but yields of the latter were reduced by formation of polymeric side products. Proof of the structure of this compound as 1,2,3-trihydroxyoctadecane was obtained by periodate oxidation. The long-chain aldehyde was identified as palmitaldehyde by vapor phase chromatography and from the 2,4-dinitrophenylhydrazone; formaldehyde was characterized as the dimedon derivative.

The supernatant liquid from the crystallization of the octadecanetriol yielded a yellow wax (10%). It contained *ca.* 3% triol and decolorized bromine and permanganate solutions, and its infrared spectrum resembled that of 1-hydroxy-3-ketooctadecane. This fraction was not characterized further.

Experimental Section

Deamination of Dihydrosphingosine.—Sphingosine was isolated from beef brain and spinal cord according to the procedure of Carter, *et al.*[2] The free base was hydrogenated over platinum in ethanol to the dihydro form. To 2.0 g of base in 50 ml of glacial acetic acid, two 1.0-g portions of $NaNO_2$ were added with a 30-min interval between additions. The reaction mixture was stirred magnetically in an amber bottle at room temperature. *Ca.* 30 min after the last addition of nitrite, four volumes of water were added. The reaction products were removed with ether which was washed with 10% $NaHCO_3$ and water. The syrup obtained after removal of the ether was dried over P_2O_5 to an amorphous yellowish solid: yield 1.80 g; mp 38–50°. It gave a negative reaction with ninhydrin in 95% ethanol.

Column Chromatography.—A silicic acid (Mallinckrodt) column, 2.5 × 20 cm, was prepared as previously described[8] except that the final chloroform wash was followed by one with petroleum ether. After loading with 3.6 g of the deaminated product in warm petroleum ether, the column was developed successively with 500 ml each of chloroform–petroleum ether (55:45, v/v) and methanol–chloroform (10:90, v/v). The eluates were concentrated to dryness, and the residues were stored over P_2O_5 until further use.

Chloroform–Petroleum Ether Fraction, 1-Hydroxy-3-ketooctadecane (V).—An amorphous, yellowish wax was obtained from the chloroform–petroleum ether eluate: yield 2.8 g; mp 39–41°. It gave a positive Tollens' reaction and decolorized a solution of $KMnO_4$ but not of bromine. The infrared absorption bands in chloroform were at 3500 cm^{-1} (m), 1710 cm^{-1} (m), 1510 cm^{-1} (w), 1470 cm^{-1} (s), 1380 cm^{-1} (w), 1210 cm^{-1} (s), and doublet 1080 and 1050 cm^{-1} (s).

Anal. Calcd for $C_{18}H_{36}O_2$ (284.3): C, 75.98; H, 12.76; O, 11.26. Found: C, 75.57; H, 12.66; O, 11.13.

Reduction to DL-1,3-Dihydroxyoctadecane (VI).—Compound V, 2.6 g in 75 ml of dry ether containing 500 mg of $LiAlH_4$, was refluxed for 4 hr. The product was isolated as described previously[9] and was crystallized from petroleum ether: yield 1.4 g; mp 62–65°. It gave a positive Tollens' reaction (3 hr) and decolorized a solution of $KMnO_4$ but not of bromine.

Anal. Calcd for $C_{18}H_{38}O_2$ (286.3): C, 75.44; H, 13.38; O, 11.18. Found: C, 75.20; H, 13.17; O, 11.24.

Oxidation to Palmitic Acid (VII).—To a magnetically stirred solution of 2.5 g of compound V in 50 ml of cold glacial acetic acid, surrounded by an ice bath, was added 1.5 g of CrO_3. The bath was removed after 15 min, and the reaction mixture was stirred for an additional 2 hr. After dilution of the reaction mixture with four volumes of water, the product was isolated and converted to the amide as described previously:[3] yield 566 mg; mp 104–106°.

Anal. Calcd for $C_{16}H_{33}ON$ (255.3): C, 75.22; H, 13.03. Found: C, 75.86; H, 12.97.

Preparation of 1-Acetoxy-3-ketooctadecane (VIII).—Compound V, 2.5 g, was treated with 4 ml of acetic anhydride in 30 ml of dry pyridine. The reaction mixture was poured into ice water and the product was extracted into ether which was washed with water and removed under reduced pressure. The syrup, dried over P_2O_5, was placed on a 1.5 × 9.0 cm silicic acid column in the same manner as described for the resolution of the deamination mixture. The column was developed with 75 ml of petroleum ether which was discarded and with 100 ml of chloroform–petroleum ether (55:45, v/v) which was concentrated and dried: yield of light yellow syrup, 1.3 g. The infrared and nuclear magnetic resonance spectra showed strong carbonyl but no hydroxyl group absorption and no aldehyde function, respectively.

Anal. Calcd for $C_{20}H_{38}O_3$ (326.3): C, 73.55; H, 11.74; O, 14.71. Found: C, 73.15; H, 11.55; O, 14.54.

Preparation of 1-Methoxy-3-hydroxyoctadecane (IX).—To 2.1 g of compound V in 30 ml of dimethylformamide, surrounded by an ice bath, were added 3.5 ml of methyl iodide and 3.5 g of Ag_2O. The reaction mixture was stirred magnetically overnight at room temperature in an amber bottle, and the product was isolated as described previously.[10] The syrupy residue, after removal of solvent and drying over P_2O_5, was fractionated on a small silicic acid column similar to that used for the purification of compound VIII. The first 100 ml of petroleum ether eluate was concentrated and the dried syrup was reduced with $LiAlH_4$ and isolated in the same manner as described for the preparation of compound VI: yield of light yellow syrup, 1.1 g. Infrared absorption bands were present at 1105 cm^{-1} (s) and 3500 cm^{-1} (m) for the ether and hydroxyl groups, respectively.

Anal. Calcd for $C_{19}H_{40}O_2$ (300.3): C, 75.92; H, 13.43; OCH_3, 10.33. Found: C, 75.39; H, 13.23; OCH_3, 10.14.

Methanol–Chloroform Fraction, 1,2,3-Trihydroxyoctadecane (III).—The residue was treated with 1 ml of saturated aqueous KOH in 50 ml of ethanol for *ca.* 4 hr at room temperature. After dilution of the reaction mixture with several volumes of water, the product was removed with ether which was washed until neutral. The dried residue obtained after removal of solvent was crystallized several times from chloroform–petroleum ether (1:15): yield, 289 mg. The triol reduced Tollens' reagent and decolorized a solution of $KMnO_4$ but not of bromine.

Anal. Calcd for $C_{18}H_{38}O_3$ (302.3): C, 71.45; H, 12.67; O, 15.88. Found: C, 71.49; H, 12.61; O, 15.94.

Degradation of 1,2,3-Trihydroxyoctadecane.—A solution of 150 mg of triol and 300 mg of periodic acid in 15 ml of methanol was warmed at 50° for 1 hr and the reaction products were isolated as described previously.[3] The long-chain aldehyde was identified as palmitaldehyde by vapor phase chromatography[11] and as the 2,4-dinitrophenylhydrazone: yield, 104 mg; mp 105–106°. The short-chain aldehyde was characterized *via* the dimedon derivative as formaldehyde: yield, 30 mg; mp 190°.

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Rearrangement of Amides with Iodine Pentafluoride[1]

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The mild fluorinating agent, iodine pentafluoride, is known to dehydrogenate amines to produce nitriles, imines, and azo compounds,[2] and to dehydrate formamides to isonitriles.[3] Now, primary amides, when

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(1) This research was carried out under Army Ordnance Contract DA-01-021 AMC-11536 (Z).

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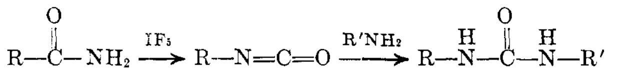
exposed to iodine pentafluoride in pyridine solution, have been found to undergo rearrangement to give products similar to those obtained under Hofmann conditions.[4]



$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \xrightarrow{IF_5} R{-}N{=}C{=}O \xrightarrow{R'NH_2} R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R'$$

The *t*-butyl isocyanate produced from pivalamide after 2 hr at 110° in pyridine–iodine pentafluoride, was isolated as di-*t*-butylurea (78%). Hexanamide and octanamide rearranged readily under similar conditions, and after aqueous work-up the product was a mixture of isocyanate and carbamoyl fluoride. Reaction with *t*-butylamine converted both products to the urea (57% from hexanamide, 41% from octanamide).[5]

Some iodination of benzamide, or its rearranged product, was observed in 1 hr at 93°; an iodinated carbanilide was isolated upon hydrolysis of the reaction mixture.[5]

Because of the complex nature of the reagent used here, it has not been possible to determine if an N-halogenated amide is an intermediate here,[4] or if dehydrogenation of the amide leads to a nitrene directly.[5]

It is worth noting that benzophenone hydrazone was converted to a mixture of benzophenone azine and benzophenone (after aqueous work-up) by iodine pentafluoride in methylene chloride alone. There was no evidence for the formation of a C–F bond. When the hydrazone was oxidized in pyridine solution, only a small amount of the same two products were obtained; the major products were water soluble.

Experimental Section

Reaction of Pivalamide, Iodine Pentafluoride, and Pyridine.—A mixture of 4.0 g of pivalamide, 3 ml of iodine pentafluoride, and 25 ml of pyridine was heated at 110° for 2 hr. The reaction mixture was cooled, poured into water, and extracted with methylene chloride. The extract was washed with water, 10% aqueous hydrochloric acid, and water, and dried over magnesium sulfate. The infrared spectrum and vpc trace of a portion of this that had been concentrated by distillation indicated only *t*-butyl isocyanate. The methylene chloride solution was treated with 10 ml of *t*-butylamine. Removal of the methylene chloride left 1,3-di-*t*-butylurea, 5.4 g, subliming at 240°, lit.[5] mp 242–243°.

Anal. Calcd for $C_9H_{20}N_2O$: C, 62.74; H, 11.70; N, 16.26. Found: C, 62.79; H, 11.62; N, 15.93.

Rearrangement of Hexanamide with Iodine Pentafluoride.—A 4.6-g sample of hexanamide was treated with iodine pentafluoride (3 ml)–pyridine as described above. The organic product extracted into methylene chloride was, by infrared spectrum, a mixture of isocyanate (4.4 μ) and carbamoyl fluoride (5.6 μ). The ^{19}F nmr spectrum exhibited the carbamoyl fluoride peaks at ϕ +15.5, J_{HF} = 8 cps.[6] The methylene chloride solution was treated with *t*-butylamine (10 ml) and gave N-*n*-pentyl-N'-*t*-butylurea, 4.19 g, mp 59–61°.

Anal. Calcd for $C_{10}H_{22}N_2O$: C, 64.47; H, 11.90; N, 15.04. Found: C, 64.23; H, 11.95; N, 14.12.

Rearrangement of Benzamide with Iodine Pentafluoride.—A mixture of benzamide (5.3 g), iodine pentafluoride (3.0 ml), and pyridine (30 ml) was heated on a steam bath for 1 hr. The mixture was poured over ice and partitioned between methylene chloride and water. A solid, 3.5 g, was removed by filtration. This solid was an iodinated diphenyl urea, mp 243–245° dec.

Anal. Found: C, 41.10; H, 3.30; N, 7.46; I, 41.0.

Anal. Calcd for a monoiodocarbanilide ($C_{13}H_{11}N_2OI$): C, 46.17; H, 3.28; N, 8.38; I, 37.5.

Oxidation of Benzophenone Hydrazone with Iodine Pentafluoride.—A solution of 2.0 ml (0.029 mole) of iodine pentafluoride in 100 ml of methylene chloride was stirred at 15° while 2.9 g (0.015 mole) of benzophenone hydrazone in 50 ml of methylene chloride was added over a 3-hr period. The solution was stirred at 15° for 30 min; then water was added and the methylene chloride solution was washed with water and dilute sodium thiosulfate solution. A residue of 2.78 g was obtained from the methylene chloride extract. This residue was recrystallized from hexane; the first crop was benzophenone azine, 0.81 g, mp 160–161°, identified by infrared spectrum and mixture melting point.[7] The solution was chilled and benzophenone, 0.62 g, mp 47–48°, was obtained.

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The Synthesis of Piperitenone *via* Mesityl Oxide and Methyl Vinyl Ketone

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The monoterpenoid, piperitenone (IV), is of interest because it can be converted to a wide variety of important monoterpenoids. It has been obtained by several chemical routes[1a,b] as well as from essential oils.[1c,d] The most practical synthesis[1b] from geranic acid has been shown to give almost equal yields of IV and a bicyclic cyclobutanone.[2] Recently, Bergmann and Bracha[3] have described the synthesis of piperitenone in 41% yield by the condensation of mesityl oxide with methyl vinyl ketone using sodium *t*-pentoxide in toluene. However, this work has been refuted by Naves[4] who claimed that the product of the reaction was isoxylitone (VI), the self-condensation product of mesityl oxide. The reaction has been studied in considerable detail by several groups[5–7] and the general consensus is that under the Bergmann reaction conditions the principal product is isoxylitone, and piperitenone is formed in only 8% yield. Moreover, the mixture is almost impossible to separate by distillation. We also have repeated Bergmann's work and obtained only a low yield of piperitenone contaminated with isoxylitone and several other products as well as polymeric material due to the self-condensation of methyl vinyl ketone. More recently, Wiemann[8] has obtained piperitenone

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