The Acid from the Polymerized Ester.—The polymerized ester was hydrolyzed by dissolving it in 15 parts of acetone and adding to the boiling solution 5 equivalents, based on the monomolecular ester, of alcoholic potassium hydroxide. The latter was added, drop by drop, at such a rate that the material remained in solution continually during the hydrolysis. After the mixture had been heated for 6 hours about $^2/_3$ of the solvent was removed by distillation, the solution diluted somewhat and the remainder of the solvent driven off with steam. The residue was poured into a considerable volume of water and ice and acidified with dil. sulfuric acid. After 8 hours the liquid was decanted from the precipitated material. The yield of the slightly yellow, amorphous acid thus obtained was quantitative.

Analysis. Calc. for $(C_{11}H_{10}O_2)_x$: C, 75.86; H, 5.74. Found: C, 75.51; H, 6.00.

The finely powdered acid was intimately mixed with 3 times its weight of anhydrous barium hydroxide and an equal weight of coarse sand. A layer of the mixture was placed in a combustion tube which was closed at one end. The tube was heated until the material had become somewhat viscous and a suction flask was then attached to the open end of the tube. The apparatus was evacuated through the suction flask and heat again applied to the tube. The amorphous material swelled, gradually decomposed and a dark colored oil was slowly driven into the receiver. The latter was dissolved in absolute ether and dried with fused sodium sulfate. A portion of the oil, b. p.$_{10\ mm.}$ 120–140°, was analyzed.

Analysis. Calc. for $C_{10}H_{10}$ (phenylbutadiene): C, 92.23; H, 7.77. Found: C, 90.65; H, 7.65.

Summary

1. The preparation of allyl ester of cinnamalacetic acid and its hexabromide is described.

2. When heated the ester polymerized to a considerable extent to an amorphous, amber-like material which had the same percentage composition as the monomolecular ester.

3. The polymerized ester was readily hydrolyzed to an amorphous acid which had the same percentage composition as cinnamalacetic acid. When the acid was heated with barium hydroxide a mixture of liquid compounds, undoubtedly hydrocarbons, resulted; the latter were formed by the elimination of carbon dioxide from the amorphous acid.

Ann Arbor, Michigan

[Contribution from the Chemical Laboratory of the University of Michigan]

THE NITRATION OF 1,1′-BINAPHTHYL

By C. S. Schoepfle

Received April 12, 1923

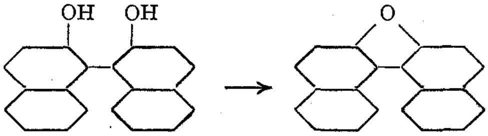
In the course of an investigation it became necessary to prepare 4-nitro-1,1′-binaphthyl for use as an intermediate. A mononitro- and dinitro-1,1′-binaphthyl are described in the literature by Julius[1] who obtained the former by nitrating 1,1′-binaphthyl in acetic acid at room temperature with twice its weight of 47.5% nitric acid. In attempting to repeat this experiment we found that there was no appreciable nitration of the bi-

---

[1] Julius, *Ber.*, 19, 2550 (1886).

naphthyl under these conditions. When 70% nitric acid and a higher temperature were used, nitration was readily effected, but a mononitro derivative was obtained which was not identical with the compound described. It was concluded, therefore, that the 2 samples of binaphthyl likewise were not identical.

The 1,1′-binaphthyl (IV) used in our experiments was prepared by the action of copper powder upon 1-bromonaphthalene, and melted at 157°; it agreed in every respect with a sample of 1,1′-binaphthyl prepared by the action of anhydrous cupric chloride upon 1-naphthyl-magnesium bromide.[2] The material used by Julius, which melted at 154°, was obtained from the distillation of β-binaphthol (I) with zinc dust, a method that had been described previously by Walder.[3] We attempted to prepare 1,1′-binaphthyl by this process, following the conditions stated as closely as possible. However, we obtained a compound melting at 156° which obviously was not 1,1′-binaphthyl and, indeed, an intimate mixture of the two compounds showed a lowered melting point, 120–125°. As we suspected, on analysis it proved to be β-binaphthylene oxide (II). As a further check, β-binaphthylene oxide was prepared from β-naphthol according to Walder's method,[3] wherein he dehydrates this material with zinc chloride at 270°. The product obtained by this procedure was identical with that obtained by the distillation of β-binaphthol with zinc dust. Both compounds gave the same picric acid derivative, melting at 159° (uncorr.), which agrees in its properties with the β-binaphthylene oxide picrate described by Eckstein[4] who gives the melting point as 163° (corr.). Attempts to prepare a picric acid compound with the true 1,1′-binaphthyl under the same conditions were unsuccessful. It was thought that possibly the β-binaphthylene oxide might be an intermediate product in the formation of binaphthyl from β-binaphthol, so the oxide itself was distilled with zinc dust but it distilled unchanged.



I II

The compounds prepared by Julius, then, must be nitro derivatives of β-binaphthylene oxide. To verify this conclusion, β-binaphthylene oxide was nitrated according to his directions, and a mononitro compound melting at 187° was obtained, which agrees in its properties with the supposed mononitro-1,1′-binaphthyl that he describes and for which he gives the melting point of 188°. The dinitro-β-binaphthylene oxide was also pre-

---

[2] Krizewsky and Turner, *J. Chem. Soc.*, **115**, 559 (1919).

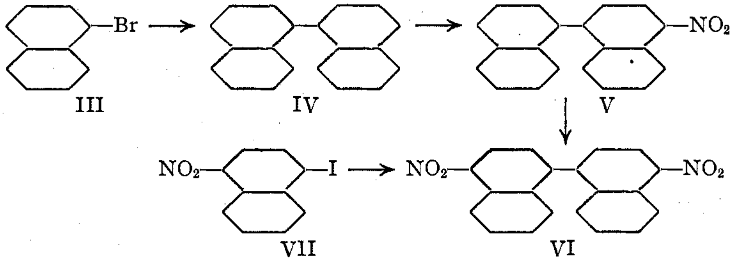
[3] Walder, *Ber.*, **15**, 2166 (1882).

[4] Eckstein, *ibid.*, **38**, 3661 (1905).

pared following Julius' directions, and this again agrees in its properties with the dinitro compound which he obtained, except that after recrystallization from xylene it melts at 306–307° instead of at 280° as stated.

It is evident, therefore, that (1) the distillation of β-naphthol with zinc dust gives β-binaphthylene oxide and not 1,1′-binaphthyl, and (2) that the compounds described in the literature as the mono- and dinitro-derivative of 1,1′-binaphthyl are actually mono- and dinitro-β-binaphthylene oxide, respectively.[5]

The true mononitro-1,1′-binaphthyl (V) is obtained in 85% yield by nitrating 1,1′-binaphthyl in acetic acid with 70% nitric acid, and melts at 104°. When excess of nitric acid is used, a dinitro derivative melting at 246° is obtained in 60% yield, with small amounts of 2 other isomeric compounds melting at 228° and 144°, respectively. The further nitration of the mononitrobinaphthyl gives practically the same results, with a 70% yield of the dinitrobinaphthyl which melts at 246°. This compound was thought to be 4,4′-dinitro-1,1′-binaphthyl (VI). Therefore, it was synthesized by the action of copper powder upon 4-nitro-1-iodonaphthalene (VII) and, indeed, the 2 products proved to be identical. Consequently, since 4,4′-dinitro-1,1′-binaphthyl is formed in at least 70% yield upon nitration of the mononitrobinaphthyl, the latter must be 4-nitro-1,1′-binaphthyl.



Experimental Part

β-Binaphthylene oxide (II).—β-Binaphthol (I) was prepared according to Walder's directions[3] by oxidizing β-naphthol with anhydrous ferric chloride in ether solution, and was distilled with 15 times its weight of zinc dust. The oil which distilled solidified on cooling and was crystallized from acetic acid. The compound crystallizes either in long, slender needles or in light yellow leaflets; m. p., 156°. It was obtained colorless after being recrystallized repeatedly, but the melting point remained unchanged.

Analyses. Calc. for binaphthyl, $C_{20}H_{14}$: C, 94.45; H, 5.55. Calc. for binaphthylene oxide, $C_{20}H_{12}O$: C, 89.52; H, 4.51. Found: C, 89.55, 89.47; H, 4.47, 4.44.

Two g. of this compound and 2 g. of picric acid were dissolved in hot benzene, from which the picrate crystallizes in large needles of deep red color melting at 159°.[4]

Analyses. Calc. for $C_{20}H_{12}O.C_6H_2(NO_2)_3OH$: picric acid, 46.1. Found: 46.2, 46.4.

---

[5] The diamino derivative which Julius obtained by reduction of his dinitro compound must also be regarded as a derivative of β-binaphthylene oxide.

Five g. of the compound obtained from the distillation of β-binaphthol with zinc dust was dissolved in 37.5 cc. of hot acetic acid and the solution cooled quickly to produce fine crystals; 5 g. of nitric acid, d. 1.3, was added at room temperature and the mixture allowed to stand overnight. The crystals were then separated, dried and recrystallized from benzene. Compact needles of a light yellow color were obtained; m. p., 187°;[6] yield, 5.7 g.

Analyses. Calc. for nitrobinaphthyl, $C_{20}H_{13}NO_2$: C, 80.24; H, 4.38; N, 4.68. Calc. for nitrobinaphthylene oxide, $C_{20}H_{11}NO_3$: C, 76.66; H, 3.54; N, 4.47. Found: C, 76.73, 76.53; H, 3.69, 3.67; N, 4.32.

The dinitro derivative was prepared by a similar procedure from 40 g. of nitric acid, d. 1.3, by heating to 60°. The compound was recrystallized from xylene, from which small, orange-yellow needles were obtained;[7] m. p., 306–307°; yield, 6.5 g.

Analyses. Calc. for dinitro-binaphthyl, $C_{20}H_{12}N_2O_4$: C, 69.75; H, 3.51; N, 8.14. Calc. for dinitro-binaphthylene oxide, $C_{20}H_{10}N_2O_5$: C, 67.03; H, 2.81; N, 7.82. Found: C, 67.52, 67.38; H, 2.89, 2.84; N, 7.51.

1,1′-Binaphthyl (IV).—The best method available for the preparation of any considerable amount of 1,1′-binaphthyl is probably that of Ullmann and Bielecki[8] who treat 1-iodonaphthalene with copper powder at 285°, obtaining a 74% yield. The principal disadvantage of this method lies in the fact that iodonaphthalene is not easily prepared. Since 1-bromonaphthalene on the other hand is readily obtainable, it seemed desirable to substitute this for iodonaphthalene in the reaction. We have found, indeed, that bromonaphthalene reacts with copper powder at a temperature of approximately 275° to give a satisfactory yield of binaphthyl; the speed of the reaction is of course dependent upon the fineness of the copper powder. The presence of a small amount of iodine appears to have a favorable influence upon the yield.

Two hundred g. of bromonaphthalene, 75 g. of copper powder, and 5 g. of iodine are heated for 4 to 5 hours in a metal bath which is kept at a temperature of 280–285°. If the mixture is stirred occasionally, the copper powder and cuprous bromide show no tendency to agglomerate. After the reaction product has cooled, it is treated with about an equal amount of benzene and filtered, and the residue washed well with benzene. The addition of a few grams of diatomaceous earth facilitates the filtering of the finely divided cuprous bromide. The filtrate is concentrated to remove the benzene, and is then fractionally distilled under reduced pressure.

The fraction distilling below 220°, at a pressure of 13 mm. of mercury, consists of naphthalene and bromonaphthalene with a small amount of binaphthyl. About 35 g. of bromonaphthalene is recovered.

The fraction distilling from 220° to 265° contains most of the binaphthyl, which when pure boils at approximately 240° at the same pressure. The distillate is recrystallized from acetic acid. When the solution is rapidly cooled the binaphthyl crystallizes in colorless leaflets, but with slow cooling, large crystals are obtained which melt at 157°; yield, 47 g. By redistilling the fractions boiling below 220° and above 265°, respectively, an additional 4 g. of binaphthyl is obtained. The total yield based upon the amount of bromonaphthalene used up in the reaction is 50%.

Analyses. Calc. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.04, 94.12; H, 5.52, 5.63.

If the filtrate from the recrystallization of the binaphthyl is concentrated and allowed to stand for several days, a crystalline product is obtained which consists of a

---

[6] Hodgkinson and Limpach, *J. Chem. Soc.*, **59,** 1100 (1891).

[7] Knecht and Unzeitig, *Ann.*, **209,** 140 (1881).

[8] Ullmann and Bielecki, *Ber.*, **34,** 2184 (1901).

mixture of 1,1'- and 1,2-binaphthyl, with a smaller amount of 2,2'-binaphthyl. The latter two compounds are probably formed by a rearrangement of the 1,1'-binaphthyl. The 3 isomers can be separated by fractional recrystallization from petroleum ether.

The red oil which distils above 265° solidifies on cooling and is treated with ether, from which 1.5 to 2 g. of very fine, colorless crystals is obtained. When recrystallized from benzene, the compound melts at 282–283° and is probably identical with the compound that Weitzenböck and Seer[9] obtained from the action of aluminum chloride upon 1-bromonaphthalene, which they suppose to be dinaphthyl-naphthalene. A small amount of perylene may also be isolated from this fraction.

4-Nitro-1,1'-binaphthyl (V).—Ten g. of finely crystalline binaphthyl is suspended in 100 cc. of acetic acid, 5 g. of nitric acid, d. 1.42, is added and the mixture heated on the steam-bath for 30 minutes at a temperature of 90–95°. When the solution has cooled, 8 g. of nitrobinaphthyl has crystallized. About 10 cc. of water is added to the hot filtrate, which upon cooling deposits an additional 2 g. of crystals; yield, 85%. When recrystallized from alcohol, the compound is obtained in light yellow needles melting at 104°. It is readily soluble in benzene or ether, less soluble in acetic acid, and slightly soluble in alcohol or petroleum ether.

Analyses. Calc. for $C_{20}H_{13}NO_2$: C, 80.24; H, 4.38; N, 4.68. Found: C, 80.02, 80.06; H, 4.52, 4.42; N, 4.65.

4,4'-Dinitro-1,1'-binaphthyl (VI).—Ten g. of finely crystalline binaphthyl is suspended in 100 cc. of acetic acid, 5 g. of nitric acid, d. 1.42, is added, and the mixture heated on the steam-bath until a clear solution is obtained. The solution is then treated with an additional 15 g. of nitric acid, d. 1.42, and the heating continued for 2 hours during which time most of the dinitro-binaphthyl crystallizes. The solution is cooled and filtered whereby 8 g. of light yellow crystals is obtained; yield, 60%. After recrystallization from benzene, the compound melts at 246°. It is moderately soluble in hot benzene, slightly soluble in cold benzene, and very slightly soluble in acetic acid, alcohol, ether or petroleum ether.

Analyses. Calc. for $C_{20}H_{12}N_2O_4$: C, 69.75; H, 3.51; N, 8.14. Found: C, 69.64, 69.69; H, 3.61, 3.56; N, 8.03.

The filtrate from the nitration mixture is added to water and the precipitate is filtered, dried and dissolved in a mixture of ether and alcohol. After the solution has stood for several days, it deposits a crystalline product from which 2 other isomeric dinitro-binaphthyls can be isolated in small amounts. They are separated from each other by treating the material with cold benzene, in which 1 isomer is soluble while the other is but slightly soluble. The insoluble portion of the material is separated and dissolved in hot benzene, from which the compound crystallizes in light yellow crystals; m. p., 228°. It has approximately the same solubilities as 4,4'-dinitro-binaphthyl. The isomer which is soluble in cold benzene is obtained in light yellow crystals, m. p., 144°, by concentrating the solution and adding petroleum ether. It is readily soluble in benzene, less soluble in alcohol, ether or acetic acid, and but slightly soluble in petroleum ether.

Analyses. Calc. for $C_{20}H_{12}N_2O_4$: C, 69.75; H, 3.51; N, 8.14. Found for the compound melting at 228°; C, 69.85; H, 3.71; N, 8.25. Found for the compound melting at 144°: C, 69.67; H, 3.59; N, 8.27.

The 4,4'-dinitrobinaphthyl may also be obtained from the mononitro derivative, although there is no advantage to be gained by isolating the latter. Five g. of mononitro-binaphthyl is dissolved in 50 cc. of acetic acid, 10 g. of nitric acid, d. 1.42, is added, and the mixture is heated for several hours on the steam-bath. A few drops of fuming

---

[9] Weitzenböck and Seer, *Ber.*, **46**, **1994** (1913).

nitric acid are usually required to start the nitration;[10] 4.1 g. of 4,4′-dinitrobinaphthyl is obtained; yield, 71%. The 2 isomeric compounds melting at 228° and 144°, respectively, can be isolated from the solution by the procedure given above.

Synthesis of **4,4′-dinitro-1,1′-binaphthyl** (VI).—1-Acetonaphthalide is nitrated in acetic acid[11] and the mixture of the 4- and 2-nitro-acetonaphthalides thus obtained is treated with a limited amount of alcoholic potash, which hydrolyzes the 4-compound but not the 2-compound. To separate the 4-nitronaphthyl amine from the unchanged 2-nitro-acetonaphthalide,[12] the material is dissolved in hot acetic acid and the solution saturated with hydrogen chloride, whereby the former is precipitated as the hydrochloride while the latter remains in solution. The hydrochloride is filtered off, dried and dissolved in hot 95% alcohol, from which the pure amine crystallizes in yellow needles melting at 192°. 4-Nitro-1-iodonaphthalene is prepared by diazotizing this compound and treating with hydriodic acid.[13] Since the amine is but slightly soluble in water and dil. acids, it is dissolved in hot acetic acid, hydrochloric acid is then added, and the solution is cooled; the hydrochloride is thus precipitated in very fine crystals, so that diazotization may take place readily.

Five g. of 4-nitro-1-iodonaphthalene, 2 g. of naphthalene, and 5 g. of copper powder are heated for 4 hours at 220–230°. The naphthalene is added to wash down the material which sublimes on the sides of the flask during the heating. The mixture is cooled, and extracted with hot benzene, the benzene evaporated and the product allowed to stand exposed to air for 24 hours in order to remove the naphthalene by sublimation. The residue is then dissolved in a large amount of hot alcohol, refluxed with animal charcoal, and the solution filtered and concentrated. 4,4′-Dinitro-1,1′-binaphthyl crystallizes upon cooling the solution, and after recrystallization from benzene, melts at 246°; yield, 1.5 g. It is identical in every way with the compound obtained by the direct nitration of 1,1′-binaphthyl, and an intimate mixture of the two shows no change in melting point. No attempt was made to determine the structure of the two isomeric derivatives which were obtained by direct nitration in addition to the main product, 4,4′-dinitrobinaphthyl.

Summary

1. It has been shown that β-binaphthol when distilled with zinc dust gives β-binaphthylene oxide and not 1,1′-binaphthyl as stated in the literature.

2. The compounds described in the literature as mono- and dinitro-1,1′-binaphthyl are mono- and dinitro-β-binaphthylene oxide, respectively.

3. A convenient method for the preparation of 1,1′-binaphthyl is described.

4. 4-Nitro- and 4,4′-dinitro-1,1′-binaphthyl have been prepared and described, and the structures verified by synthesizing the latter from 4-nitro-1-iodonaphthalene.

ANN ARBOR, MICHIGAN

---

[10] Klemenc and Ekl, *Monatsh.*, **39**, 641 (1918).

[11] Lellmann and Remy, *Ber.*, **19**, 797 (1886); **20**, 891 (1887).

[12] Meisenheimer and Patzig, *ibid.*, **39**, 2541 (1906).

[13] Meldola, *J. Chem. Soc.*, **47**, 519 (1885).