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°.

LATROBE, PA.

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

Alkylation of Acylhydrazines. The Synthesis of Trimethylamine-benzimide

R. L. HINMAN[1] AND MINERVA C. FLORES[2]

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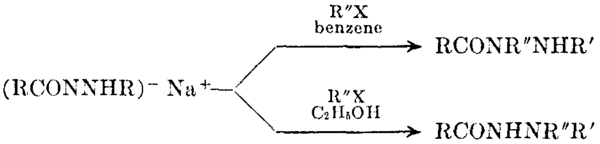
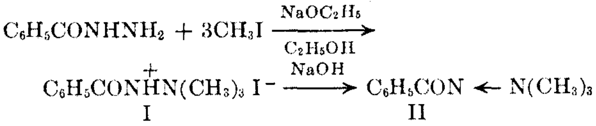
Trimethylamine-benzimide has been prepared from benzoylhydrazine and from 1-benzoyl-2,2-dimethylhydrazine by reaction with methyl iodide in the presence of sodium ethoxide. Under similar conditions 1-isonicotinyl-2,2-dimethylhydrazine was converted to trimethylamine-isonicotinimide, rather than 1-isonicotinyl-1,2,2-trimethylhydrazine, 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-



$$C_6H_5CONHNH_2 + 3CH_3I \xrightarrow[C_2H_5OH]{NaOC_2H_5}$$

$$\underset{\text{I}}{C_6H_5CONH\overset{+}{N}(CH_3)_3\,I^-} \xrightarrow{NaOH} \underset{\text{II}}{C_6H_5CON \leftarrow N(CH_3)_3}$$

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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).

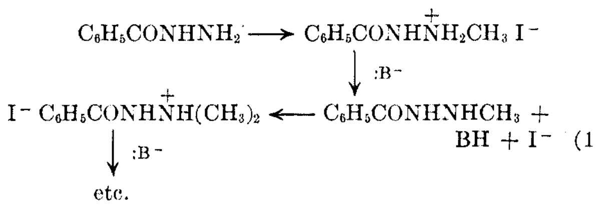
[6] A survey of the literature has revealed that substitution of an alkyl group for a hydrogen on the acylated nitrogen of an acylhydrazine is generally accompanied by a marked decrease in melting point. Thus, benzoylhydrazine melts at 112°, whereas 1-benzoyl-1-methylhydrazine is an oil. It would be 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).

cation of this hypothesis was obtained by hydrogenolysis of the nitrogen-nitrogen bond by Raney nickel in ethanol. From both the hydriodide and the free base benzamide was obtained. In addition trimethylamine was obtained from the cleavage of II. The best conditions found to date for the prep-

$$\underset{\text{II}}{C_6H_5CON \leftarrow N(CH_3)_3} \xrightarrow[C_2H_5OH]{Ni} C_6H_5CONH_2 + N(CH_3)_3$$

aration of II from benzoylhydrazine require a reaction time of 10 hr., and a molar ratio of benzoyl hydrazine, sodium ethoxide, and methyl iodide of 1:2:4, respectively. The relative quantity of sodium ethoxide is particularly critical. With a mole ratio of benzoylhydrazine, sodium ethoxide, and methyl iodide of 1:2:2, respectively, the yield of I was 36%. When the ratio was 1:1:2, respectively, the yield of I was only 8%. Since the alkylation of benzoylhydrazine undoubtedly occurs in a stepwise fashion, the sodium ethoxide must be consumed in removing a proton after each step of the alkylation (Equation 1). When only one mole of base is present per mole



$$\begin{tikzcd} & C_6H_5CONHNH_2 \arrow[r] & C_6H_5CONH\overset{+}{N}H_2CH_3\ I^- \arrow[d, ":B^-"] \\ I^-\ C_6H_5CONH\overset{+}{N}H(CH_3)_2 \arrow[d, ":B^-"] & & C_6H_5CONHNHCH_3 + BH + I^- \arrow[ll] \\ \text{etc.} & & \end{tikzcd} \quad (1)$$

of benzoylhydrazine, the principal reaction probably stops when 1-benzoyl-2,2-dimethylhydrazinium iodide is formed. Conversion of a small quantity of the last compound to 1-benzoyl-2,2-dimethylhydrazine by reaction of the hydriodide with sodium ethoxide before the latter is exhausted would account for the formation of the small amount of trimethylamine-benzimide which was isolated.

Benzoylhydrazine itself must also be capable of acting as the base in Equation 1, since 1-benzoyl-2,2-dimethylhydrazine was isolated in 8% yield from the alkylation of benzoylhydrazine in neutral solution. Thirty-two percent of the starting material was recovered. Since the reaction time was twenty-four hours, and a large excess of methyl iodide was used, it is unlikely that the recovered benzoylhydrazine simply did not undergo alkylation. More likely it was converted to its salt by proton-abstraction from alkylated molecules, and was thereby prevented from undergoing alkylation itself.

As would be expected, 1-benzoyl-2,2-dimethylhydrazine was converted by methyl iodide to 1-benzoyl-2,2,2-trimethylhydrazinium iodide by simply refluxing an alcoholic mixture of the two reagents. The use of 1 mole of sodium ethoxide per mole of 1-benzoyl-2,2-dimethylhydrazine and an excess of methyl iodide produced trimethylamine-benzimide directly.

Recently reported results of the alkylation of 1-isonicotinyl-2,2-dimethylhydrazine conflict with the results reported here for the reaction of 1-benzoyl-2,2-dimethylhydrazine. It has been claimed[8] that the reaction of methyl iodide with 1-isonicotinyl-2,2-dimethylhydrazine in the presence of sodium ethoxide yields 1-isonicotinyl-1,2,2-trimethylhydrazine. No proof of structure was given.

$$C_5H_5NCONHN(CH_3)_2 \xrightarrow[NaOC_2H_5]{CH_3I} C_5H_5NCON(CH_3)N(CH_3)_2$$

The fact that the melting point of the product (191.5–193.5°) is much higher than that of the starting material (120–121°)[9] raises considerable doubt about the position of the newly introduced methyl group.[6] The methylation of 1-isonicotinyl-2,2-dimethylhydrazine was therefore repeated according to the original directions, and the compound of m.p. 191.5–193.5° was obtained. Hydrogenolysis of this material with Raney nickel yielded isonicotinamide and trimethylamine, proving that the product of the methylation of 1-isonicotinyl-2,2-dimethylhydrazine is actually trimethylamine-isonicotinimide (IV).

$$C_5H_5NCONHN(CH_3)_2 \xrightarrow[NaOC_2H_5]{CH_3I} C_5H_5NCON \leftarrow N(CH_3)_3 \quad \text{IV}$$

Other compounds prepared by alkylation of 1-isonicotinyl - 2,2 - dimethylhydrazine with higher alkyl halides were assumed by the same authors to have the structures of 1-isonicotinyl-1,2,2-trialkylhydrazines. From the present work, however, it seems likely that some, if not all, of these compounds are of the amine-imide type. The water-solubility of the compound described as 1-isonicotinyl-1-benzyl-2,2-dimethylhydrazine is more in accord with an amine-imide structure. Until a conclusive proof of structure has been carried out, the structures of this series of compounds will remain in doubt.

In exploring the scope of the conversion of benzoylhydrazines to amine-imides, the reaction of benzoylhydrazine and *n*-propyl bromide was investigated. Even with a mole ratio of 1:2:6 (acylhydrazine: base: alkyl halide) the only product isolated was 1-benzoyl-2,2-di-*n*-propylhydrazine.[10] No reaction occurred when 1-benzoyl-2,2-di-*n*-propylhydrazine was refluxed with ethanolic solutions of *n*-propyl bromide or methyl iodide. The formation of trialkylamine-benzimides or their hydrohalides under the conditions used in this study is therefore limited to the reactions of benzoylhydrazines bearing small alkyl groups in the dialkyl stage of alkylation.[11]

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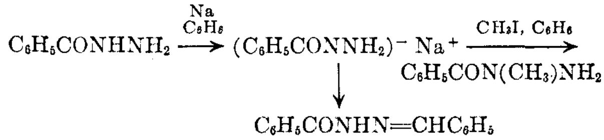
[8] H. H. Fox and J. T. Gibas, *J. Org. Chem.*, **21**, 356 (1956).

[9] H. H. Fox and J. T. Gibas, *J. Org. Chem.*, **20**, 60 (1955).

The trialkylamine-benzimides prepared in this investigation represent the first examples of amine-imides in which one nitrogen bears a simple acyl group. Previously reported examples have borne the tosyl group and various other substituents.[7]

We turned our attention next to the reaction of methyl iodide with the sodium salt of benzoylhydrazine in benzene. Using a mole ratio of benzoylhydrazine, sodium and methyl iodide of 1:1:1, a large part of the sodium salt of benzoylhydrazine was recovered unreacted. The products consisted of a small quantity of 1-benzoyl-1-methylhydrazine and a larger amount of a neutral solid, which proved to be 1-benzoyl-2-benzylidenehydrazine.[12]



$$C_6H_5CONHNH_2 \xrightarrow{\substack{Na\\C_6H_6}} (C_6H_5CONNH_2)^- Na^+ \xrightarrow{CH_3I,\ C_6H_6} C_6H_5CON(CH_3)NH_2$$
$$\downarrow$$
$$C_6H_5CONHN{=}CHC_6H_5$$

From this result it was expected that 1-benzoyl-1,2,2-trimethylhydrazine would be formed from 1-benzoyl-2,2-dimethylhydrazine, when the latter was refluxed with sodium and then treated with methyl iodide. However, trimethylamine-benzimide was isolated in this case.

The results obtained in this study support the general observation that alkylation of an acylhydrazine in neutral solution takes place on the unacylated nitrogen. In the presence of sodium ethoxide in ethanol alkylation of an acylhydrazine also takes place on the unacylated nitrogen. When the salt of the acylhydrazine is formed in an inert solvent and alkylated therein, alkylation *may* take place on the nitrogen which bears the acyl group. Since salts are presumably formed under both of the last two sets of conditions,[10,13] the difference in the products may be due to incomplete conversion of the acylhydrazine to its salt in ethanolic sodium ethoxide with the result that it is actually the unreacted acylhydrazine which undergoes alkylation. Hydrolysis of salts of this type in ethanol has been reported.[13a,b]

EXPERIMENTAL[14]

Reaction of benzoylhydrazine and methyl iodide in the presence of sodium ethoxide. A solution of methyl iodide (56.8 g., 0.4 mole) in 25 ml. of absolute ethanol was added to a stirred solution of 4.6 g. (0.2 mole) of sodium and 13.6 g. (0.1 mole) of benzoylhydrazine in 140 ml. of absolute ethanol (previously dried with sodium and diethyl phthalate). Initially, the solution was a deep yellow, but after 10 hr. of refluxing the color was pale yellow, and the *p*H was 4–5. The stirred reaction mixture was then cooled until a white crystalline precipitate was deposited. The filtered solid weighed 15.0 g. (49%) and melted at 187–189° (dec.). Three crystallizations from absolute ethanol gave an analytical sample, m.p. 194–196° (dec.), which gave a yellow precipitate with aqueous silver nitrate, decomposed aqueous sodium bicarbonate, and had the composition of 1-benzoyl-2,2,2-trimethylhydrazinium iodide.

Anal. Calcd. for $C_{10}H_{15}N_2OI$: C, 39.21; H, 4.90; N, 9.01. Found: C, 39.13; H, 5.03; N, 9.08.

Trimethylamine-benzimide. The procedure above was repeated, but in working up the reaction mixture the solvent was distilled under reduced pressure. The residue from the distillation was made basic with 6*N* sodium hydroxide and extracted with chloroform. After the combined extracts had been dried over magnesium sulfate, the solvent was removed under reduced pressure and *n*-pentane was added to the residue. The white crystals which formed were collected on a filter. Recrystallization from a mixture of chloroform and *n*-pentane provided an analytical sample, m.p. 168–169°.

Anal. Calcd. for $C_{10}H_{14}N_2O$: C, 67.41; H, 7.86; N, 15.72. Found: C, 67.15; H, 7.85; N, 15.07.

Trimethylamine-benzimide was also obtained when a sample of 1-benzoyl-2,2,2-trimethylhydrazinium iodide was treated with 6*N* sodium hydroxide and the solution then extracted with chloroform. Evaporation of the chloroform left the product as a crystalline residue.

Hydrogenolysis of trimethylamine-benzimide. A mixture of 0.6 g. of trimethylamine-benzimide, 10 g. of Raney nickel, and 50 ml. of absolute ethanol was refluxed with vigorous stirring for 3 hr.[15] The liberated gas was entrained with nitrogen and passed through a solution of hydrochloric acid. The Raney nickel was collected on a filter and the alcoholic

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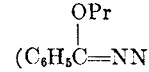
(10) It has been reported [D. Liberman, F. Grumbach, and N. Rist, *Compt. rend.*, **237**, 338 (1953)] that the reaction of benzoylhydrazine and *n*-propyl bromide in the presence of sodium ethoxide yields a product with one alkyl group on oxygen and one on the terminal nitrogen



$(C_6H_5\overset{OPr}{\overset{|}{C}}{=}NNHPr)$. However, the infrared spectrum of the product shows the two characteristic bands of a secondary amide in the carbonyl region, where it is almost identical with the spectrum of 1-benzoyl-2,2-dimethylhydrazine. It seems certain that both propyl groups are attached to the terminal nitrogen. Similar structures bearing alkyl groups on oxygen and nitrogen, proposed for the products of alkylations of isonicotinylhydrazine, have been refuted by Fox and Gibas [*J. Org. Chem.*, **21**, 349 (1956)], who also showed that both alkyl groups are attached to the terminal nitrogen.

(11) Our experiments also suggest that if two alkyl groups are small, a larger, third one can be introduced. Thus, 1-benzoyl-2,2-dimethylhydrazine reacted with *n*-propyl bromide, yielding a product which had the characteristics of an amine-imide hydrobromide, *i.e.* it contained ionic bromine, was sufficiently acidic to decompose bicarbonate, and was converted to a bromine-free compound on treatment with base. Neither the hydrobromide nor the supposed free base could be purified sufficiently for analysis, however, and the study was terminated without a satisfactory structure proof.

(12) 1-Benzoyl-2-benzylidenehydrazine may have been formed in a manner similar to the well known MacFayden-Stevens synthesis of aldehydes from 1-acyl-2-sulfonylhydrazines; *i.e.* during the reaction with sodium, part of the benzoylhydrazine was converted to benzaldehyde or an equivalent fragment, which then reacted with more benzoylhydrazine to give the hydrazone. The last substance has been isolated on other occasions from reactions of benzoylhydrazine under alkaline conditions: see for example, Th. Curtius, *Ber.*, **33**, 2560 (1900); Th. Curtius and R. Melsbach, *J. prakt. Chem.*, [2], **81**, 505 (1901). In this laboratory 1-benzoyl-2-benzylidenehydrazine was obtained in low yield from the attempted reduction of benzoylhydrazine with lithium aluminum hydride.

(13) (a) Th. Curtius and G. Struve, *J. prakt. Chem.* [2], **50**, 295 (1894); (b) Th. Curtius and O. Trachmann, *J. prakt. Chem.*, [4], **51**, 165 (1895).

(14) Melting points are uncorrected.

(15) R. L. Hinman, *J. Org. Chem.*, **22**, 148 (1957).

filtrate evaporated to dryness. After recrystallization from water the residue melted at 126–127°, and did not depress the m.p. of an authentic sample of benzamide. The yield was 0.21 g. (51%). The hydrochloric acid solution was also evaporated to dryness. The residue was recrystallized from a mixture of absolute ethanol and ether, and then melted at 276–278° (dec.). It did not depress the m.p. of an authentic sample of trimethylamine hydrochloride.

Hydrogenolysis of 1-benzoyl-2,2,2-trimethylhydrazinium iodide. The procedure used for the hydrogenolysis of trimethylamine-benzimide was employed and an 88% yield of benzamide was obtained.

Reaction of benzoylhydrazine, sodium, and methyl iodide in benzene. A mixture of 13.6 g. (0.1 mole) of benzoylhydrazine, 2.3 g. (0.1 mole) of sodium, and 150 ml. of dry benzene was refluxed with vigorous stirring until the sodium had disappeared (about 48 hr.). A creamy, water-soluble precipitate formed. After the mixture had been cooled, 14.2 g. (0.1 mole) of methyl iodide in 30 ml. of benzene was added and stirring was continued for 15 min. more. The mixture was filtered and the filtrate was evaporated to dryness, giving approximately 0.5 g. of an oil (A) which was shown to be 1-benzoyl-1-methylhydrazine (see below). The filtered solid (B), which melted above 300°, was partially soluble in water, giving a basic solution. Neutralization of this solution with hydrochloric acid produced a creamy, water-insoluble precipitate (C), which melted at 204–206°. Compound C was also obtained by recrystallization of B from an acetic acid–water mixture. The melting point of an authentic sample of the benzoylhydrazone of benzaldehyde (m.p. 206°[16]) when mixed with compound C showed no depression. The solid (B), isolated by filtration of the original reaction mixture, was therefore the sodium salt of 1-benzoyl-2-benzylidenehydrazine. The over-all yield of the hydrazone (C) was 4.5 g. (40%).

p-Nitrobenzaldehyde (0.2 g.), was added to approximately 0.2 g. of the oil (A) obtained in the previous experiment in 7 ml. of glacial acetic acid. The homogeneous mixture was heated to boiling and after cooling, crystallization was induced by addition of water. The crystals, which were collected on a filter, melted at 172–174°. A mixed melting point with an authentic sample of the 1-benzoyl-1-methylhydrazone of *p*-nitrobenzaldehyde (reported m.p. 172–173°[17]) showed no depression.

The reaction of benzoylhydrazine and methyl iodide in neutral solution. A solution of benzoylhydrazine (6.8 g., 0.05 mole) in 10 ml. of absolute ethanol and 71 g. (0.5 mole) of methyl iodide was refluxed for 24 hr. At the end of this period, the acidic solution (*p*H 1–2) was concentrated under reduced pressure. The residue was a dark oil which partially crystallized on standing. The crystals were collected by filtration, and the filtrate (A) was set aside. The crystals, m.p. 185–187°, were water-soluble and the water solution gave a positive test for iodide with silver nitrate. This compound, which was apparently 1-benzoyl-2,2-dimethylhydrazinium iodide, was treated with 6*N* sodium hydroxide and the solution was extracted with chloroform; upon evaporation of the solvent a white crystalline product was obtained, m.p. 99–103°, which did not depress the melting point of an authentic sample of 1-benzoyl-2,2-dimethylhydrazine. The yield was 0.65 g. (8%). The hydrochloride of the product was prepared and it did not depress the melting point of an authentic sample of 1-benzoyl-2,2-dimethylhydrazinium chloride (see below). From the residual dark oil (filtrate A) benzoylhydrazine (2.2 g., 32%) was recovered by neutralization with 6*N* sodium hydroxide and extraction with chloroform.

When the above procedure was repeated without the addition of absolute ethanol, the yield of 1-benzoyl-2,2-dimethylhydrazine was 0.6 g. (7%).

1-Benzoyl-2,2-dimethylhydrazinium chloride. Hydrogen chloride was bubbled through a solution of 0.5 g. of 1-benzoyl-2,2-dimethylhydrazine in 23 ml. of chloroform for 30 min. After evaporation of the solvent on a steam bath, the solid residue was recrystallized from a mixture of chloroform and *n*-hexane to provide an analytical sample, m.p. 187–188° (dec.).

Anal. Calcd. for $C_9H_{13}N_2OCl$: C, 53.80; H, 6.48; N, 13.96. Found: C, 53.36; H, 6.36; N, 14.53.

Reaction of 1-benzoyl-2,2-dimethylhydrazine and methyl iodide in the presence of sodium ethoxide. Methyl iodide (9 g., 0.063 mole) in 10 ml. of absolute ethanol was added to a solution of 0.6 g. (0.025 mole) of sodium in 60 ml. of absolute ethanol and 4.1 g. (0.025 mole) of 1-benzoyl-2,2-dimethylhydrazine.[5] The mixture was refluxed for 10 hr., at the end of which the *p*H of the solution was 4–5. The solvent was distilled under reduced pressure and the residue was treated as in the procedure described above for the isolation of trimethylamine-benzimide. The yield was 2.1 g. (48%) of trimethylamine-benzimide, m.p. 167–169°.

Reaction of 1-benzoyl-2,2-dimethylhydrazine, sodium, and methyl iodide, in benzene. (A) In a 1:1:1 mole proportion. A mixture of 4.1 g. (0.025 mole) of 1-benzoyl-2,2-dimethylhydrazine, 0.6 g. (0.025 mole) of sodium, and 50 ml. of dry benzene, was refluxed for 6 hr. During this period a precipitate separated. After the solution had been cooled, 3.5 g. (0.025 mole) of methyl iodide in 10 ml. of benzene was added and the reaction mixture was refluxed for 1 hr. more. The solvent was distilled under reduced pressure and the residue was dissolved in chloroform and washed with water. The chloroform solution was dried over magnesium sulfate and the solution evaporated to dryness. The residual oil crystallized on standing giving a few crystals of trimethylamine-benzimide, m.p. 162–164° (167–169° after recrystallization from a mixture of chloroform and *n*-hexane).

(B) With a 1:1:2 mole proportion and 10-hr. reflux period. The reaction was carried out using procedure A but 7.1 g. (0.05 mole) of methyl iodide was used and the reaction was refluxed for 10 hr. instead of 1 hr. after the addition of this reagent. The yield was 2.1 g. (48%) of trimethylamine-benzimide, m.p. 167–169°.

Trimethylamine-isonicotinimide. Methyl iodide (3.6 g,. 0.025 mole) was added to a solution of 0.6 g. (0.025 mole) of sodium and 4.1 g. (0.025 mole) of 1-isonicotinyl-2,2-dimethylhydrazine[9] in 50 ml. of absolute ethanol. The mixture was refluxed for 5 hr. (*p*H 7–8), at the end of which the ethanol was removed and the residue was treated with an excess of ammonium hydroxide which was also removed under reduced pressure. The residue was extracted with chloroform and the chloroform solution was dried over magnesium sulfate and then distilled partially under reduced pressure; crystallization was induced by addition of isopentane. The white crystals melted at 191–192° (reported[8] m.p. 191.5–193.5°) and weighed 1.8 g. (40%).

Hydrogenolysis of trimethylamine-isonicotinimide. A mixture of 1 g. of the product of the previous reaction, 15 g. of Raney nickel, and 60 ml. of 95% ethanol was refluxed with vigorous stirring for 3 hr. The liberated gas was entrained with nitrogen and passed through a solution of hydrochloric acid. The Raney nickel was collected on a filter and the filtrate evaporated to dryness; the residue was recrystallized from a mixture of chloroform and *n*-pentane, yielding white crystals which melted at 155–156° (reported[18] m.p. of isonicotinamide 155.5–156°).

The hydrochloric acid solution was evaporated to dryness and the residue, after recrystallization from a mixture of absolute ethanol and ether, melted at 272–274° (dec.). The melting point of a mixture with an authentic sample of trimethylamine hydrochloride showed no depression.

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(16) A. Michaelis and E. Hadanck, *Ber.*, **41**, 3288 (1908).

(17) R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).

(18) I. Heilbron and H. H. Bunbury, *Dictionary of Organic Compounds*, Vol. 3, Eyre and Spottisworde, London 1953, p. 97.

1-Benzoyl-2,2-di-n-propyl-hydrazine. Prepared by the method of Liberman, Grumbach, and Rist[10] (mole ratio of benzoylhydrazine: sodium ethoxide: *n*-propyl bromide = 1:2:2, reaction time, 10 hr.), the yield was 30%. When the mole ratio was increased to 1:2:6, and the reaction time to 18 hr., the yield was 70%. M.p. and reported[10] m.p. 100–101°. The infrared spectrum of a sample in a potassium bromide pellet showed two strong bands at 1535 cm.$^{-1}$ and 1653 cm.$^{-1}$, characteristic of a secondary amide.[19] A strong band characteristic of bonded N—H appeared at 3210 cm.$^{-1}$ 1-Benzoyl-2,2-dimethylhydrazine has similar bands at 1555, 1653, and 3250 cm.$^{-1}$

1-Benzoyl-2,2-di-*n*-propylhydrazine was recovered unchanged from 20 hr. of refluxing with a large excess of either *n*-propyl bromide or methyl iodide in ethanolic solution.

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[19] L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* John Wiley, New York, 1954, p. 175. See also; R. L. Hinman, *J. Am. Chem. Soc.,* **78,** 1645 (1956).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KENTUCKY]

Ultraviolet Spectra of *N*-Sulfinyl Amines. Influence of Structure and Solvent[1]

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The ultraviolet spectra of some *N*-sulfinylanilines have been determined in ether and in several alcohols. The effect of substituents on the spectra and on the reaction of *N*-sulfinylanilines with alcohol is discussed.

The ultraviolet absorption spectra of some aliphatic and aromatic *N*-sulfinyl amines in hexane and cyclohexane have been reported by Mangini and Leandri.[2]

The work reported here is concerned with the spectra of some of these compounds in ether and in alcohols. In the cases where we have measured the spectra of compounds reported by Mangini and Leandri we find that there is little difference, if any, between the spectra in ether and in cyclohexane. Our work in ether has been primarily concerned with studying steric effects of ring substituents in *N*-sulfinylaniline. Such work, together with the spectra in alcohol, is of value in interpreting the structure of the NSO group.

The aliphatic *N*-sulfinyl amines characteristically absorb at about 230–240 $m\mu$. The aromatic derivatives have a first primary band[3] at about 314–330 $m\mu$, and in addition have a second primary band at about 230–240 $m\mu$. The exact position of the first primary band is influenced to a small extent by the nature and position of a single substituent on the aromatic ring.

We interpret the second primary band (at 230–240 $m\mu$) as being due to the ordinary isolated NSO grouping. The first primary band (at 314–330 $m\mu$) is apparently due to the overall conjugated system consisting of the NSO group and the aromatic ring.

To obtain evidence that the band at 313–330 $m\mu$ is due to the conjugation of the NSO group with the aromatic ring we have prepared 2,4-dimethyl-*N*-sulfinylaniline and 2,6-dimethyl-*N*-sulfinylaniline and have compared the spectra of these two compounds.

In order for the NSO group to be conjugated with the aromatic ring the sulfur and nitrogen must be coplanar with the ring. Molecular models show that there will be considerable interference between the NSO group of *N*-sulfinylaniline and methyl groups in the *ortho* position. A comparison of the spectra of 2,4-dimethyl-*N*-sulfinylaniline shows that the interference caused by two *ortho* methyls has a pronounced effect on the spectra. 2,4-dimethyl-*N*-sulfinylaniline has a log ϵ of 4.05 at 337 $m\mu$. In the 2,6-isomer the first primary band at 337 $m\mu$ has shifted to shorter wave lengths and has decreased in intensity to such an extent (log ϵ 3.27) that it is apparent only as a shoulder at 285 $m\mu$ of the second primary band. This result is in agreement with the idea outlined above that the first primary band is due to the over-all system consisting of the aromatic ring and the NSO group.

A secondary band which is either absent or is fused with the first primary band in 2,4-dimethyl-*N*-sulfinylaniline is accentuated by the two *ortho* methyl groups and appears at 367 $m\mu$, log ϵ 3.24.

The shift of the first primary band to longer wave lengths in 2-methyl-, 4-methyl-, and 2,4-dimethyl-*N*-sulfinylanilines appears to be related to the methyl substituents. Thus unsubstituted *N*-sulfinylaniline has a maximum at 314 $m\mu$. The introduction of a methyl group in the 4-position shifts the maximum 14 $m\mu$ to 328 $m\mu$. A 2-methyl substituent shifts the maximum 8 $m\mu$ to 322 $m\mu$. In 2,4-dimethyl-*N*-sulfinylaniline the shift is 23 $m\mu$. This is approximately equal to the

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[2] A. Mangini and G. Leandri, *Spectrochim. Acta,* **8,** 283 (1956). Also paper presented at XVIth International Congress of Pure and Applied Chemistry, Paris, July 1957.

[3] L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.,* **69,** 2715 (1947).