The barium was precipitated from the combined filtrates by sulfuric acid and the barium-free solution was concentrated *in vacuo* to dryness. The residue was recrystallized from about 50 parts of ethyl alcohol and then from 20 parts of methyl alcohol. The yield was 1.5 g. (65%). The 2,4:3,5-dimethylene-L-idosaccharic acid rotated $[\alpha]^{20}\mathrm{D}$ +76.3 in aqueous solution (*c*, 0.83) in agreement with the specific rotation $[\alpha]^{20}\mathrm{D}$ +76.4° for a sample of acid prepared by the epimerization of dimethyl 2,4:3,5-dimethylene-D-glucosaccharate as described in the following section. The melting point of the compound was determined by Dr. C. P. Saylor of the National Bureau of Standards in a microscope furnace of the type designed by Stadnichenko[13] and found to be 298.5–299.0°; in the same apparatus the melting point of the acid which was prepared by epimerization was found to be 297.8°. Dr. Saylor also found that the products prepared by each procedure showed the same crystallographic and optical properties. The compound belongs to the monoclinic system and crystallizes as rectangular plates which are greatly flattened parallel to the base and bounded by clino- and orthopinacoids; nearly all individuals are complexly twinned parallel to the base. The refractive indices $n^{27}\mathrm{D}$ are α = 1.526, β = 1.534 and γ = 1.581 (all ±0.001). The crystals are biaxial and positive in sign, the optical axial angle being about 40°, but variable, and the plane of the optic axis is normal to the long direction.

Anal. Calcd. for $C_8H_{10}O_8$: C, 41.03; H, 4.30; neutralization equivalent, 234. Found: C, 40.96; H, 4.21; neutralization equivalent, 237.

2,4:3,5-Dimethylene-L-idosaccharic Acid from Dimethyl 2,4:3,5-Dimethylene-D-glucosaccharate.—The epimerization was conducted essentially by the procedure of Haworth, Jones, Stacey and Wiggins.[7] The dimethyl 2,4:3,5-dimethylene-D-glucosaccharate, which was obtained in a yield of 15% by the methylenation of potassium hydrogen glucosaccharate, melted at 156–157° in agreement with their value of 157.5°. It was recrystallized from 18 parts of methyl alcohol and showed a specific rotation $[\alpha]^{20}\mathrm{D}$ +34.9° in chloroform solution (*c*, 0.99). A solution of 10 g. of the ester and 20 g. of barium hydroxide octahydrate in 300 cc. of water was refluxed for six hours; the barium ions were balanced out by *N* sulfuric acid, the barium sulfate was separated by filtration and the filtrate was concentrated *in vacuo* to dryness. The dry residue was extracted with warm acetone to remove some impurities, and the insoluble portion was recrystallized from 3 parts of water or 20 parts of methyl alcohol. The acid showed a specific rotation $[\alpha]^{20}\mathrm{D}$ +76.4° in aqueous solution (*c*, 1.3) and crystallographic optical examination showed it to be identical with the acid obtained by oxidation of dimethylene-L-iditol. The yield was 5.1 g. (57%). Haworth, Jones, Stacey and Wiggins[7] reported a specific rotation $[\alpha]^{16}\mathrm{D}$ +73.7 in water (*c*, 1.817) and a melting point of 292° (dec.) for this compound.

Dimethyl 2,4:3,5-Dimethylene-L-idosaccharate.—One-gram samples of 2,4:3,5-dimethylene-L-idosaccharic acid, prepared in one case by oxidation of the 2,4:3,5-dimethylene-L-iditol and in the other by epimerization of 2,4:3,5-dimethylene-D-glucosaccharic acid, were esterified by the method of Haworth, Jones, Stacey and Wiggins.[7] The reaction products (1.0 g., 91%) were recrystallized from about 200 parts of boiling water and submitted to Mr. J. J. Fahey, of the United States Geological Survey, for comparison as to identity. He reported that the esters from the two sources were identical. The compound crystallizes in the monoclinic system; its refractive indices $n^{20}\mathrm{D}$ are α = 1.508, β = 1.511 and γ = 1.515, all ±0.001; the optic axial angle is about 60° and the dispersion of violet is greater than red. A saturated aqueous solution of the compound at 20° (*c* = 0.064) showed a rotation $[\alpha]^{20}\mathrm{D}$ +80 ± 2°. A saturated solution in methyl cellosolve at 20° (*c* = 0.043) also showed $[\alpha]^{20}\mathrm{D}$ +80 ± 2°. The ester also has been prepared recently by the condensation of paraformaldehyde with calcium L-idosaccharate under the catalytic action of warm sulfuric acid.[12]

Summary

The dimethylene-L-iditol that is obtained in nearly quantitiative yield by slow evaporation of a mixture of L-iditol, aqueous formaldehyde and concentrated hydrochloric acid has been shown to be 2,4:3,5-dimethylene-L-iditol. This is the structure which is to be expected in the case of iditol by applying to its configuration the generalizations that we published recently.

A number of derivatives of the diacetal are described.

Evidence is presented which shows that this dimethylene-L-iditol is in all probability the acetal which Lobry de Bruyn and Alberda van Ekenstein, and later Bertrand and Lanzenberg, described in its enantiomorphous forms.

BETHESDA, MARYLAND RECEIVED JANUARY 11, 1945

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[13] *Cf.* p. 677 of "Temperature, its Measurement and Control in Science and Industry," Reinhold Publishing Corp., New York, N. Y., 1941.

[CONTRIBUTION FROM THE ESSO LABORATORIES, CHEMICAL DIVISION, THE STANDARD OIL DEVELOPMENT COMPANY]

Oxidation of N-Phenyl-2-naphthylamine

BY JOHN REHNER, JR., FRED W. BANES AND SAMUEL B. ROBISON

In the course of some work on oxidation in synthetic rubbers it was found desirable to investigate the nature of the oxidation products of N-phenyl-2-naphthylamine. Kinetic schemes that have been proposed[1] in attempts to explain the rate of oxidation of rubber have left unanswered the specific nature of the product into which the added antioxidant is transformed in the presumed chain termination reactions.

As one of the most effective[2] and widely used members of the group of secondary arylamines displaying considerable antioxidant activity in various hydrocarbons and oils N-phenyl-2-naphthylamine possesses an industrial importance in notable contrast to the scanty literature on its oxidation products. Graebe and Knecht[3] found that when the amine is passed through a red-hot tube 5-benzo[*b*]carbazole is formed, in addition to ammonia, hydrogen cyanide, and other substances. Streiff[4] found that phthalic acid is

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[1] Morgan and Naunton, Proc. Rubber Techn. Conf. London, 1938, p. 599. The Bibliography given by Dufraisse in Davis and Blake, "Chemistry and Technology of Rubber," Reinhold Publ. Corp., New York, N. Y., 1937, p. 440, contains references to earlier chain reaction theories of antioxidant behavior.

[2] Jones and Craig, *Ind. Eng. Chem.*, **23**, 23 (1931).

[3] Graebe and Knecht, *Ann.*, **202**, 1 (1880).

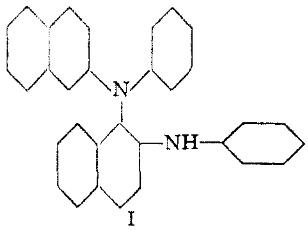
[4] Streiff, *ibid.*, **209**, 151 (1881).

formed when the amine is oxidized with chromium trioxide in glacial acetic acid.

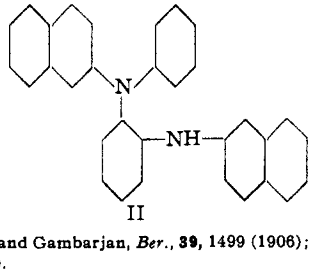
It was considered impractical to attempt to isolate the oxidation products formed by atmospheric oxidation of the amine in rubber-like polymers, inasmuch as only a small percentage of the substance is ordinarily incorporated in such materials, the task of complete extraction is complicated by slow diffusion in the rubber, and contamination of the extract by considerable amounts of low polymer species, addition agents, and catalyst residues is difficult to avoid. It was therefore decided to carry out the oxidation in the absence of rubber.

Permanganate Oxidation.—When the amine was treated for two hours with potassium permanganate in a cold acetone solution containing a small amount of formalin, a tarry residue was obtained on evaporation; ether extraction yielded a crystalline product described below. When formalin was omitted and the reaction mixture was allowed to stand for two days at room temperature, the yield of this product was increased by more than threefold. It was expected that this substance might be *sym*-diphenyldinaphthylhydrazine, since the oxidation of diphenylamine or di-*p*-tolylamine under the same experimental conditions is known to yield the corresponding tetrasubstituted hydrazines.[5] However, an investigation of the purified substance and some of its derivatives disclosed that this product is the isomeric semidine, N-(2-naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine, which is analogous to the product obtained by Wieland and Süsser[6] on permanganate oxidation of dinaphthylamine, and it is unlikely that the semidine was formed by rearrangement of the hydrazine as an intermediate.[7]

The experiment chosen to decide between the two possible structures, I and II, of the semidine was based on the closely related fact that hydrolysis of N-phenyl-2-naphthylamine or N-*o*-(or *p*-)-tolyl-2-naphthylamine with concentrated hydrochloric acid at 240° yields aniline or *o*-(or *p*-)-toluidine and 2-naphthol.[8] Hydrolysis of the semidine under these conditions was found to yield almost the theoretical amount of aniline, and neither 2-naphthylamine nor naphthalene could be found in the reaction products. These results are consistent with structure I.[9]

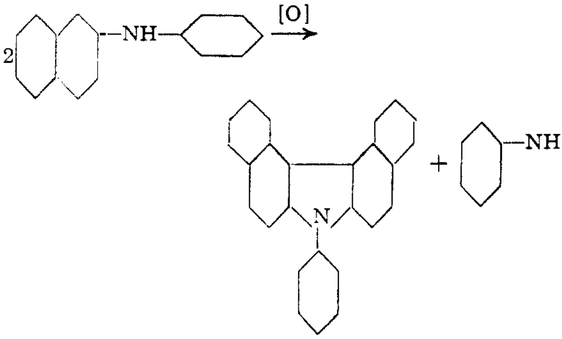


I



II

When the tar remaining after extraction of the semidine was distilled under reduced pressure, there were obtained a small amount of diacetone alcohol, which was doubtless derived from the solvent, a fraction containing a considerable proportion of unreacted N-phenyl-2-naphthylamine, and one containing a very viscous tar which could not be recrystallized from ordinary solvents even after redistillation followed by mercury vapor distillation. Reaction of the tar with picric acid and decomposition of the resulting picrate yielded 7-phenyl-dibenzo[*c*,*g*]carbazole[10] (III), which is probably formed by the condensation of two molecules of the parent amine with elimination of one molecule of aniline.



III

Lead Dioxide Oxidation.—When a benzene solution of the amine was treated with lead dioxide for two days at room temperature a tar was obtained. Ether extraction of the latter yielded some unreacted amine, but the extract was found not to contain any of the semidine described above. Distillation of the extracted tar under reduced pressure yielded additional unreacted amine and two tar fractions. Reaction of one of these fractions with picric acid formed a dipicrate which was decomposed to yield an unidentified yellow crystalline substance having the composition $C_{27}H_{20}N_3O_2$. From the remaining tar fraction there was obtained, by isolation as the picrate, a considerable amount of 7-phenyl-dibenzo[*c*,*g*]carbazole which was found to be identical with that (III) obtained on permanganate oxidation.

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(5) Wieland and Gambarjan, *Ber.*, **39**, 1499 (1906); Wieland, *ibid.*, **40**, 4260 (1907).

(6) Wieland and Süsser, *Ann.*, **392**, 169 (1912).

(7) Wieland and Süsser, ref. 6, showed that a naphthylaminotrinaphthylamine is definitely not formed by rearrangement of tetranaphthylhydrazine.

(8) Friedländer, *Ber.*, **16**, 2089 (1883).

(9) An attempt to synthesize the semidine by an independent method involving reaction of the parent amine with sodium ethylate and iodine, ref. 6, proved unsuccessful.

(10) Walder, *Ber.*, **15**, 2166 (1882), prepared this substance from di-2-naphthol and zinc aniline chloride.

Absorption Spectra of Oxidation Products.—Figure 1 gives the absorption curves for a purified sample of N-phenyl-2-naphthylamine and for those oxidation products that were isolated in an essentially pure state. With one exception[11] the spectra were determined in the region 230–390 mμ. It is observed that oxidative condensation of two molecules of the parent amine to form the semidine has only a minor effect on the spectrum. On the other hand, when condensation takes place with the elimination of a molecule of aniline, the resulting carbazole derivative has absorption characteristics resembling those of the parent substance below about 320 mμ, but displays three absorption maxima instead of one in the range of 320–370 mμ. The unidentified compound $C_{27}H_{20}N_3O_2$ is observed to be quite different from the other substances in its absorption features. The possible bearing of these results on the problem of determining spectrophotometrically the amount of N-phenyl-2-naphthylamine in a rubber-like material that may have undergone an appreciable amount of oxidation is apparent. Table I contains the wave lengths of the maxima and minima, and the corresponding values of the specific absorption coefficient *K*, for the curves shown in Fig. 1.

TABLE I

ABSORPTION CHARACTERISTICS OF N-PHENYL-2-NAPHTHYLAMINE AND SOME OF ITS OXIDATION PRODUCTS IN ISO-OCTANE

Wave length, mμ	*K* (l./g. cm.) Maxima	Minima
	N-Phenyl-2-naphthylamine	
342	16.1	
326		13.7
308	85.2	
282		50.5
271	105.1	
240		78.5
238	83.0	
231		63.7
	N-(2-naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine	
352	22.0	
333		17.2
303	90.5	
286		67.1
274	115.0	
261		85.7
246	98.0	
234		78.8
	7-Phenyl-dibenzo[*c*,*g*]carbazole	
365	76.0	
354		34.7
348	56.5	
335		25.4
334	25.7	
322		14.1
305	59.1	
298		46.2
281	110.5	
258		61.9
243	99.9	
234		82.8
	$C_{27}H_{20}N_3O_2$[11]	
388	1.9	
379		1.78
241	122.0	

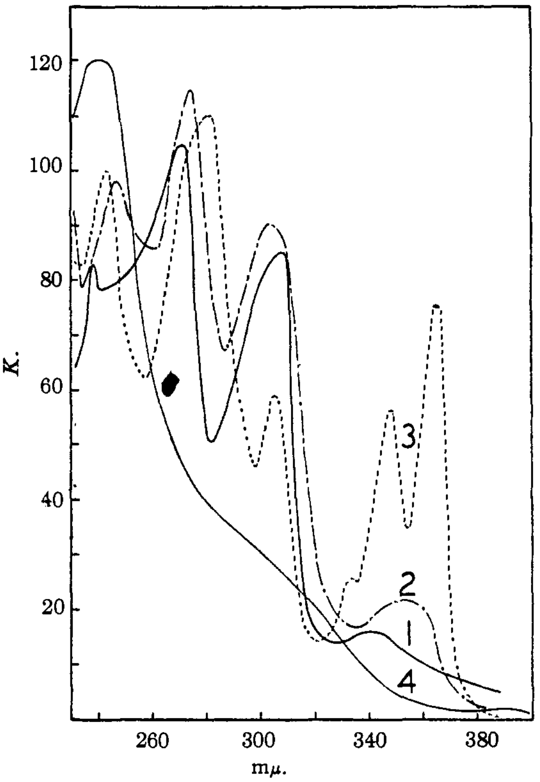

Fig. 1.—Ultraviolet absorption spectra of N-phenyl-2-naphthylamine (curve 1), N-(2-naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine (curve 2), 7-phenyldibenzo[*c*,*g*]-carbazole (curve 3), and $C_{27}H_{20}N_3O_2$ (curve 4) in iso-octane solution.

Experimental[12]

Permanganate Oxidation of N-Phenyl-2-naphthylamine.—Two hundred fifty grams of a commercial grade of the amine, m. p. 104.5–107°, was dissolved in 2 liters of dry acetone and the solution was cooled to 5–8°. One cc. of formalin (40%) was added, and to the cooled, stirred solution there was added in small portions 63 g. of finely powdered potassium permanganate. After two hours of stirring 50 cc. of alcohol was added and the mixture was heated to boiling and filtered to remove manganese dioxide. The latter was extracted with 500 cc. of acetone and the combined filtrates were evaporated to dryness to yield 320 g. of a dark tar. This was taken up in 500 cc. of ether, filtered and evaporated to dryness to yield 270 g. of a dark tar (A). During concentration of the solution about 14 g. of brownish crystals was deposited. These were separated and recrystallized twice from ether to yield almost colorless crystals (I), m. p. 164–165°, uncor.

N-(2-Naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine.—The oxidation experiment was repeated with omis-

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[11] The low solubility of the compound $C_{27}H_{20}N_3O_2$ in iso-octane necessitated dilution with about 20% of ethylene dichloride.

[12] Melting points are corrected unless otherwise noted.

sion of the formalin and alcohol, and the reaction mixture was allowed to stand for forty-eight hours at room temperature. This procedure yielded 46 g. of crude crystals which, after recrystallization, proved to be identical with crystals I; m. p. 163–164°, uncor.; mixed m. p. with I unchanged. *Anal.* Calcd. for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42; mol. wt., 436. Found: C, 87.90; H, 5.44; N, 6.56; mol. wt. (in benzene), 404, 418. This substance does not appear to have been reported previously. It gave a colorless solution in benzene, was insoluble in glacial acetic acid and concentrated hydrochloric acid, and was slightly soluble in concentrated sulfuric acid, the latter solution being colorless. On addition of sodium nitrite to a suspension of the substance in hydrochloric acid a permanent green color was instantly developed. These properties indicate a secondary amine rather than a tetrasubstituted hydrazine.

Attempted Benzidine Rearrangement of I.—A solution of 0.1 g. of I in 5 cc. of ether was added dropwise with shaking to 15 cc. of cold 20% hydrochloric acid and the mixture was allowed to stand for thirty minutes. The product was filtered off and washed with dilute hydrochloric acid and with ether. It was then suspended in 25 cc. of hot 2% hydrochloric acid containing a few per cent. of alcohol, made slightly alkaline with sodium hydroxide, the mixture was warmed for fifteen minutes, and the product was filtered off, washed and dried. Crystallization from an aniline–alcohol mixture, followed by washing with cold alcohol and drying *in vacuo*, yielded a product (II) of m. p. 155–158°, uncor.

The product II was dissolved in 150 cc. of alcohol and refluxed for four hours with 5 cc. of 5% sodium hydroxide. The solution was neutralized with carbon dioxide, evaporated to dryness, and the residue extracted with hot xylene. The product obtained on evaporation was crystallized from a hot xylene–alcohol mixture and the starting material I, m. p. 163–164°, uncor., was recovered.

Attempted Reduction of I.—A solution of 0.1 g. of I in 50 cc. of alcohol was refluxed for six hours with a large excess of zinc dust and glacial acetic acid containing a small proportion of concentrated hydrochloric acid. The solution was filtered, concentrated to a small volume, neutralized with sodium carbonate and extracted twice with ether. Evaporation of the ether yielded a crystalline residue, m. p. 160–162°, uncor., resembling the starting material.

Dipicrate of I.—A solution of I in alcohol containing a little xylene was treated with alcoholic picric acid. A slow deposition of long yellow needles occurred. Recrystallization from a hot alcohol–benzene mixture yielded the dipicrate, m. p. 117–118° (uncor.). *Anal.* Calcd. for $C_{32}H_{24}N_2 \cdot 2C_6H_2OH(NO_2)_3$: N, 12.5. Found: N, 13.4.

Hydrochloride of I.—One gram of I was dissolved in 50 cc. of dry ether containing 5 cc. of benzene, and dry hydrogen chloride was passed through the solution. The white reaction product was formed almost immediately. Removal of the solvent and excess hydrogen chloride by evacuation at room temperature yielded the hydrochloride. The product slowly liberated hydrogen chloride at room temperature and had no definite melting point. *Anal.* Calcd. for $C_{32}H_{24}N_2 \cdot HCl$: Cl, 7.5. Found: Cl, 7.29, 7.05.

A benzene solution of the hydrochloride was shaken with aqueous sodium hydroxide, separated, washed and evaporated to dryness. The resulting oily residue was taken up in ether to yield I, m. p. 163–164° (uncor.); mixed m. p. with I unchanged.

Nitrosamine of I.—Two grams of I was dissolved in a mixture of 25 cc. of glacial acetic acid and 60 cc. of acetone, and a solution of 1 g. of sodium nitrite in 50 cc. of water was added with stirring. The yellow precipitate which formed immediately was filtered off, washed with water, acetone, and ether, and recrystallized from a methanol–benzene–ether mixture. The product was dried in a darkened vacuum desiccator at room temperature to yield a yellowish-white powder, m. p. 180° (dec.). *Anal.* Calcd. for $C_{32}H_{23}N_2 \cdot NO$: N, 9.0. Found: N, 10.5, 10.4.

Acetyl Derivative of I.—0.5 gram of I was dissolved in a mixture of 20 cc. of glacial acetic acid and 10 cc. of acetic anhydride and refluxed overnight with exclusion of moisture. The reaction mixture was poured into a large volume of a methanol–water mixture and the resulting emulsion was coagulated by the addition of 2 cc. of concentrated calcium chloride solution. The product was filtered off, washed with alcohol and dried *in vacuo* at room temperature to yield a gray-white powder, m. p. 170–175°, uncor. (dec.). *Anal.* Calcd. for $C_{32}H_{23}N_2 \cdot C_2H_3O$: C, 85.33; H, 5.48; N, 5.86. Found: C, 85.20, 84.98; H, 5.35, 5.33; N, 6.21, 6.18.

Hydrolysis of I.—Ten grams of I and 40 cc. of concentrated hydrochloric acid were each divided into four equal portions and the mixtures were sealed in glass tubes. The latter were placed in a brass-lined steel bomb containing some concentrated hydrochloric acid for the purpose of minimizing the pressure within the tubes, and the system was heated for six hours at 238–244°. After the contents had cooled and the bomb had been opened, the tubes were found to have been explosively shattered. Explosion probably occurred in the neighborhood of 200°, as was indicated by a sudden increase in the thermocouple reading in this temperature region. The reaction mixture was treated with excess sodium hydroxide and filtered, and the residue was washed with hot dilute sodium hydroxide. The combined filtrates were extracted twice with ether, and evaporation of the ether yielded about 2 cc. of aniline, b. p. 183°. This product was identified by the bleaching powder and isocyanide tests, and by conversion into phenylthiourea and benzamide.

The residue remaining after ether extraction was extracted with hot alcohol, and a brown oily residue was recovered on evaporation of the filtrate. Extraction of the oil with hot water yielded a small additional amount of aniline. The remainder of the oil was dissolved in hot benzene, filtered and evaporated to dryness. On taking up the resulting residue in a little ether and cooling in ice-water, a tan crystalline product was deposited. Recrystallization from a benzene–ether mixture yielded about 0.1 g. of almost colorless crystals, m. p. 141.5–142.5°, which gave a blue fluorescence in ether and an unchanged melting point on mixture with 7-phenyl-dibenzo[*c*,*g*]carbazole (to be described below). No evidence was found for the presence of 2-naphthylamine or naphthalene in the reaction products.

Distillation of Tar A.—53 grams of tar A was distilled under reduced pressure to give three fractions: (1) A yellow liquid, b. p. 108–112° (735 mm.), which was microdistilled to yield about 4 cc. of a colorless liquid, b. p. 155–165°. *Anal.* Calcd. for diacetone alcohol: C, 62.03; H, 10.41; mol. wt., 116; $d^{20}{}_4$ 0.938; $n^{9}{}_{\mathrm{D}}$ 1.430; b. p. 164–166°. Found: C, 61.85, 61.88; H, 10.41, 10.50; N, negative; mol. wt. (in *p*-bromotoluene), 107; $d^{20}{}_4$ 0.920; $n^{20}{}_{\mathrm{D}}$ 1.420. The product was converted to the 2,4-dinitrophenylhydrazone, m. p. 167–169°, uncor.; mixed m. p. with the dinitrophenylhydrazone (m. p. 173–175°, uncor.) prepared with an authentic sample of diacetone alcohol, 171–173°, uncor. (2) Ten grams of an orange semi-solid mass, b. p. 210–250° (20 mm.), exhibiting strong blue fluorescence in alcohol. Crystallization from cyclohexane yielded N-phenyl-2-naphthylamine, m. p. 108–109°; mixed m. p. unchanged. (3) About 27 g. of a dark glassy tar (B), b. p. 315–321° (10 mm.), which was very soluble in cyclohexane and benzene, slightly soluble in naphtha, and could not be crystallized even after redistillation and mercury vapor distillation.

7-Phenyl-dibenzo[*c*,*g*]carbazole.—Tar B (1.38 g.) reacted with picric acid (2.05 g.) in a small amount of hot benzene to form, on cooling, a red crystalline picrate. Two recrystallizations from hot benzene yielded 1.0 g. of picrate melting at 168.5–169.5°. Concentration of the filtrates yielded a second crop weighing 0.4 g. One and three-tenths grams of the picrate was decomposed with hot dilute ammonium hydroxide to form an oily semi-solid mass. Crystallization from an ether–alcohol mixture yielded 0.15 g. of tan crystals which were crystallized three times from ether–alcohol mixtures to give colorless crystals, m. p. 143.5–144.5°. This product gave a violet color with concentrated sulfuric acid, a red color with hot ferric chloride solution, and a strong blue fluorescence in alcohol.

It was very soluble in ether and benzene and slightly soluble in alcohol and glacial acetic acid. *Anal.* Calcd. for $C_{26}H_{17}N$: C, 90.93; H, 4.99; N, 4.08; mol. wt., 343; m. p. (lit.[10]) 144°. Found: C, 90.26, 90.55; H, 4.97, 5.01; N, 4.20, 4.27; mol. wt., 350, 354, 335, 337 (average 344); m. p. 143.5–144.5°.

7-Phenyl-dibenzo[*c,g*]carbazole Dipicrate.—Conversion of a sample of the carbazole to the picrate by the procedure described above yielded the red crystalline product. *Anal.* Calcd. for $C_{26}H_{17}N \cdot 2C_6H_2OH(NO_2)_3$: N, 12.23; m. p. (lit.[10]) 169°. Found: N, 12.10, 12.05; m. p. 168.5–169.5°.

Lead Dioxide Oxidation of N-Phenyl-2-naphthylamine.—Two hundred fifty grams of the amine was dried *in vacuo* at 70°, dissolved in 5 liters of dry benzene, and stirred with 250 g. of lead dioxide for 48 hours at room temperature. The solution was filtered and evaporated to yield a dark tar. When the tar was taken up in about 1 liter of ether, about 75 g. of a crystalline residue remained. A portion of the residue was recovered from ether and was identified as unreacted amine, m. p. 108°; mixed m. p. unchanged. On evaporation of the ether extract 157 g. of a dark tar (C) was obtained. Seventy-five grams of C was distilled under reduced pressure to give three fractions: (1) Forty-seven and five-tenths grams of a white crystalline product, b. p. 235–270° (20 mm.), which was recrystallized twice from a cyclohexane–acetone mixture and identified as additional unreacted N-phenyl-2-naphthylamine. (2) Five grams of a red viscous tar, b. p. 275–285° (20 mm.), which could not be crystallized, but after reaction with 5.8 g. of picric acid in a small amount of hot benzene, a red crystalline picrate separated immediately. This was recrystallized twice from benzene and decomposed with hot dilute ammonium hydroxide to yield 2 g. of a dark tar which underwent an almost complete transition to yellowish crystals on standing at 10° for several days. Recrystallization twice from a benzene–alcohol–acetone mixture yielded yellow crystals, m. p. 190° (dec.). *Anal.* Calcd. for $C_{27}H_{20}N_3O_2$: C, 77.49; H, 4.82; N, 10.04; mol. wt., 418. Found: C, 76.86; H, 4.79; N, 10.84; ash, 0.0; mol. wt. (in camphor), 412. The dipicrate melted at 156° (dec.). *Anal.* Calcd. for $C_{27}H_{20}N_3O_2 \cdot 2C_6H_2OH(NO_2)_3$: C, 53.43; H, 2.99; N, 14.38. Found: C, 57.24; H, 3.05; N, 12.33. (3) Twelve grams of a very viscous red tar, b. p. 320–350° (20 mm.), which reacted with 19.9 g. of picric acid in hot benzene to yield a red crystalline picrate. Recrystallization twice from hot benzene and decomposition with hot dilute ammonium hydroxide gave 3.9 g. of dirty yellow crystals. These were recrystallized 3 times from benzene–alcohol mixtures to yield pale green crystals, m. p. 137–140°, which gave the same color tests, fluorescence, and solubility properties as were described above for the 7-phenyl-dibenzo[*c,g*]carbazole isolated from the permanganate oxidation products; mixed m. p. with the latter, 140–142°. Conversion to the picrate gave a product with m. p. 165–168°; mixed m. p. with the corresponding picrate obtained from the permanganate oxidation product, 165–168.5°.

Absorption Spectra.—The measurements were made with a Beckman quartz prism spectrophotometer, a hydrogen discharge tube serving as the light source. Readings were taken at 1 mμ intervals in the vicinity of maxima and minima, and at 5 mμ intervals elsewhere. Solute concentrations of about 0.01 g./l. were employed. Selected lots of the purified solvents were used, and suitable corrections were made for background absorption.

Acknowledgment.—The authors wish to thank Mr. Julius V. Sommer for some of the analyses reported in this work, and Miss Jean Hund for technical assistance in the spectrophotometric measurements.

Summary

1. The oxidation of N-phenyl-2-naphthylamine by potassium permanganate in acetone and by lead dioxide in benzene has been carried out.

2. From the permanganate oxidation products there have been isolated N-(2-naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine, and 7-phenyl-dibenzo[*c,g*]carbazole.

3. From the lead dioxide oxidation products there have been isolated 7-phenyl-dibenzo[*c,g*]-carbazole and an unidentified product having the composition $C_{27}H_{20}N_3O_2$.

4. Some derivatives of N-(2-naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine and of $C_{27}H_{20}N_3O_2$ have been synthesized and described.

5. The ultraviolet absorption spectra, in isooctane solution, of N-phenyl-2-naphthylamine and some of its oxidation products have been compared and the spectral characteristics have been recorded.

ELIZABETH, NEW JERSEY RECEIVED DECEMBER 29, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL COMPANY, INC.]

The Absorption Spectra of the Vitamins and Provitamins D[1]

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Observations on the ultraviolet absorption spectra of the various D vitamins[2,3,4,5] and provitamins[6] have been reported in the literature by various authors. There also have been reported spectra of several of the esters of these compounds, particularly of the nitro substituted benzoyl esters.[5,7]

It is the purpose of this paper to describe the spectra of the D vitamins, provitamins and several of their esters, including those mentioned by Huber and Barlow,[5] with a view to characterization and possible assay of vitamin preparations and intermediates by absorption spectrophotometry. We have examined particularly the 3,5-dinitrobenzoates, the 3,5-dinitro-4-methylbenzoates, the 3-nitro-4-methylbenzoates, and the 4-nitrobenzoates of vitamins D_2 and D_3, ergosterol and 7-dehydrocholesterol. These have been studied variously in alcohol, hexane, and chloroform solutions.

The D provitamins, such as ergosterol (I), 7-

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[2] Brockmann and Busse, *Z. physiol. Chem.*, **256**, 252 (1938).

[3] Anderson, Bacharach and Smith, *Analyst*, **62**, 430 (1937).

[4] Schenck, *Naturwiss.*, **25**, 159 (1937).

[5] Huber and Barlow, *J. Biol. Chem.*, **149**, 125 (1943).

[6] Hogness, Sidwell and Zscheile, *J. Biol. Chem.*, **120**, 239 (1937).

[7] Windaus and Rygh, *Nachr. Ges. Wiss. Göttingen*, Math.-physik. Klasse, **25**, 202 (1928).