1 hr. at room temperature and then for 15 min. at 40°. The mixture was nearly clear at this time. A slight vacuum was applied to remove hydrogen chloride and the resulting solution of the imino chloride was cooled to 15°. A solution of hydrazoic acid (330 ml.; 5.5% or 0.424 mole) was added dropwise from a funnel replacing the dry port. A slight vacuum was maintained on the system to prevent escape of hydrazoic acid to the hood and room. The mixture was stirred at 25° for 2 hr. and under reflux (no vacuum) for 3 hr. The benzene was removed by distillation (under reduced pressure) and the residue treated with 100 ml. of water and sufficient sodium hydroxide to make alkaline (*p*H 8.5). The resulting solid was filtered by suction and washed with water. There was obtained 27.9 g. of crude product, m.p. 113.6–118.6°; on three recrystallizations from benzene the melting point was still not sharp. It was suspected that there was unreacted amide present (in these compounds mixed melting points rarely show depression), and the total crude material was boiled under reflux in 400 ml. of 10% sulfuric acid. This gave a product free of amide, m.p. 118.8–120.3°, from benzene.

In the preparations of the other new tetrazoles similar purifications were followed. The data for these compounds are in Table II.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, ST. VINCENT COLLEGE]

Sterically Hindered Reactions of Grignard Reagents with Schiff Bases

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N-Benzylidene-*tert*-butylamine added methyllithium and allylmagnesium bromide, but not methylmagnesium iodide. Lithium aluminum hydride smoothly reduced *N*-benzylidene-*tert*-butylamine to *N*-*tert*-butylbenzylamine. With allylmagnesium bromide, *N*-benzylidene-*n*-octadecylamine formed *N*-*n*-octadecyl(α-allylbenzyl)amine. *N*-Benzylidenemethylamine reacted with *tert*-butylmagnesium chloride to give *N*-methyl(α-*tert*-butylbenzyl)amine and with *n*-octadecylmagnesium iodide to give *N*-methyl(α-octadecylbenzyl)amine.

Campbell *et al.*[1] treated a number of *N*-benzylidenealkylamines with various alkylmagnesium halides to synthesize *N*-alkyl(α-alkylbenzyl)amines:

$$C_6H_5—CH{:}N—R' + RMgX \longrightarrow C_6H_5—CH(R)—NHR'$$

They found that, when equimolar amounts of Grignard reagent and aldimines were used, satisfactory yields (60–75%) were obtained only with the most reactive Grignard reagents and the simplest Schiff bases. Thus with *N*-benzylidenemethylamine ethylmagnesium bromide gave a 75% yield of *N*-methyl(α-ethylbenzyl)amine, but with *N*-benzylideneethylamine only a 39% yield of *N*-ethyl(α-ethylbenzyl)amine was obtained.

The present work was undertaken to obtain some knowledge of: (1) the effect of bulky alkyl groups in the Schiff base on the reactivity of the C:N; and (2) the steric requirements of the alkyl Grignard reagent. *N*-Benzylidene-*tert*-butylamine was selected as a bulky *N*-alkyl Schiff base, and *tert*-butylmagnesium chloride as a Grignard of high steric requirement.

N-Benzylidene-*tert*-butylamine was prepared by Hurwitz[2] in a 63% yield. However, he recorded no physical constants. Methylmagnesium iodide would not add to this Schiff base even under forcing conditions. This indicates that the steric requirements of the *N*-*tert*-butyl group are appreciable. On the other hand methyllithium did add to give *tert*-butyl(α-methylbenzyl)amine. Organolithium compounds are known to be much more reactive than the corresponding Grignard reagents.[3]

The failure of methylmagnesium iodide to react with *N*-benzylidene-*tert*-butylamine prompted an attempt to add allylmagnesium bromide. Gilman and Eisch[4] found that this latter Grignard reagent added in a 1,2-manner to aromatic ketimines having high steric requirements. In line with Gilman's observation we found that allylmagnesium bromide gave good yields of *N*-*tert*-butyl(α-allylbenzyl)-amine. The reactivity of this Grignard reagent as compared to that of methylmagnesium iodide seems to confirm Gilman's view that the mechanism of this 1,2-addition to the azomethine linkage proceeds by a nucleophilic attack of the allyl anion on the positively polarized carbon atom adjacent to the nitrogen in the Schiff base. The reactivity of allylmagnesium bromide was also shown by its addition to the high molecular weight *N*-benzylidene-*n*-octadecylamine to form *N*-octadecyl(α-allylbenzyl)amine.

N-Benzylidenemethylamine was used to test the reactivity of *tert*-butylmagnesium chloride. During the progress of this work Thies and Schoenenberger[5] carried out the same reaction but were unable to isolate any product from addition. They obtained only starting material and the dimer of the Schiff base, *N*,*N*′-dimethyl-1,2-diphenylethylenediamine. In this work the 1,2-addition product,

(1) K. N. Campbell, C. H. Helbing, M. P. Florkowski, and B. K. Campbell, *J. Am. Chem. Soc.*, **70**, 3868 (1948).

(2) M. D. Hurwitz, U. S. Patent **2,582,128**, (Jan. 8, 1952); *Chem. Abstr.*, **46**, 8146 (1952).

(3) H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **55**, 1265 (1933).

(4) H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **79**, 2150 (1957).

(5) H. Thies and H. Schoenenberger, *Arch. Pharm.*, **289**, 408 (1956).

TABLE I

N-ALKYL(α-ALKYLBENZYL)AMINES, (C_6H_5—CH(R)—NHR′)

R—	R′—	B. P., °C./mm. Hg	Yield, %	n_D^{25}	d_4^{25}	% N Calcd.	% N Found	Amine Hydrochloride M. P., °C.	% N Calcd.	% N Found
CH_3	*t*-C_4H_9	93/14	26	1.4896	0.884	7.91	7.96	240	6.55	6.59
H	*t*-C_4H_9	109–110/25	63	1.4942	0.899	8.58	8.57	245–247[a]	7.00	7.00
C_3H_5	*t*-C_4H_9	87–88/3	45	1.4954	0.888	6.89	6.94	186–187	5.85	5.87
C_3H_5	*n*-$C_{18}H_{37}$	27–29[b]	48			3.51	3.53[c]	124–126.5	3.22	3 20
t-C_4H_9	CH_3	92–92.5/10	22	1 5014	0.905	7.90	8.01	314–315	6.56	6.51
n-$C_{18}H_{37}$	CH_3	34.5–35[b]	11			3.75	3.78	118.5–119	3.42	3.40

[a] Recrystallized from 1–3 *n*-butyl alcohol–ethyl acetate. A. Einhorn and H. Pfeiffer [*Ann.*, **310**, 225 (1900)] report a melting point of 228°. [b] Melting point. [c] Material analyzed melted at 22–26°.

N-methyl(α-*tert*-butylbenzyl)amine was isolated in a 22% yield.

The facile tendency of *N*-benzylidenemethylamine to undergo addition was also demonstrated by the additon of *n*-octadecylmagnesium iodide to give *N*-methyl(α-*n*-octadecylbenzyl)amine in fair to good yields.

Gilman, Kirby, and Kinney[6] reported a case of 1,4-addition of phenylmagnesium bromide to *N*-diphenylmethyleneaniline under conditions involving high temperature and a long period of heating. To show that substitution did not occur in the ortho position of the benzene ring of our Schiff bases, we oxidized the addition products from: (1) *tert*-butylmagnesium chloride and *N*-benzylidenemethylamine; (2) methyllithium and *N*-benzylidene-*tert*-butylamine; and (3) allylmagnesium bromide and *N*-benzylidene-*tert*-butylamine. In all cases benzoic acid was obtained showing that there was only one substituent on the benzene ring.

In connection with this work a new Schiff base, *N*-benzylidene-*n*-octadecylamine, and five new secondary amines (Table I) have been characterized.

EXPERIMENTAL[7]

N-Benzylidene-tert-butylamine. To 30.0 g. of redistilled *tert*-butylamine (Eastman Grade) was added 44.5 g. of freshly distilled benzaldehyde at 2–3°. Stirring was continued for 30 min., and the reaction was allowed to stand 2 days over a few grams of sodium hydroxide. The aqueous layer which formed was removed and extracted with ether. The ether extract was added to the water-insoluble material and dried over potassium hydroxide. After removal of the ether, the product was distilled to give 60.0 g. (90%): b.p. 92°/8 mm., n_D^{25} 1.5179, d_4^{25} 0.904.

The procedure described by Freeman[8] was used to determine quantitatively the Schiff base as benzaldehyde 2,4-dinitrophenylhydrazone. Milliequivalents used: 1.074, 0.941. Found: 1.060, 0.940.

Methylmagnesium iodide and benzylidene-tert-butylamine. To the Grignard reagent prepared from 24.0 g. of magnesium and 125 g. of methyl iodide was added dropwise 43.0 g. of benzylidene-*tert*-butylamine (b.p. 110–112°/29 mm.) dissolved in an equal volume of ether, over a period of 20 min. The mixture was refluxed for 2 hr. It was hydrolyzed with ice. On acidification with concentrated hydrochloric acid a yellow solid formed, which was filtered off and added to a solution of 10 g. of concentrated hydrochloric acid in 100 ml. of water. The two liquid layers which formed overnight were separated. The organic layer yielded 9.7 g. of benzaldehyde: b.p. 60°/10 mm., $n_D^{17.8}$ 1.5461; oxidation product, m.p. 122–123°. The water layer was evaporated. It yielded a solid which after washing with ether weighed 18.6 g. Part of the solid was redissolved in water, filtered, and the filtrate made basic with sodium hydroxide and extracted with ether. On treatment with hydrogen chloride gas, the dried ether solution precipitated a white solid. The solid was filtered and treated with concentrated sodium hydroxide in contact with ligroin. Phenyl isothiocyanate was added to the dried ligroin solution. The precipitate which formed melted at 122–123°. Mixture m.p. with 1-phenyl-3-*tert*-butylthiourea prepared in ligroin from *tert*-butylamine and phenyl isothiocyanate, 122–124°.

The filtrate from the original Grignard mixture, consisting of an ether and a water phase, was next worked up. The ether was separated, dried over anhydrous magnesium sulfate, and then distilled yielding 6 g. of benzaldehyde, b.p. 83–85°/30 mm. It was identified as its air oxidation product, benzoic acid, m.p. 118–119°, and its 2,4-dinitrophenylhydrazone, m.p. 239–240°.

The water phase from the Grignard was made strongly basic with ammonium hydroxide and some ammonium chloride added to dissolve magnesium hydroxide. Extraction with ether and subsequent distillation gave 2.1 g. of unreacted *N*-benzylidene-*tert*-butylamine, determined as benzaldehyde-2,4-dinitrophenylhydrazone.[8] Milliequivalents used: 0.980. Found: 1.00

In another run when the Grignard reaction was forced in dry toluene at 100° for 2 hr. the same yellow solid was obtained. No addition product was isolated.

Lithium aluminum hydride and N-benzylidene-tert-butylamine. The reaction was carried out according to the procedure of Nystrom and Brown.[9] Lithium aluminum hydride (9.5 g., 0.25 mole) was dissolved in 400 ml. of ether. Forty grams (0.25 mole) of *N*-benzylidene-*tert*-butylamine was added dropwise in 35 min. The mixture was refluxed 4.5 hr. and then allowed to stand for 2 hr. It was hydrolyzed in the usual manner. The ether layer was separated and dried over anhydrous magnesium sulfate. After removal of the ether, the product distilled to give 32.5 g. (80%): b.p. 109–109.5°/23 mm., n_D^{25} 1.4956. This contained about 5% unreacted Schiff base which was removed by refluxing 0.5 hr. with dilute hydrochloric acid, washing with ether, making basic with sodium hydroxide, and extracting the amine with

(6) H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Am. Chem. Soc.*, **51**, 2252 (1929).

(7) The boiling points and melting points reported in this work are uncorrected. Those reported in Table I were taken with 76 mm. immersion thermometers.

(8) S. K. Freeman, *Anal. Chem.*, **25**, 1750 (1953).

(9) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).

ether. After drying, distillation gave 25.6 g. of pure amine, n_D^{25} 1.4942.

Methyllithium and N-benzylidene-tert-butylamine. An ether solution of 0.43 mole of methyllithium prepared by the procedure of Tegner[10] was added dropwise under nitrogen with stirring to 28.4 g. (0.177 mole) of freshly distilled benzylidene-*tert*-butylamine dissolved in 75 ml. of ether. The reaction mixture was refluxed for 10.5 hr., and then poured into 250 g. of ice. The organic layer was extracted with ether, dried over anhydrous magnesium sulfate, and distilled to give: 23 g., b.p. 88–90°/11 mm., n_D^{25} 1.4950. After removing unreacted Schiff base by acid hydrolysis, as described in the reduction with lithium aluminum hydride, distillation gave 8.0 g., n_D^{25} 1.4896.

The hydrochloride was prepared by passing dry hydrogen chloride into an ether solution of the amine. It was recrystallized from an equal mixture of ligroin (b.p. 90–100°) and butyl alcohol, m.p. 240°. Oxidation of the amine with sodium dichromate and sulfuric acid gave a poor yield of benzoic acid, m.p. and mixture m.p. 123–124°.

Allylmagnesium bromide and N-benzylidene-tert-butylamine. Fifty-three grams (0.330 mole) of *N*-benzylidene-*tert*-butylamine dissolved in an equal volume of ether was added dropwise to 0.385 mole of allylmagnesium bromide prepared as described by Mikulasova, Hrivik, and Simek.[11] The reaction mixture was refluxed for 2 hr. and then allowed to stand sealed for 19 hr. It was hydrolyzed with ice and then acidified with hydrochloric acid. A white solid formed which was filtered off 2 days later and dried. After washing with ether, 52.5 g. was obtained, m.p. 182–183°. Recrystallization from equal volumes of ligroin (90–120) and butyl alcohol gave 44.0 g. (56%): m.p. 186–187°. Further recrystallization did not change the melting point.

To obtain the free amine 44 g. of the *N-tert*-butyl(α-allylbenzyl)amine was added to 200 ml. of a 6% solution of sodium hydroxide and allowed to stand overnight. The organic layer was taken up with ether, dried over anhydrous magnesium sulfate, and distilled, yielding 30 g. of a colorless liquid: b.p. 87–88°/3 mm. The product gave no precipitate when tested with a 2*N* hydrochloric acid solution of 2,4-dinitrophenylhydrazine.

One gram of the distillate was oxidized with alkaline permanganate[12] and yielded 0.11 g. benzoic acid, m.p. 121.5–122.5°.

N-Benzylidene-n-octadecylamine. To a filtered solution of 23.4 g. of *n*-octadecylamine[13] in 200 ml. of methanol was added slowly, at 60°, 20.0 g. of benzaldehyde which had been previously washed with sodium carbonate solution. The mixture was permitted to cool slowly to room temperature and then kept at 5° for 4 hr. The solid which separated was filtered and washed with a little cold methanol, yield 27.5 g., m.p. 35.5–37°. Recrystallization from 500 ml. of methanol gave 23.5 g. of *N*-benzylidene-*n*-octadecylamine, m.p. 36–37°.

Anal. Calcd. for $C_{25}H_{43}N$: N, 3.91%. Found: N, 3.95%.

Allylmagnesium bromide and N-benzylidene-n-octadecylamine. Allylmagnesium bromide was prepared as indicated for the preparation of *N-tert*-butyl(α-allylbenzyl)amine, 36.3 g. of allyl bromide being used. To this was added, in 45 min., 21 g. of *N*-benzylidene-*n*-octadecylamine dissolved in 100 ml. of ether. The reaction mixture was refluxed 2 hr. and then allowed to stand overnight. The solid obtained by acid hydrolysis was filtered, dried, washed thoroughly with ether, and after two recrystallizations from a mixture of equal volumes of ligroin (90–120) and butyl alcohol weighed 19 g. (74%): m.p. 117–120°.

Conversion, in the usual manner, of the hydrochloride to the free amine gave a reddish liquid, which was crystallized by dissolving in methanol, and prolonged cooling. The filtered crystals, after drying in a vacuum desiccator, melted at 22–26°. Another recrystallization raised the melting point to 27–29°, yield 11.4 g. Dry hydrogen chloride was passed into an ether solution of the recrystallized amine to reconvert it to *N*-*n*-octadecyl(α-allylbenyl)amine hydrochloride, m.p. 124–126.5° after one recrystallization.

tert-Butylmagnesium chloride and N-benzylidenemethylamine. tert-Butylmagnesium chloride was prepared by a standard procedure.[14] Two moles (185 g.) of *tert*-butyl chloride was used. Addition of the initial batch of halide should be made cautiously. To the *tert*-butylmagnesium chloride, 60.0 g. (0.50 mole) of *N*-benzylidenemethylamine (b.p. 64–64.5°/8 mm.) was added in 0.5 hr. About 650 ml. of dry toluene was then added, and the ether was distilled off until the temperature of the reaction mixture reached 95°. It was maintained at this temperature and stirred for 1 hr. It was then cooled, sealed, and allowed to stand overnight. It was hydrolyzed with ice, made acidic with hydrochloric acid, and allowed to stand for 2 days to hydrolyze unreacted Schiff base. The ether-toluene layer was then separated, and the acid layer made basic with concentrated ammonium hydroxide. Solid ammonium chloride was added until most of the solid dissolved and the amine was extracted with ether. The ether layer was dried over solid potassium hydroxide and then distilled, yielding 24 g. of a colorless liquid, b.p. 53–70°/1 mm. The distillate residue solidified overnight. After washing with ether it melted at 132–134°. At the melting point it sublimed. The sublimate melted at 133°. This was probably *N*,*N*′-dimethyl-1,2-diphenylethylenediamine. Thies and Schoenenberger[5] recorded a melting point of 135° for this compound.

The distillate (b.p. 53–70°/1 mm.) was dissolved in ether and treated with dry hydrogen chloride to give 27.5 g. of a white solid, which after recrystallization from a solution of equal volumes of ligroin (90–120) and butyl alcohol melted at 314–315°. The nitrogen content (Table I) corresponded to that of *N*-methyl(α-*tert*-butylbenzyl)amine hydrochloride. Conversion, in the usual way, to the free amine gave 19.4 g. of *N*-methyl(α-*tert*-butylbenzyl)amine. Alkaline permanganate oxidation[12] of the amine gave, after 5 hr. refluxing with vigorous stirring, 0.2 g. of benzoic acid, which after recrystallization from water had a m.p. and mixture m.p. of 122–123°. No phthalic acid was produced in the oxidation.

When the Grignard reaction was not forced a slightly lower yield (14%) of the pure amine was obtained.

n-Octadecylmagnesium iodide and N-benzylidenemethylamine. This reaction was conducted several times. The results are considered anomalous because of unexplainable variations in the yields. The following run is described as typical.

n-Octadecyl iodide was prepared by a published procedure.[15] In a 1-l. three-neck flask equipped in the usual manner for Grignard preparations were placed 20 g. (0.83 g.-atom) of magnesium turnings and 120 g. of ethyl ether. A few crystals of iodine and about 0.5 ml. of methyl iodide were used to start the reaction. Sixty grams (0.158 mole) of *n*-octadecyl iodide dissolved in 200 g. of ether was added over a period of 4 hr. The reaction mixture was stirred for an additional 0.5 hr., and then 15 g. (0.126 mole) of *N*-benzylidenemethylamine dissolved in an equal volume of ether was added in 0.5 hr. while the reaction mixture was maintained at 32°. The product was then refluxed for 2 hr., after which the reaction flask was tightly corked and allowed to stand overnight. Hydrolysis and acidification with hydrochloric acid yielded a solid which was filtered from the ether-water

(10) C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952).

(11) D. Mikulasova, A. Hrivik, and I. Simek, *Chem. zvesti*, **10**, 622 (1956); *Chem. Abstr.*, **51**, 8002 (1957).

(12) B. L. Emling, J. E. Beatty, and J. R. Stevens, *J. Am. Chem. Soc.*, **71**, 703 (1949).

(13) Armeen 18D, supplied through the courtesy of Armour and Co.

(14) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York (1954), pp. 26, 27.

(15) C. A. Kind and W. Bergman, *J. Org. Chem.*, **7**, 424 (1942).

mixture. The ether was separated and preserved. The solid was washed thoroughly with dilute hydrochloric acid and then with water. It was dried and then shaken with ether for 40 min. The ether was added to that from the hydrolysis mixture. The solid was next washed twice with ligroin (60–90) and after drying weighed 14.6 g., m.p. 101–104°. Two recrystallizations from ethanol gave 7.5 g. (14.6%) of *N*-methyl(α-*n*-octadecylbenzyl)amine hydrochloride, m.p. 115–117.5°. Yields from several additional runs varied greatly, the two largest being 55% (m.p. 118–118.5°) and 48% (m.p. 118.5–119°).

In the run described the ether phase on evaporation gave 17.6 g. of octadecane, which on recrystallization from ethanol melted at 25–26°. The ligroin on partial evaporation and cooling gave 4.7 g. of hexatriacontane, m.p. 73–76°.

N-Methyl(α-*n*-octadecylbenzyl)amine hydrochloride (10 g.) was converted to the free amine by refluxing with an excess of 15% sodium hydroxide, extraction of the cold mixture with ether, and subsequent evaporation of the ether; yield 7.3 g. This was dissolved in methanol, filtered, and the methanol removed under vacuum to give 6.8 g.: m.p. 34.5–35°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Alkylation of Acylhydrazines. The Synthesis of Trimethylamine-benzimide

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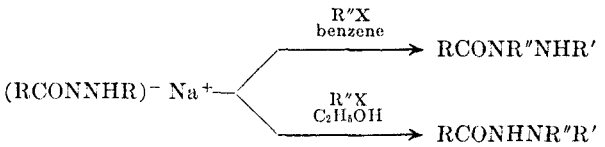
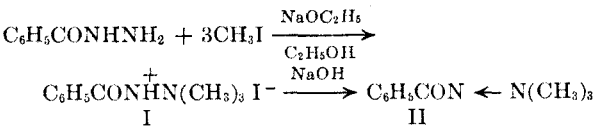
Trimethylamine-benzimide has been prepared from benzoylhydrazine and from 1-benzoyl-2,2-dimethylhydrazine by reaction with methyl iodide in the presence of sodium ethoxide. Under similar conditions 1-isonicotinyl-2,2-dimethylhydrazine was converted to trimethylamine-isonicotinimide, rather than 1-isonicotinyl-1,2,2-trimethylhydrazine, as previously reported. The reaction of benzoylhydrazine with *n*-propyl bromide, however, yielded only 1-benzoyl-2,2-di-*n*-propylhydrazine. Treatment of benzoylhydrazine with sodium in benzene, followed by methyl iodide, produced a small quantity of 1-benzoyl-1-methylhydrazine. A similar procedure converted 1-benzoyl-2,2-dimethylhydrazine to trimethylamine-benzimide.

Previous investigations of the alkylation of acylhydrazines have revealed that alkylation of the salt of a monoacylhydrazine in a nonpolar solvent such as ether or benzene takes place on the acylated nitrogen.[3] When alkylation is carried out in ethanol, the alkyl groups are introduced on the unacylated nitrogen.[3a,c,4] Treatment of the



acylhydrazine itself with alkylating agents in neutral solvents effects alkylation of the unacylated nitrogen[5], in accord with the electron-withdrawing properties of the acyl group. Although this pattern of behavior appears to be fairly general, the acylhydrazines studied have generally borne a substituent on the unacylated nitrogen. It was the purpose of the work reported here to examine the alkylation of a simple monoacylhydrazine (RCONHNH$_2$). The methylation of benzoylhydrazine was selected since the likely products are all known, easily accessible compounds.

From the reaction of an ethanolic solution of benzoylhydrazine, sodium ethoxide, and methyl iodide (mole ratio 1:2:2, respectively) an acidic product (I), containing ionic iodine, was isolated. Compound I was converted to the free base (II) by dissolving it in sodium hydroxide and extracting with chloroform. Analysis of the basic material and its hydriodide showed that three methyl groups had been introduced. Although the composition of 1-benzoyl-1,2,2-trimethylhydrazine agrees with the analytical data, from the high melting point[6] of II (167–169°) and the marked acidity of its hydriodide (decomposes bicarbonate) we inferred that the product of the reaction of benzoylhydrazine and methyl iodide in the presence of two moles of sodium ethoxide is the hydriodide of trimethylamine-benzimide (I), which is converted by base to trimethylamine-benzimide (II)[7]. Verifi-



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(2) Abstracted from the M.S. thesis submitted by Minerva C. Flores to the Graduate College of the State University of Iowa, August 1957.

(3) (a) P. C. Freer and P. L. Sherman, *J. Am. Chem. Soc.*, **18**, 574 (1896); (b) C. D. Harries, *Ber.*, **27**, 697 (1894); (c) W. Stühmer and E. A. Elbrachter, *Arch. Pharm.*, **285**, 161 (1952).

(4) K. von Auwers and G. Wegener, *J. prakt. Chem.*, (2), **102**, 243 (1923).

(5) See for example: R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

(6) A survey of the literature has revealed that substitution of an alkyl group for a hydrogen on the acylated nitrogen of an acylhydrazine is generally accompanied by a marked decrease in melting point. Thus, benzoylhydrazine melts at 112°, whereas 1-benzoyl-1-methylhydrazine is an oil. It would be expected that 1-benzoyl-1,2,2-trimethylhydrazine would melt below 106°, the m.p. of 1-benzoyl-2,2-dimethylhydrazine.

(7) For an explanation of the nomenclature of compounds of this type see H. H. Sisler, G. M. Omietanski, and B. Rudner, *Chem. Revs.*, **57**, 1021 (1957).