hours). The crude product was obtained by diluting the reaction mixture with ice and water.

α-*p*-Tolylsulfonyl-*n*-butyramide (XI).—The crude product from the ethylation of 51 g. (0.24 mole) of α-*p*-tolylsulfonylacetamide (V) in 250 ml. of absolute alcohol weighed 33 g. (60%). Three recrystallizations from benzene gave 21 g. (35%), m. p. 175–175.5°.

α-*p*-Tolylsulfonyl-α-isoamylacetamide (XII).—From 26 g. (0.12 mole) of V in 100 ml. of absolute alcohol a crude yield of 26 g. (76%), m. p. 133–135° (uncorr.) was obtained. After recrystallization from dilute alcohol the product weighed 15 g. (44%), m. p. 151.5–152°.

α-*n*-Butylsulfonyl-*n*-butyramide (XIII).—From 8.5 g. (0.05 mole) of α-*n*-butylsulfonylacetamide (VI) in 200 ml. of sodium ethoxide solution only 3.0 g. of product was obtained by dilution with ice and water. An additional 2.0 g. was obtained by concentrating the filtrate. The combined products were recrystallized from ligroin. The yield of purified material was 4.2 g. (40%), m. p. 125–125.5°.

α-Benzylsulfonyl-*n*-butyramide (XIV).—The product from 21.3 g. (0.1 mole) of α-benzylsulfonylacetamide (VII) in 200 ml. of sodium ethoxide solution was recrystallized from 1 l. of boiling water. The purified product weighed 14 g. (62%), m. p. 196–198°.

Ackowledgment.—The authors are grateful to the Faculty Research Committee of the University of Pennsylvania for a grant to aid this investigation.

Summary

The preparation of α-sulfonyl (I) and α,α-disulfonyl (II) derivatives of amides has been in-

$$\underset{\text{I}}{RSO_2CHR'CONH_2} \qquad \underset{\text{II}}{(RSO_2)_2CHCONH_2}$$

vestigated. The influence of temperature on the yields of metathesis products from mercaptides and sulfinates has been described.

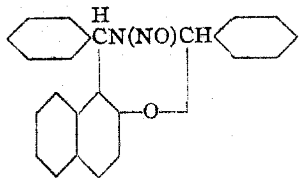
PHILADELPHIA, PENNA. RECEIVED NOVEMBER 12, 1937

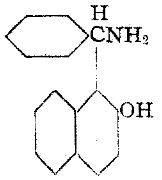
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Action of Nitrous Acid on Phenyl-beta-Naphtholaminomethane. III

BY FRANCIS EARL RAY AND WALTER R. HAEFELE

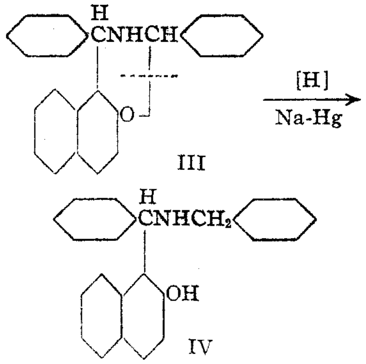
A previous paper of this title[1] explained the formation of N-nitroso-1,3-diphenyl-4,2-β-naphtho-iso-oxazine, I, and 1,6-dinitro-2-naphthol from phenyl-β-naphtholaminomethane, II, and nitrous acid by assuming a preliminary dissociation of the amine into benzaldehyde, β-naphthol and ammonia.


I


II

We now wish to report further on reactions of this type. While some of the structures can be advanced only tentatively, the present status of the work is recorded inasmuch as the authors are unable, at this time, to continue the research.

The iso-oxazine, III, as well as the nitroso derivative, I, give no reaction with ferric chloride. When, however, the iso-oxazine, III, is reduced with sodium amalgam, the compound obtained melts at 143° and gives a strong violet color with ferric chloride.



III
IV

The iso-oxazine does not form a salt but the reduction product readily forms stable, crystalline salts. Analyses and molecular weight determinations all point to the compound being phenyl-β-naphthol-N-benzylaminomethane, IV. In distinction from the iso-oxazine this compound is not hydrolyzed by boiling hydrochloric acid.

Evidently reduction attacked the molecule at the carbon–oxygen bond as shown by the dotted line in III.

The nitroso-iso-oxazine, I, was reduced under similar conditions and white needles melting at 141° were obtained. At first it was thought that this substance was identical with that obtained above, but a mixed melting point showed almost

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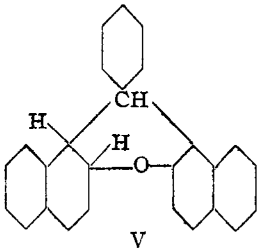
[1] Ahmed and Hemphill with Ray, THIS JOURNAL, **56**, 2403 (1934).

20° difference. In addition the compound contained no nitrogen and gave no reaction with ferric chloride. It was unaffected by boiling with hydrochloric acid.

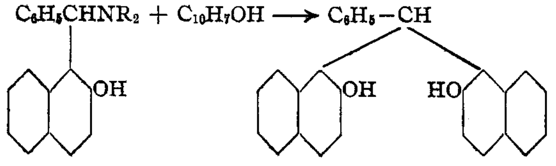
Analyses and molecular weight determinations gave $C_{27}H_{20}O$. No indication could be obtained of hydrogen attached to the oxygen. It seems reasonable to suppose an ether linkage but all attempts to hydrolyze it resulted in tarry products. The carbon skeleton requires one benzyl and two naphthalene nuclei, therefore we have assigned formula V to this compound.



V

The two extra hydrogens have been assigned on the basis of analyses. The theoretical requirement for this compound, $C_{27}H_{20}O$, is 5.55% of hydrogen. Analyses gave 5.63 and 5.74. For $C_{27}H_{18}O$ the hydrogen requirement is only 5.03.

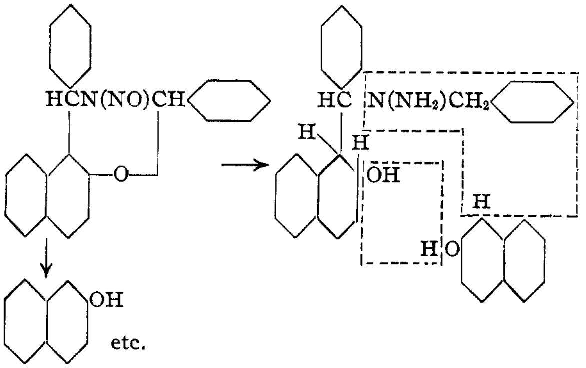
Littman and Brode[2] obtained phenyl-di-β-naphtholmethane by the following reaction



$C_6H_5CHNR_2 + C_{10}H_7OH \longrightarrow C_6H_5-CH$

It melted at 197–198° and was identical with the substance prepared by Hewitt and Turner[3] from benzaldehyde and β-naphthol.

The formation of compound V would require a combination of Littman and Brode's mechanism preceded by the decomposition given previously.[1]

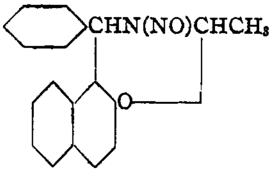


Probably an unstable hydrazine is formed which then reacts with the β-naphthol formed by the decomposition mechanism.

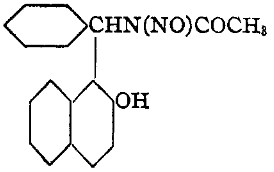
It is, of course, impossible to say when the extra hydrogens were acquired. Much tarry matter was always present which made it impossible to isolate other substances which may have been formed.

During the course of previous experiments[1] *nitrous anhydride* was passed into phenyl-β-naphtholaminomethane, II, in acetic anhydride and ether. A white or faintly yellow colored compound which crystallized in rhombs was obtained melting at 125°. It gave a Liebermann test for the nitroso group, no test with ferric chloride, and was stable to alkali. On hydrolysis with hydrochloric acid phenyl-β-naphtholaminomethane hydrochloride was deposited in crystalline form. The mother liquor gave the iodoform reaction and the cacodyl oxide test. No volatile primary amine was found but nitrous acid was identified by passing the gaseous products through α-naphthylamine sulfanilate.

This nitroso compound was not identical with the nitroso derivative of the condensation product of acetaldehyde and phenyl-β-naphtholaminomethane,[4] VI. We will designate this new nitroso compound as VIII.



VI



VII

It could not be the nitroso derivative of the acetyl compound, VII, as this has a different carbon–hydrogen composition. Also, a substance with formula VII would give a color reaction with ferric chloride. The analyses eliminate the possibility of the hydroxyl group being acetylated.

In the hope of shedding additional light on the problem, this compound, VIII, was also reduced with sodium amalgam. White needles resulted melting at 137°. Analyses and molecular weight determinations gave the formula $C_{34}H_{33}NO_2$. It gave a ferric chloride reaction and, on hydrolysis with hydrochloric acid, the hydrochloride of phenyl-β-naphtholaminomethane. For reference purposes we will call this compound IX. The formula that seems to agree best with the data for

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(2) Littman and Brode, THIS JOURNAL, **52**, 1655 (1930).

(3) Hewitt and Turner, *Ber.*, **34**, 202 (1901).

(4) M. Betti, *Gazz. chim. ital.*, **33**, I, 28 (1903).

VIII is $C_{21}H_{20}N_2O_2$, and for IX, $C_{34}H_{33}NO_2$. At the present time it is not possible to write thoroughly satisfactory structural formulas for these compounds. Compound VIII undoubtedly contains one phenyl and one naphthyl group to each nitrogen besides carbon residues derived from the acetic anhydride. On the other hand, IX contains two phenyl and two naphthyl rings to each nitrogen. One of the naphthyl rings probably is partially reduced also.

Experimental Part

Phenyl-β-naphthol-N-benzylaminomethane, IV.—A solution of 3 g. of 1,3-diphenyl-4,2-β-naphtho-iso-oxazine, III, in 100 cc. of alcohol was treated with 100 g. of 2% sodium amalgam. During the addition of the amalgam the solution was stirred and a steady stream of carbon dioxide was passed in. The temperature was maintained at 60°. The solution was filtered from sodium bicarbonate and on evaporation under reduced pressure fine rhombic crystals were obtained which were recrystallized from a mixture of alcohol and acetone; m. p. 143°; yield 2 g.

Anal. Calcd. for $C_{24}H_{21}NO$: C, 85.5; H, 6.2; mol. wt., 339. Found: C, 85.71, 85.86; H, 6.28, 6.25; mol. wt. (benzene), 316, 332.

Treatment with alcoholic hydrochloric acid gave a compound melting at 176° from which alkali regenerated the original amine.

Anal. Calcd. for $C_{24}H_{22}NOCl$: Cl, 9.48. Found: Cl, 9.50, 9.55.

Phenyl-1,1′-(1,2-dihydro-di-β-naphthyl-ether)-methane, V.—The same procedure was followed in the reduction of the nitroso derivative of 1,3-diphenyl-4,3-β-naphtho-iso-oxazine; white needles melting at 141° from acetone and alcohol. No reaction was obtained with ferric chloride.

Anal. Calcd. for $C_{27}H_{20}O$: C, 90.00; H, 5.55; mol. wt., 360. Found: C, 89.79, 89.73; H, 5.63, 5.74; mol. wt., 322, 329.

Preparation of the Nitroso Compound, VIII.—A mixture of 15 g. of phenyl-β-naphtholaminomethane, 35 cc. of acetic anhydride, 25 cc. of glacial acetic acid, and 30 cc. of anhydrous ether was allowed to stand for two hours with frequent stirring. It was then cooled to −20° and nitrous anhydride passed into the mixture until a deep blue color resulted. The solid dissolved during the course of an hour. The solution was then poured into a beaker and 50–75 cc. of cold water added. As soon as effervescence ceased, 200 cc. of alcohol was added and on stirring the solution deposited white rhombic crystals which soon acquired a faint yellow tinge. Recrystallization from acetone and alcohol gave large well-defined crystals melting at 125°. The best yields are obtained when equimolar proportions of amine and acetylated amine are present.

Anal. Calcd. for $C_{21}H_{20}N_2O_2$: C, 76.05; H, 5.85; N, 8.45. Found: C, 76.32, 76.33; H, 6.16, 6.06; N, 8.8.

The compound is soluble in acetone, pyridine, chloroform and acetic acid; slightly soluble in alcohol.

Compound IX was obtained by reducing compound VIII as previously described. It recrystallized from alcohol in needles and melted at 137°. With ferric chloride a blue color was formed. Hydrolysis with hydrochloric acid gave the salt of phenyl-β-naphtholaminomethane and benzaldehyde.

Anal. Calcd. for $C_{34}H_{31}NO_2$: C, 84.2; H, 6.40; N, 2.89. Calcd. for $C_{34}H_{33}NO_2$: C, 83.78; H, 6.78; N, 2.87. Calcd. for $C_{34}H_{35}NO_2$: C, 83.44; H, 7.16; N, 2.86. Found: C, 82.95, 83.04; H, 6.64, 6.84; N, 2.85, 2.87.

Summary

The reactions of derivatives of phenyl-β-naphtholaminomethane with sodium amalgam have been studied. Only 1,3-diphenyl-4,2,β-naphtho-iso-oxazine gave a direct reduction product. The other compounds all involved molecular rearrangements. Structures have been assigned tentatively to some of these substances.

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