

An analogous, chelated structure also seems reasonable for **20**. However, the nmr spectra of **20** displays characteristics that are typical of compounds exhibiting hindered bond rotation. When the nmr spectrum of **20** was determined in $CDCl_3$, upfield methyl signals were observed at δ 2.81, 2.87, and 3.30. In addition, two singlets of equal intensity were observed at δ 2.97 and 3.50 which integrated for approximately 0.5 H. The low-intensity peaks were found not to be due to impurities. When the spectrum of **20** was determined in DMSO-d_6, singlets of equal intensity were observed at δ 2.65 (sharp), 2.75 (broad), and 3.18 (broad). Peak sharpening was observed on warming the DMSO-d_6 solution.

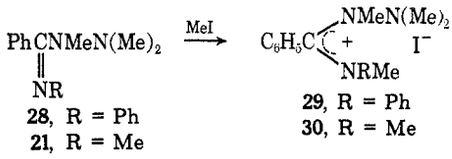
These results, coupled with those described below for **24**, indicate that the N^1- and N^2-methyl groups of **20** assume two unequally populated, magnetically nonequivalent conformations in $CDCl_3$ and the interconversion of these forms is facilitated in DMSO-d_6. Restricted rotation about either the C–N[2 9] or N–N[10] bonds could account for the spectral characteristics of **20**. Coalescence in DMSO-d_6 could be accounted for by assuming that the rotational barrier (either C–N or N–N) is lowered by affording NH the opportunity to hydrogen bond with the acceptor solvent, thus destabilizing structure **20**.



Results similar to those described above for the conversion of **5** to **20** were obtained for the methylation of **23**. The latter compound also undergoes methylation at N^2 on reaction with methyl iodide to give a salt to which we have assigned the charge-delocalized structure **24** to the cation. In the conversion of **23** to **24**, we have assumed that the alkylation is accompanied by a N^2 to N^3 proton transfer. The latter assumption seems valid, since the N^1,N^1-dimethyl analog (**25**) has been shown by us[1] to give **26** on treatment with methyl iodide. The iodide **24** was amorphous and was characterized by conversion to the picrate and free base **27**. The structure of the latter compound was firmly established by its synthesis from *N*-phenylbenzimidoyl chloride and 1,2-dimethyl-1-phenylhydrazine. The picrate of **24** also displayed a nmr spectrum that indicated hindered rotation about either the C–N^2 or N–N bonds. When determined in DMSO-d_6, **24** picrate displayed methyl singlets of equal intensity at δ 2.95 and 3.45, each of which integrated for approximately 2.5 H, and low-intensity singlets at δ 3.02 and 3.45, each of which integrated for approximately 0.5 H. On warming the DMSO-d_6 solutions from 34 to 50°, coalescence was observed and peak sharpening occurred on further heating. Cooling to 34° restored the original four-singlet pattern. As with **20**, which differs only by having an N^3-methyl substituent in place of the N^3-phenyl substituent in **24**, a choice between C–N^2 and N–N rotation cannot be made with certainty.



In paper I, we reported that the completely substitued hydrazide imide, **28**, gives **29** on reaction with methyl iodide. We have found that substitution of the N^3-phenyl group of **28** by a methyl group does not affect the site of methylation, since the tetramethylated hydrazide imide, **21**, also undergoes substitution at N^3 to give a salt of analogous structure (**30**). It is of interest to note that these two N^1,N^1-dimethylated hydrazide imides undergo substitution with methyl iodide at N^3 while the N^1,N^1-dimethylated amidrazones **7**, **9**, and **11** undergo methylation at N^1. The differences in alkylation site in these compounds can be best explained by simple steric considerations. The nucleophilicity of the hydrazinic moiety of **21** and **28** is decreased by the steric effect of the methyl substituent at N^2 in these hydrazide imides. Thus, the less hindered imino nitrogen (N^3) becomes the most nucleophilic and the "crowded," charge-delocalized cations **29** and **30** are preferentially formed.



This study indicates that, with the exception of the N^1,N^1-dimethyl-substituted amidrazones, **7**, **9**, and **11**, amidrazones and hydrazide imides exhibit amidine-type behavior when treated with alkyl halides; *i.e.*, alkylation occurs at either N^2 or N^3 to produce charge-delocalized (amidinium type) ions.

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 as the internal standard.

N-**Methylbenzamide Dimethylhydrazone** (**4**).—*N*-Methylbenzimidoyl chloride[11] (15.3 g) was slowly added to a stirred

(10) For discussion of N–N rotational barriers and leading references see M. J. S. Dewar and B. Jennings, *J. Amer. Chem. Soc.*, **91**, 3655 (1969).

(11) I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, **95**, 126 (1962).

solution containing 6.0 g of 1,1-dimethylhydrazine and 10.1 g of triethylamine in 50 ml of dry benzene. After an initial exothermic reaction, the reaction mixture was kept at room temperature overnight. An equal volume of benzene was added to the reaction mixture and the precipitated triethylamine hydrochloride was removed by two extractions with 50 ml of water. The dried benzene extract was evaporated *in vacuo* at 100° and the residue was distilled, giving 10.4 g of product as a light yellow oil: bp 134–136° (20 mm); nmr ($CDCl_3$) δ 2.51 [d, 3, J = 4 Hz, $NHCH_3$ (s with $NDCH_3$)], 2.33 [s, 6, $N(CH_3)_2$], 6.0 (broad, 1, $NHCH_3$), and 7.3 (m, 5).

Anal. Calcd for $C_{10}H_{15}N_3$: C, 67.8; H, 8.5; N, 23.7. Found: C, 67.4; H, 8.5; N, 23.8.

***N*-Methylbenzamide Methylphenylhydrazone (5).**—Reaction of 10.0 g of *N*-methylbenzimidoyl chloride with a solution containing 7.9 g of 1-methyl-1-phenylhydrazine and 6.6 g of triethylamine in 50 ml of dry benzene afforded (after work-up as described for **4**) a yellow oil which was treated with 50 ml of petroleum ether (bp 60–80°) and refrigerated for 3 days. The partially solidified reaction mixture was filtered and the yellow solid was washed with cold petroleum ether, giving 6.2 g of crude **5**, mp 50–65°. Several recrystallizations from petroleum ether gave yellow crystals: mp 72–73°; nmr ($CDCl_3$) δ 2.62 [d, 3, J = 4 Hz, $NHCH_3$ (s with $NDCH_3$)], 2.92 (s, 3), 5.85 (broad, 1, $NHCH_3$), 7.0 (m, 10).

Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.3; H, 7.2. Found: C, 75.3; H, 7.3.

***N,N*-Dimethylbenzamide Dimethylhydrazone (9).**—This compound was obtained in 54% yield by the condensation of *N,N*-dimethylbenzamide with 1,1-dimethylhydrazine.[7] Distillation gave **9** as a yellow oil: bp 124–128° (20 mm); nmr (neat) δ 2.09 (s, 6), 2.57 (s, 6), 7.22 (s, 5).

Anal. Calcd for $C_{11}H_{17}N_3$: C, 69.1; H, 9.0; N, 22.0. Found: C, 69.2; H, 9.0; N, 21.8.

The picrate was recrystallized from ethanol, mp 121–122°.

Anal. Calcd for $C_{17}H_{20}N_6O_7$: C, 48.6; H, 4.8; N, 20.0. Found: C, 48.4; H, 4.7; N, 19.8.

1,1,1-Trimethyl-2-(α-dimethylaminobenzylidene)hydrazinium Salts (10).—One gram of **9** was treated with 2 ml of methyl iodide. After 24 hr, the solution was diluted with ether to give 1.4 g of **10** iodide, mp 132° (prior sintering). Recrystallization from ethanol gave white crystals: mp 154–155° (sample inserted at 140° and heated 2°/min); nmr (D_2O) δ 2.75 (s, 6), 3.15 (s, 9), 7.5 (m, 5).

Anal. Calcd for $C_{12}H_{20}IN_3$: C, 43.3; H, 6.1; N, 12.6. Found: C, 43.3; H, 5.9; N, 12.6.

The tosylate salt of **10** was obtained by treating 2 g of **13** with 3 ml of methyl *p*-toluenesulfonate. After 24 hr at room temperature, the reaction mixture was warmed on the steam bath, cooled, and diluted with ether. The gummy salt was washed with several portions of dry ether and dried at 100° *in vacuo:* nmr (D_2O) δ 2.92 (s, 9), 2.51 (s, 6), 2.12 (s, 3), 7.2 (m, 9).

Acid Hydrolysis of 10.—A solution containing 10.0 g of **10** iodide in 100 ml of 2 *N* HCl was heated under reflux for 30 hr. On cooling, 4.0 g of crude benzoic acid, mp 113–114° (confirmed by ir), precipitated. A portion of the filtrate was made basic and heated to boiling. Dimethylamine was evolved and trapped as the picrate, mp 160–162°. Treatment of another portion of the basic solution with benzenesulfonyl chloride gave *N,N*-dimethylbenzenesulfonamide, mp 41–43°. Identity of the derivatives was established by comparison of their ir spectra with those of authentic samples. Concentration of the acid solution resulted in the formation of iodine and attempts to isolate a 1,1,1-trimethylhydrazinium salt failed.

A solution of the tosylate salt (3.5 g) in 20 ml of 2 *N* HCl was heated under reflux for 24 hr. After filtration of benzoic acid, the solution was evaporated *in vacuo* to a solid. Recrystallization from ethanol afforded 1.2 g of crude 1,1,1-trimethylhydrazinium tosylate, mp 198–202°. Identity was established by comparison of its ir and nmr spectra with that of an authentic sample.[1]

***N,N*-Dimethylpropionamide Dimethylhydrazone (11).**—This compound was obtained in 55% yield by condensation of *N,N*-dimethylpropionamide with 1,1-dimethylhydrazine.[7] Distillation gave **11** as a colorless oil: bp 65–66° (25 mm); nmr (neat) δ 0.97 (t, 3, J = 8 Hz), 2.55 (q, 2, J = 8 Hz), 2.20 (s, 6), 2.73 (s, 6).

Anal. Calcd for $C_7H_{17}N_3$: C, 58.7; H, 12.0; N, 29.3. Found: C, 58.9; H, 12.3; N, 29.5.

The picrate was recrystallized from ethanol, mp 136–137°.

Anal. Calcd for $C_{13}H_{20}N_6O_7$: C, 41.9; H, 5.4; N, 22.6. Found: C, 42.1; H, 5.6; N, 22.7.

1,1,1-Trimethyl-2-(α-dimethylaminopropylidene)hydrazinium Iodide (12).—Two grams of **11** was treated with 4 ml of methyl iodide. After 24 hr at room temperature **12** separated as an oil, which was dissolved in acetone. Addition of dry ether to the acetone solution precipitated the product as a hygroscopic solid, 2.7 g, mp 98–101°. Recrystallization from acetone–ether gave white crystals: mp 99–101°; nmr (D_2O) δ 1.18 (t, 3, J = 8 Hz), 2.70 (q, 2, J = 8 Hz), 2.90 (s, 6), 3.45 (s, 9).

Anal. Calcd for $C_8H_{20}IN_3$: C, 33.9; H, 7.1; N, 14.7. Found: C, 33.6; H, 7.2; N, 14.3.

Dimethyl(1,2-dimethyl-2-phenylhydrazinomethylene)ammonium Iodide (15).—Three grams of **14**[6] was treated with 6 ml of methyl iodide. After 2 days at room temperature, the product was precipitated by addition of 20 ml of dry ether, giving 3.2 g of **15**, mp 151–152°. Recrystallization from ethanol gave white crystals: mp 156–157°; nmr ($CDCl_3$) δ 2.81 (s, 3), 3.08 (s, 3), 3.90 (s, 6), 7.5 (m, 5), 8.42 (s, 1).

Anal. Calcd for $C_{11}H_{18}IN_3$: C, 41.4; H, 5.7; N, 13.2. Found: C, 41.8; H, 5.9; N, 13.0.

Dimethyl[α-(1,2-dimethyl-2-phenylhydrazino)propylidene]ammonium Iodide (17).—Two grams of **16**[7] was added to 2 ml of methyl iodide. After 24 hr at room temperature the solid product was precipitated with dry ether and recrystallized from acetone–ether to give 2.8 g of **17**, mp 142–143°. Further recrystallization from acetone–ether gave white crystals: mp 149–150°; nmr δ 1.04 (t, 3, J = 8 Hz), 2.75 (q, 2, J = 8 Hz), 3.12 (s, 3), 3.21 (s, 3), 3.30 (s, 6), 7.2 (m, 5).

Anal. Calcd for $C_{13}H_{22}N_3I$: C, 45.0; H, 6.4. Found: C, 44.8; H, 6.6.

Basic Hydrolysis of 17.—A solution of 2 g of **17** in 25 ml of 6 *N* NaOH was heated under reflux for 8 hr. The cooled reaction mixture was saturated with salt and extracted with ether. Evaporation of the dried ether extracts gave 0.43 g of 1,2-dimethyl-1-phenyl-2-propionylhydrazine. The nmr spectrum of this material was found to be identical with that of an authentic sample which was prepared as described below.

1,2-Dimethyl-1-phenyl-2-propionylhydrazine.—Two grams of 1,2-dimethyl-1-phenylhydrazine[12] was treated with 2.0 g of propionic anhydride. The reaction mixture was heated on the steam bath for 30 min, cooled, and dissolved in ether. The ether solution was extracted with dilute sodium carbonate and washed with water. The dried ether solution was evaporated and the residue was distilled to give 1.7 g of product as a colorless oil; bp 165–166° (22 mm); nmr ($CDCl_3$) δ 0.99 (t, 3, J = 8 Hz), 2.30 (q, 2, J = 8 Hz), 2.80 (s, 3), 2.92 (s, 3), 6.8 (m, 5).

Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.7; H, 8.4. Found: C, 68.7; H, 8.1.

***N*-Methylbenzimidic Acid Trimethylhydrazide (21).**—The amidrazone **4** (3.9 g) was slowly added to 12 ml of methyl iodide. The exothermic reaction was moderated with external cooling. Anhydrous ether was added and the crystalline product was filtered off, giving 5.5 g of the hydriodide **19**, mp 203–204°. Recrystallization from ethanol gave white crystals: mp 205–206°; nmr ($CDCl_3$) δ 2.80 [d, 3, J = 2 Hz, $NHCH_3$ (s with $NDCH_3$)], 2.75 (s, 6), 2.97 (s, 3), 9.8 (broad, 1, $NHCH_3$), and 7.60 (s, 5).

Anal. Calcd for $C_{11}H_{18}IN_3$: C, 41.4; H, 5.7; N, 13.2. Found: C, 41.5; H, 5.5; N, 13.1.

The free base **21** was obtained by treating 1.0 g of **19** with 10 ml of 10% NaOH followed by extraction with ether. Evaporation of the dried ether extract gave 0.5 g of **21**, mp 67–71°. Recrystallization from petroleum ether gave white crystals: mp 71–72°; nmr ($CDCl_3$) δ 2.20 (s, 6), 2.70 (s, 3), 2.75 (s, 3), and 7.2 (m, 5).

Anal. Calcd for $C_{11}H_{17}N_3$: C, 69.1; H, 9.0; N, 22.0. Found: C, 68.9; H, 9.1; N, 22.0.

***N*-Methylbenzimidic Acid 1,2-Dimethyl-2-phenylhydrazide (22).**—Addition of 0.5 g of the amidrazone **5** to 2 ml of methyl iodide resulted in the separation of the hydriodide **20**, which was dissolved in hot ethanol and reprecipitated with ether, giving 0.7 g of white crystals, mp 195–197°. Recrystallization from ethanol–ether gave white crystals: mp 196–197°; nmr ($CDCl_3$) δ 2.81 (s, *ca.* 3), 2.87 (s, *ca.* 2.5), 3.30 (s, *ca.* 2.5), 2.97 (s, *ca.* 0.5), 3.50 (s, *ca.* 0.5), 9.8 (broad, 1), 7.2 (m, 10); nmr (DMSO-d_6) δ 2.65 (s, 3), 2.75 (s, 3), 3.18 (s, 3), 10.1 (broad, 1), 7.4 (m, 10).

(12) C. D. Harries, *Ber.*, **27**, 696 (1894).

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

The free base **22** was obtained by the procedure described for **21**. Recrystallization from petroleum ether gave pale yellow crystals: mp 76–78°; nmr ($CDCl_3$) δ 2.64 (s, 3), 2.78 (s, 3), 2.87 (s, 3), and 6.9 (m, 10).

Anal. Calcd for $C_{16}H_{19}N_3$: C, 75.5; H, 7.6. Found: C, 75.6; H, 7.4.

***N*-Phenylbenzimidic Acid 2-Methyl-2-phenylhydrazide (23).**—*N*-Phenylbenzimidoyl chloride[13] (8.6 g) was slowly added to a solution of 5.0 g of 1-methyl-1-phenylhydrazine and 4.0 g of triethylamine in 25 ml of dry benzene. After the exothermic reaction had subsided, the reaction mixture was allowed to stand at room temperature overnight. An equal volume of benzene was added and the reaction mixture was extracted with water. Evaporation of the dried benzene solution gave 11 g of crude product, mp 91–97°. Recrystallization from petroleum ether gave yellow crystals: mp 100–101°; nmr (DMSO-d_6) δ 3.03 (s, 3), 6.5–8.1 (m, 16).

Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.7; H, 6.4; N, 13.9. Found: C, 79.6; H, 6.3; N, 14.1.

***N*-Phenylbenzimidic Acid 1,1-Dimethyl-2-phenylhydrazide (27).**—The hydrazide imide **23** (2.5 g) was added to 10 ml of methyl iodide. After 5 days at room temperature the hydriodide **24** was precipitated with dry ether as an amorphous solid (2.5 g). This material could not be successfully crystallized. Treatment of the hydriodide with 50 ml of 6 *N* NaOH followed by extraction with chloroform afforded, after evaporation of the dried extracts, the free base (1.1 g) as a yellow oil.

The picrate on recrystallization from ethanol formed yellow needles: mp 168–169°; nmr (DMSO-d_6) δ 2.95 (s, *ca.* 2.5), 3.02 (s, *ca.* 0.5), 3.30 (s, *ca.* 2.5), 3.45 (s, *ca.* 0.5), 7.3 (m, 15), 8.5 (s, 2), 12.1 (broad, 1).

Anal. Calcd for $C_{27}H_{24}N_6O_7$: C, 59.6; H, 4.4; N, 15.4. Found: C, 59.6; H, 4.7; N, 15.2.

The picrate was also prepared by the following route. *N*-Phenylbenzimidoyl chloride[13] (4.3 g) was added to a solution containing 2.7 g of 1,2-dimethyl-1-phenylhydrazine[12] and 2.0 g of triethylamine in 25 ml of dry benzene. After 5 days at room temperature the oily product (5.0 g) was isolated as described for **23**. The picrate obtained from this product had a melting point and nmr spectrum identical with that described above.

Dimethyl[α-(Trimethylhydrazino)benzylidene]ammonium Iodide (30).—A solution containing 1 g of **21** in 2 ml of methyl iodide was gently warmed to induce an exothermic reaction. Anhydrous ether was added and the solid product was filtered off, giving 1.4 g of **30**, mp 177–183°. Recrystallization from ethanol gave white crystals: mp 186–188°; nmr ($CDCl_3$) δ 2.72 (s, 6), 2.90 (s, 6), 3.60 (s, 3), 7.6 (m, 5).

Anal. Calcd for $C_{12}H_{20}IN_3$: C, 43.3; H, 6.1. Found: C, 43.3; H, 6.2.

Registry No.—**4,** 38435-15-3; **5,** 38435-16-4; **9,** 38435-17-5; **9** picrate, 38435-18-6; **10** iodide, 38435-19-7; **10** tosylate, 38435-20-0; **11,** 38435-21-1; **11** picrate, 38435-22-2; **12** iodide, 38521-57-2; **13** (R = Ph; R′ = Me; X = TsO), 38435-23-3; **14,** 38435-24-4; **15,** 38435-25-5; **16,** 38435-26-6; **17,** 38435-27-7; **19,** 38435-28-8; **20,** 38435-87-9; **21,** 38435-88-0; **22,** 38435-89-1; **23,** 38554-60-8; **27** picrate, 38435-90-4; **30,** 38435-91-5; *N*-methylbenzimidoyl chloride, 21737-87-1; 1,1-dimethylhydrazine, 57-14-7; 1-methyl-1-phenylhydrazine, 618-40-6; *N*,*N*-dimethylbenzamide, 611-74-5; *N*,*N*-dimethylpropionamide, 758-96-3; 1,2-dimethyl-1-phenyl-2-propionylhydrazine, 38435-93-7; 1,2-dimethyl-1-phenylhydrazine, 29195-01-5; propionic anhydride, 123-62-6; *N*-phenylbenzimidoyl chloride, 4903-36-0.

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

Monomethylation of Aromatic Amines *via* Sodium Borohydride Mediated Carbon–Nitrogen Bond Cleavage

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Arylaminomethylsuccinimides (I) displaying a variety of substituents are rapidly and conveniently converted into the corresponding *N*-methyl aromatic amines (II) upon treatment with sodium borohydride in dimethyl sulfoxide. The presence of ester, amide, or nitrile functions does not affect the facility with which this reaction occurs. The reaction mechanism appears to involve base-catalyzed elimination of succinimide from I followed by reduction of the resulting aldimine intermediate.

Of numerous methods available for the monomethylation of primary aromatic amines, none is without serious deficiencies. Direct or Eschweiler–Clarke[1] alkylation is complicated by the formation of tertiary amines as well as other products; hydrolytic cleavage of *N*-methyl-*p*-toluenesulfonanilides or *N*-methylformanilides[2] requires sufficiently drastic conditions as to preclude the use of starting materials exhibiting labile ester, amide, or nitrile groups; lithium aluminum hydride reduction of formanilides or aryl isocyanates is applicable only to those substrates which do not bear substituents which will also be altered under the reaction conditions. We wish to report that sodium borohydride, the use of which in the hydrogenolysis of alkyl and aralkyl halides and tosylates[3a–d] has received increasing attention, can also be employed to effect the cleavage of carbon–nitrogen bonds with the consequential formation of *N*-methyl aromatic amines. Furthermore, the procedure reported herein may be utilized in the presence of ester, amide, or nitrile functions.

The reaction of aromatic amines with aqueous formaldehyde and succinimide in refluxing ethanol was reported by Winstead, *et al.*,[4] to provide good yields of *N*-arylaminomethylsuccinimides (I). Treatment of these aminal-type substances with sodium borohydride

(1) M. L. Moore, *Org. React.*, **5**, 301 (1949).

(2) R. M. Roberts and P. J. Vogt, *J. Amer. Chem. Soc.*, **78**, 4778 (1956).

(3) (a) H. M. Bell and H. C. Brown, *ibid.*, **88**, 1473 (1966); (b) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969); (c) R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969); (d) J. Jacobus, *Chem. Commun.*, 338 (1970).

(4) M. B. Winstead, K. V. Anthony, L. L. Thomas, R. G. Strachan, and H. J. Richwine, *J. Chem. Eng. Data*, **7**, 414 (1962).