

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

## Oxidation of Primary, Secondary, and Tertiary Amines with Neutral Potassium Permanganate. II

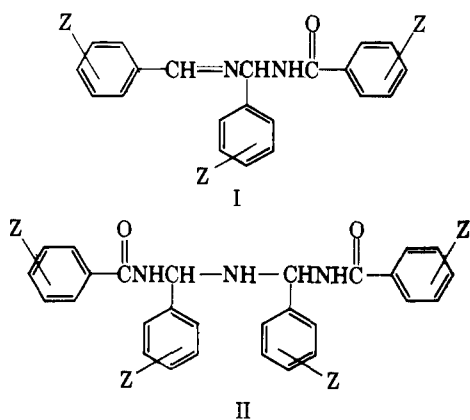
BY HAROLD SHECHTER<sup>1a</sup> AND SURJAN SINGH RAWALAY<sup>1b,c,d</sup>

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Oxidation of benzhydramine (III) with buffered permanganate at 25° gave *N*-diphenylmethylenbenzhydramine and ammonia; in hot excess permanganate, benzophenone azine (VII) is formed. Reaction of benzophenoneimine (IV) with neutral permanganate in aqueous *t*-butyl alcohol yielded VII and benzophenone. Dibenzylamines are oxidized to their corresponding *N*-[ $\alpha$ -(dibenzylamino)-benzyl]-benzamides (XI–XIII); alternate structures have been proposed for the products previously reported from such oxidations. *N*-Phenylbenzhydramine (XXII) is converted by permanganate to *N*-diphenylmethylenaniline (XXIII) and *N*-(diphenylmethyl)-*N,N'*-1,1-tetraphenylmethanediamine (XXIV). Tributylamine (XXV) reacts with neutral permanganate to give *N,N*-dibutylformamide (XXXI), *N,N*-dibutylbutyramide (XXX), dibutylamine (XXVIII), butyraldehyde (XXIX), and butyric acid. Benzaldehyde and benzoic acid are the products of oxidation of tribenzylamine (XXXII). Possible mechanisms of these various oxidations are discussed.

Primary carbinamines are oxidized by unbuffered potassium permanganate to aldehydes<sup>2a</sup> and carboxylic acids.<sup>2b</sup> Certain control of reaction of specific secondary carbinamines with unbuffered permanganate to give nitroso compounds<sup>2c,d</sup> oximes,<sup>2c,d</sup> and imines<sup>2e</sup> results from effecting oxidation in the presence of simple aldehydes or ketones.<sup>3</sup> Tertiary carbinamines are converted slowly to nitro compounds by aqueous permanganate.<sup>2f</sup> Secondary dialkylamines have been oxidized to their corresponding carboxylic acids<sup>2b</sup>; secondary and tertiary amines containing substituted benzyl groups are converted to their corresponding benzaldehydes or benzoic acids by acidic potassium permanganate.<sup>2g</sup>

It has been recently reported<sup>4</sup> that neutral permanganate as derived from potassium permanganate and excess calcium sulfate in aqueous *t*-butyl alcohol is an excellent oxidant for conversion of substituted benzylamines to substituted *N*-[ $\alpha$ -(benzylidene)-benzyl]-benzamides (I) and *N,N*-(iminodibenzylidene)-bis-



(1) (a) To whom inquiries may be directed. (b) The principal results of the present study have been abstracted from the Ph.D. dissertation of S. S. Rawalay, The Ohio State University, 1962. (c) This research was sponsored primarily by the U. S. Army Research Office, Grant DA-ARO(D)-31-124-G182, ARO(D)2367-C. (d) The present authors wish to acknowledge the support and facilities provided by M. Tubis, Department of Radiology, School of Medicine of the University of California, Los Angeles, and Department of Radioisotope Research, Veterans Administration Center, Los Angeles, Calif., for study of oxidations of 4,4'-dichlorodibenzylamine and 4,4'-dimethyldibenzylamine with permanganate.

(2) (a) E. Carstanjen, *J. prakt. Chem.*, **89**, 466 (1863); (b) O. Wallach and L. Claisen, *Ber.*, **8**, 1237 (1875); (c) I. Okamura, R. Sakurai, and T. Tanabe, *Chem. High Polymers* (Tokyo), **9**, 279 (1952); (d) I. Okamura and R. Sakurai, *ibid.*, **9**, 434 (1952); (e) S. Goldschmidt and W. Beuschel, *Ann.*, **447**, 197 (1926); (f) N. Kornblum, R. J. Cutter, and W. J. Jones, *J. Am. Chem. Soc.*, **78**, 4003 (1956); (g) R. A. Labriola, M. Ishii, and I. Mariani, *Anales. Asoc. Quim. Argentina*, **33**, 156 (1945).

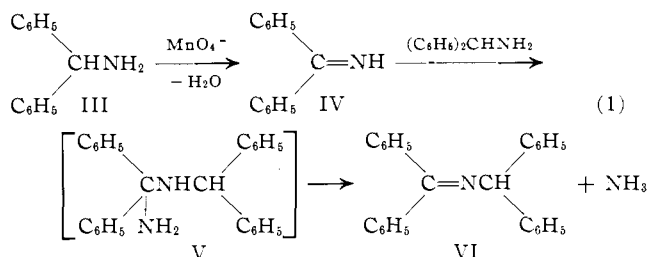
(3) It is not clear in such systems whether permanganate oxidizes the amines, their corresponding Schiff bases, or other intermediates derived from reaction of the amines with the aldehydes or ketones.

(4) H. Shechter, S. S. Rawalay, and M. Tubis, *J. Am. Chem. Soc.*, **86**, 1701 (1964).

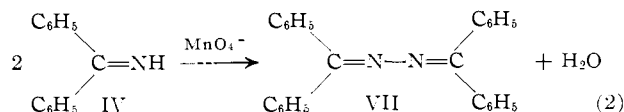
[benzamides] (II). It was suggested that in these complex transformations important reactions involve oxidation of the benzylamines to benzalimines, condensation of the benzalimines and benzylamines, and subsequent oxidation to products. As an extension of a study of the utility of neutral permanganate as an oxidant of amines and to obtain additional information of the courses and mechanisms of such reactions, an investigation has been made of oxidation of benzhydramine, various dibenzylamines, *N*-phenylbenzhydramine, tributylamine, and tribenzylamine, respectively.

### Results and Discussion

**Oxidation of Benzhydramine.**—Reaction of benzhydramine (III) with potassium permanganate and calcium sulfate in water-acetone (1:10) at 25° yields an unstable adduct (presumably V) which decomposes into *N*-diphenylmethylenbenzhydramine (VI, 74%) and ammonia. On the basis of the products of the present study and the previous report<sup>2e</sup> that benzhydramine (III) is oxidized by potassium permanganate in acetone to benzophenoneimine (IV), it is apparent that a process of the type indicated in eq. 1 occurs in conversion of III to VI. The present system is thus of interest in that in the oxidation medium, condensation to give V takes place rather than hydrolysis or oxidation of the reaction intermediates to benzophenone.

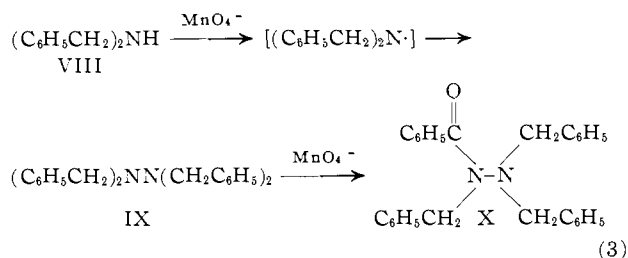


When benzhydramine (III) was oxidized by refluxing buffered permanganate (1.5 equiv.) in water-*t*-butyl alcohol (1:1), benzophenone azine (VII) was isolated in 73% yield. To account for the surprisingly efficient formation of VII, it appears almost certain that III is initially converted to benzophenoneimine (IV); oxidative coupling of IV may then give VII. If this reaction sequence (eq. 2) is indeed followed, it is evident that the rate of oxidative coupling of IV is considerably faster than its hydrolysis to benzo-



phenone and ammonia. Support for the mechanism suggested for conversion of III to VII has been presently obtained by demonstrating that authentic benzophenoneimine (IV) is converted to VII (>32% yield) along with benzophenone (55% yield) by warm neutral permanganate in aqueous *t*-butyl alcohol. Oxidative coupling of IV by permanganate to VII is not a unique process since the conversion may also be effected by oxygen in the presence of cuprous chloride.<sup>5</sup>

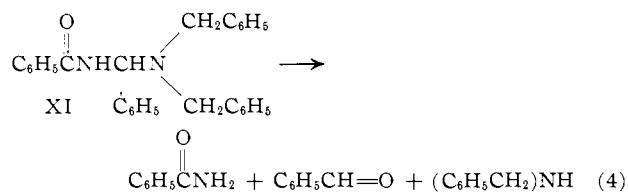
**Oxidation of Dibenzylamines**—Reaction of dibenzylamine (VIII) with aqueous potassium permanganate has been previously reported<sup>6</sup> to give benzoyltrisbenzylhydrazine (X), m.p. 181°, as a major product. It was postulated that tetrabenzylhydrazine (IX) is a reaction intermediate, and the following mechanism for formation of X from VIII (eq. 3) was proposed. The authors<sup>6</sup> claimed to have proved the structure of X by



comparison of its melting point with an authentic sample, by its reduction with zinc dust in acetic acid to dibenzylamine and *N*-benzylbenzamide, and by its hydrolysis in cold dilute acid to benzaldehyde, dibenzylamine, and benzamide.

The products reported for hydrolysis of X are indeed surprising. Since oxidations of benzylamines<sup>4</sup> and benzhydramine do not involve oxidative coupling to hydrazines but rather conversion to the corresponding imines which undergo nucleophilic addition of the parent amines, it became of interest to reinvestigate the oxidation of dibenzylamine with permanganate.

When dibenzylamine was oxidized in the present study with potassium permanganate-calcium sulfate in water-*t*-butyl alcohol (1:1), a product assigned the structure *N*-[ $\alpha$ -dibenzylaminobenzyl]-benzamide (XI) was obtained in 62% yield.



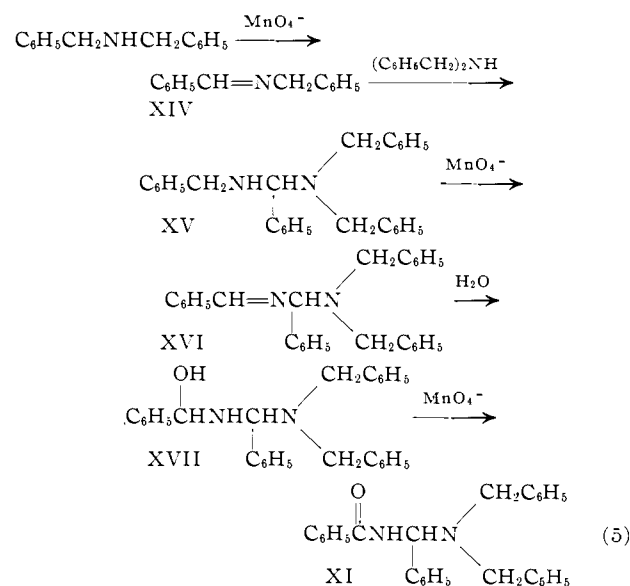
The melting point of XI (179–181°), its analysis and molecular formula, and its products of hydrolysis in acid: benzamide, benzaldehyde, and dibenzylamine (eq. 4) indeed correspond to that previously reported<sup>6</sup> for X. The infrared spectrum of XI exhibited strong absorption at 2.98  $\mu$  for an NH group; the infrared spectrum of X cannot exhibit such absorption. The identity of XI was demonstrated by its mixture melting point and comparison of its infrared spectrum with a sample of XI established previously<sup>6</sup> as the structure of the product of reduction of *N*-[ $\alpha$ -(benzylideneamino)-benzyl]-benzamide with sodium borohydride. Benzoyltrisbenzylhydrazine (X) was then prepared from tribenzylhydrazine and benzoyl chloride in 88% yield. Surprisingly enough, X melted at 108–109° instead of 181° as previously reported. Furthermore, X gave neither benzaldehyde, dibenzylamine, nor benzamide on hydrolysis with acids.

(5) R. Meyer and D. Pillon, U. S. Patent 2,870,206, Jan. 20, 1959.

(6) S. Goldschmidt and V. Voeth, *Ann.*, **435**, 265 (1924).

The oxidations were extended<sup>1d</sup> to 4,4'-dichlorodibenzylamine and 4,4'-dimethyldibenzylamine. The products isolated, *N*-[ $\alpha$ -[bis-(*p*-chlorobenzyl)-amino]-*p*-chlorobenzyl]-*p*-chlorobenzamide (XII, 64%) and *N*-[ $\alpha$ -[bis-(*p*-methylbenzyl)-amino]-*p*-methylbenzyl]-*p*-toluamide (XIII, 68%), are of structures analogous to that of X obtained from oxidation of dibenzylamine. The structure of XIII was assigned upon demonstrating its identity with that of the product previously obtained<sup>4</sup> from reduction of *N*-[*p*-methyl- $\alpha$ -[(*p*-methylbenzylidene)-amino]-benzyl]-*p*-toluamide with sodium borohydride.<sup>7</sup>

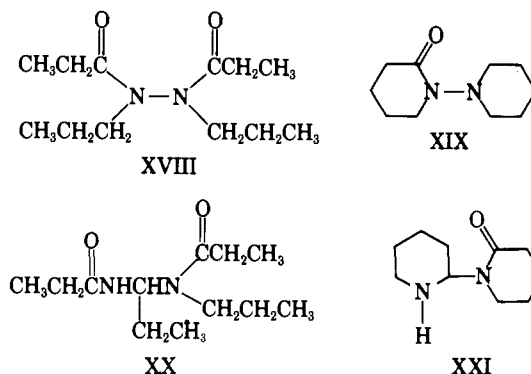
The mechanism of oxidation of dibenzylamines to complex products such as XI–XIII is unknown. A possible reaction sequence (eq. 5)<sup>8,9</sup> which is consistent with that proposed for oxidation of benzylamines<sup>4</sup> involves conversion of the dibenzylamine to its Schiff



(7) Secondary amines containing substituted benzyl groups have been previously oxidized<sup>2b</sup> by potassium permanganate in acid media to the corresponding benzaldehydes and isolated as 2,4-dinitrophenylhydrazones. It is quite possible that amides corresponding to XI were the actual oxidation products.

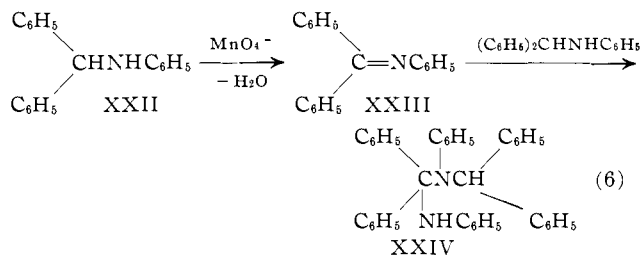
(8) In oxidation of an intermediate such as XV, dehydrogenation involving the tertiary benzyl hydrogen to give  $\text{C}_6\text{H}_5\text{CH}_2\text{N}=\text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$  (XV') may occur more rapidly than that at the secondary benzyl position yielding XVI. Simple processes may be envisaged for isomerizing or oxidizing XV' to XV or XI.

(9) It has also been previously reported<sup>6</sup> that oxidations of dipropylamine and piperidine with permanganate yield 1,2-dipropyl-1,2-dipropionylhydrazine (XVIII) and 1,1'-bipiperidine-2-one (XIX), respectively. The structures of XVIII and XIX were assigned as a result of their analyses, molecular weights, and thermal decomposition to *N*-propylpropionamide and *N*-propylidenepropionamide and to 2-piperidone and 3,4,5,6-tetrahydropyridine, respectively. On the basis of the patterns of oxidation observed in this laboratory for primary<sup>4</sup> and secondary amines, the present authors should like to suggest XX and XXI as alternate structures of the products derived from dipropylamine and piperidine with permanganate.



base (XIV), subsequent addition of the dibenzylamine to the Schiff base, oxidation, hydration, and final oxidation.<sup>8</sup>

**Oxidation of N-Phenylbenzhydrylamine.**—Reaction of N-phenylbenzhydrylamine (XXII) with neutral potassium permanganate (1.0 equiv.) in water-acetone (1:20) at 25–30° has been found to give N-(diphenylmethyl)-N,N',1,1-tetraphenylmethanediamine (XXIV) as the principal product (79% yield) along with N-diphenylmethylethaniline (XXIII). The structure of XXIV was assigned on the basis of its analysis, molecular weight, spectral properties, and its efficient synthesis by reaction of authentic XXII and XXIII. An apparent sequence for conversion of XXII by permanganate to XXIII and XXIV is indicated in eq. 6. Oxida-



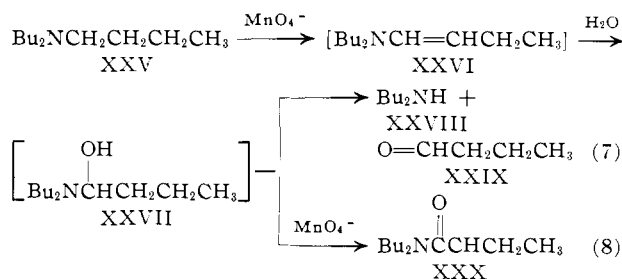
tion of XXII to the intermediate Schiff base XXIII could only be effected in trace quantities; even upon reaction of XXII with excess permanganate. XXIV was the major product. An oxidation pattern in which a secondary benzhydrylamine is dehydrogenated to its Schiff base which undergoes rapid addition of the parent amine parallels that proposed for oxidation of benzylamines<sup>4</sup> and dibenzylamines with permanganate.

The structure of XXIV is of interest with respect to results obtained previously for reduction of nitrones.<sup>10</sup> Reduction of  $\alpha$ ,N-diphenylnitronone with zinc and ammonium chloride yielded N-benzylideneaniline<sup>10</sup>; triphenylnitronone to behave similarly should give XXIII, m.p. 116°. Instead of XXIII, triphenylnitronone yielded a product, m.p. 83°, for which no structure was given other than it appeared to be a molecular addition compound<sup>10</sup> of XXII and XXIII. The product is presently assigned the structure XXIV since it is identical with that obtained from oxidation of XXII.

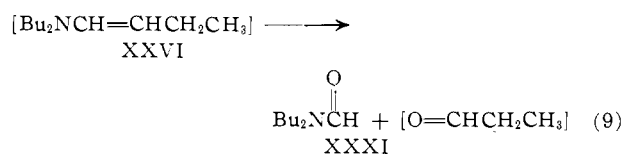
**Oxidation of Tributylamine and Tribenzylamine.**—In order to obtain information concerning the products and mechanisms of reaction of tertiary amines with neutral permanganate, a study has been made of oxidation of tributylamine (XXV) and of tribenzylamine (XXXII). Reaction of XXV with insufficient permanganate in aqueous *t*-butyl alcohol gave dibutylamine (XXVIII, 8%), butyraldehyde (XXIX, 12%), N,N-dibutylbutyramide (XXX, 10%), butyric acid (17%), and unchanged XXV (43%). N,N-Dibutylformamide (XXXI) and propionic acid were also obtained in small yields.

It is suggested that oxidation of XXV yields initially or in part the corresponding enamine XXVI. Dehydrogenation of tertiary amines to the corresponding enamines has been previously proposed for their oxidations with mercuric acetate,<sup>11a</sup> hydrated manganese dioxide,<sup>11b</sup> ozone,<sup>11b</sup> and peroxides.<sup>11c</sup> In the present system water may add to the double bond of the enamine XXVI to give XXVII which is cleaved to XXVIII and XXIX (eq. 7) or oxidized to XXX (eq. 8).

Oxidation of tributylamine (XXV) in the presence of minimal amounts of water was studied in an attempt



to determine the influence of the aqueous environment on the courses of reaction. Insufficient neutral permanganate and XXV at 25–30° in anhydrous acetone thus gave N,N-dibutylformamide (XXXI, 15%), XXVIII (9%), and XXX (4%) along with unchanged XXV (46%), carboxylic acids (2%), aldehydes, and other carbonyl compounds. In the absence of water other than that produced by reduction of the permanganate, formation of XXXI may have resulted from oxidative cleavage of XXVI (eq. 9).



The reactions of the tertiary amine, tribenzylamine (XXXII), with neutral permanganate were then investigated. Oxidation of XXXII is of interest because it only contains oxidizable hydrogen on the carbon atoms  $\alpha$  to the amine function. Reaction of XXXII with insufficient permanganate in aqueous *t*-butyl alcohol occurs rapidly to give benzaldehyde (17%), benzoic acid (31%), and recovered XXXII (42%). In a system in which formation of an enamine is structurally inhibited,<sup>12a</sup> oxidation thus effects dealkylation. It is of note that dibenzylamine is not formed in oxidation of XXXII.<sup>12b</sup> The present results thus parallel those reported previously for oxidation<sup>2g</sup> of N,N-dialkylbenzylamines by acidic permanganate to the corresponding benzaldehydes and benzoic acids.

### Experimental

**Oxidation of Benzhydrylamine (III).** Procedure 1.—A water-acetone mixture (1:10, 44 ml.) of III (2.0 g., 0.0109 mole), potassium permanganate (1.2 g., 0.0076 mole, 1 equiv.), and zinc sulfate<sup>13</sup> (1.0 g., 0.0035 mole) was stirred for 0.75 hr. The reaction mixture was filtered and the filtrate evaporated. The oily residue decomposed on storage to give ammonia and N-diphenylmethylenbenzhydrylamine (VI); yield 1.4 g. (74%), m.p. and mixture m.p. 150–151°, lit.<sup>14</sup> m.p. 152–153°.

Procedure 2.—Benzhydrylamine (III, 5.0 g., 0.0272 mole) was added in one portion to a stirred mixture of potassium permanganate (4.5 g., 0.0285 mole, 1.5 equiv.) and calcium sulfate dihydrate (2.5 g., 0.0145 mole) in water-*t*-butyl alcohol (1:1, 100 ml.) at 70°. The mixture was refluxed for 8 hr. and filtered. The inorganic residue was washed with diethyl ether. The com-

(12) (a) The results of the present investigations coupled with the fact that *t*-carbinamines are oxidized much more slowly by permanganate than are *p*- and *s*-carbinamines suggest that initial attack by the oxidant occurs on oxidizable hydrogen on the carbon atoms  $\alpha$  to the amine function. It is not known whether an amine is oxidized to radical or carbonium ion intermediates by permanganate. The relative ease of oxidation at  $\alpha$ -positions of amines upon comparison to that observed for alcohols, ethers, and hydrocarbons and the much greater rate of oxidation of an amine than its conjugate acid implies that hybridization in the oxidation transition state involves the nonbonded electrons on nitrogen. (b) On the basis of the mechanisms presently proposed for reaction of amines and permanganate, the fact that dibenzylamine is not formed in oxidation of tribenzylamine suggests that  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NCHC}_6\text{H}_5$  is not a reaction intermediate.

### OH

(13) Zinc sulfate and magnesium sulfate have been used successfully in the present studies for buffering potassium permanganate. Calcium sulfate, however, was found to be the superior reagent.

(14) A. Rahman and M. O. Farooq, *Rec. trav. chim.*, **73**, 423 (1954).

(10) L. Alessandri, *Gazz. chim. ital.*, **51**, pt. 1, 75 (1921).

(11) (a) N. J. Leonard and W. K. Musker, *J. Am. Chem. Soc.*, **82**, 5148 (1960), and related previous papers from their laboratory; (b) H. B. Henbest and M. J. W. Stratford, *Chem. Ind. (London)*, 1170 (1961); (c) D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4901 (1937).

bined filtrate was evaporated and the benzophenone azine (VII)<sup>15a</sup> crystallized from ether as bright yellow needles; yield 3.6 g. (73%), m.p. 159–162°, lit.<sup>15b</sup> m.p. 162°.

**Oxidation of Benzophenoneimine (IV).**—Benzophenoneimine hydrochloride<sup>16</sup> (4.0 g., 0.0184 mole) was added rapidly to a warm stirred mixture of potassium permanganate (1.0 g., 0.006 mole, 0.5 equiv.), calcium sulfate (0.6 g., 0.00348 mole), and sodium hydroxide (0.78 g., 0.0195 mole) in water-*t*-butyl alcohol (1:1, 50 ml.). The mixture was refluxed for 8 hr., cooled, extracted with ether, and filtered. The filtrate was evaporated and the residue chromatographed on neutral alumina using petroleum ether (30–60°) as the eluent to give benzophenone (1.85 g., 55%, m.p. and mixture m.p. 46–48°) and VII (1.05 g., 32%, m.p. 160–162°, lit.<sup>15b</sup> m.p. 162°).

**Oxidation of Dibenzylamine (VIII).**—*t*-Butyl alcohol (40 ml.) was added to a stirred mixture of potassium permanganate (2.65 g., 0.0168 mole) and calcium sulfate dihydrate (1.8 g., 0.01 mole) in water (40 ml.). After 5 min., VIII (5.0 g., 0.025 mole) was poured slowly into the oxidizing medium. After a reaction period of 10 min., the mixture was cooled and extracted with ether. The ether extract was washed with water and evaporated, and the residue crystallized from benzene to yield XI (3.21 g., 62%) as white needles. Its identity was established from its mixture melting point and by comparison of its infrared spectrum with XI of established structure as prepared previously.<sup>4</sup>

**Benzoyltribenzylhydrazine (X).**—Benzoyl chloride (4.0 g., 0.028 mole) was added to a stirred suspension of tribenzylhydrazine hydrochloride (2.0 g., 0.0084 mole) and anhydrous sodium carbonate (4.0 g., 0.038 mole) in pyridine (50 ml.) at 80°. The mixture was refluxed for 1 hr., cooled, and added to water (250 ml.). An oily material separated which solidified on standing. The product was filtered, dried, and crystallized from ethanol to give X (2.11 g., 88%) as colorless plates, m.p. 108–109°; mol. wt. calcd. 407, found 401. Its infrared spectrum showed the absence of NH but the presence of an amide carbonyl group (6.04  $\mu$ ). Addition of X in ethanol to excess 2,4-dinitrophenylhydrazine gave no benzaldehyde 2,4-dinitrophenylhydrazone; X remained unchanged on standing in hydrochloric acid for 4 hr.

*Anal.* Calcd. for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O: C, 82.73; H, 6.45; N, 6.89. Found: C, 82.89; H, 6.29; N, 6.89.

**Oxidation of 4,4'-Dichlorodibenzylamine.**—Reaction of *p*-chlorobenzylamine and *p*-chlorobenzyl bromide in anhydrous diethyl ether and recrystallization of the product from ethanol gave 4,4'-dichlorodibenzylamine hydrobromide as colorless needles, m.p. 285–288°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>NBrCl<sub>2</sub>: N, 4.04. Found: N, 4.28.

An aqueous solution of 4,4'-dichlorodibenzylamine hydrobromide (5.0 g., 0.0144 mole) and sodium hydroxide (0.6 g., 0.015 mole) was poured into a mixture of potassium permanganate (1.9 g., 0.012 mole, 1.25 equiv.) and calcium sulfate dihydrate (1.5 g., 0.0087 mole) in water (40 ml.)-*t*-butyl alcohol (40 ml.). After 10 min. the mixture was cooled and extracted with ether. Evaporation of the ether and crystallization of the product from benzene gave XII as white crystals; yield 2.5 g. (64%), m.p. 188–190°. The infrared spectrum of the product exhibited absorption for NH (3.07  $\mu$ ) groups.

*Anal.* Calcd. for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>OCl<sub>4</sub>: C, 61.78; H, 4.07; N, 5.14. Found: C, 61.39; H, 4.09; N, 5.47.

**Oxidation of 4,4'-Dimethyldibenzylamine.**—4,4'-Dimethyldibenzylamine hydrobromide was prepared from equimolar quantities of *p*-methylbenzylamine and *p*-methylbenzyl bromide in diethyl ether and recrystallization from ethyl alcohol; m.p. 297–298°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>20</sub>NBr: N, 4.57. Found: N, 4.66. *t*-Butyl alcohol (40 ml.) was added to a stirred solution of potassium permanganate (2.2 g., 0.014 mole, 1.25 equiv.) and calcium sulfate dihydrate (1.5 g., 0.0087 mole) in water (40 ml.). After the mixture had been stirred for 5 min., 4,4'-dimethyldibenzylamine, generated from 4,4'-dimethyldibenzylamine hydrobromide (5.0 g., 0.016 mole) and sodium hydroxide (0.65

g., 0.016 mole) in water, was added in one portion. Isolation and then crystallization of the product from benzene gave XIII as a white solid; yield 2.56 g. (68%), m.p. 146–148°. lit.<sup>4</sup> m.p. 146–148°. Its infrared absorption, analysis, and properties are identical with the product of reduction of *N*-[*p*-methyl- $\alpha$ -(*p*-methylbenzylidene)-amino]-benzyl]-*p*-toluamide with sodium borohydride.<sup>4</sup>

**Oxidation of *N*-Phenylbenzhydrylamine (XXII).**—To a stirred mixture of potassium permanganate (0.41 g., 0.0026 mole, 1.0 equiv.) and zinc sulfate (0.5 g., 0.0017 mole) in water-acetone (1:20, 42 ml.) was added XXII. After 4 hr. the mixture was filtered and the solvents evaporated. *N*-(Diphenylmethyl)-*N,N'*,1,1-tetraphenylmethanediamine (XXIV, 0.78 g., 79%) was crystallized from ethanol as colorless prisms, m.p. 82–83°, lit.<sup>10</sup> m.p. 83°; mol. wt. calcd. 517, found 499. The melting point of XXIV was not depressed by admixture of the product prepared from equimolar quantities of XXII and XXIII in acetone and subsequent crystallization from ethanol. The infrared spectrum of XXIV showed absorption for NH at 3.05  $\mu$ . There was no distinguishable absorption for a C=N group.

**Oxidation of Tributylamine (XXV).** Procedure 1.—To a stirred mixture of potassium permanganate (85 g., 0.54 mole) and calcium sulfate dihydrate (50 g., 0.29 mole) in water-*t*-butyl alcohol (1:1, 1000 ml.) at 10° was added XXV (50 g., 0.27 mole). After reaction was complete (~7 min.), the mixture was filtered, the inorganic residue washed with ether, and the combined filtrates extracted with ether. Gas-liquid chromatography<sup>17</sup> of the ether extract confirmed the presence of XXV, dibutylamine (XXVIII, 8%), and *N,N*-dibutylbutyramide (XXX) along with trace quantities of *N,N*-dibutylformamide (XXXI). The mixture of products on removal of solvents was fractionated to give XXV (21.3 g., 43%, b.p. 53–54° (1 mm.)) and XXX (5.1 g., 10%, b.p. 74–76° (0.5 mm.)),  $n_D^{20}$  1.4442.

The aqueous layer was concentrated, acidified, and extracted with ether to give butyric acid (12.5 g., 17%); the butyric acid was converted to methyl butyrate and identified by gas-liquid chromatographic analysis.<sup>18</sup> Butyraldehyde (XXIX, 6.9 g., 12%) was isolated as its 2,4-dinitrophenylhydrazone (31.5 g.), m.p. and mixture m.p. 122°.

Procedure 2.—Compound XXV (50 g., 0.27 mole) was added in 2 min. to a stirred mixture of potassium permanganate (85 g., 0.54 mole) and calcium sulfate dihydrate (50 g., 0.29 mole) in anhydrous acetone (700 ml.) at 10°. After 15 min. the mixture was filtered and the residue washed with water. The combined filtrates were extracted with ether. The ether extract on removal of solvents gave XXVIII (3.25 g., 9%), XXV (23.0 g., 46%), XXXI (6.5 g., 15%), and XXX (2.0 g., 4%) as analyzed by gas-liquid chromatography. The aqueous layer was concentrated, acidified, and extracted with ether; a small quantity of organic acids (~1.0 g., ~2%) remained upon evaporation of the solvent from the ether extract.

**Oxidation of Tribenzylamine (XXXII).**—Compound XXXII (5.0 g., 0.0174 mole) was added rapidly to a stirred mixture of potassium permanganate (5.0 g., 0.032 mole) and calcium sulfate dihydrate (3.0 g., 0.017 mole) in water (50 ml.)-*t*-butyl alcohol (50 ml.). After 20 min. the mixture was cooled and extracted with ether. The ether extract was washed with water. Benzaldehyde (17%, as its 2,4-dinitrophenylhydrazone, 2.55 g., m.p. and mixture m.p. 235–237°) and XXXII (2.1 g., 42%, m.p. and mixture m.p. 90–92°) were isolated on removal of the ether. There was no NH absorption in the infrared spectrum of the crude oxidation product; the absence of dibenzylamine (XXVIII) was confirmed by gas-liquid chromatographic analysis.<sup>19</sup>

The inorganic residue from the ether extraction was washed with water. The aqueous extract on acidification and subsequent ether extraction gave benzoic acid (2.0 g., 31%), m.p. and mixture m.p. 121–122°.

(17) (a) The assistance of P. B. Sargeant and G. Baum in these analyses is gratefully acknowledged. (b) A 15-ft. column of 5% by weight of silicone oil No. 550 on Fluoropack with helium as carrier gas was used at 125°.

(18) A 5-ft. column of 23% by weight silicone grease on firebrick with helium as carrier gas at 46° was used.

(19) Oxidation of XXXII containing XXVIII under the conditions of the above experiment indicated that XXVIII survived the oxidation.

(15) (a) Product VII gave the proper quantitative analysis. (b) C. Ruchardt and G. N. Schrauzer, *Ber.*, **93**, 1840 (1960).

(16) A. Lachman, *Org. Syn.*, **10**, 28 (1930).