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Syntheses of Some Binaphthalenes

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Syntheses of binaphthalene derivatives are described with the particular aim of connecting two naphthalene units in an unsymmetrical manner. 1.2'-Binaphthalenes were formed in a reaction between 2.3-dichloro-1.4-naphthoquinone and 1- or 2--naphthol, but the reaction can proceed further to pentacyclic quinones. Some methoxynaphthalenes were treated with vanadium oxytrichloride to give the corresponding binaphthalene derivatives. Some syntheses of unsymmetrically substituted binaphthalenes from 2-naphthol and its methoxy analog are also described.

Numerous binaphthalenes or binaphthoquinones have been found in various plants or are produced by microorganisms. They are generally formed from phenolic substrates by oxidative biogenetic pathways. Synthetic binaphthalenes play an important role in studying weak intermolecular interactions in the host-guest relationship and they have been used for resolving amino acids by complexation,[1] for asymmetric reduction of ketones to optically active alcohols[2,3] and for other stereoselective transformations.

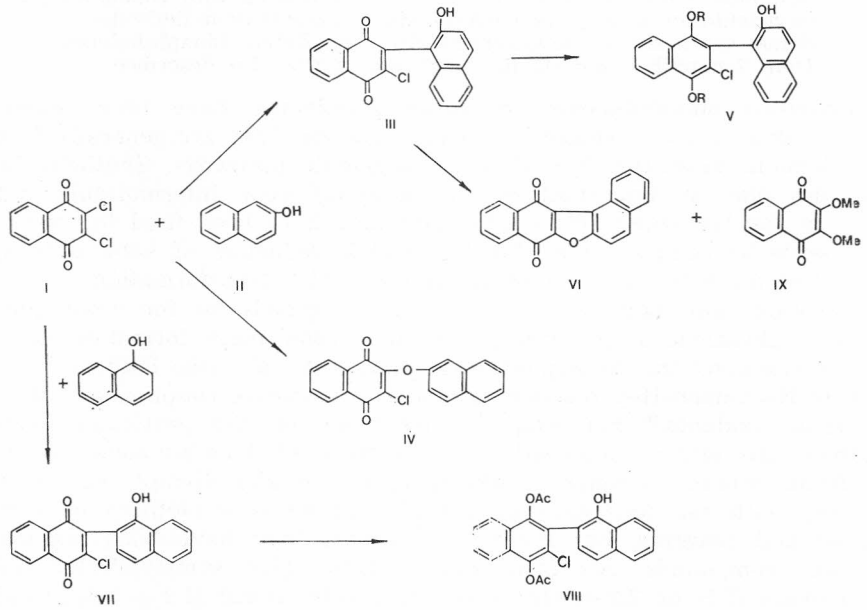
The most important and commonly used methods for the direct joining of two naphthalene rings through carbon-carbon bond formation are the Ullmann reaction,[4] the decomposition of diazonium salts (the Pschorr[5,6] or the Gomberg-Bachmann-Hey reaction[7–9]), phenolic oxidative coupling and the use of various oxidants.[10] For example, depending on the particular oxidant, naphthols are either dimerized to derivatives of binaphthalene or dinaphthofuran, whereas stronger oxidizing agents usually disrupt the naphthalene ring with the formation of acids.[11,12] There is a plethora of various methods and reagents, but for the most part they have been applied to particular compounds. All mentioned methods give symmetrically linked naphthalenes (1.1′ or 2.2′-), the unsymmetrically linked (1.2′-) being seldom formed. In addition, since they are of limited use, these methods have many disadvantages they are more or less confined to the synthesis of symmetrical binaphthalenes, they lack regioselectivity, they usually require severe reaction conditions and the yields are generally low. Therefore, it is almost impossible

* Dedicated to prof. M. Lj. Mihailović on the occasion of his 60th birthday.

to predict which synthetic approach will be successful or will give the optimum yield of the desired product.

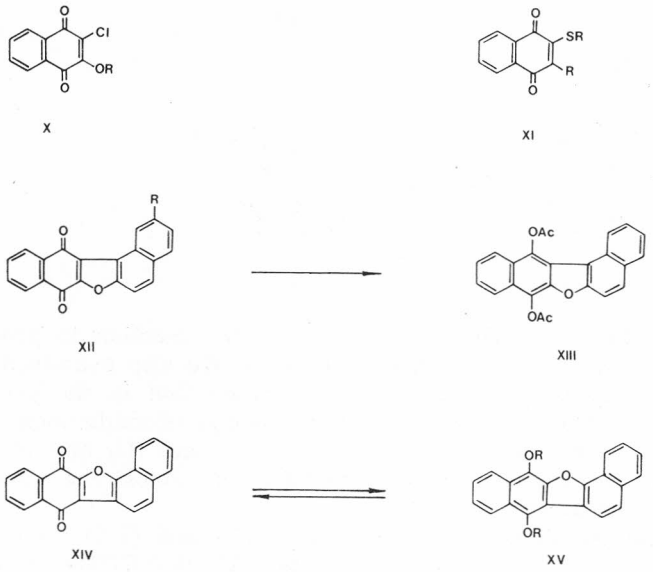
We have been interested in the synthesis of unsymmetrically linked and/or substituted binaphthalenes as well as in new developments of regioselective synthetic approaches. We should like to describe here some experiments which were performed with this aim.

We studied the reaction between 2.3-dichloro-1,4-naphthoquinone (*I*) and naphthols. In principle, this is an arylation with a reactive halo compound since haloquinones can be regarded as vinylogs of acyl halides.[13] Although phenols are *O*-alkylated in the presence of a base, it was found that sodium 2-naphtholate is methylated with methyl iodide to give the anticipated 2-methoxynaphthol (25%) and in addition also 1-methyl-2-naphthol as the main product (39%).[14] This is typical of an ambident ion for which it is known that in protic solvents C-alkylation is favoured.[15] Another interesting example is the reaction between 2-naphthol (or other phenols) and 1-methyl-1.2.5.6-tetrahydropyridine-4-carbonitrile under the basic conditions giving a substituted naphthol rather than a product resulting from a Michael addition reaction to the activated double bond.[16] Although it was reported that (*II*) is *O*-arylated with (*I*)[17], the *C*-arylated structure (*III*)[18] was later assigned to this product. In order to trace the eventual formation of (*IV*) we synthesized this compound from the sodium 2-naphtholate and (*I*) in benzene and the product was different from (*III*). Furthermore, we have also prepared the *C*-arylated analog from 1-naphthol (*VII*).



In order to obtain a better insight into these reactions we performed theoretical calculations. Standard geometries for naphthalene together with the bond lengths and angles were used to calculate the geometries for 1- and 2-naphtholate. The C—O bond was optimized in agreement with the Davidon-Fletcher-Powell algorithm for the gradient method of optimization.[19] Net

charges on particular carbon and oxygen atoms were calculated by the semi-empirical MNDO (modified NDDO) method[20,21] and these are presented in Scheme 1. It should also be mentioned that the total energy difference for 2-naptholate and 1-naphtholate is very small (16.3 kJ/mol), the value being higher for the first one.

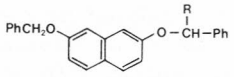


X XI XII XIII XIV XV

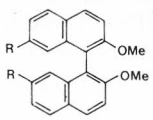
From the calculated net charges for 1- and 2-naphtholate at various positions it appears that for 1-naphtholate, in addition to the oxygen atom, the carbon atom at position 2 should be most nucleophilic and thus the preferred attack would be expected either at oxygen or at C_2 and with less probability at C_4. In a similar manner for 2-naphtholate, in addition to the oxygen atom, position 1 would be expected to be attacked preferentially by electrophiles. This has been found experimentally. Some negative charge is delocalized into the other ring, but this is insignificant when compared to the phenolate part of the bicycle.

Scheme 1

We could establish that for the synthesis of these binaphthalenes the employed base is of outmost importance for the outcome of the reaction. Tertiary bases like pyridine are not useful since (*I*) forms with pyridine a pyridinium salt which is converted in protic solvents into 1.4-dioxo-3-pyridinium-2-naphthoxide, a betaine.[22] In the presence of naphthol, however, this pyridinium salt reacts smoothly to form a pentacycle (*VI*). Also in one pot reaction of (*I*) and (*II*) in pyridine the dinaphthofuranquinone was obtained.[23] Anhydrous sodium acetate proved to be the most suitable promotor since

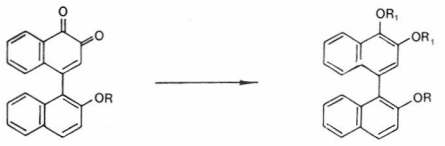


XVI



XVII

XVIII



XIX XX

anhydrous potassium carbonate also caused the reaction to proceed towards the formation of dinaphthofuranquinone (*VI*). We also examined the addition of lithium hydroxide since it had been shown that in the presence of this base C-alkylation of 2-naphtholate with benzyl bromide took place selectively.[24] In our hands, the reaction between (*I*) and (*II*) and in the presence of lithium hydroxide yielded compound (*III*) in almost the same yield when compared to the acetate addition.

The obtained binaphthalene quinones (*III*) and (*VII*) were easily transformed into the corresponding diacetates (*V*, R = COMe, and *VIII*) upon reductive acetylation and the hydrosulfide reduction of *III* afforded the hydroxy compound (*V*, R = H). The hydroxyl group in *III*, however, is unreactive towards diazomethane and triethyloxonium tetrafluorobarate.

The binaphthalene derivative *III* is easily cyclized to dinaphtho(2.1-b; 2′.3′-d)furan-8.13-quinone (*VI*) in the presence of various bases. But there are some unusual transformations. For example, compound *III* when treated with methanolic sodium methylate (1.5 hour under reflux) is converted into a mixture of the pentacycle (*VI*) and 2.3-dimethoxy-1.4-naphthoquinone (*IX*) (2 : 1 by weight). The latter compound is formed most probably as a result of a retro-Michael reaction and subsequent transformation with methylate. In view of these findings we decided to try the dimerization with some other reactive naphthoquinones. 2-Chloro-3-methoxy-1.4-naphthoquinone (*X*, R=Me) was allowed to react with *II* in anhydrous pyridine and in the presence of 4-dimethylaminopyridine. No binaphthalene derivative was formed and 2--chloro-3-hydroxy-1.4-naphthoquinone (*X*, R=H) could be isolated. It appears that the formed intermediate, a 1.4-dioxo-2-methoxynaphthyl-2-pyridinium salt,[25] acted as demethylating agent for *X* (R=Me). Even when anhydrous sodium acetate was used in the reaction between *X* (R=Me) and *II* the pentacycle *VI* was formed. Finally, it is interesting that 2.3-bis(methylthio)--1.4-naphthoquinone (*XI*, R=SMe) reacted with (*II*) in boiling pyridine to give only 2-methylthio-1,4-naphthoquinone (*XI*, R=H).

The easy formation of pentacycles prompted us to investigate them in more detail with the particular aim of eventual furan ring opening. 2.7-Dihydroxynaphthalene was easily transformed with (*I*) into the pentacycle (*XII*,

R=OH) if a small amount of 4-dimethylaminopyridine was added to the reaction mixture. Pentacyclic quinones are readily converted upon reductive acetylation into the corresponding diacetoxy derivatives (*XIII* or *XV*, R=COMe) and further to the dihydroxy derivative (*XV*, R=H). To the best of our knowledge, there are only a few reports on the ring opening of dinaphthofurans. In one case the furan ring was cleaved with potassium hydroxide and a binaphthalene derivative was obtained,[27] whereas in the second case the same reagent was employed but no compounds were isolated and the ring opening was proposed because of blue coloration.[28] This is in contrast with the dibenzofurans where many cases of ring opening, though at elevated temperatures, are known.[29] Since hot alkaly, sodium hydride, boiling trifluoroacetic acid or attempted hydrogenolysis in the presence of Raney nickel did not affect the pentacyclic system, we tried lithium in boiling dioxane.[30] The experiment was not successful and for more severe reaction conditions lithium in boiling ethylenediamine was applied. Upon work up of the reaction mixture, we could establish that the diacetate (*XV*, R=COMe) was converted via the dihydroxy compound and subsequent oxidation in the air back into the quinone (*XIV*).

We also designed some experiments for the synthesis of binaphthalenes by oxidative dimerization of hydroxy and alkoxynaphthalenes. In an attempt to prepare 2.7-dibenzyloxynaphthalene (*XVI*, R=H) as starting material we could observe that, in addition to the anticipated product, subsequent benzilation caused the formation of the tribenzylated compound (*XVI*, R=CH_2Ph). The IR and NMR spectroscopic data are in accord with the proposed structure. There is no carbonyl absorption in IR spectrum which would be present in an alternative structure, *i. e.* in 1.1-dibenzyl-7-benzyloxynaphthalen-2-one For oxidative dimerization of alkoxynaphthalenes we employed vanadium oxytrichloride since the related oxytrifluoride had already found a useful application in transformations of benzylisoquinolines[31] and bibenzyls.[32] 1-Methoxy-, 2-methoxynaphthalene and 2.7-dimethoxynaphthalene formed the corresponding binaphthalenes instantly at room temperature (*XVII*, R=H; *XVIII; XVII*, R=OMe). Use of silylated starting material, *i. e.* of 1.5- or 2.7-bis(*t*-butyldimethylsilyloxy) naphthalene, was not successful, most probably due to the lability of the protecting group. Also, 1.4-naphthoquinone was inert to this reagent. Finally, the attempted dimerization of 2-acetoxynaphthalene with hydrogen peroxide in glacial acetic acid and in the presence of ammonium molybdate failed. Evidently, for a success of this method a free hydroxyl group is required, as shown in the preparation of *XIX* (R=H).

On the other hand, trihydroxybinaphthalene *XX* (R=R_1=H) and its methoxy analog (*XX*, R=Me, R_1=H) were prepared from the corresponding quinones (*XIX*, R=H or Me) with sodium hydrosulfite. In an attempted purification of *XX* (R=Me, R_1=H) by column chromatography on alumina the compound was easily oxidized back to the red quinone (*XIX*, R=Me). Reductive acetylation of the quinone *XIX* (R=H) yielded the corresponding triacetoxy compound (*XX*, R=R_1=COMe). We also prepared the trimethoxy compound (*XX*, R=R_1=Me) by methylation with dimethyl sulfate. Attempted methylation of *XX* (R=R_1=H) with a mixture of methyl iodide and silver oxide did not afford the expected trimethoxy compound and a red compound with m. p. 182—186 °C and $M^+ = 438$ was obtained. Evidently, the starting

material was oxidized by silver oxide to the quinone and some further transformation occurred. The structure of this product was not further investigated.

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EXPERIMENTAL

The melting points were measured with a Kofler micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer CHN Analyzer 240C. NMR spectra were taken with a JOEL JNM C60-HL spectrometer with the use of tetramethylsilane as an internal standard and chemical shifts are expressed in δ values. Mass spectra were taken with a Hitachi-Perkin-Elmer RMU-6L mass spectrometer and the high resolution mass spectra with a CEC-20--110C instrument. 2'-Methoxy-1.1'-binaphthalene-3.4-dione (*XIX*, R = Me) was prepared according to the literature, m. p. 190—194 °C (Lit.[33] gives m. p. 191—193 °C). Dinaphtho(1.2-b; 2'.3'-d)-furan-7.12-quinone (*XIV*) was obtained from *I* and 1-naphthol, m. p. 229—232 °C (Lit.[34] gives m. p. 231 °C). Other starting compounds were commercially available.

3'-Chloro-2-hydroxy-1.2'-binaphthalene-1'.4'-dione (III)

A mixture of 2-naphthol (*II*) (1.44 g), lithium hydroxyde (0.4 g)and 2.3-dichloro--1,4-naphthoquinone (*I*) (2.27 g) in acetonitrile (50 ml) was heated under reflux for 15 hours. The product which separated upon cooling was filtered, washed with water and crystallized from 2-propanol (yield 1.1 g, 33%), m. p. 175—176 °C (Lit.[8] gives m. p. 178—179 °C) and mixed m. p. undepressed with an authentic sample. Mass spectrum: $M^+ = 335$.

3-Chloro-1'-hydroxy-2.2'-binaphthalene-1.4-dione (VII)

A suspension of 1-naphthol (7.2 g) *I* (11.3 g) and anhydrous sodium acetate (4.1 g) in 2-propanol (250 ml) was heated for 10 hours. The hot reaction mixture was decanted, the residue was filtered and washed with hot 2-propanol. The product was suspended in water, filtered and crystallized from 1-propanol (yield 11.73 g, 70%), m. p. 224—230 °C (dec.). High resolution mass spectrum: $M^+ = 334.041$ (calculated 334.0397).

Anal. $C_{20}H_{11}ClO_3$ (334.04) calc'd: C 71.75; H 3.31%
found: C 71.18; H 3.20%

3-Chloro-1.4-diacetoxy-1'-hydroxy-2.2'-binaphthalene (VIII)

A mixture of the above dione (*VII*) (2 g), acetic anhydride (40 ml) and anhydrous sodium acetate (1.3 g) was heated to boil and treated with zinc powder. The reaction mixture was filtered hot and the residue washed with hot glacial acetic acid. The filtrate was evaporated in vacuo and the residue was treated with water and filtered. The product can be crystallized from 1-propanol or glacial acetic acid (yield 2.37 g, 94%), m. p. 255—260°C. Mass spectrum: $M^+ = 420$.

Anal. $C_{24}H_{17}ClO_5$ (420.07) calc'd: C 68.49; H 4.07%
found: C 68.72; H 4.32%

1'.4'-Diacetoxy-3'-chloro-2-hydroxy-1.2'-binaphthalene (V, R=COMe)

A mixture of the quinone *III* (14 g), acetic anhydride (250 ml) and anhydrous sodium acetate (9.1 g) was heated to boil and then treated with an excess of zinc dust until the colour disappeared. The mixture was filtered hot and the residue washed with hot glacial acetic acid. The combined filtrates were evaporated in vacuo, the oily residue was treated with *n*-hexane, with water to eliminate inorganic material, and then again with *n*-hexane. The residue was crystallized from ethanol (yield 8.71 g, 49.5%), m. p. 158—160 °C. High resolution mass spectrum:

$M^+ = 420.079$, calc'd for $C_{24}H_{17}ClO_5 = 420.0764$. NMR ($CDCl_3$): $\delta = 2.15$ and 2.45 (s, COMe), 7.02—7.82 (m, 12 H and OH).

Anal. $C_{24}H_{17}ClO_5$ (420.07) calc'd: C 68.49; H 4.07%
found: C 67.92; H 4.18%

3'-Chloro-1'.2.4'-trihydroxy-1.2'-binaphthalene (V, R=H)

A solution of the quinone *III* (1.67 g) in dichloromethane (60 ml) was treated with aqueous sodium hydrosulfite (7 g in 50 ml water). The mixture was shaken until the red colour of the quinone disappeared. The product which separated was filtered, the organic layer was separated and dried over sodium sulfate. The product was crystallized from *n*-heptane or cyclohexane (yield 1.37 g, 81.5%), m. p. 193—196 °C. Mass spectrum: $M^+ = 336$. NMR (DMSO-d_6): $\delta = 6.88$—8.18 (m, 10 H).

Anal. $C_{20}H_{13}ClO_3$ (336.76) calc'd.: C 71.33; H 3.89%
found: C 71.14; H 3.89%

2-Chloro-3-(2'-naphthyloxy)-1.4-naphthoquinone (IV)

To a solution of sodium methylate (prepared from 0.23 g sodium and 5 ml methanol) *II* (1.44 g) was added and the mixture was evaporated to dryness. Benzene (10 ml) and naphthoquinone *I* (2.26 g) were added and the mixture was heated under reflux for 30 minutes. Upon cooling, an oily product separated and slowly crystallized. The crystals were separated and washed with benzene. The compound was crystallized from benzene (yield: 0.95 g, 28%), m. p. 208—209 °C. Mass spectrum $M^+ = 334$.

Anal. $C_{20}H_{11}ClO_3$ (334.04) calc'd: C 71.76; H 3.31%
found: C 72.07; H 3.50%

Reaction Between 2-Chloro-3-methoxy-1.4-naphthoquinone (X, R=Me) and II

a) A mixture of 2-chloro-3-methoxy-1.4-naphthoquinone[35] (*X*, R = Me) (1.11 g), *II* (0.72 g), anhydrous pyridine (8 ml) and 4-dimethylaminopyridine (0.1 g) was heated under reflux for 1 hour. The product which separated on cooling was filtered and washed with ethyl acetate. The red compound was dissolved in water and upon acidification a yellow product separated. It was crystallized from ethanol (yield 0.7 g, 67%), m. p. 220—222 °C. (Lit.[36] gives m. p. 214 °C for 2-chloro-3-hydroxy-1.4-naphthoquinone). Mixed m. p. with an authentic sample was undepressed. Mass spectrum: $M^+ = 208$.

b) A mixture of 2-chloro-3-methoxy-1.4-naphthoquinone (*X*, R = Me) (1.11 g), *II* (0.72 g), anhydrous sodium acetate (0.41 g) and 2-propanol (25 ml) was heated under reflux for 17 hours. TLC examination revealed that no reaction took place. To the reaction mixture potassium carbonate (0.4 g) was added and heating was continued for 4 hours. The product, which separated upon cooling, was filtered, suspended in water and filtered again. The product was crystallized from glacial acetic acid with addition of some water (yield: 0.38 g, 25,5%), m. p. 273—278 °C. A mixed m. p., with an authentic sample of dinaphtho(2.1-b; 2'.3'-d)-furan-8.13--quinone (Lit.[37] gives m. p. 270—271 °C, lit.[38] gives m. p. 271—273 °C) was undepressed. Mass spectrum: $M^+ = 298$.

Reaction Between 2.3-Bis(methylthio)-1.4-naphthoquinone and II

A mixture of the quinone[39] (*XI*, R = SMe) (0.25 g), *II* (0,144 g), and pyridine (5 ml) was heated under reflux for 2 days. The mixture was evaporated in vacuo and the residual dark oil was triturated with *n*-heptane. The product was filtered, washed with some ethanol and upon crystallization from benzene the compound (yield 10 mg) had m. p. 180—182 °C and was identified as 2-methylthio-1.4-naphthoquinone (*XI*, R = H) (Lit.[39] gives m. p. 180—184 °C). Mass spectrum: $M^+ = 204$.

Anal. $C_{11}H_8O_2S$ (204.24) calc'd: C 64.70; H 3.95%
found: C 64.90; H 3.93%

In the filtrate the presence of unchanged starting quinone and *II* were identified.

2-Hydroxy-dinaphtho-(2.1-b; 2'.3'-d)furan-8.13-quinone (XII R=OH)

A mixture of *I* (2.3 g), 2.7-dihydroxynaphthalene (1.6 g), pyridine (15 ml) and 4-dimethylaminopyridine (0.3 g) was heated under reflux for 2 hours. Upon cooling, the solid material was filtered and suspended in ethanol and heated to boil. The product was filtered hot and washed with some ethanol (yield 2.60 g, 81%), m. p. >290 °C. The compound was identical with the authentic sample (Lit.[38] gives m. p. >340 °C).

8.13-Diacetoxy-dinaphtho-(2.1-b; 2'.3'-d)furan (XIII)

A boiling mixture of dinaphtho-(2.1-b;2'.3'-d)furan-8.13-quinone (*XII*, R = H), (0.9 g) and anhydrous sodium acetate (0.65 g) in acetic anhydride (20 ml) was treated portionwise with zinc powder and upon heating under reflux for 20 minutes the mixture was filtered hot and the residue washed with hot glacial acetic acid. Upon cooling the crystals separated, they were filtered and crystallized from glacial acetic acid (yield 1.1 g, 95%), m. p. 257—260 °C. Mass spectrum: $M^+ = 384$.

Anal. $C_{24}H_{16}O_5$ (384.37) calc'd: C 74.99; H 4.20%
found: C 74.29; H 4.16%

7.12-Diacetoxy-dinaphtho-(1.2-b; 2'.3'-d)furan (XV, R=COMe)

It was obtained from the corresponding quinone (*XIV*) in essentially the same manner as described above in 88% yield, m. p. 268—270 °C (from glacial acetic acid). Mass spectrum: $M^+ = 384$.

Anal. $C_{24}H_{16}O_5$ (384.37) calc'd: C 74.99; H 4.20%
found: C 74.80; H 4.16%

7.12-Dihydroxy-dinaphtho-(1.2-b; 2'.3'-d)furan (XV, R=H)

The above diacetoxy compound (*XV*, R = COMe) (0.5 g) was heated under reflux in aqueous sodium hydroxide (5 ml of 10%) for 15 minutes. The brown solution was acidified with hydrochloric acid (1 : 1) and the obtained product was filtered and dried in the air. Upon crystallization from ethanol (yield 0.22 g, 56%) the compound had m. p. 215—217 °C. Mass spectrum: $M^+ = 300$.

Anal. $C_{20}H_{12}O_3$ (300.30) calc'd: C 79.99; H 4.03%
found: C 79.81; H 3.66%

Reaction of 7.12-Diacetoxy-dinaphtho-(1.2-b; 2'.3'-d)furan (XV, R=COMe) with Lithium-ethylenediamine

Lithium (35 mg) was dissolved in anhydrous ethylenediamine (5 ml), the diacetate (*XV*, R = COMe) (0.77 g) was added and the mixture was heated under reflux for 30 minutes. The solvent was evaporated in vacuo, the residue was treated with water and acidified to pH 4. The separated product was filtered and crystallized from glacial acetic acid (yield 0.36 g, 60%), m. p. 232—233 °C. On the basis of analytical data, mass spectrum and mixed m. p. with an authentic specimen the compound was identified as the pentacyclic quinone (*XIV*).

Benzylation of 2.7-Dihydroxynaphthalene

To a warm solution of sodium ethylate in ethanol (prepared from 4.6 g sodium and 50 ml ethanol) 2.7-dihydroxynaphthalene (16 g) were added. After addition of benzyl chloride (25.2 g) the mixture was heated under reflux for 1 hour. The product which separated upon cooling was filtered, washed with water and crystallized from ethanol (yield 2.26 g). The obtained crystals with m. p. 154—158 °C were identified as 2.7-bis(benzyloxy)-naphthalene (*XVI*, R = H). Mass spectrum: $M^+ = 340$. IR spectrum: no carbonyl absorption.

Anal. $C_{24}H_{20}O_2$ (340.40) calc'd: C 84.68; H 5.92%
found: C 84.92; H 5.98%

To the ethanolic filtrate water was added and upon acidification an oil separated. After addition of ethanol and resting at room temperature some crystals separated (yield 3.92 g). For analysis the product was crystallized from ethanol, m. p. 104 °C. Mass spectrum: $M^+ = 430$. The compound is 2-benzyloxy-7-(1'.2'-diphenylethyloxy-1')-naphthalene (*XVI*, R = CH_2Ph). IR: no carbonyl absorption. NMR ($CDCl_3$): δ 4.98 (s, CH_2), 5.64 (d, CH_2CH), 4.92 (t, $CHCH_2$), J = 6.0 Hz.

Anal. $C_{31}H_{26}O_2$ (430.52) calc'd: C 86.48; H 6.09%
found: C 86.20; H 6.15%

2.2'-Dimethoxy-1.1'-binaphthalene (XVII, R=H)

A three-necked flask, fitted with a mechanical stirrer and gas inlet and outlet, was flushed with nitrogen and a solution of 2-methoxynaphthalene (4.74 g) in dichloromethane (30 ml) was put into the it. Under stirring though a syringe vanadium oxytrichloride (3 ml) was added portionwise. Stirring was continued for 30 minutes and the reaction mixture was filtered. The product (4.5 g) was heated with hydrochloric acid (1 : 1, 50 ml), filtered and washed with water. It was dissolved in hot glacial acetic acid and precipitated with addition of some water (yield 0.31 g, 7%), m. p. 160 °C (Lit.[40] gives m. p. 190—191 °C). Mass spectrum: $M^+ = 314$. The molecule is an adduct with acetic acid, as evident from analysis.

If the reaction was performed in trifluoroacetic acid instead of dichloromethane and the reaction mixture diluted with water, the product was obtained in a 47% yield. It was crystallized from cyclohexane, m. p. 215—220 °C. High resolution mass spectrum: $M^+ = 314.131$ ($C_{22}H_{18}O_2$ requires 314.1307). NMR ($CDCl_3$): δ = 3.65 and 3.68 (s, OMe), 7.05—7.93 (m, 12 H).

Anal. $C_{22}H_{18}O_2$ (314.13) calc'd: C 84.05; H 5.77%
found: C 83.92; H 5.60%

4.4'-Dimethoxy-1.1'-binaphthalene (XVIII)

The compound was prepared in essentially the same manner as above in dichloromethane as solvent. The product was crystallized from cyclohexane (yield 84%), m. p. 250—255 °C (Lit.[40] gives m. p. 252—253 °C, lit.[33] m. p. 256—257 °C). Mass spectrum: $M^+ = 314$.

Anal. $C_{22}H_{18}O_2$ (314.13) calc'd: C 84.05; H 5.77%
found: C 84.14; H 5.84%

2.2'.7.7'-Tetramethoxy-1.1'-binaphthalene (XVII, R=OMe)

It was obtained in essentially the same manner from 2.7-dimethoxynaphthalene in 68% yield, m. p. 190 °C (from glacial acetic acid and water). Mass spectrum: $M^+ = 374$.

Anal. $C_{24}H_{22}O_4$ (374.42) calc'd: C 76.98; H 5.92%
found: C 77.06; H 5.45%

2.3'.4'-Trihydroxy-1.1'-binaphthalene (XX, R=R$_1$=H)

A solution of 2'-hydroxy-1.1'-binaphthalene-3.4-dione (*XIX*, R = H)[41] (1.25 g) in dichloromethane (120 ml) was shaken with an aqueous solution of sodium hydrosulfite (7 g in 50 ml water) until the red colour of the starting compound disappeared. The organic layer was separated and dried in a nitrogen atmosphere over sodium sulfate. The solvent was evaporated and the residue crystallized from *n*-heptane or chloroform (yield 1.0 g, 80%), m. p. 184—192 °C (dec.). Mass spectrum: $M^+ = 302$.

Anal. $C_{20}H_{14}O_3$ (302.31) calc'd: C 79.45; H 4.67%
found: C 79.32; H 4.67%

From (*XIX*, R = H), by reductive acetylation with acetic anhydride and zinc dust, 2'.3.4-triacetoxy-1.1'-binaphthalene (*XX*, R = R_1 = CH_3CO) was obtained, m. p. 154 °C (from glacial acetic acid) together with some diacetate, m. p. 106 °C, isolated from the filtrate after addition of water.

The triacetate crystallized with a molecule of acetic acid and its mass spectrum had $M^+ = 429$.

Anal. $C_{26}H_{20}O_6 \cdot CH_3COOH$ (488.47) calc'd: C 68.84; H 4.95%
found: C 69.12; H 4.57%

The diacetate crystallized with a molecule of water and had mass spectrum $M^+ = 386$.

Anal. $C_{24}H_{18}O_5 \cdot H_2O$ (404.40) calc'd: C 71.28; H 4.99%
found: C 71.06; H 4.82%

3.4-Dihydroxy-2'-methoxy-1.1'-binaphthalene (XX, R=Me, R_1=H)

A solution of 2'-methoxy-1.1'-binaphthalene-3.4-dione (*XIX*, R = Me) (1.57 g)[33] in dichloromethane (80 ml) was shaken with a solution of sodium hydrosulfite (7 g in 50 ml water) until the red colour of the starting compound disappeared. The organic layer was separated, dried over sodium sulfate, the mixture was filtered and the salt washed with hot dichloromethane. The combined filtrates yielded, after evaporation, the product which was crystallized from benzene (yield 0.33 g, 21%), m. p. 167—174 °C. Mass spectrum: $M^+ = 316$.

Anal. $C_{21}H_{16}O_3$ (316.34) calc'd: C 79.73; H 5.10%
found: C 80.62; H 5.33%

2'.3.4-Trimethoxy-1.1'-binaphthalene (XX, R=R_1=Me)

Freshly prepared 3.4-dihydroxy-2'-methoxy-1.1'-binaphthalene (*XX*, R = Me, R_1 = H) (0.79 g) was dissolved in aqueous sodium hydroxide (180 ml of 2 M) and dioxane (18 ml) and dimethyl sulfate (7.5 ml) were added. The mixture was shaken in an atmosphere of nitrogen for 0.5 hr. The reaction mixture was extracted with chloroform, the layers were separated and the suspension in aqueous phase filtered. The solid material was treated with some hydrochloric acid (1 : 1), filtered and crystallized from benzene and n-hexane (yield 0.52 g, 60%), m. p. 148—152 °C. Mass spectrum: $M^+ = 344$.

Anal. $C_{23}H_{20}O_3$ (344.39) calc'd: C 80.21; H 5.55%
found: C 79.92; H 5.47%

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POVZETEK

Sinteze nekaterih binaftalenov

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Opisane so sinteze nekaterih binaftalenov s posebnim ozirom na možnosti povezave dveh naftalenovih delov in na nesimetričen način. 1.2'-binaftaleni nastanejo pri reakciji med 2,3-dikloro-1,4-naftokinonom in 1- ali 2-naftolom, lahko pa reakcija poteče dalje do petčlenskih kinonov. Izvedeni so bili tudi poskusi dimerizacije s pomočjo vanadijevega oksitriklorida in z različnimi metoksinaftaleni. Končno so opisane še nekatere sinteze nesimetrično substituiranih 1.1'-binaftalenov iz 2-naftola ali njegovega metoksi analoga.