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

Nitrosative Cleavage of *N'*,*N'*-Dialkylhydrazides and Tertiary Amines

PETER A. S. SMITH AND HARRY G. PARS[1]

Received April 29, 1959

N-Benzamidopiperidine (I) and *N*-benzamidopyrrolidine (IV) have been found to undergo attack by nitrous acid at the tertiary nitrogen atom, resulting in ring cleavage to give a carboxylic acid (II) and an aldehyde (V), respectively, each bearing a benzoylnitrosohydrazino substituent. Evidence for similar reactions was obtained with *N*-benzamido-2,6-lupetidine (VII), *N*-benzamidomorpholine and *N'-tert*-butyl-*N'*-neopentylbenzhydrazide. *N*-*p*-toluenesulfonamidopiperidine gave di-*p*-toluenesulfonylhydroxylamine, and *N*-benzoyloxypiperidine gave only its nitrate salt. The cleavage reactions are presumed to take place through formation of a nitrosammonium ion (IX), followed by elimination of nitroxyl (NOH) to give an aldimmonium or hydrazonium ion (X), which then hydrolyzes. It is demonstrated to occur even with the sample tertiary amines tribenzylamine and tributylamine.

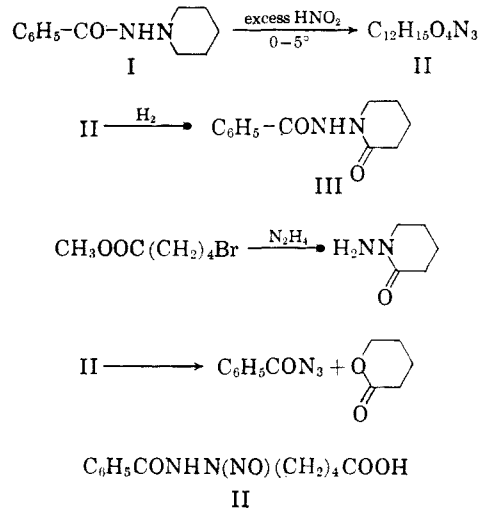
Some hydrazine derivatives, notably *N*,*N*-dialkylhydrazines, react with nitrous acid to produce nitrous oxide, one of whose nitrogen atoms comes from the hydrazine.[2] The research which we are about to describe was begun in the hope of carrying out such a reaction with *N'*,*N'*-dialkylhydrazides, which might be expected to give dialkylamides as the organic products. Such a reaction might have unusual utility in synthesis, inasmuch as its application to cyclic hydrazides, such as pyrazolidones, would bring about ring-contraction, giving lactams one atom smaller than the original ring.

In this paper we describe the nitrosation of a group of *unsym*-dialkylhydrazides in which the hydrazide structure is open chain. Neither they nor cyclic hydrazides, whose nitrosation will be described in another communication, gave the desired reaction. Instead, a totally different behavior was observed, in which nitrogen-to-carbon instead of nitrogen-to-nitrogen bonds were ultimately broken.

The required hydrazides were prepared by acylating *unsym*-dialkylhydrazines by customary methods. The hydrazines were prepared by reducing nitrosamines with either lithium aluminum hydride or zinc dust and aqueous acetic acid. The nitrosamines were most conveniently prepared by heating water solutions of the amine hydrochloride with sodium nitrite on a steam bath for several hours.

N-Benzamidopiperidine (I) was the first compound studied. It was found to react with excesss nitrous acid at 0° to give a crystalline acidic substance (II), $C_{12}H_{15}N_3O_4$. Infrared absorption at 1665 cm.$^{-1}$ and 1700 cm.$^{-1}$ indicated the presence of two carbonyl groups, probably amide and carboxyl; broad absorption in the 3200 cm.$^{-1}$ regions, attributable to associated hydroxyl (and perhaps obscuring N—H) supported the latter assignment.

Catalytic reduction of II produced 1-benzamido-2-piperidone (III), prepared independently from 1-amino-2-piperidone, obtained from the reaction of methyl δ-bromovalerate with hydrazine. Compound II gave Liebermann's nitroso test and readily decomposed to give benzoyl azide and a neutral liquid product whose infrared spectrum suggested impure δ-valerolactone. Potentiometric titration showed the presence of two acidic functions, and a *p*-bromophenacyl ester could be prepared. On the basis of these observations, the structure shown (II) and the indicated reactions were deduced.

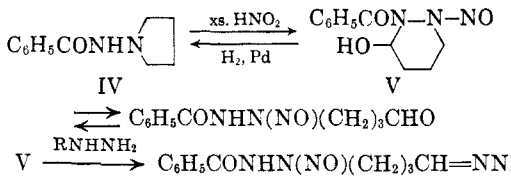


Nitrosation of *N*-benzamidopyrrolidine (IV) produced a crystalline solid, $C_{11}H_{13}O_3N_3$ (V), which formed a semicarbazone and a 2,4-dinitrophenylhydrazone. Its infrared spectrum showed but one carbonyl group (1655 cm.$^{-1}$), probably amide rather than aldehyde or ketone, and hydroxyl absorption at 3380 cm.$^{-1}$ It dissolved in sodium bicarbonate solution, but not in water, and gave Liebermann's nitroso test. On attempted bromination, benzoyl azide was produced. Catalytic hydrogenation gave 1-benzamidopyrrolidine.

From these observations we deduce the carbinolamine structure (V), which is assumed to be in labile equilibrium with an open-chain aldehyde.

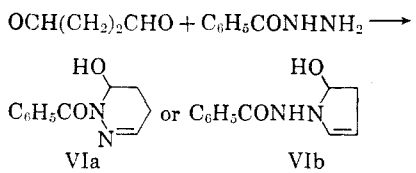
(1) From the doctoral dissertation of H. G. P., 1958; Union Carbide Corp. Fellow, 1956; Procter and Gamble Co. Fellow, 1956–1957.

(2) E. Fischer, *Ann.*, **190**, 158 (1877).



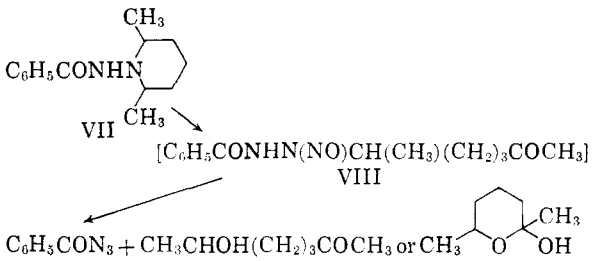
An alternate structure in which the nitroso group is on the amide nitrogen and the carbinolamine ring is five-membered is improbable in two respects. *N*-Nitrosocarboxamides show carbonyl absorption at considerably higher frequencies (1700 cm.$^{-1}$) than do ordinary amides[3]; compound V, however, absorbs at 1656 cm.$^{-1}$, comparable to the 1645 cm.$^{-1}$ band of the parent compound, 1-benzamidopyrrolidine. The alternate structure, having no amide hydrogen and not being able to tautomerize to such a structure, cannot account for the observed acidity. It might also be noted that such an alternate structure could not give rise to benzoyl azide without rearrangement, whereas structure V can cleave in a natural fashion to give benzoyl azide.

We attempted an independent synthesis of structure V from succindialdehyde. Treatment with benzhydrazide gave a monohydrazone, presumably the carbinolamine (VIa or b), since its infrared spectrum showed no carbonyl absorptions above 1640 cm.$^{-1}$, the amide position. This compound unfortunately could not be selectively reduced to 1-benzoylpyridazolidine, which would have allowed the synthesis to be completed by nitrosation, but was reduced all the way to 1-benzamidopyrrolidine, a result which supports structure VIb.



Nitrosation of 1-benzamido-2,6-lupetidine (VII) was much more difficult than nitrosation of 1-benzamidopiperidine, and no significant reaction was observed after 5 days at 0–5°. At 25–30°, however, nitrosation occurred, but the primary product of nitrosation apparently does not survive such reaction conditions, as diphenylurea, undoubtedly derived from benzoyl azide, was the only product positively identified in repeated attempts.

If the reaction followed a course parallel to that of the two previous hydrazides, the primary product would have been the ketone VIII, which under the influence of the warm, acidic reaction conditions would be expected to break up into benzoyl azide and 6-hydroxyheptanone-2. Although this compound could not be positively identified, the evidence suggests that a neutral oil isolated from the reaction mixture had this structure or was a simple transformation product of it.



6-Hydroxyheptanone-2 would be expected to exist largely as a hemiacetal, thus sequestering the chemically available carbonyl group from infrared detection. Weak absorption was actually observed at 1720 cm.$^{-1}$, the saturated ketone position, and also at 1660 cm.$^{-1}$, as well as strong, broad absorption at 3360 cm.$^{-1}$ attributable to hydroxyl. A trace of impure 2,4-dinitrophenylhydrazone was obtained, and hypoiodite oxidation gave iodoform. Phenyl isocyanate reacted vigorously, but only diphenylurea could be isolated. The chemical behavior of δ-hydroxy ketones suggests that the manner in which the oil was handled might have brought about dehydration to a dihydropyran, and perhaps polymerization.

N'-tert-butyl-*N'*-neopentylbenzhydrazide reacted more readily than 1-benzamido-2,6-lupetidine, but the primary product of nitrosation could not be isolated. Benzoyl azide was detected by its azide absorption (2180 cm.$^{-1}$) in the infrared and by conversion through phenyl isocyanate to diphenylurea. The presence of pivalic acid was suggested by the odor and by infrared absorption at 1700 cm.$^{-1}$, but the small amount available precluded a thorough investigation.

N-Benzamidomorpholine reacted with nitrous acid at 0–5° to give water-soluble products. Chloroform extraction of the neutralized solution yielded an oil which gave Liebermann's nitroso test and showed infrared absorption at 1680–1690 cm.$^{-1}$, but efforts to crystallize it or convert it to a derivative failed.

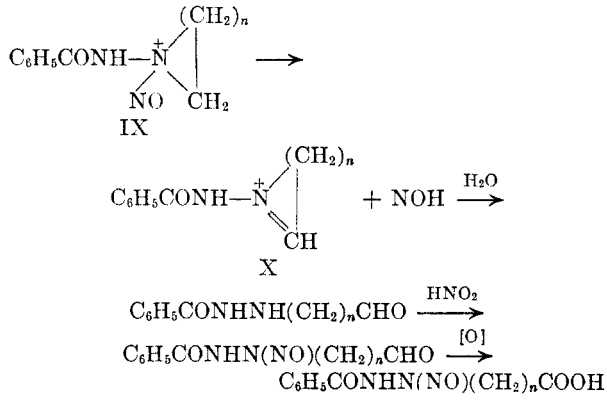
N-p-toluenesulfonamidopiperidine was prepared in order to have a compound in which the two hydrazine nitrogen atoms are strongly differentiated. Reaction with nitrous acid took place rapidly at 0–5°, with precipitation of an impure solid, from which di-*p*-toluenesulfonylhydroxylamine was obtained by several recrystallizations. No other products from this quite unexpected reaction could be isolated.

N-benzoyloxypiperidine, an isostere of *N*-benzamidopiperidine, gave a crystalline precipitate when treated with cold nitrous acid. It proved to be only the nitrate (sic!) salt of the starting material, and no evidence of further reaction was detected.

The foregoing results can for the most part be correlated if it is assumed that initial nitrosation occurs at the tertiary nitrogen atom, *i.e.*, the most remote from the carbonyl group, to give a nitrosammonium derivative (IX). It is not unreasonable to

(3) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

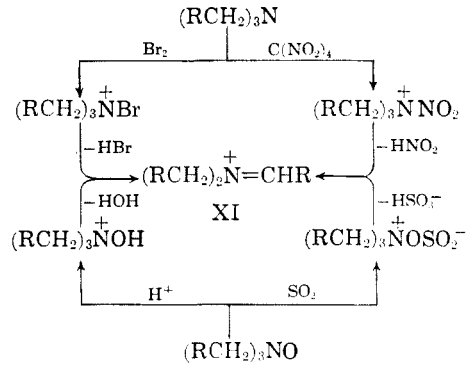
suppose that such a structure would undergo elimination in the manner indicated, giving a hydrazonium ion (X) which would hydrolyze readily. Nitrosation of the resulting hydrazino carbonyl compound would give the type of product obtained from benzamidopyrrolidine, while oxidation of the aldehyde function to carboxyl by oxides of nitrogen would give the type of product obtained from benzamidopiperidine.



The fundamental process in this scheme can be seen to consist of the cleavage of a tertiary amine structure by means of nitrous acid. Such a process has been encountered before, in Reade's and others work with dialkylaniline derivatives.[4] In one such example,[4b] *p*-dimethylaminobenzenesulfonic acid reacted with nitrous acid to give, among other products, *N*-nitroso-*N*-methyl-*p*-nitroaniline and formaldehyde. Disregarding the nuclear changes, the events at the tertiary nitrogen atom are quite analogous to those that we have encountered with dialkyl hydrazides. Reactions of presumably similar type have also been encountered in the treatment of the alkaloids aconitine and delphinine with nitrous acid.[5]

Hughes, Ingold, *et al.*[6] have proposed a mechanism to account for the reactions observed by Reade and co-workers. They, too, assume the initial formation of a nitrosammonium ion, but they propose that it breaks up by homolytic cleavage of the N—N bond, giving nitric oxide and an ammonium radical ion, rather than by elimination as we propose. Their scheme is completed by further cleavage of the ammonium radical ion to a secondary amine and a carbonium radical ion, R—CH·$^+$ which reacts successively with water and nitrosonium ion to give aldehyde and another nitric oxide molecule.

In support of the elimination path that we have put forth may be mentioned the closely analogous reactions of tertiary amines with bromine,[7] of amine oxides with sulfur dioxide,[8] of tertiary amines with tetranitromethane,[9] and the acid-induced cleavage of amine oxides.[10] In all of these a trialkylammonium ion is produced having as a fourth N-attached substituent a group capable of existence as a reasonably stable anion. Elimination of the latter group with a hydrogen from an α-carbon produces a dialkylimmonium ion (XI), hydrolysis of which gives the observed secondary amine and aldehyde (or derivative). While all of these reactions can be satisfactorily accounted for in terms of an elimination, some of them are unlikely to occur by a free-radical process. The analogous elimination in a nitrosammonium ion would produce nitroxyl, NOH. Although this is a less familiar substance, there are many examples of elimination reactions recorded[11] where nitroxyl is the species probably eliminated, such as, for example, from 4-nitroso-4-methylpentanone-2 to give mesityl oxide,[11a] from β-nitroso nitroalkenes to give nitro olefins,[11b] and from nitroso hydroxylamines to give C-nitroso compounds.[11c] Nitroxyl rapidly dimerizes to hyponitrous acid if not otherwise interfered with, such as by oxidation to nitric oxide, and ultrimately appears as nitrous oxide.[12] In the experiments reported here, it is uncertain whether nitroxyl would survive oxidation by nitrous and nitric acids to a sufficient extent to give rise to significant quantities of nitrous oxide.



(4) (a) G. P. Crowley, G. J. G. Milton, T. H. Reade, and W. M. Todd, *J. Chem. Soc.*, 1286 (1940); H. M. Halliday and T. H. Reade, *J. Chem. Soc.*, 138 (1940); A. C. Hutchison and T. H. Reade, *J. Chem. Soc.*, 93 (1940); (b) A. M. M. Davidson and T. H. Reade, *J. Chem. Soc.*, 1701 (1939); (c) G. J. G. Milton and T. H. Reade, *J. Chem. Soc.*, 1749 (1936); C. Donald and T. H. Reade, *J. Chem. Soc.*, 53 (1935); W. G. MacMillan and T. H. Reade, *J. Chem. Soc.*, 2863 (1929); M. F. Aitken and T. H. Reade, *J. Chem. Soc.*, 1896 (1926); H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 470 (1941); E. Koch, *Ber.*, **20**, 2460 (1887).

(5) A. Lawson, *J. Chem. Soc.*, 80 (1936); W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **136**, 323 (1940). W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **136**, 303 (1940).

(6) J. Glazer, E. D. Hughes, C. K. Ingold, A. T. James, G. T. Jones, and E. Roberts, *J. Chem. Soc.*, 2671 (1950).

(7) J. Meisenheimer, *Ber.*, **46**, 1148 (1913).

(8) H. Z. Lecher and W. B. Hardy, *J. Am. Chem. Soc.*, **70**, 3789 (1948).

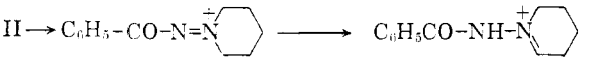
(9) E. Schmidt and H. Fischer, *Ber.*, **53**, 1529 (1920).

(10) M. Polonovski, *Bull. soc. chim.*, **41**, 1186 (1927).

(11) *Inter alia*, (a) K. D. Anderson, C. J. Crumpler, and D. L. Hammick, *J. Chem. Soc.*, 1679 (1935); (b) O. Wallach, *Ann.*, **336**, 30 (1904); H. Wieland, *Ber.*, **36**, 2558 (1903); (c) R. Berend and E. Konig, *Ann.*, **263**, 221 (1891).

(12) W. C. Bray, M. E. Simpson, and A. A. Mackenzie, *J. Am. Chem. Soc.*, **41**, 1363 (1919).

The objection might be raised that elimination should occur in the direction of the other nitrogen atom, which holds the most acidic hydrogen. The structure that would result from this, $RCON{=}\overset{+}{N}R_2$, would be the quaternary ammonium analog of an azo compound, and it is reasonable to suppose that it would undergo tautomerism to the hydrazone structure, as do known azo compounds,[18] thereby giving the same result as if elimination had taken place toward an α-carbon in the first place. Such tautomerization would be expected to be retarded most by a sulfonyl group, which may be responsible for the different behavior of *N*-*p*-toluenesulfonamidopiperidine.



If the foregoing interpretation is correct, *unsym*-diarylhydrazides, having no hydrogen atoms on the carbons α to the tertiary nitrogen, should not undergo the same sort of nitrosative cleavage. To investigate this point, we prepared *N*-benzamidocarbazole. This compound did, indeed, resist the action of nitrous acid until forcing conditions were used, whereupon amorphous green substances were formed, indicative of ring nitrosation. This resistant behavior can also be attributed to the greatly reduced basicity of the tertiary nitrogen atom, however. In an attempt to force nitrosation to occur at the amide nitrogen, *N*-benzamidopiperidine was treated with sodium hydride to prepare its sodium salt. Treatment of this salt with nitrosyl chloride produced a very impure organic substance that gave Liebermann's nitroso test, but we were unable to bring about sufficient conversion to make possible its investigation.

The recognition of nitrosative dealkylation of both *unsym*-dialkylhydrazides and dialkylaniline raises the question of why this reaction is not ordinarily observed with tertiary amines in general. We noted that both dialkylanilines and hydrazides are in general much weaker bases than tertiary aliphatic amines. Although nitrosation is commonly carried out in a strongly acidic solution, such weakly basic substances would not be entirely converted to ammonium ions, and sufficient free base would be expected to be in equilibrium to make *N*-nitrosation feasible. With the aliphatic amines, however, their greater basic strength (several powers of 10 in K_b) would result in their being so completely tied up as ammonium ions as to be more nearly inert to ordinary nitrosating conditions. The difference to be expected would be very much the same as that demonstrated for aromatic and aliphatic primary amines by Kornblum and Iffland,[14] for which a suitable range of acidity exists where aromatic amino groups are diazotized while aliphatic amino groups are unaffected.

The well known nitrous acid test for distinguishing among primary, secondary, and tertiary amines is commonly carried out in excess mineral acid, the *p*H being in the range 2 to 4. We felt that more nearly neutral solutions would provide a more favorable environment for nitrosative attack on aliphatic tertiary amines. We accordingly attempted the nitrosation of tribenzylamine in an acetic acid–sodium acetate–buffered solution; the evidently sluggish reaction required heating on a steam bath. In a short time nonbasic products were indeed formed, and were identified as *N*-nitrosodibenzylamine and benzaldehyde, analogous to the products of the cleavage of the dialkylhydrazides In order to establish that this result was not one peculiar to benzyl groups with their unusually active α-hydrogens, we attempted the reaction with tri-*n*-butylamine. The expected products, *N*-nitrosodibutylamine and butyraldehyde, were formed in good yield. We conclude from these observations that nitrosative dealkylation may be a general, albeit sometimes sluggish, reaction of tertiary amines having an α-hydrogen, if the proper conditions of acidity are chosen, and that the usual nitrous acid test for distinguishing among the classes of amines owes its reliability to the use of a combination of high acidity and low temperature that minimizes reaction with tertiary amines.

EXPERIMENTAL[15]

N-Aminopiperidine. *N*-Nitrosopiperidine was reduced with zinc dust in dilute acetic acid at 30–35°, according to the directions of Knorr,[16] and isolated as the hydrochloride in about 85% yields. Alternatively, lithium aluminum hydride reduction was used, following the procedure used by Schueler and Hanna[17] for reducing *N*-nitrosodimethylamine; the yields were about the same, but in this case the free base was isolated.

N-Benzenesulfonamidopiperidine. One g. of *N*-aminopiperidine, 8 ml. of 10% sodium hydroxide solution, and 2.1 g. of benzenesulfonylchloride were shaken together for 2 hr. An oil which separated solidified after cooling and scratching; it was discarded. The cooled filtrate was acidified to *p*H 6.7, whereupon a solid precipitated, wt. 1.1 g., m.p. 90–95°. Two recrystallizations from aqueous ethanol gave an analytical sample of *N*-benzenesulfonamidopiperidine, m.p. 99–100°.

Anal. Calcd. for $C_{11}H_{16}N_2O_2S$: C, 55.00; H, 6.67. Found: C, 54.81; H, 6.78.

N-Benzamidopiperidine (I). Crude *N*-aminopiperidine hydrochloride (23 g.) was benzoylated with 28 ml. of benzoyl

(13) T. W. J. Taylor and W. Baker, *Sidgwick's Organic Chemistry of Nitrogen*, Oxford University Press, London, 1942, p. 434 *et seq.*

(14) N. Kornblum and D. Iffland, *J. Am. Chem. Soc.*, **71**, 2137 (1949).

(15) Melting and boiling points are uncorrected. Analyses are by Mrs. Anna Griffin of the University of Michigan or by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were determined with a Perkin Elmer Model instrument.

(16) L. Knorr, *Ann.*, **221**, 297 (1883).

(17) F. W. Schueler and C. Hanna, *J. Am. Chem. Soc.*, **73**, 4996 (1951).

chloride under Schotten-Baumann conditions. The white solid initially obtained was a mixture of mono- and dibenzoyl compound. Cold dilute hydrochloric acid dissolved the former, leaving *N-dibenzimidopiperidine*, wt. 1.7 g., m.p. 112–113°, after recrystallization from ethanol; infrared absorption (Nujol) at 1670–1690 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 74.21; H, 6.62; N, 9.11.

The acid extracts were made alkaline, precipitating 23 g. (50% over-all from nitrosopiperidine) of *N*-benzamidopiperidine, m.p. 190–194°. Two recrystallizations from aqueous ethanol gave an analytical sample, m.p. 195–197° (Knorr reports 195–195.5°); infrared absorption (Nujol) at 3160 and 1640 cm.$^{-1}$

Anal. Calcd. for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.42; H, 7.90; N, 13.48.

Nitrosation of N-benzamidopiperidine; 5-(2-benzoyl-1-nitrosohydrazino)pentanoic acid (II). *N*-Benzamidopiperidine (1.0 g., 4.9 mmol.) was dissolved in 100 ml. of 10% hydrochloric acid in a 250-ml. glass-stoppered flask and cooled to 0°. A solution of 5 g. (72 mmol.) of sodium nitrite in 20 ml. of water was added dropwise with continuous swirling over a 15-min. period; a considerable quantity of oxides of nitrogen was evolved. The open flask was kept in an ice-salt bath for nearly 1 hr. after the addition, and was then stoppered and stored at 0–5° for 1 to 2 days. The fluffy, white crystals that precipitated were collected and washed well with ice water; wt. 700 mg. (51%), m.p. 100–102°. Recrystallization from water gave an analytical sample, m.p. 110–112°.

Anal. Calcd. for $C_{12}H_{15}N_3O_4$: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.38, 54.42; H, 5.54, 5.59; N, 15.86, 15.82. Mol. Wt. (Rast) 276, 283 (theory 265). Equiv. wt. (thymolphthalein end point) 136.

The infrared spectrum (Nujol) above 1600 cm.$^{-1}$ showed bands at 3200, 1700, and 1665 cm.$^{-1}$ The compound was insoluble in cold water, but soluble in cold 5% sodium bicarbonate solution. Its potentiometric titration curve is characteristic of a dibasic acid. It gave Liebermann's nitroso test. Treatment with diazomethane gave an oil which could neither be distilled nor crystallized; it showed infrared absorption characteristic of esters at 1730 cm.$^{-1}$

p-Bromophenylacyl ester of II. The acid (II, 500 mg.) in 3 ml. of water was made neutral to litmus with dilute sodium hydroxide, a solution of 500 mg. of *p*-bromophenacyl bromide in 5 ml. of ethanol was added, and the mixture was refluxed for 1 hr. The oil which separated on cooling gave 100 mg. of solid, m.p. 91–96°, when triturated with ether. Several recrystallizations from ethanol gave an analytical sample, m.p. 94–96°; infrared absorpion (Nujol) at 3180, 1735, 1695, and 1675 cm.$^{-1}$

Anal. Calcd. for $C_{20}H_{20}N_3O_5Br$: C, 51.94; H, 4.32; N, 9.09; Br, 17.31. Found: C, 51.97; H, 4.39; N, 9.06; Br, 17.42.

Decomposition of II *to benzoyl azide (attempted bromination).* The acid (II, 1.2 g., 4.5 mmol.) was dissolved in reagent grade chloroform (100 ml.). The solution was placed in the dark and 0.25 ml. of bromine was added. After the mixture had stood stoppered in the dark for 24 hr., the bromine color had disappeared. The solution was washed well with dilute sodium bicarbonate solution, then water, and dried over magnesium sulfate. The infrared spectrum showed strong absorption at 2180 cm.$^{-1}$, characteristic of azide. The solution was then refluxed overnight. The absorption at 2180 cm.$^{-1}$ disappeared and a new band at 2260 cm.$^{-1}$, characteristic of isocyanate, appeared. Treatment with 0.5 ml. of aniline caused the deposition of 290 mg. of diphenylurea, m.p. 220–230° (30% over-all from the acid); several recrystallizations from ethanol raised the m.p. to 235–236°, undepressed when mixed with an authentic sample (reported[18] 238–239°).

(18) I. Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, 1953, Vol. I, p. 426.

The chloroform filtrate was washed with dilute hydrochloric acid, 5% sodium bicarbonate solution, then water, and dried over magnesium sulfate. Evaporation of the solvent left a few drops of oil, whose infrared spectrum showed, *inter alia*, a strong, sharp band at 1730 cm.$^{-1}$ and a weaker one at 1190 cm.$^{-1}$ Repeated attempts to obtain a solid derivative by treatment with hydrazine were unsuccessful.

Similar decomposition to give benzoyl azide was observed when acid (II) was allowed to stand at room temperature in the acidic solution in which it had been formed, and also in attempts to denitrosate it with aqueous hydrochloric or hydrobromic acid, and directly from *N*-benzamidopiperidine upon nitrosation with nitrogen dioxide.

Catalytic hydrogenation of II. The acid (II, 1.32 g., 5.0 mmol.) was dissolved in 50 ml. of absolute ethanol and hydrogenated at 1 atmosphere pressure at room temperature over palladium catalyst (500 mg., 5% on carbon, Baker and Co.). The solution absorbed 87% of the theoretical amount of hydrogen in 45 min., at which time the hydrogenation was stopped. The catalyst was filtered off and the solvent evaporated at room temperature. The solvent vapors smelled of ammonia and turned moistened litmus paper blue. The residue, a colorless oil (850 mg.), crystallized on standing at room temperature for 24 hr. Recrystallization from benzene-cyclohexane mixture gave 350 mg. (32%) of 1-benzamido-2-piperidone, m.p. 156–165°. Several additional recrystallizations yielded an analytically pure sample, m.p. 165–167°. An authentic sample of 1-benzamido-2-piperidone (*vide infra*) showed no depression of melting point on admixture with the above sample, and the infrared spectra (Nujol) (principal absorptions at 3240, 1685, and 1650 cm.$^{-1}$) were identical.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.11; H, 6.41; N, 12.87.

1-Amino-2-piperidone. A solution of hydrazine hydrate (2.5 g.,50 mmol. of 99–100%) in 150 ml. of absolute methanol was stirred at room temperature while methyl δ-bromovalerate (9.75 g., 50 mmol.) dissolved in 150 ml. of absolute methanol was added dropwise over a period of 30 min. The solution was stirred for 24 hr., after which sodium methoxide (1.15 g., 50 mmol.) in 50 ml. of methanol was added, dropwise, over a period of 30 min. The solution was stirred at room temperature overnight. The solvent was then distilled off on the steam bath, whereupon sodium bromide precipitated from the residual liquid and was filtered off with the aid of some cold methanol. The filtrate was distilled, yielding 3.1 g. (54%) of 1-amino-2-piperidone, b.p. 78–80°/0.8 mm. An analytical sample was obtained by redistilling, collecting the fraction boiling at 70–72°/0.4 mm.; $n_D^{23.5°}$ 1.5104; principal infrared absorption (chloroform) at 3320 and 1630 cm.$^{-1}$

Anal. Calcd. for $C_5H_{10}N_2O$: C, 52.61; H, 8.83; N, 24.54. Found: C, 52.44; H, 8.85; N, 24.48.

p-Chlorobenzalhydrazone. 1-Amino-2-piperidone (100 mg.) and *p*-chlorobenzaldehyde (100 mg.) were heated to reflux in 5 ml. of ethanol. Upon cooling, 120 mg. of *1-p-chlorobenzylideneamino-2-piperidone* crystallized, m.p. 146–151°. Recrystallization from ethanol gave an analytical sample, m.p. 150–152°, principal infrared absorption (Nujol) at 1665 cm.$^{-1}$

Anal. Calcd. for $C_{12}H_{13}N_2OCl$: C, 60.88; H, 5.54; N, 11.84; Cl, 15.05. Found: C, 60.84; H, 5.59; N, 11.90; Cl, 14.89.

1-Benzamido-2-piperidone. 1-Amino-2-piperidone (500 mg.) was warmed with benzoyl chloride in the presence of excess in benzene. After dilution with water, the product was extracted with chloroform and dried over anhydrous magnesium sulfate. Evaporation left 480 mg. of 1-benzamido-2-piperidone, m.p. 161–165°. Recrystallization from benzene-cyclohexane mixture raised the melting point to 164–166°. This compound was found to be identical with the catalytic hydrogenation product of II (*vide supra*) by a mixed melting point determination and through identical infrared spectra.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84 Found: C, 66.25; H, 6.43; N, 12.81.

1-Benzamidopyrrolidine (IV). *N*-nitrosopyrrolidine was prepared in 64% yield by the method of Petersen[19]; b.p. 104–106°/20 mμ; reported,[19] 214°/760 mm. A mixture of 28 g. (0.28 mol.) of it with 141 g. (2.8 mol.) of zinc dust and 300 ml. of water was stirred while 150 ml. of 50% acetic acid was moderated by occasional cooling so as to keep the temperature at 30–35°. Fifteen min. after completion of the addition, the mixture was heated to 75°, 10 ml. of dilute hydrochloric acid was added, and the mixture was filtered. The combined filtrate and water washings were made strongly alkaline with *ca.* 40% sodium hydroxide solution and steam-distilled. When the distillate no longer reduced Tollens' reagent (about 500 ml. collected), it was acidified with concd. hydrochloric acid and evaporated to dryness, leaving a cake of crude *N*-aminopyrrolidine hydrochloride, wt. 36 g. This was then benzoylated under Schotten-Baumann conditions. The crude, white solid obtained was treated with dilute hydrochloric acid, and the acid-insoluble dibenzoylated material was filtered off and recrystallized from ethanol. The yield of *1-(dibenzoylamino)pyrrolidine* was 11.0 g. (12%), m.p. 97–98°. It showed infrared absorption (Nujol) at 1680 cm.$^{-1}$

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.47; H, 6.22; N, 9.54.

The acid-soluble monobenzoyl derivative was recovered by cooling the acidic filtrate (above) and basifying with concentrated sodium hydroxide solution. The precipitated solid was filtered and recrystallized from dilute ethanol, yielding 18.9 g. (30%), based on 1-nitrosopyrrolidine of 1-benzamidopyrrolidine, m.p. 160–163°. An analytical sample, m.p. 161–163°, was prepared by recrystallizing twice from dilute ethanol. Its principal infrared absorption occurred at 3200 and 1645 cm.$^{-1}$

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.46; H, 7.31; N, 14.72.

4-(2-Benzoyl-1-nitroschydrazino)butanal (V). 1-Benzamidopyrrolidine (1 g., 5.3 mmol.) was dissolved in 50 ml. of 10% hydrochloric acid and nitrosated as described for 1-benzamidopiperidine by adding sodium nitrite (5.0 g., 72 mmol.) in 10 ml. of water. A white, crystalline solid, wt. 900 mg. (75%), m.p. 103–104°, precipitated after one to two days. Recrystallization from water raised the melting point to 105–107°.

Anal. Calcd. for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.57; N, 17.86. Found: C, 56.18; H, 5.61; N, 17.94.

Equiv. Wt. Calcd.: 235. Found: 227 (thymolphthalein indicator).

The compound was insoluble in cold water but soluble in cold, dilute (5%) sodium bicarbonate solution. It gave Liebermann's nitroso test. Its infrared spectrum (Nujol) in the high-frequency region (above 1600 cm.$^{-1}$) showed bands at 3380 (sharp), and 1655 cm.$^{-1}$

Semicarbazone of V. The "aldehyde" (V, 500 mg.), semicarbazide hydrochloride (500 mg.) and sodium acetate (750 mg.) in 10 ml. of 50% ethanol were heated in a water bath at 70° for 10 min. The solution was then cooled and 10 ml. of water was added. Prolonged cooling, addition of 10 ml. more water and scratching yielded 490 mg. of semicarbazone, m.p. 116–118°. Two recrystallizations from water gave an analytical sample, m.p. 117–118°, infrared absorption (Nujol) at 3420, 3290, 1690, 1660, and 1630 cm.$^{-1}$

Anal. Calcd. for $C_{12}H_{16}N_6O_3$: C, 49.31; H, 5.52; N, 28.75 Found: C, 49.34; H, 5.46; N, 28.83.

2,4-Dinitrophenylhydrazone of V. The aldehyde (V, 500 mg.) was dissolved in 20 ml. of 95% ethanol and treated with 400 mg. of 2,4-dinitrophenylhydrazine dissolved in 2 ml. of concd. sulfuric acid, 3 ml. of water, and 10 ml. of 95% ethanol. After 2 hr., 630 mg. of solid precipitated, m.p. 88–94°. Two recrystallizations from 95% ethanol gave an analytical sample, m.p. 126–128°.

Anal. Calcd. for $C_{17}H_{17}N_7O_6$: C, 49.15; H, 4.09; N, 23.61. Found: C, 49.24; H, 4.13; N, 23.56.

(19) F. C. Petersen, *Ber.*, **21**, 290 (1888).

Decomposition of V *to benzoyl azide (attempted bromination).* The aldehyde (V, 500 mg., 2.1 mmol.) was dissolved in 50 ml. of reagent chloroform and treated with bromine (0.13 ml.) in the dark. Tarry material settled out of the chloroform solution on standing overnight. The solvent was decanted and washed with 5% sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. The presence of benzoyl azide was indicated by its infrared spectrum, having a sharp band at 2180 cm.$^{-1}$ A little aniline was added and the solution was evaporated to dryness. The oily residue was washed well with dilute acid and the resulting solid was filtered and recrystallized several times from absolute ethanol, yielding 10–15 mg. of diphenylurea, m.p. 234–236° (lit.,[18] 238–239°). Admixture with an authentic sample gave no depression of its melting point, and the infrared spectra were identical.

Catalytic hydrogenation of V. The aldehyde (V, 1.18 g., 5.0 mmol.) was dissolved in 50 ml. of glacial acetic acid and hydrogenated at 1 atmosphere at room temperature over palladium catalyst (500 mg., 5% on carbon, Baker and Co.). The solution absorbed 75% of the theoretical amount of hydrogen in 10 hr., and thereafter no more. The catalyst was filtered off and the solvent was evaporated in an air stream at room temperature, leaving a tan-colored residue. Upon recrystallization from carbon tetrachloride (Norit), 1-benzamidopyrrolidine (IV, 565 mg., 59%) was obtained, m.p. 150–158°. Several additional recrystallizations from carbon tetrachloride gave a sample, m.p. 158–160°, which required drying in a vacuum oven at 100° in order to remove adhering solvent. This compound and the one prepared by the benzoylation of 1-aminopyrrolidine (*vide supra*) were shown to be identical through undepressed mixed melting points, identical infrared spectra, and by elemental analysis.

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.53; H, 7.42; N, 14.68.

Succindialdehyde mono(benzoylhydrazone) (VI). The aqueous solution of succindialdehyde (prepared according to the directions of Keagle and Hartung[20] from succindialdoxime[21]) was mixed with an equimolar amount of benzhydrazide (6.1 g., 0.045 mol.) dissolved in methanol (50 ml.). The solution, which warmed slightly on mixing, was swirled and cooled well in an ice bath. A finely dispersed solid precipitated almost immediately and the cooling and swirling were continued for 1 hr. This unidentified solid was filtered off and washed with cold, 50% methanol; yield, 1.8 g., m.p. 218–220°. The filtrate was stripped of methanol, whereupon 4.4 g. (43% over-all from oxime) of white, crystalline succindialdehyde mono(benzoylhydrazone) separated, m.p. 120–122°. Recrystallization from benzene and low-boiling petroleum ether gave an analytical sample, m.p. 123–124°. It showed infrared absorption (Nujol) at 3430 (sharp), 1640, 1618, and 1580 cm.$^{-1}$

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.78. Found: C, 64.80; H, 5.69; N, 13.45.

Catalytic reduction of VI. Succindialdehyde mono(benzoylhydrazone) (VI, 1.02 g., 5.0 mmol.) dissolved in 50 ml. of acetic acid was hydrogenated at 1 atmosphere at room temperature over palladium catalyst (500 mg., 5% on carbon, Baker and Co.). The solution absorbed 110% of the theoretical amount of hydrogen in 27 hr. The catalyst was filtered off and the solvent was evaporated, leaving an oil (800 mg.), which crystallized after several hours at room temperature. Recrystallization from carbon tetrachloride (Norit) gave 300 mg. of a white powder, m.p. 155–160°. Further recrystallization from dilute ethanol gave 1-benzamidopyrrolidine (IV), m.p. 159–161°. Identification was established by means of superimposable infrared spectra and mixed melting point determinations with a sample prepared by the benzoylation of 1-aminopyrrolidine (*vide supra*).

(20) L. C. Keagle and W. H. Hartung, *J. Am. Chem. Soc.*, **68**, 1608 (1946).

(21) S. P. Findlay, *J. Org. Chem.*, **21**, 645 (1946).

Nitrosation of tribenzylamine. A solution of 1 g. (3.5 mmol.) of tribenzylamine and 13.6 g. of sodium acetate in 100 ml. of 60% acetic acid was warmed to 70–75° on the steam bath and stirred while 5 g. of sodium nitrite in 10 ml. of water was added dropwise over a period of 5–10 min. The mixture was stirred at this temperature for 30 min. after the addition, and the solution was then concentrated to a volume of 25–30 ml. The resulting oily suspension was extracted with ether (two 50-ml. portions) and the ether washed several times with 5% sodium bicarbonate solution, then water, and dried over anhydrous potassium carbonate. Evaporation left an oil, which solidified in several hours; yield, 300 mg. (38%), m.p. 55–58°. Recrystallization from ethanol-water gave *N*-nitrosodibenzylamine, m.p. 58–60° (lit.,[22] 61°), undepressed when mixed with an authentic sample. The infrared spectrum was identical with that of the authentic sample.

The other product in this nitrosation, benzaldehyde, was isolated in a separate experiment. Tribenzylamine (1.0 g., 3.5 mol.) was nitrosated as just described. After the initial reaction, mixture was cooled, 100 ml. of water was added, and the mixture was treated with 690 mg. of 2,4-dinitrophenylhydrazine dissolved in 3 ml. of concentrated sulfuric acid, 3 ml. of water, and 30 ml. of ethanol. The orange precipitate which came down was filtered and dried; yield, 300 mg. (30%), m.p. 200–220°. Recrystallization from ethyl acetate gave a sample of benzaldehyde 2,4-dinitrophenylhydrazone melting at 234–236° (lit.,[23] 237°), undepressed when mixed with an authentic sample.

Nitrosative cleavage of dibenzylamine. Dibenzylamine (17.4 g., 0.9 mol.) was nitrosated with aqueous nitrous acid at 75–80° in strong hydrochloric acid by the method described by Hatt[24] for nitrosating dimethylamine. The ether extracts obtained were dried and evaporated, leaving a light yellow oil. Recrystallization from ethanol-water gave 13.7 g. (68%) of *N*-nitrosodibenzylamine, m.p. 58–59°. The combined filtrates from these recrystallizations were treated with 2,4-dinitrophenylhydrazine reagent (prepared by dissolving 5.3 g. in 40 ml. of concd. sulfuric acid, 40 ml. of water, and 200 ml. of ethanol). The orange precipitate was collected, dried and weighed; yield, 3.3 g., m.p. 200–215°. Several recrystallizations from ethyl acetate gave a product which melted at 234–237°, undepressed by mixture with an authentic sample of benzaldehyde 2,4-dinitrophenylhydrazone.

Nitrosation of tri-n-butylamine. Freshly distilled tri-*n*-butylamine (25 g., 0.135 mol.) dissolved in 100 ml. of 50% acetic acid was placed in a 500-ml. three-neck, round-bottom flask equipped with a mechanical stirrer, dropping funnel, and a water separator with reflux condenser attached. The solution was heated at 80–85° on the steam bath with good stirring while 67 g. (1 mol.) of sodium nitrite in 100 ml. water was added dropwise over a period of 45 min. After the first 10–15 ml. of nitrite solution was added, some material began to distill over into the water separator. The main reaction mixture was heated and stirred for 15 min. after the addition was complete. The total distillate collected in the water separator was 8.5 ml. The organic phase, 5 ml., of this distillate was dried over magnesium sulfate and distilled; the fraction boiling below 75° weighed 2.1 g. This liquid gave a silver mirror with Tollens' reagent, and was shown to be *n*-butyraldehyde by converting a small portion to its 2,4-dinitrophenylhydrazone, m.p. 119–121° (lit.,[23] 122°), undepressed by admixture with an authentic sample.

The main reaction mixture was cooled and the dark yellow oil which separated (upper layer) was drawn off. The aqueous solution (lower layer) was extracted twice with 50-ml. portions of ether. The combined organic layers were washed successively with dilute hydrochloric acid (to remove unreacted amine), water, sodium bicarbonate solution and again with water. After drying over anhydrous magnesium sulfate, the liquid was distilled, yielding 14.4 g. (67%) of *N*-nitroso-di-*n*-butylamine, a light yellow liquid, b.p. 98–103°/8 mm. This liquid was redistilled for analysis, b.p. 54–57°/0.1 mm. (lit.,[25] 234–237°).

Anal. Calcd. for $C_8H_{18}N_2O$: C, 60.72; H, 11.47. Found: C, 61.04; H, 11.69.

1-Benzamido-2,6-lupetidine (VII). 1-Amino-2,6-lupetidine[26] (1.0 g.) was benzoylated under Schotten-Baumann conditions. The white solid obtained was recrystallized from 50% ethanol, yielding 1.4 g. (76%) of 1-benzamido-2,6-lupetidine, m.p. 165–170°. An analytical sample prepared by successive recrystallizations from 50% ethanol melted at 179–180° and showed infrared absorption (Nujol) at 3210 and 1650 cm.$^{-1}$

Anal. Calcd. for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.41; H, 8.69; N, 11.97.

Nitrosation of 1-benzamido-2,6-lupetidine. 1-Benzamido-2,6-lupetidine (4.0 g., 0.017 mol.) was dissolved in 200 ml. of 10% hydrochloric acid and cooled in an ice bath. Excess sodium nitrite (20 g.) was added and the solution allowed to warm to room temperature. After 3 days, a yellow oil separated. The two-phase mixture was neutralized with sodium bicarbonate (30 g.) and warmed on a steam bath for 15–20 min. During this operation the oil turned to a brownish granular solid, which was filtered off; yield, 1.1 g. Several recrystallizations from ethanol gave diphenylurea, m.p. 234–235°, undepressed by mixture with an authentic sample; the infrared spectra were identical.

The neutralized filtrate was then extracted continuously with ether for 24 hr. The ether extracts were dried over anhydrous magnesium sulfate and distilled, yielding 760 mg. of a colorless liquid, b.p. approx. 125°/29 mm. The liquid gave a positive iodoform test and a positive test with 2,4-dinitrophenylhydrazone reagent, but attempts to isolate enough hydrazone for characterization were unsuccessful. A few drops of the liquid reacted exothermically with phenyl isocyanate to give diphenylurea. The infrared spectrum (film) of the liquid showed broad absorption at 3120–3400, 1720, 1660, and 1600 cm.$^{-1}$, and was of such a character as to suggest that the material was a mixture; attempts to isolate and identify any of the components were unsuccessful.

N'-neopentyl-N'-tert-butylbenzhydrazide. *N*-Neopentyl-*N*-*tert*-butylhydrazine[27] (1.3 g., 8.2 mmol.) was benzoylated under Schotten-Baumann conditions. The yield of crystalline hydrazide was 1.2 g., m.p. 153–157°. Two recrystallizations from aqueous ethanol gave an analytical sample, m.p. 158–159°, infrared absorption (Nujol) at 3280 and 1650 cm.$^{-1}$

Anal. Calcd. for $C_{16}H_{26}N_2O$: C, 73.24; H, 9.99; N, 10.68. Found: C, 73.17; H, 9.81; N, 10.87.

Nitrosation of N'-tert-butyl-N'-neopentylbenzhydrazide. The hydrazide (800 mg., 3.0 mmol.) was dissolved in 80 ml. of 10% hydrochloric acid and the solution cooled to 0–5° in an ice-salt bath. Excess sodium nitrite (5 g.) dissolved in 10 ml. of water was added dropwise over a period of 10–15 min. The low temperature was maintained for 24 hr., whereupon an oil precipitated, and was extracted with two 50-ml. portions of chloroform. The extracts were washed with 5% sodium bicarbonate solution, then water, and dried over anhydrous magnesium sulfate. An infrared spectrum of the dried chloroform solution indicated the presence of benzoyl azide (strong bands at 2180 and 1695 cm.$^{-1}$), along with other secondary products from the nitrosation. The benzoyl azide was rearranged to phenyl isocyanate by

(22) T. Curtius and H. Franzen, *Ber.*, **34**, 552 (1901).

(23) N. R. Campbell, *Analyst*, **61**, 391 (1936).

(24) H. H. Hatt, *Org. Syntheses*, **Coll. Vol. II**, 211 (1943).

(25) V. Meyer, J. Barbieri, and F. Forster, *Ber.*, **10**, 130 (1877).

(26) C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Am. Chem. Soc.*, **77**, 4100 (1955).

(27) Kindly provided by Mr. Julian Lakritz (Doctoral thesis, University of Michigan, 1959).

refluxing the chloroform solution overnight. Addition of aniline (2–3 drops) to the solution gave a precipitate of diphenylurea, identified by mixture m.p. with an authentic sample.

The remainder of the material in the chloroform solution was not identified, but upon evaporating to dryness, the characteristic odor of pivalic acid could be detected. The acidified bicarbonate extracts also smelled of pivalic acid. The presence of this acid was further indicated by the infrared spectrum of the residue from the evaporation of the chloroform filtrate. There was broad absorption in the carbonyl region at 1700 cm.$^{-1}$ and in the 2500–3200 cm.$^{-1}$ region, as well as azide absorption at 2180 cm.$^{-1}$ Unfortunately, there was not enough material for purification and analysis, or for repetition of the experiment.

1-(p-Toluenesulfonamido)piperidine. 1-Aminopiperidine (10 g., 0.1 mol.) and *p*-toluenesulfonyl chloride (20.8 g., 0.108 mol.) were shaken well with 80 ml. of 10% sodium hydroxide solution for 2 hr., during which time an oil separated. The oil solidified on cooling and was removed by filtration; yield, 4.6 g., m.p. 55–62°. This solid was not identified, but it was presumed to be crude diacylated 1-aminopiperidine. The filtrate was acidified to a *p*H of 5–6 by the careful addition of dilute hydrochloric acid. The solid which then precipitated was collected and washed well with water; yield, 11.5 g. (44%) of 1-*p*-toluenesulfonamidopiperidine, m.p. 113–116°. Several recrystallizations from aqueous ethanol gave an analytical sample, m.p. 121–122°.

Anal. Calcd. for $C_{12}H_{18}N_2O_2S$: C, 56.68; H, 7.14; N, 11.02; S, 12.59. Found: C, 56.78; H, 7.09; N, 10.94; S, 12.68.

Nitrosation of 1-p-toluenesulfonamidopiperidine. 1-*p*-Toluenesulfonamidopiperidine (1.0 g., 3.9 mmol.) was dissolved in 60 ml. of 50% acetic acid and cooled to 0–5° in an ice bath. Excess sodium nitrite (5 g.) dissolved in 10 ml. of water was added dropwise over 15 to 20 min. The solid which precipitated was collected by filtration and washed well with cold water; yield, 650 mg., m.p. 70–80°. On recrystallization from aqueous methanol (twice) and benzene (twice), white crystals, soluble in dilute sodium hydroxide, were obtained, m.p. 123–124° (with gas evolution), undepressed by mixture with an authentic sample of *N,N*-(di-*p*-toluenesulfonyl)hydroxylamine (lit.,[28] m.p. 125°).

Anal. Calcd. for $C_{14}H_{15}NO_5S$: C, 49.27; H, 4.43; N, 4.10; S, 18.77 Found: C, 49.37; H, 4.66; N, 4.06; S, 18.39.

Nitrosation of N-benzamidomorpholine. *N*-Benzamidomorpholine, prepared by the method of Knorr,[29] was found to show infrared absorption at 1575 and 1640–1655 cm.$^{-1}$ A solution of 2.0 g. (0.98 mmol.) in 100 ml. of 10% hydrochloric acid was cooled to 0–5° in an ice bath. Excess sodium nitrite (10 g.) dissolved in 15 ml. of water was added and the temperature maintained at 0–5° for 48 hr. The solution was carefully neutralized with solid sodium bicarbonate and extracted with five 60-ml. portions of chloroform. The extracts were dried over anhydrous magnesium sulfate and the solvent evaporated *in vacuo*. A yellow, oily residue remained (1 g.), which gave Liebermann's nitroso test. An infrared spectrum (film) of this oil indicated that a reaction had taken place which was similar to the nitrosation of 1-benzamidopiperidine, in that a carbonyl group(s) absorbing at 1680–1690 cm.$^{-1}$ had apparently been introduced in place of the original amide carbonyl which absorbed at 1640–1650 cm.$^{-1}$ and broad absorption above 3200 cm.$^{-1}$ suggested associated hydroxyl. Efforts to crystallize the oil were unsuccessful, as were efforts to convert it to a *p*-bromophenacyl ester.

Attempted nitrosation of N-benzoyloxypiperidine. *N*-Benzoyloxypiperidine was prepared by the method of Gambarajar,[30] and found to show infrared absorption (Nujol) at 1725 cm.$^{-1}$ A solution of 700 mg. (3.0 mmol.) of it in 40 ml. of 10% hydrochloric acid was cooled to 0–5° in an ice bath. Excess sodium nitrite (4 g.) dissolved in 10 ml. of water was added and the temperature maintained for 24 hr. A solid precipitated during this period, and was filtered off and washed well with cold filter; yield, 450 mg., m.p. 70–105° dec. Several recrystallizations from benzene gave an analytical sample, m.p. 110–112° (with gas evolution). This compound was shown to be the nitrate salt of *N*-benzoyloxypiperidine by comparison with an authentic sample (*vide infra*); an admixture showed no depression of the melting point, and the infrared spectra were identical.

Anal. Calcd. for $C_{12}H_{16}N_2O_5$: C, 53.72; H, 6.01; N, 10.44. Found: C, 53.72, 53.77; H, 6.04, 5.96; N, 10.44, 10.39.

Nitrate salt of N-benzoyloxypiperidine. Cold, 35% nitric acid (35 ml.) was added to a solution of 500 mg. of *N*-benzoyloxypiperidine in 35 ml. of cold, 20% hydrochloric acid, and the mixture was allowed to stand for 10 min. in the ice bath. A white crystalline solid precipitated and was filtered off, washed well with cold water, sucked dry, and recrystallized several times from benzene, yielding 400 mg. of salt, m.p. 114–115° (with gas evolution).

N-benzamidocarbazole. Nitrosocarbazole[31] (1.0 g., 5.0 mmol.) was dissolved in a mixture of glacial acetic acid (2.5 ml.) and moist ether (13 ml.). Zinc dust (4 g.) was added portionwise to the ice-cooled solution at such a rate as to keep the temperature below 10°. After the addition was complete, the reaction was allowed to stand at room temperature for 24 hr. The initially yellow solution turned colorless during this period, after which time it was filtered. The filtrate was evaporated to dryness, leaving a purple-tinged solid, presumably 1-aminocarbazole. This was benzoylated directly by treating with sodium hydroxide solution (50 ml., 10%) and benzoyl chloride (2 ml.), and shaking well for 15–20 min. The resulting solid was filtered off and recrystallized (Norit) several times from an ethanol-water mixture, yielding 500 mg. of *N*-benzamidocarbazole (17% over-all from carbazole), m.p. 230–232°, infrared absorption (Nujol) at 3340 and 1670 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.52; H, 4.98; N, 9.68.

Attempted nitrosation of N-benzamidocarbazole. Several attempts to nitrosate *N*-benzamidocarbazole with a variety of nitrosating agents were unsuccessful. The reagents used include nitrous acid (aqueous and nonaqueous), nitrosyl chloride, and nitrogen tetroxide. The last of these methods gave unidentifiable green-colored mixtures.

Attempted preparation of 1-(N-nitrosobenzamido)piperidine. 1-Benzamidopiperidine (2.0 g., 0.01 mol.) and sodium hydride (240 mg., 0.01 mol.) were added to 250 ml. of nitrobenzene and heated with good stirring on a steam bath overnight. As the solution was warmed, it appeared to evolve a gas (presumably hydrogen) and the suspended sodium hydride was apparently transformed into a suspension of the sodium salt of 1-benzamidopiperidine. The solution was cooled to 5–10° while dry, gaseous nitrosyl chloride was bubbled into the reaction mixture. The addition of nitrosyl chloride was continued for 10–15 min. (10–15 bubbles per min.), whereupon the solution turned wine-red. The reaction mixture was then warmed to 75–80° and maintained there for 1 hr. The reaction mixture was concentrated *in vacuo* to approximately 50 ml. Trituration with dry ether precipitated an amorphous tan solid. Isolation of this finely divided material was effected by portionwise centrifuging. The solid thus obtained was thoroughly washed with ether, yielding 350 mg., m.p. 125–150°. This gave Liebermann's nitroso test, and its infrared spectrum indicated that some alteration of starting material had occurred, in that N—H absorption at 3180 cm.$^{-1}$ was weak, and absorption in the carbonyl region consisted of overlapping bands at 1680, 1660, and 1645 cm.$^{-1}$ Attempts to purify the mixture by recrystallization or by passing through an alumina column were unsuccessful.

ANN ARBOR, MICH.

(28) E. von Meyer, *J. prakt. Chem.*, **63**, 173 (1901).
(29) L. Knorr, *Ber.*, **35**, 4476 (1902).
(30) S. Gambarajar, *Ber.*, **58**, 1776 (1925).
(31) H. Wieland and A. Susser, *Ann.*, **392**, 127(1912).