In cases where the products were high boiling and did not distill, the reaction mixture was neutralized with dilute hydrochloric acid and extracted with ether, benzene, or chloroform. After removal of the solvent, the product was either crystallized or distilled. With the cyclic diols, however, no cleavage products were isolated (probably on account of high water solubility, since these products would be expected to be diols and hydroxy acids).

The products obtained from the diols numbered II, VI, IX, X, and IV (Table I) were passed through a gas-phase chromatographic column employing tricresyl phosphate on celite. All the peaks observed were consistent with the materials already known to be present, as given in Table I.

The methods of identifying the cleavage products are listed in Table III.

Alkaline pyrolysis by the above general procedure appeared to give practically no cleavage in the following cases: (1) 2-methyl-4-methoxy-2-pentanol, 44 g. of an initial 50 g. being recovered after treatment with 100 g. of potassium hydroxide at temperatures up to 280°. (2) 4-Methyl-4-methoxy-2-pentanol, with similar recovery after similar treatment. (3) 1,2-Propanediol. (4) Glycerol. (5) 2-Ethyl-1-hexanol. (6) 2,2-Dimethyl-1-propanol. (7) 2-Methyl-2-butanol, although 1% of 2-butanone, b.p. about 90°, m.p. of DNP 116–117°, was obtained, reminiscent of the cleavage of 2-butyl-2-hexanol to 2-hexanone at 600°.[34]

trans-1,3-Dihydroxycyclohexane. Resorcinol was catalytically reduced over Raney nickel catalyst, forming a mixture of *cis-* and *trans*-1,3-dihydroxycyclohexane, b.p. 145–147° (15 mm. in 90% yield).[35] This product contains approximately equal amounts of both isomers.[35,36]

An intimate mixture of 20 g. of this material and 50 g. of powdered, 85% potassium hydroxide was heated at 170° for 15 min., followed by cooling, addition of water, and extraction with hot benzene. After drying and removal of solvent, 6.5 g. of *trans*-1,3-dihydroxycyclohexane, b.p. 137–144° (15 mm.) m.p. 110–115° (from acetone), m.p. trityl ether, 197–198° (lit.[35,36] values, b.p. 135° (13 mm.), m.p. 118°, trityl ether m.p. 199°).

The same procedure was used for pyrolysis of the other cyclic diols.

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(34) V. Grignard and F. Chambret, *Compt. rend.*, **182**, 299 (1926).

(35) H. Lindemann and H. Baumann, *Ann.*, **477**, 78 (1930).

(36) W. Rigby, *J. Chem. Soc.*, 1586 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DEPAUL UNIVERSITY]

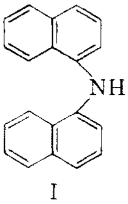
Synthesis of Dinaphthylamines and Tetranaphthyl Hydrazines[1]

EUGENE LIEBER[2] AND S. SOMASEKHARA

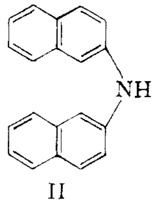
Received April 6, 1959

An improved procedure for the synthesis of the three isomeric 1,1′-, 2,2′- and 1,2′-dinaphthylamines has been devised and their oxidation, by neutral permanganate in acetone, to the corresponding symmetrical tetranaphthyl hydrazines achieved. The treatment of *N*-acetyldinaphthylamines under the same conditions results in recovery of starting material. New properties for the *N*-acetyldinaphthylamines are described. The syntheses of 1,2-dimethyl-1,2-di(1-naphthyl)- and 1,2-diphenyl-1,2-di(1-naphthyl)-hydrazines are also described.

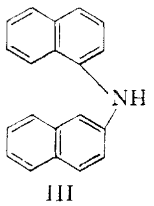
The synthesis of heavily tetra-substituted hydrazines was undertaken with the objective of studying their dissociation in solution to disubstituted nitrogen radicals. The procedure adopted for obtaining the desired hydrazines from the corresponding secondary amines was the method described by Wieland[3] for converting diphenylamine to tetraphenyl hydrazine by oxidation with neutral potassium permanganate. As a prelude to the synthesis of tetranaphthyl hydrazines, the synthesis of three isomeric dinaphthylamines, namely, the 1,1′ (I); the 2,2′ (II); and, the 1,2′ (III), was investigated. A survey of the literature[4-8] revealed that



I



II



III

I, II, and III have been synthesized by a variety of procedures. These, in general, comprised heating naphthols or naphthylamine, either singly on in admixture, at temperatures ranging from 150–300° for extended periods of time, in the presence of substances such as ammonia chloride, zinc chloride, calcium chloride, and sodium acetate. In our hands these methods led only to tarry solids from which only the starting materials could be recovered on a very depleted scale. The method finally adopted was a variation of the procedure described by Merz and Weith[4,5] and represents a distinct improvement over that previously described. The procedure consists in gently heating a mixture of equal parts of a naphthylamine, a naphthol, freshly fused zinc chloride and ammonium chloride to the molten state. A spontaneous, exothermic reaction sets in

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(1) This investigation was sponsored by the Basic Research Group, Corps of Engineers, U. S. Army, Fort Belvoir, Virginia. The authors gratefully acknowledge this assistance.

(2) To whom all correspondence should be addressed. Present address: Dept. of Chemistry, Roosevelt University, Chicago 5, Ill.

(3) C. Weygand, *Organic Preparations*, Interscience Publishers, Inc., New York, N. Y., 1945, p. 244.

(4) V. Merz and W. Weith, *Ber.*, **13**, 1300 (1880).

(5) V. Merz and W. Weith, *Ber.*, **14**, 2344 (1881).

(6) G. Benz, *Ber.*, **16**, 8 (1883).

(7) A. Calm, *Ber.*, **15**, 613 (1882).

(8) L. Landshoff, *Ber.*, **11**, 639 (1978).

almost immediately and lasts for ten to fifteen minutes. The reaction mixture is worked up after thirty minutes. In this manner a 70% yield of II was obtained, while I and III were obtained in 25% yields.

Neutral permanganate in acetone proved a convenient reagent for obtaining the tetranaphthyl hydrazines from I, II, and III. In order to demonstrate that only the hydrogens on the secondary amine nitrogen were involved in the permanganate oxidation, *N*-acetyl derivatives of I and II were prepared by adopting the procedure described by Hurd and Dull[9] for the *N*-acetylation of carbazole. Benz[6] reported a melting point of 217° for the *N*-acetyl derivative of I and 114–115° for that of II. The purified products obtained in this investigation melted at 101–103° for the *N*-acetyl derivative of I, while that of II melted at 80–82°. When these acetyl derivatives were subjected to neutral permanganate oxidation, under the same conditions used for the secondary amines, they were recovered almost quantitatively, demonstrating that the hydrogen atoms on the naphthalene ring were not involved in the oxidation.

Two additional secondary amines, namely, *N*-phenyl-1-naphthylamine and *N*-methyl-1-naphthylamine have also been oxidized to their respective hydrazines with neutral permanganate. However, similar attempts with *N*-ethyl-1-naphthylamine and *N*-phenyl-2-naphthylamine led only to either recovery of starting material or resinous solids which could not be crystallized.

EXPERIMENTAL[10,11]

2,2'-Dinaphthylamine (II). Ten g. (0.07 mole) 2-naphthol, 2-naphthylamine (10 g.; 0.07 mole), ammonium chloride (10 g.) and freshly fused zinc chloride (10 g.) were thoroughly mixed and melted to a brown liquid by gentle heating. A vigorous reaction set in almost immediately and lasted for 15 min. The reaction mixture was maintained in the molten condition for an additional 30 min., cooled to room temperature, and thoroughly crushed under boiling water (200 ml.) to remove all the ammonium chloride and most of the zinc chloride. The solid residue obtained on filtering was treated with hot 10% KOH solution to remove any unreacted 2-naphthol and basic zinc chloride that might have been formed during the reaction. The product was then treated with hot dilute hydrochloric acid in order to remove any 2-naphthylamine present. The solid residue was finally washed with 10% KOH solution and water. It was then taken up in pyridine, charcoal treated, and precipitated with water to obtain the dinaphthylamine as a fine powder. Recrystallization from benzene yielded 12.5 g. (70%) of silvery-yellow platelets, m.p. 172.5°, literature[4] 170.5°.

Anal. Calcd. for $C_{20}H_{15}N$: N, 5.20. Found: N, 5.26.

In the ultraviolet, absorption maxima are exhibited at 265 and 316 mμ with log ε of 4.71 and 4.53, respectively.

1,1'-Dinaphthylamine (I). The procedure and quantities described above were carried out with 10 g. (0.07 mole) of 1-naphthylamine. The brown solid finally obtained was given a charcoal treatment in ethanol and crystallized from ethanol as pale-yellow platelets, m.p. 113.5–114.5°, literature,[8] 111°. The yield was 7 g. (35%).

Anal. Calcd. for $C_{20}H_{15}N$: N, 5.20. Found: N, 5.16.

In the ultraviolet, absorption maxima are exhibited at 248 and 338 mμ with log ε at 4.53 and 4.21, respectively.

1,2'-Dinaphthylamine (III). The procedure described above was carried out with a mixture of 7.2 g. (0.05 mole) each of 1-naphthylamine and 2-naphthol. The pale-brown solid obtained was given 2 charcoal treatments in ethanol and crystallized from aqueous ethanol. A yield of 3.6 g. (27%) of crystalline material, m.p. 98–100°, literature,[6] 111°. Attempts to raise the m.p. by recrystallization were unsuccessful.

Anal. Calcd. for $C_{20}H_{15}N$: N, 5.20. Found: N, 5.40.

In the ultraviolet, absorption maxima are exhibited at 254 and 344 mμ with log ε of 4.73 and 4.30, respectively.

1,1,2,2-Tetra(2-naphthyl)hydrazine. One-hundredth mole (2.7 g.) of II was dissolved in acetone (distilled from permanganate) and the solution cooled in an ice bath. Potassium permanganate (1.2 g.) was added in 6 portions over a period of 2 hours, care being taken to see that the pink color of the solution disappeared before making the next addition of potassium permanganate. At the end of 2 hr., 1 additional g. of potassium permanganate was added in 1 lot, and the reaction allowed to stand at room temperature for 1 hr. Ordinary acetone (20 ml.) was added to remove the remaining pink color and the resulting mixture filtered free of manganese dioxide. The filtrate on concentration and dilution with 95% ethanol, yielded 1.7 g. (65%) of a brownish-yellow solid, m.p. 210–215°. This could not be crystallized from either acetone, alcohol, chloroform, or benzene. It was, therefore, purified by repeated dissolution in acetone and precipitation with ethanol. After 3 such treatments, a yellow powder having a constant m.p. of 256–259° was obtained. It was very sparingly soluble in ethanol but very soluble in acetone, chloroform, and benzene.

Anal. Calcd. for $C_{40}H_{28}N_2$: C, 89.54; H, 5.22; N, 5.22. Found: C, 89.37; H, 5.16; N, 4.96.

In the ultraviolet, absorption maxima are exhibited at 256 and 316 mμ with log ε of 4.71 and 4.53, respectively.

1,1,2,2-Tetra(1-naphthyl)-hydrazine. This was obtained in 60% yield from I by the procedure described above. The analytical sample melts at 235–238°.

Anal. Calcd. for $C_{40}H_{28}N_2$: N, 5.22. Found: N, 5.13.

In the ultraviolet, absorption maxima are exhibited at 248 and 358 mμ with log ε of 4.31 and 4.09, respectively.

1,2-Di(1-naphthyl)-1,2-di(2-naphthyl)hydrazine. This was obtained in 45% yield from III by the procedure described above. The analytical sample melted at 240–242°.

Anal. Calcd. for $C_{40}H_{28}N_2$: C, 89.54; H, 5.22; N, 5.22. Found: C, 89.08; H, 5.62; N, 5.36.

In the ultraviolet, absorption maxima are exhibited at 250 and 330 mμ with log ε of 4.58 and 4.00, respectively.

1,2-Dimethyl-1,2-di(1-naphthyl)hydrazine. From *N*-methyl-1-naphthylamine in 10% yield, m.p. 187–190°.

Anal. Calcd. for $C_{22}H_{20}N_2$: C, 84.61; H, 6.40; N, 8.97. Found: C, 84.20; H, 6.13; N, 9.13.

1,2-Diphenyl-1,2-di(1-naphthyl)hydrazine. From *N*-phenyl-1-naphthylamine by the above procedure; m.p. 177–180°.

Anal. Calcd. for $C_{32}H_{24}N_2$: N, 6.42. Found: N, 6.24.

N-Acetyl-2,2'-dinaphthylamine. One and a half g. of II was refluxed with acetic anhydride (8 ml.) for 3 hr. The reaction was then poured into warm water (50 ml. at 50°). The mixture was neutralized with K_2CO_3, producing an oily substance. This was taken up in acetone-alcohol mixture, charcoal treated, the filtrate concentrated, cooled, and diluted with water. On standing, fragile needles precipitated, very soluble in acetone, benzene, and hot ethanol. Recrystallization, was effected from ethanol, m.p. 80–82°.

Anal. Calcd. for $C_{22}H_{17}NO$: N, 4.50. Found: N, 4.24.

N-Acetyl-1,1'-dinaphthylamine. From I in 50% yield, m.p. 101–103°.

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(9) C. D. Hurd and M. F. Dull, *J. Am. Chem. Soc.*, **54**, 2432 (1932).

(10) Melting points are uncorrected.

(11) Micro analyses by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 4.50. Found: N, 4.32.

Oxidation of N-acetyldinaphthylamines. The procedure with *N*-acetyl-2,2′-dinaphthylamine was typical. One-half gram of the amide was dissolved in acetone (50 ml. distilled from permanganate). After cooling in an ice bath, 0.08 g. $KMnO_4$ was added. The oxidizing agent was not decolorized on standing at 0° for 1 hr. or overnight at room temperature. Since no decolorization had taken place, additional permanganate was not added. The pink color of the solution was then discharged by the addition of ethanol (5 ml.) and gentle warming. It was filtered and concentrated. Dilution of the concentrate with ice water regenerated the starting material in nearly quantitative yield. A similar result was obtained on oxidation of *N*-acetyl-1,1′-dinaphthylamine.

CHICAGO 14, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

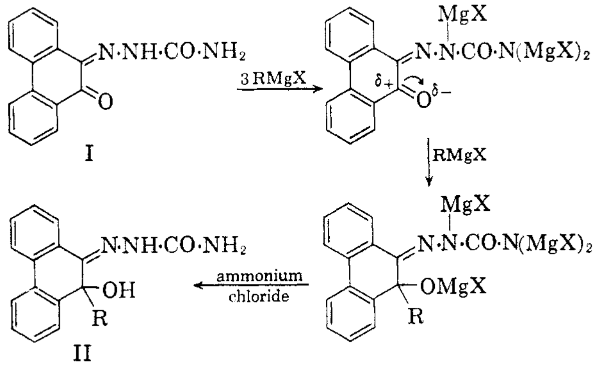
Studies of Quinoid Structures. III.[1] Action of Grignard Reagents on Phenanthrenequinone Monosemicarbazone, Chrysenequinone Monosemicarbazone, and Benzil Monosemicarbazone

WILLIAM IBRAHIM AWAD, ABDEL REHIM ABDEL RAOUF, AND AIDA MOUSTAFA KAMEL

Received April 17, 1959

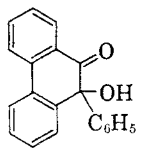
The preferential addition of alkyl and arylmagnesium halides to the carbonyl group of phenanthrenequinone monosemicarbazone, chrysenequinone monosemicarbazone, and benzil monosemicarbazone is described. The constitution of the products is discussed. Infrared data are given for these monosemicarbazones and some of their Grignard products.

Awad and Raouf[1,2] found that Grignard reagents add preferentially to the carbonyl group of phenanthrenequinonimine, chrysenequinonimine, phenanthrenequinone monoxime, and chrysenequinone monoxime. This investigation is now extended to phenanthrenequinone monosemicarbazone, chrysenequinone monosemicarbazone, and benzil monosemicarbazone. The reaction seems to proceed according to scheme A.



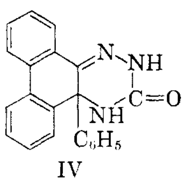
IIa. R = CH_3; IIb. R = C_2H_5; IIc. R = C_6H_5; IId. R = $C_{10}H_7(\alpha)$
Scheme A

The constitution of the Grignard products is based upon the following: (1) the preferential addition of the Grignard reagent to the carbonyl group,[1-4] (2) the action of acetic acid on (IIc) to yield the ketone (III),[1,2] (3) the infrared spectral study (inter-alia), (4) elemental analysis, (5) the inactivity of acetophenone semicarbazone towards Grignard reagent under the conditions of the experiment.

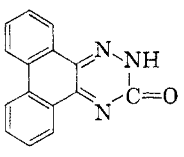


III

When (IIc) was heated with alcoholic hydrochloric acid, water is lost to give (IV). The constitution of (IV) is based upon: (1) elemental analysis, and (2) a comparative study of its infrared spectra with that of (V).[5]



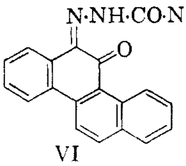
IV



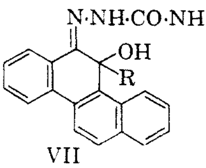
V

(or its enol form).

Similarly, chrysenequinone monosemicarbazone for which structure (VI) was assigned on steric grounds[1,6] reacted with Grignard reagents to give compounds for which structure (VII) was given.



VI



VII

VIIa. R = CH_3; VIIb. R = $C_{10}H_7(\alpha)$

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(1) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **23**, 282 (1958).

(2) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **22**, 881 (1957).

(3) O. Diels and F. ter Meer, *Ber.*, **42**, 1940 (1909).

(4) O. Diels and J. M. Johlin, *Ber.*, **44**, 403 (1911).

(5) Schmidt, Schairer, and Glatz, *Ber.*, **44**, 276 (1911).

(6) W. I. Awad and A. R. A. Raouf, *J. Am. Chem. Soc.*, **77**, 3913 (1955).