The xylene phase was freed of solvent, the residue was distilled at 2 mm., and the distillate was collected in two fractions: (1) b.p. 200–210°, a yellow oil, $n^{25}{}_D$ 1.4877, wt. 0.7 g.; (2) b.p. 210–240°, a yellowish solid, wt. 1.5 g. Both of these fractions gave negative acyloin tests.[38]

p,p′-Tetramethylene-1-phenyl-4-cyclohexylbutane (II, $m = n = 4$).—*p,p′*-Tetramethylene-1,4-diphenylbutane,[3c] 0.95 g. (0.0036 mole), was hydrogenated with 0.1 g. of PtO_2 in a mixture of 10 ml. of glacial acetic acid and 20 ml. of ethyl acetate. The theoretical amount of hydrogen was absorbed in 4 hours and the reaction was stopped. The solution was filtered free of catalyst and was poured into pentane. The pentane phase was washed, dried and the solvents were removed in vacuum. The residual oil was dissolved in pentane and adsorbed on a 125-g. column of alumina (act. I).[30] The column was washed with pure pentane, and the eluate was collected in 25-ml. fractions. Fractions 1–3 contained nothing, fraction 4 contained 0.08 g. of oil. Fractions 3–6 contained 0.70 g. of the desired product, and fractions 9–12 (eluted with ether) gave 0.17 g. of recovered starting material. The product in fractions 3–6, 0.70 g. (71%), had m.p. 47.8–48.4°. For analysis a sample was crystallized from ethanol, needles, m.p. 48.0–48.6°.

Anal. Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 89.04; H, 11.10.

p,p′-Trimethylene-1-cyclohexyl-4-phenylbutane (II, $m = 3, n = 4$).—The reaction and work-up were carried out in a manner similar to that described for the homolog (II, $m = n = 4$). From 150 mg. of the paracyclophane was obtained 25 mg. (16%) of the pure product, needles, m.p. 31.4–32.1°.

Anal. Calcd. for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 88.80, 88.54; H, 10.34, 10.95.

LOS ANGELES, CALIFORNIA

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[38] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[CONTRIBUTION FROM THE MEDICAL RESEARCH LABORATORY, VETERANS ADMINISTRATION HOSPITAL, AND THE DEPARTMENT OF CHEMISTRY, BAYLOR UNIVERSITY COLLEGE OF MEDICINE]

Studies in the Naphthalene Series. I. Oxidative Coupling of 1-Naphthol

BY J. D. EDWARDS, JR., AND J. L. CASHAW

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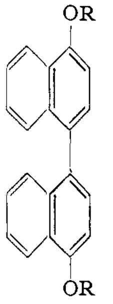
The structure V, 2,2′-bi-1-naphthol, assigned to one of the oxidation products of 1-naphthol has been shown to be correct. All possible interconversions between this binaphthol and its mono- and dimethyl ether have been made. A study of the ultraviolet absorption spectra of the various binaphthyls prepared is presented.

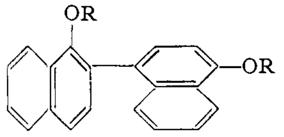
The oxidative coupling of 1-naphthol by means of ferric chloride was first reported by Dianin.[1] That 4,4′-bi-1-naphthol (I) is formed has been shown,[2-4] but it was only recently[5] that a second product was isolated from this reaction and assigned the structure 2,2′-bi-1-naphthol (V) (m.p. 220°).[6] The evidence presented in support of structure V by Ioffe was convincing but not conclusive.

Since we were interested in the synthesis of certain substituted 2,2′-bi-1-naphthols by oxidation of the appropriate 1-naphthols, it was desirable to prove the structure of the oxidation product V of 1-naphthol reported by Ioffe and study some of its reactions.

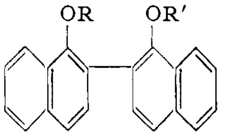
The synthesis of the dimethyl ethers of the three binaphthols, 4,4′-, 2,4′- and 2,2′-bi-1-naphthol (I, III and V) expected from the oxidative coupling of 1-naphthol, was realized by application of the Ullmann reaction. 4,4′-Dimethoxy-1,1′-binaphthyl (II) was formed by the coupling of 4-iodo-1-methoxynaphthalene or from 4-bromo-1-methoxynaphthalene.[7] The product proved to be identical with that obtained by the methylation[2,8] of I



I, R = H
II, R = CH_3



III, R = H
IV, R = CH_3



V, R = R′ = H
VI, R = H; R′ = CH_3
VII, R = R′ = CH_3

which was isolated from the oxidation of 1-naphthol. The identity of this product[2-4] establishes the structure of 4-bromo- and 4-iodo-1-methoxynaphthalene. The 4-iodo-1-methoxynaphthalene was prepared by the interaction of 1-methoxynaphthalene and iodine monochloride.

The synthesis and coupling of 2-iodo-1-methoxynaphthalene were carried out according to the directions of Clemo[3] and gave 1,1′-dimethoxy-2,2′-binaphthyl (VII); mol. wt. (Rast), 300.

From the coupling of a mixture of 2- and 4-iodo-1-methoxynaphthalenes, three compounds were isolated by fractional crystallization. It was shown that two of these were identical with II and VII. The remaining one was therefore 1,4′-dimethoxy-1′,2-binaphthyl (IV).

The complete methylation of V proved to be quite difficult. It was accomplished by repeatedly using large excesses of potassium hydroxide and dimethyl sulfate in diethylene glycol as a solvent. The product was identical with synthetic VII. The structure V postulated by Ioffe[5] for the binaphthol obtained from the oxidation of 1-naphtho-

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[1] A. P. Dianin, *J. Russ. Phys. Chem., Soc.*, **6**, 187 (1874).

[2] A. Corbellini and E. Debenedetti, *Gazz. chim. ital.*, **59**, 391 (1929).

[3] G. R. Clemo, J. G. Cockburn and R. Spence, *J. Chem. Soc.*, 1265 (1931).

[4] W. M. Cumming and G. Howie, *ibid.*, 528 (1932).

[5] I. S. Ioffe and B. K. Kirchevtsov, *J. Gen. Chem.* (*USSR*), **9**, 1136 (1939).

[6] Apparently Ioffe[5] was unaware of the work by Clemo[3] who had synthesized 1,1′-dimethoxy-2,2′-binaphthyl (VII) and on demethylation obtained V (m.p. 212°), and of W. M. Cumming and G. D. Muir, *J. Roy. Tech. Coll.* (*Glasgow*), **4**, 61 (1937); *C. A.*, **31**, 4310 (1937), who obtained a compound postulated as V (m.p. 213°) by the alkaline fusion of 2,2′-binaphthyl-1,1′-disulfonic acid.

[7] E. C. Spaeth, T. A. Geissman and T. L. Jacobs, *J. Org. Chem.*, **11**, 399 (1946).

[8] E. Ostermayer and J. Rosenhek, *Ber.*, **17**, 2453 (1884).

is therefore correct. All the standard procedures for methylation when applied to V gave a compound, the analysis of which indicated it to be a monomethyl ether. The infrared spectrum also indicated the presence of a free hydroxyl group. This same monomethyl ether also was obtained by the partial demethylation of the synthetic dimethoxy compound VII with hydrogen bromide–acetic acid. Methylation of this monomethyl ether gave back the dimethoxy compound VII, but only if the extreme conditions outlined above for the complete methylation of V were used. Structure VI, 1-hydroxy-1′-methoxy-2,2′-binaphthyl, is therefore assigned to this monomethyl ether. Cleavage of the monomethyl ether VI and the dimethoxy compound VII to the dihydroxy compound V was achieved by the use of aluminum chloride.

Since 2,2′-binaphthyl, contrary to 1,1′- and 1,2′-binaphthyl, is free of steric hindrance,[9] the introduction of hydroxyl and methoxyl groups in the 1,1′- positions of 2,2′-binaphthyl should cause strong steric hindrance. That this is true was indicated also by the difficulties encountered in the methylation and demethylation studies of 2,2′-bi-1-naphthol and its derivatives. For these reasons, a study was made of the ultraviolet absorption spectra of the various binaphthyls prepared in this study. By the introduction of hydroxyl or methoxyl groups (I and II) in 1,1′-binaphthyl, the expected bathochromic shifts in the 280–320 mμ region accompanied by the loss of fine structure and broadening of the band occurred. A comparison of the spectrum of 1,2′-binaphthyl[9] to that of the dimethyl ether IV also showed a bathochromic shift and broadening of the band in the 280–320 mμ region. The lack of interference of the 1′-methoxyl group in IV is analogous to a similar effect on the introduction of an even larger (*o*-tolyl) group[10] into the 1′-position of 1,2′-binaphthyl. The spectra of 1,1′-binaphthyl, 1,2′-binaphthyl and their derivatives, as well as 2,2′-binaphthyl, all have absorption maxima in the 280–320 mμ region, whereas 1,1′-dihydroxy-, 1,1′-dimethoxy- and 1-hydroxy-1′-methoxy-2,2′-binaphthyl all have a pronounced hypsochromic shift of the maxima in the 280–320 mμ region. Such would be expected in case of steric hindrance. Since only the 2,2′-binaphthols exhibit absorption maxima in the 255–275 mμ range, differentiation of the oxidation products of various substituted 1-naphthols should be possible.

Clemo[3] postulated that the dinaphtho-(1,2,2′,1′)-furan formed by the dehydration of crude binaphthol obtained by ferric chloride oxidation of 1-naphthol, or from the oxidation of fused 1-naphthol with vanadium pentoxide, was formed from I by "an unusual *meta*-wandering of the 4,4′-binaphthyl link to the 2,2′-position." It would appear, especially since the yield of this dinaphthofuran is always very low, that it originates from the dehydration of V which is formed in a low yield rather than from a rearrangement of I.

Oxidation of I with lead tetraacetate gave in good yield [1,1′-(4,4′)-binaphthalene]-4,4′-dione, a dark purple quinone. This structure was demonstrated by reduction to I. Oxidation of V in like manner, however, gave a colorless solution, although a definite transitory color developed.

In the course of the preparation of 2-iodo-1-methoxynaphthalene, the catalytic reductions of the 2- and 4-nitro-1-methoxynaphthalenes were carried out to give the corresponding amines. Whereas acetylation of 1-methoxy-2-naphthylamine gave the monoacetyl derivative, N-acetyl-1-methoxy-2-naphthylamine, acetylation of 4-methoxy-1-naphthylamine gave a diacetyl derivative. The infrared spectrum of the diacetyl compound did not show any N–H absorption. The structure of the diacetyl derivative is therefore formulated as being N,N-diacetyl-4-methoxy-1-naphthylamine.

Acknowledgments.—The authors are indebted to Mr. Wilbert Adams for the preparation of the nitromethoxynaphthalenes and for the corresponding amino derivatives, and to Mr. B. B. Smith of W. H. Curtin Company for making available a Beckman model DR spectrophotometer and assistance in the determination of the spectra.

Experimental[11]

4-Iodo-1-methoxynaphthalene.—To a solution of 25 g. of 1-methoxynaphthalene in 50 ml. of glacial acetic acid in a 300-ml. flask equipped with a stirrer, was added dropwise with cooling 28 g. of iodine monochloride in 50–60 ml. of glacial acetic acid. The flask was placed in a water-bath at 50° and stirred for 2 hours while a slow stream of air was passed through to remove the hydrogen chloride formed. The contents of the flask were then poured onto crushed ice and, after standing a few hours, the aqueous layer was decanted from the dark oil. The dark oil was washed several times with water, dissolved in ether and washed with sodium bisulfite. The resulting light yellow ethereal extract was washed with water, dried over sodium sulfate, filtered and concentrated over a steam-bath. The residual oil was dissolved in petroleum ether (30–60°) and crystallized at Dry Ice temperature to give 22 g. (45% yield) of colorless crystals, m.p. 54–56°.

Anal. Calcd. for $C_{11}H_9IO$: C, 46.50; H, 3.19. Found: C, 46.55; H, 3.25.

4,4′-Dimethoxy-1,1′-binaphthyl (II).—One gram of 4-iodo-1-methoxynaphthalene and 4 g. of copper powder[12] were heated in an oil-bath at 220–230° for 2 hours. In the same manner 6 g. of 4-bromo-1-methoxynaphthalene,[7] 6 g. of copper powder[12] and a crystal of iodine were heated at 250–260° for 5 hours. After cooling, the products were worked up separately by kneading with hot benzene, filtration and concentration. Upon diluting with methanol and standing overnight in the refrigerator, the crystalline material was filtered and dried, yield 15–20%. Sublimation of the product under vacuum followed by recrystallization from benzene–methanol gave colorless crystals, m.p. 259–260°.

Anal. Calcd. for $C_{22}H_{18}O_2$: mol. wt., 314; C, 84.05; H, 5.77. Found: mol. wt. (Rast), 294; C, 84.19; H, 5.57.

The above products were shown to be identical by mixture melting points with the compound obtained by the methylation[2] of the binaphthol (I).

1,4′-Dimethoxy-1′,2-binaphthyl (IV).—A mixture of 16 g. of 4-iodo-1-methoxynaphthalene, 4 g. of 2-iodo-1-methoxynaphthalene and 20 g. of copper powder[12] was heated at 230–240° with occasional stirring for 5 hours. The resulting solid material was extracted three times with boiling benzene and filtered to give a light red solution. The latter was concentrated to 25 ml. and diluted with methanol. After standing overnight, 4.6 g. of crystalline material was filtered off and shown to be identical with II.

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[9] R. A. Friedel, M. Orchin and L. Reggel, This Journal, **70**, 199 (1948).

[10] M. Orchin, L. Reggel and R. A. Friedel, *ibid.*, **73**, 1449 (1951).

[11] All melting points are uncorrected. The microanalyses reported were carried out by the Huffman Microanalytical Laboratories, Wheatridge, Colorado.

[12] E. C. Kleiderer and R. Adams, This Journal, **55**, 4225 (1933).

Evaporation of the filtrate gave a red oil which was taken up and fractionally crystallized from ligroin (90–120°) to give first a few crystals of II, then 0.2 g. of 1,1′-dimethoxy-2,2′-binaphthyl (VII), and finally 0.3 g. of a colorless crystalline material, m.p. 125.5–126.5°. This product was shown by infrared analysis and mixture melting points to be different from II and VII and is therefore 1,4′-dimethoxy-1′,2-binaphthyl (IV).

Anal. Calcd. for $C_{22}H_{18}O_2$: mol. wt., 314; C, 84.05; H, 5.77. Found: mol. wt. (Rast), 294; C, 84.07; H, 5.72.

Oxidation of 4,4′-Di-1-naphthol (I).—To a suspension of 1 g. of the binaphthol I in 30 ml. of glacial acetic acid there was added portionwise with continuous stirring 1.6 g. of lead tetraacetate[13] suspended in 25 ml. of glacial acetic acid. An immediate dark purple coloration occurred. Stirring was continued for 30 minutes, 5 drops of ethylene glycol was added and the stirring continued for 15 minutes. On filtering and drying, 0.85 g. of purple crystals was obtained. The product was recrystallized from ethyl acetate–ligroin (30–60°). It does not have a melting point, which is characteristic of many extended quinones.

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25. Found: C, 84.61; H, 4.20.

To a warmed solution of 0.5 g. of the quinone dissolved in methanol, an aqueous solution of sodium hydrosulfite was added dropwise until a colorless solution was obtained. Addition of water and filtration gave 0.2 g. of a colorless material which on recrystallization from glacial acetic acid melted at 298–300°. A mixture melting point with 4,4′-bi-1-naphthol (I) was not depressed.

On passing dry hydrogen chloride gas through a chloroform solution of the quinone, a colorless compound was formed rapidly in good yield.

1-Hydroxy-1′-methoxy-2,2′-binaphthyl (VI).—(a) To a solution of 1 g. of V in 25 ml. of ether, there was added an ethereal solution of diazomethane prepared from 4.1 g. of N-methyl-N-nitroso-N′-nitroguanidine[14] and a few drops of dilute ethanol. After standing overnight, the ether was evaporated and the residue was recrystallized from ligroin (90–120°) to give 0.35 g. (32%) of colorless crystals, m.p. 140–142°. Infrared analysis indicated the presence of an hydroxyl group (3300 cm.$^{-1}$).

Anal. Calcd. for $C_{21}H_{16}O_2$: mol. wt., 300; C, 83.98; H, 5.37; OCH_3, 10.33. Found: mol. wt. (Rast), 305; C, 84.17; H, 5.51; OCH_3, 10.27.

(b) Two grams (0.007 mole) of V was dissolved by heating in 150 ml. of water containing 5.6 g. (0.14 mole) of sodium hydroxide. To this stirred solution was added dropwise 5.5 ml. of dimethyl sulfate and the solution was refluxed for 2 hours; then 5.5 ml. of dimethyl sulfate was added and refluxing continued for an additional 2 hours. After standing overnight, the solid material was filtered and recrystallized from ligroin (90–120°); yield 0.5 g., m.p. 140–142°. This was shown to be identical with the above product.

1,1′-Dimethoxy-2,2′-binaphthyl from V.—(a) Four grams of potassium hydroxide was dissolved in 30 ml. of diethylene glycol by heating and stirring over a steam-bath. To this solution there was added 2 g. of the binaphthol V and, after solution, 3 ml. of dimethyl sulfate was added dropwise. Heating was continued for 1 hour after which the treatment with potassium hydroxide and dimethyl sulfate was repeated and the heating continued for an additional hour. After cooling, the diethylene glycol solution was poured with stirring into 300 ml. of water and the precipitate was filtered, dried and recrystallized from ligroin (90–120°), to give 0.3 g. of colorless crystals, m.p. 120–122°. This compound was shown to be identical by a mixture melting point determination with 1,1′-dimethoxy-2,2′-binaphthyl VII prepared by the Ullmann reaction.

(b) To a solution of 1 g. of the binaphthol V dissolved in 20 ml. of dry xylene there was added 0.15 g. of sodium metal. The mixture was refluxed with stirring for 2 hours protected from the atmosphere by a drying tube. The white sodium salt was filtered and washed with dry ether and then heated over a steam-bath for 3–5 hours with 5 ml. of dimethyl sulfate. After cooling the excess dimethyl sulfate was decomposed with dilute sodium carbonate and the precipitate filtered and dried. By fractional crystallization from ligroin (90–120°) there was obtained after a very small amount of II, 0.3 g. of the monomethyl ether VI and then 0.1 g. of the dimethyl ether VII.

(c) Methylation of the monomethyl ether VI using procedure (a) gave VII. Identity was established by mixture melting point and infrared analysis.

Partial Demethylation of 1,1′-Dimethoxy-2,2′-binaphthyl (VII).—(a) A mixture of 0.3 g. of synthetic VII, 5 ml. of glacial acetic acid and 1 ml. of 48% hydrobromic acid was refluxed for 2 hours. After cooling, water was added and the precipitate filtered, dried and recrystallized from ligroin (90–120°) to give 60 mg. of colorless crystals, m.p. 140–142°. A mixture melting point and infrared spectrum showed this to be identical with the monomethyl ether VI obtained from V and diazomethane.

Cleavage of the Mono- and Dimethyl Ethers of V.—(a) A mixture of 0.25 g. of the synthetic dimethyl ether VII, 0.1 g. of anhydrous aluminum chloride and 20 ml. of dry benzene was refluxed for 8 hours. The reaction mixture was treated with an excess of hydrochloric acid and the benzene layer removed and extracted with 10% sodium hydroxide. Excess dilute hydrochloric acid was added to the alkaline extract which was then extracted with ether. After drying the ethereal extract over anhydrous sodium sulfate and concentrating to dryness, the precipitate was recrystallized from ligroin (90–120°) to give 0.02 g. of a crystalline material, m.p. 218–220°. This was shown by a mixture melting point to be identical with the binaphthol V.

(b) Cleavage of the monomethyl ether VI was accomplished in the same manner and the product shown to be identical with V by a mixture melting point.

N-Acetyl-1-methoxy-2-naphthylamine.—A solution of 5 g. of 1-methoxy-2-nitronaphthalene[15] in diethyl ether was hydrogenated at 2–3 atm. in a Parr hydrogenator with platinum oxide catalyst.[16] After filtration, dry hydrogen chloride gas was bubbled through the ether solution until the precipitation of the hydrochloride was complete. After filtration and drying, 4.9 g. of the crude hydrochloride was obtained. A mixture of 3 g. of the hydrochloride, 10 ml. of acetic anhydride and 10–20 mg. of fused sodium acetate was refluxed for a few minutes and poured onto crushed ice. The precipitate was filtered and recrystallized (charcoal) from dilute methanol; yield 2 g., m.p. 130–132°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.09. Found: C, 72.47; H, 6.18.

N,N-Diacetyl-4-methoxy-1-naphthylamine.—Reduction of 4-nitro-1-methoxynaphthalene[17] and the preparation of the amine hydrochloride was carried out in the same manner as above. From 5 g. of the nitro compound 4.4 g. of the crude hydrochloride was obtained. Acetylation as above and recrystallization from methanol gave colorless crystals, m.p. 190–192°.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.45. Found: C, 69.69; H, 6.01; N, 5.58.

Absorption Spectra.—All ultraviolet absorption spectra determinations were made on a Beckman model DR spectrophotometer. Methanol was used as a solvent in all cases except for 4,4′-dimethoxy-1,1′-binaphthyl for which chloroform was used.

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[13] Arapahoe Chemical Co., Boulder, Colorado.

[14] Aldrich Chemical Co., Milwaukee, Wis.

[15] G. N. Burkhardt and H. Wood, *J. Chem. Soc.*, 143 (1929).

[16] V. L. Frampton, J. D. Edwards and H. R. Henze, THIS JOURNAL, **73**, 4432 (1951).

[17] H. H. Hodgson and E. W. Smith, *J. Chem. Soc.*, 671 (1935).