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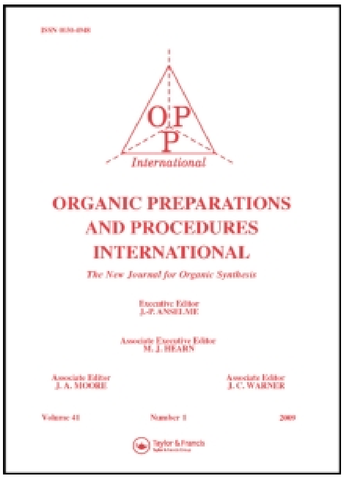

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SYNTHETIC APPROACHES TO BINAPHTHALENES. A REVIEW

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SYNTHETIC APPROACHES TO BINAPHTHALENES. A REVIEW

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INTRODUCTION

Binaphthalenes and in particular binaphthoquinones have been isolated from various plants or are produced by microorganisms.[1] They are generally formed from phenolic substrates by oxidative biogenetic pathways. Microorganisms and higher plants contain dimers of naphthoquinones. So far more than 20 such compounds have been isolated and characterized. Many of them are dimers of 5-hydroxy-1,4-naphthoquinone (juglone). On the other hand, synthetic binaphthalenes have recently become of increasing interest either in connection with the preparation of natural products and analogs of the biologically active gossypol[2-4] or for studying weak intermolecular interactions in the host-guest relationship, in particular as potentially host-guest lattice inclusions. Binding selectivity is effected by the steric requirements of the host and quest molecules to form the specific host-quest aggregates. Thus, binaphthalenes have been used extensively as chiral host for resolving amino acids,[5] for asymmetric reduction of ketones to optically active alcohols,[6,7] in the asymmetric alkylation or arylation of aldehydes,[8] for the isomerization of allylamines to chiral enamines,[9] and other stereoselective transformations.

A variety of methods exists for direct joining two naphtalene rings through carbon-carbon bond formation, the most important and commonly used being the Ullmann reaction,[10] the decomposition of diazonium salts (the Pschorr,[11,12] or the Gomberg-Bachmann-Hey reaction[13-15]), phenolic oxidative coupling, use of various oxidants[16] and a plethora of methods and reagents which were applied only to particular naphthalene derivatives. For example, depending on particular oxidant, naphthols are either dimerized to derivatives of binaphthalene or dinaphthofuran, whereas stronger oxidants usually disrupt the naphthalene ring with the formation of acids.[17,18] All the methods mentioned give symmetrically linked binaphthalene (1,1'- or 2,2'-), the unsymmetrically linked (1,2'-) being seldom formed. In addition, many of these methods have disadvantages since many are of limited use as they are more of less confined for the syntheses of symmetrical binaphthalenes or binaphthoquinones; they also lack of regioselectivity, usually require severe reaction conditions and yields are generally low. Therefore, it is almost impossible to predict which synthetic approach will be successful or will give the optimum yield of the desired product.

In addition, syntheses of chiral binaphthalenes are limited although such syntheses are of great value. Recently, there have been some reports of syntheses where axial dissymmetry has been induced during the formation of the binaphthalene rings and these approaches will be mentioned later.

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I. FORMATION OF BINAPHTHALENES FROM NAPHTHALENES

1. Thermal Dimerization

Thermally induced dimerization of naphthalene derivatives occur only in special cases. Naphthalene itself is dimerized to 2,2'-binaphthalene at 475°C and 25-50 atm.[19] The 2,2'-isomer is apparently the most stable under such extreme conditions since 1,1'-binaphthalene when passed over platinum-alumina at 490°C is isomerized into 1,2'- and 2,2'-isomers. It has been found that all three isomeric binaphthalenes are interconvertible when passed over silica gel at 490°C and the order of stability is found to be 2,2'->1,2'->1,1'-.[20] 1,1'-Binaphthalene is also of interest from the point of view that a solid state resolution occurs and the racemic (low-temperature) form is converted to the chiral (high-temperature) form[21] (for X-ray structure determination see[22,23] A rather facile dimerization to a binaphthalene occurs with 5-isopropyl-6,7-dimethoxy-3-methyl-1-naphthol. The dimer was obtained first at elevated temperatures (150°C then 215°C).[24,25] However, it was later established that dimerization of the above naphthol occurs readily even in the solid state at -10°C in an inert atmosphere to the same 2,2'-binaphthalene derivative (apogossypol tetramethyl ether).[26]

Dimerization in the crystalline state upon brief heating at 120°C was observed with methyl 5-iodo-1,6,8-trimethoxy-3-naphtholate and the 1,1'-dimer is formed in about 80% yield.[27,28] In a similar manner brief heating of related iodonaphthalenes afforded other 1,1'-binaphthalene derivatives.[29,30] A binaphthalene is formed also upon thermal dissociation of the trans-photodimer of 2-methoxynaphthalene (1) the process being accompanied by isomerization to 2',3-dimethoxy-1,2-dihydro-1,1'-binaphthalene.[31]

TABLE I. 1,1'-Binaphthalenes from Thermal Coupling of Naphthalenes

Starting Naphthalene[a]	Product	% Yield	Ref.
1,6,8(OMe) 3(COOMe) 5(I)	2,2',4,4',5,5'(OMe) 7,7'(COOMe)	74,80	27,28
1(OH) 3(COOMe) 5(I) 6,8(OMe)	2,2',4,4'(OMe) 5,5'(OH) 7,7'(COOMe)	5	29
1,6,8(OMe) 3(COOH) 5(I)	2,2',4,4',5,5'(OMe) 7,7'(COOH)	50	29
1,6,8(OMe) 5(I)	2,2',4,4',5,5'(OMe)	48	29
1,3(OH) 2(COOMe) 5(I) 7,8(OMe)	3,3',4,4'(OMe) 5,5',7,7'(OH) 6,6'(COOMe)	25	30

[a] Figures and substituents in parentheses indicate the relative positions of functional groups in the starting naphthalene and in the 1,1'-binaphthalene.

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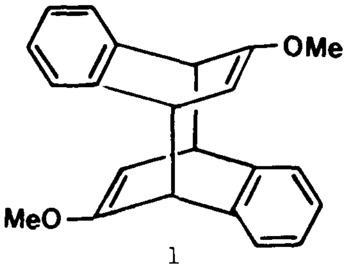

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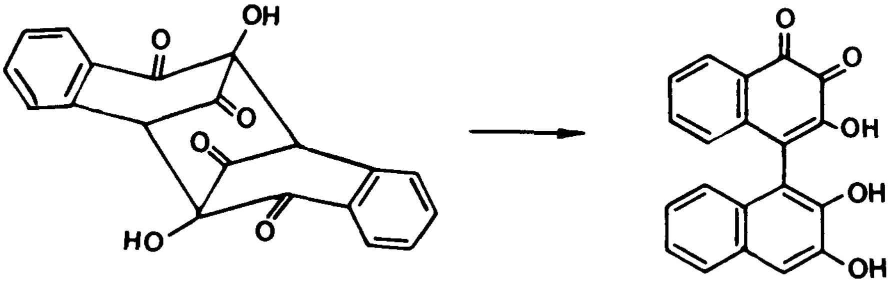
2,3-Dihydroxynaphthalene when oxidized with potassium nitrosodisulfonate is transformed into 3-hydroxy-1,2-naphthoquinone which dimerized to 2. If the dimer, for which the structure 2 has been proposed is heated in water the binaphthalene derivative (3) is formed.[32]



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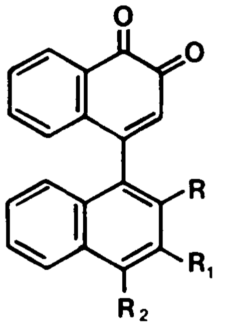
2. Dimerization under the Influence of Acids, Lewis Acids and other Catalysts

The acid-catalyzed dimerization of 1,2-naphthoquinone to the dimeric quinhydrone (4, R = H, $R_1 = R_2$ = OH) takes place under relatively mild conditions (yield 67%).[33-35] In a similar manner the crossed condensation with 1- or 2-naphthol takes place to give 4 (R = R_1 = H, R_2 = OH) in 25% yield[34] or 4 (R = OH, $R_1 = R_2$ = H).[36]

For compound 4 (R = H, $R_1 = R_2$ = OH) several tautomeric forms are possible and it has been concluded that the above form exists in polar solvents, whereas in nonpolar solvents or in solid state the 1,1′-binaphthylidene form prevails.[37] Dimerization, however, failed in the case of 1,2-naphthoquinone-3-carboxylic acid.[38]



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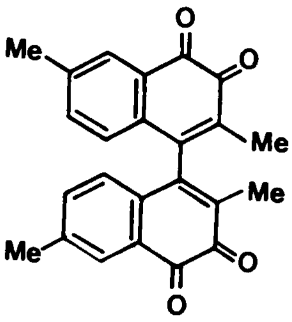

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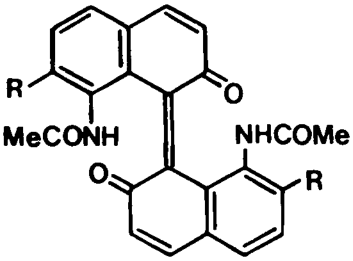

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In a similar manner acid catalyzed condensation of 3,7-dimethyl-1,2-naphthoquinone and 1,2-dihydroxy-3,7-dimethylnaphthalene yielded upon oxidation with nitric acid the diquinone 5 in 64% yield.[35]

When equimolar amounts of naphthalene and 1,4-naphthoquinone are heated in the presence of palladium(II) chloride 2,2'-binaphthalene-1,4-dione is formed in 16% yield.[39] 1,4-Naphthoquinone is dimerized in acetic acid and quinoline or pyridine (yield 67-70%),[40] but in the presence of pyridine further condensation may take place.[41] Other examples of binaphthalene formation under the influence of metals or salts are collected in Table II.

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TABLE II. Dimerization of Naphthalenes under the Influence of Metals or Salts

Starting Naphthalene	Promotor	1,1'-Binaphthalene	% Yield	Ref.
Naphthalene	$SbCl_3$ or $SnCl_4$ in glowing tube	1,1'-Binaphthalene	-	42,43
	glowing Pt	a	-	44
	Se_2Br_2,$AlCl_3$		low	45
	$FeCl_3$,$AlCl_3$ or $MoCl_5$	b	-	46
1(Et)	$AlCl_3$, MeCOCl	4,4'(Et) c	by product	47
1(OMe)	$CuCl_2$	4,4 (OMe) + 3(Cl) 4,4'(OMe)	-	48
1(OMe)	$CuBr_2$ or $CuCl_2$	4,4'(OMe)	40-70	48
	$AlCl_3$		16	49

TABLE II (continued)

Starting Naphthalene	Promotor	1,1′-Binaphthalene	% Yield	Ref.
2(OMe)	$AlCl_3$	2,2′(OMe)	low	49
1(OEt)	$AlCl_3$ or $AlCl_3$,ClCOOEt	4,4′(OEt)	39	49
	$CuBr_2$ or $CuCl_2$		60-84	48
Naphthalene	$AlCl_3$ or Ni-carbonyl or alumosilicate earth	2,2′-Binaphthalene	-	50,51 52 53
	$MoCl_5$		100	46
	i) $TeCl_4$, ii) Raney-Ni		98	54
1(Cl)	$FeCl_3$	1,1′(Cl)	low	55
1,4-Naphthoquinone	$RhCl_3$, EtOH	1,1′(OH) 4,4′(OEt)	-	56

a. Together with much 2,2′-binaphthalene. Yield of the 1,1′-isomer increases with increasing temperature.

b. In various yields, together with 1,2′- and 2,2′-isomers.

c. Structure tentatively assigned.

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3. Oxidative Coupling

Oxidative coupling of naphthols to give binaphthalene derivatives is widely used for the preparation of symmetrically substituted 1,1′- or 2,2′-binaphthalenes. Various reagents have been used for these purposes and there is no general recommendation for a specific one since oxidative transformations of naphthols usually give in addition to the anticipated binaphthalenes various polymeric and quinonoid products.

In the first step, in general, naphthoxyl radical are formed which rapidly react further, although stable radicals are also known. Further transformations of naphthoxyl radicals depend on the structural features and mechanistic possibilities have been discussed.[17,18] Sometimes, in particular with specific reagents such as silver (I)oxide, dimeric quinones are formed. In the first step, naphthoxyl radicals are formed and couple exclusively at unsubtituted ortho and para positions to give first a dimeric naphthol, which may react further to form oligomers. In order to repress these processes, the starting naphthol should have all other positions where coupling may occur blocked, except the required one. In many cases, methoxy groups are used for such purposes and they may be at a later stage transformed into a quinone carbonyl group. The advantage of oxidative coupling when compared to the naphthol/naphthoquinone addition is that the site of formation of the new carbon-carbon bond is more or less unequivocal. However, both synthetic approaches are limited or even fail,if bulky substituents are present at position 2 in naphthols and at the quinonoid carbon-carbon double bond. Stronger oxidizing agents usually disrupt the naphthalene ring with the formation of acids.

a) Ferric chloride

Dianin was first[57] to show that 1-naphthol undergoes oxidative coupling with this reagent. That 1,1'-binaphthalene-4,4'-diol is formed was shown also by others,[58-60] but it was discovered later[61] that also 2,2'-binaphthalene-1,1'-diol is formed. The assigned structure was later found to be correct.[62]

The products from oxidative dimerization of naphthols with $FeCl_3$ are presented in Table III.

In an overoxidation reaction napthols may be transformed with $FeCl_3$ into binaphthylidene derivatives. For example, 8-acetamino-2-naphthol gives upon heating with $FeCl_3$ in aqueous hydrochloric acid 6 (R = H) (63% yield) which is also obtained with Cu(II)oxide in nitrobenzene (60% yield).[80] Similarly the hydroxy analog (6, R = OH) is formed [80] whereas 4-cyclohexyl-1-naphthol gives the 4-oxo analogue 7.[81] From 4-methyl-, 4-methoxy-, 4-cyclohexyl- or 4-phenyl-1-naphthol under similar conditions the bicyclic derivatives (8, R = Me, MeO, C_6H_{11}, Ph) were obtained in 46% to quantitative yield, respectively.[36,81-85]

1,2-Naphthoquinone upon heating with $FeCl_3$ is transformed into a compound for which originally a structure of an ether

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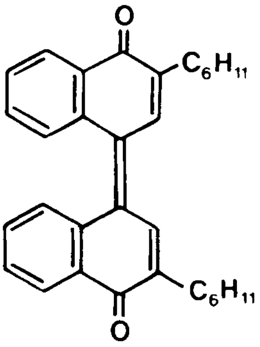
TABLE III. FeCl$_3$ Oxidations of Naphthols

Starting Naphthalene	1,1'-Binaphthalene	% Yield	Ref.
2(OH)	2,2'(OH)	-	57,63,64
		90	65
1(OH)	4,4'(OH)	-	34,57,61
2,3(OH)[a]	2,2',3,3'(OH)	73	66
		60	67
2,6(OH)	2,2',6,6'(OH)	75	68
2,7(OH)	2,2',7,7'(OH)	68	69
2(OH) 3(OMe)	2,2'(OH) 3,3'(OMe)	-	70
2(OH) 3(COOH)	2,2'(OH) 3,3'(COOH)[b]	-	71-73,74
2(OH) 7(SO$_3$H)	2,2'(OH) 7,7'(SO$_3$H)	90	75
2(OH) 6(Br)	2,2'(OH) 6,6'(Br)	58	76,77
6(OH) 7(t-Bu)	2,2'(OH) 3,3'(t-Bu)	low	78
1,2,3,4(H)	5,5',6,6',7,7',8,8'(H)		
	2,2'-Binaphthalene		
1(OH) 3(Me) 4(Cl)	1,1'(OH) 3,3'(Me) 4,4'(Cl)	86	79
5,8(OMe)	5,5',8,8'(OMe)		

a. With ammonium ferric sulfate

b. The levo and dextro form were separated.[72]

was proposed[86] but later structure 9 was assigned and confirmed.[87,88]



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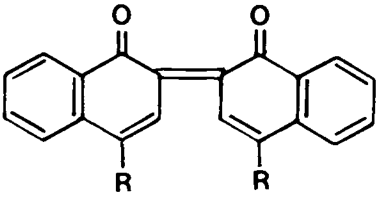

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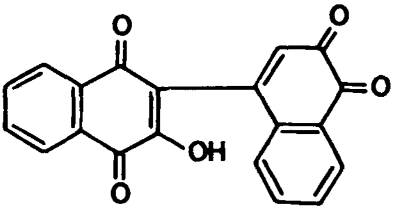

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b) Potassium ferricyanide

This reagent is frequently used for oxidative coupling of naphthols in an alkaline solution (Table IV). With this reagent overoxidation is also possible as shown later in several cases. It is however possible to overcome this drawback by using a two phase system in which the product is protected from further oxidation.

TABLE IV. Oxidative Coupling of Naphthols with $K_3Fe(CN)_6$

Starting Naphthalene	1,1'-Binaphthalene	% Yield	Ref.
6(OH) 7(t-Bu) 1,2,3,4(H)	2,2'(OH)3,3'(t-Bu) 5,5',6,6',7,7',8,8'(H)	68	78
6(OH) 7,8(Me) 1,2,3,4(H)	2,2'(OH) 3,3',4,4'(Me) 5,5',6,6',7,7',8,8'(H)	43[a]	95
	2,2'-Binaphthalene		
1(OH) 3(Me) 4(OMe)	1,1'(OH) 3,3'(Me) 4,4'(OMe)	61	96
2(OH) 1,6(t-Bu)	3,3'(OH) 4,4',7,7'(t-Bu)[b]	25	76
6(OH) 5,8(Me) 1,2,3,4(H)	1,1',4,4'(Me) 3,3'(OH) 5,5',6,6',7,7',8,8'(H)	40	95

a. In a two phase system. b. Structure tentatively assigned.

1,1'-Binaphthalene-2,2'-diol (10) which is formed from 2-naphthol is easily oxidized further by $K_3Fe(CN)_6$ or other

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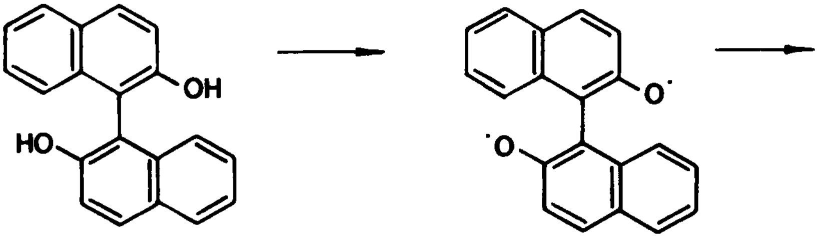
oxidants. Two crystalline products were obtained, peroxide and an ether. Both dissociate in solution forming deep-coloured radicals, formulated as 11 and 12.



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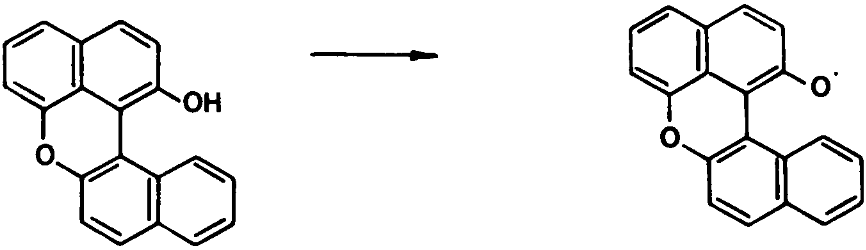

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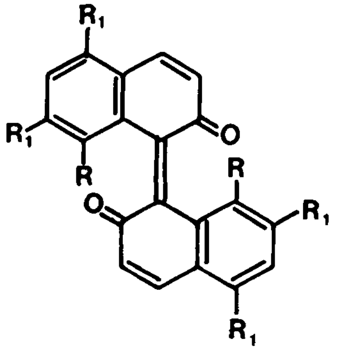
For these two species ESR spectra were measured and showed the presence of radicals. Also oxidation of 10 with Ag_2O gives a compound which is a radical in the solid state. All these dinaphthoxyl radicals are stable in the presence of air.[89]

When a solution of optically pure (S)-(+)-7-hydroxy-1,5,6-trimethyl-1,2,3,4-tetrahydronaphthalene was dimerized with $K_3Fe(CN)_6$ only one pure isomer was obtained (yield 63%). The (S,S)-trans enantiomer was obtained in a completely stereospecific manner.[90] If racemic starting material was used, a mixture of three diastereoisomeric dl-dimers were obtained in a ratio of 66:7.9:26.1. Mixed oxidation of 2-naphthol and 6-bromo-2-naphthol gave a mixture of homo- and cross-coupled products.[91]

Overoxidation of the corresponding naphthols yields the 1,1'- (13, R = Cl, R_1 = H , quantitative yield, or 13, R = NHCOMe, R_1 = Cl),[80] the 2,2'-binaphthylidene derivative (14) (yield 50%)[79] and 15.[92] Whereas the 8-substituted derivatives, for example 13 (R = NHCOMe, R_1 = Cl), are true quinones, the parent compound (13, R = R_1 = H) is regarded as diradical.[80,93]



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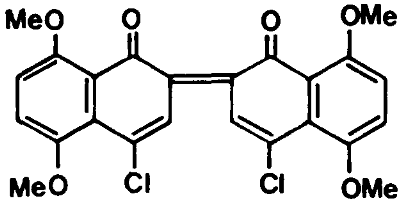

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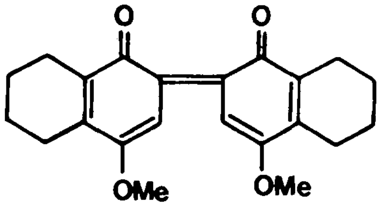

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Similarly 2-methyl-1-naphthol is transformed with $K_3Fe(CN)_6$ into 3,3′-dimethyl-1,1′-binaphthylidene-4,4′-dione in almost quantitative yield[94] and from 2-methoxy-1-naphthol 3,3′-dimethoxy-1,1′-binaphthylidene-4,4′-dione is obtained in low yield.[70]

c) Lead tetraacetate

Lead tetraacetate has been used mainly to convert phenolic compounds into the quinone-diacetates, quinol acetates and quinones and there are only a few examples of its application for the synthesis of binaphthalene derivatives.

1-Methoxynaphthalene when oxidized with lead tetraacetate gives 1,1′-binaphthalene derivatives together with a small amount of 1′,4-dimethoxy-1,2′-binaphthalene.[97] After four weeks at room temperature, 4,4′-dimethoxy-1,1′-binaphthalene was obtained in 51% yield;[98] with an excess of lead tetraacetate, 4-methoxy-1,1′-binaphthalene-3′,4′-dione is obtained in appreciable quantity.[97] 1,5-Dimethoxynaphthalene with a

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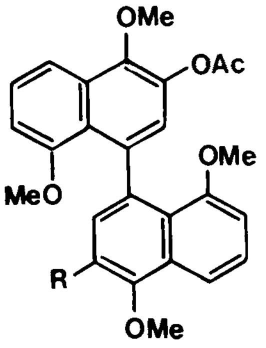
molar proportion of lead tetraacetate gives as the main product the diacetoxy dimer (16, R = OAc) together with a smaller amount of the 3-acetoxy analog (16, R = H) and a substantial amount of the dione (17, $R_1 = R_2 = H$) and its 3-acetoxy (17, R_1 = OAc, R_2 = H) and 5-acetoxy (17, R_1 = H, R_2 = OAc) derivatives. With excess of lead tetraacetate also compound 18 is formed.[97] Similar results were obtained from oxidation of 2,6-dimethoxynaphthalene.[97]



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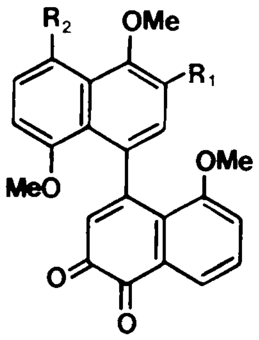

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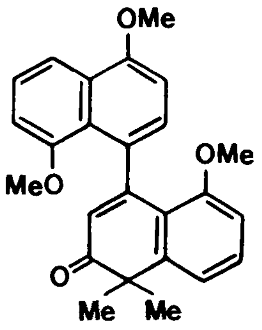

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d) Lead(IV) oxide and Silver(I) oxide

Oxidative coupling of 1-naphthols with Ag_2O to give 2,2'-binaphthalene derivatives has been used in several cases to produce polysubstituted derivatives (Table V). Similar to 5,8-dimethoxy-3-methyl-1-naphthol which is oxidized to the biquinone,[79] 4-hydroxy-1,2-dimethoxynaphthalene gives upon oxidation with Ag_2O 3,3'-dimethoxy-2,2'-binaphthalene 1,1',4,4'-tetrone.[99]

For the most part 1-naphthols are oxidized with Ag_2O into the corresponding 2,2'-binaphthylidene-1,1'-diones (Table VI). Cross coupling was also successful with a mixture of 1,5-dihydroxy-4-methoxy-7-methylnaphthalene and 4,5-dihydroxy-1-methoxy-7-methylnaphthalene with PbO_2 to give 5,8'-dihydroxy-4,4'-dimethoxy-6',7-dimethyl-2,2'-binaphthylidene-1,1'-dione.[106] In an analogous manner, co-oxidation of 4-methoxy-8-methyl-1-naphthol and 4-methoxy-5-methyl-1-naphthol with Ag_2O afforded

TABLE V. 2,2'-Binaphthalenes from Naphthols and Ag_2O

Starting Naphthalene	2,2'-Binaphthalene	% Yield	Ref.
1(OH) 4(OMe)	1,1'(OH) 4,4'(OMe)	95	100
1(OH) 3(Me) 5,8(OMe)	1,1'(OH) 3,3'(Me) 5,5',8,8'-tetrone	13[a]	79
1(OH) 3(Me) 4(OCOMe)	3,3'(Me) 1,1',4,4'(OCOMe)	low[b]	101
1(OH) 3(Me) 4(OCOMe) 8(OMe)	1,1'(OH) 3,3'(Me) 4,4'(OCOMe) 8,8'(OMe)	25[c]	102

a.Together with 8% isodiospyrin (4,1'-dihydroxy-2,3'-dimethyl-1,2'-binaphthalene-5,5',8,8'-tetrone) which was isolated previously from Diospyros lotus.[103-105] b.After subsequent acetylation. c.As by-product 1-hydroxy-3,3'-dimethyl-4-acetoxy-8,8'-dimethoxy-2,2'-binaphthalene-1',4'-dione is obtained.

in addition to the symmetrical 4,4'-dimethoxy-8,8'-dimethyl- and 4,4'-dimethoxy-5,5'-dimethyl-2,2'-binaphthylidene-1,1'-dione 4,4'-dimethoxy-5,8'-dimethyl-2,2'-binaphthylidene-1,1'-dione as the main product in 42% yield.[109] Co-oxidation of 4-methoxy-6-methyl-1-naphthol and 4-methoxy-7-methyl-1-naphthol gave a mixture of 4,4'-dimethoxy-7,7'-dimethyl-, 4,4'-dimethoxy-6,7'-dimethyl- and 4,4'-dimethoxy-6,6'-dimethyl-2,2'-binaphthylidene-1,1'-dione.[109] From 4-methoxy-6-ethoxy-1-naphthol and 4-methoxy-7-ethoxy-1-naphthol a mixture of 4,4'-dimethoxy-6,6'-diethoxy-, 4,4'-dimethoxy-6,7'-diethoxy- and 4,4'-dimethoxy-7,7'-diethoxy-1,1'-binaphthylidene-1,1'-dione was obtained.[109]

A 1,1'-binaphthylidene derivative is formed when 2-methoxy-1-naphthol is oxidized with PbO_2 to give 3,3'-dimethoxy-1,1'-binaphthylidene-1,1'-dione.[34] Also 1,2-naphthoquinone when oxidized with Ag_2O and in the presence of 1,1-dianisylethylene is transformed into the last mentioned product.[113] An unusual tetrone is formed in small yield when 1,7-dihydroxynaphthalene is oxidized with PbO_2 to give 1,1'-binaphthalene-2,2',8,8'-tetrone.[114]

It should be mentioned that the blue compound, obtained

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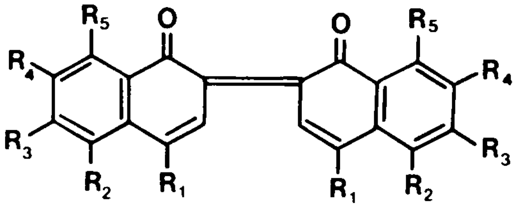
TABLE VI. 2,2'-Binaphthylidene-1,1'-diones from Naphthols and Ag_2O or PbO_2



Starting Naphthalene	Oxidant	R_1	R_2	R_3	R_4	R_5	% Yield	Ref.
1(OH) 4(OMe)	PbO_2	OMe	-	-	-	-	-	107
1(OH) 4,5(OMe)	Ag_2O	OMe	OMe	-	-	-	93	106
4(OH) 1,5(OMe)	Ag_2O	OMe	-	-	-	OMe	95	106
1(OH) 4(OMe) 6,7(OEt)	Ag_2O	OMe	-	EtO	EtO	-	91	108
1(OH) 4,5(OMe) 7(Me)	Ag_2O	OMe	OMe	-	Me	-	92	106
4(OH) 1,5(OMe) 7(Me)	Ag_2O	OMe	-	Me	-	OMe	95	106
1(OH) 4(OMe) 5(Cl)	Ag_2O	OMe	Cl	-	-	-	78	109
1(OH) 4(OMe) 5(Me)	Ag_2O	OMe	Me	-	-	-	48	109
1(OH) 4(OMe) 8(Cl)	Ag_2O	OMe	-	-	-	Cl	92	109
1(OH) 4(OMe) 8(Me)	Ag_2O	OMe	-	-	-	Me	63	109
1,5(OH) 4(OMe)	PbO_2	OMe	OH	-	-	-	68	106
4,5(OH) 1(OMe)	PbO_2[a]	OMe	-	-	-	OH	87	106
1,5(OH) 4(OMe) 7(Me)	PbO_2	OMe	OH	-	Me	-[b]	71	106,110
1,8(OH) 4(OMe) 6(Me)	PbO_2[a]	OMe	-	Me	-	OH[c]	84 -	106, 110-112

a. Or with $FeCl_3$. b. Diosindigo B. c. Identical with the blue pigment isolated from Diospyros species (Diosindigo A).

from chemical oxidation of 4-methoxy-1-naphthol and to which structure of 4,4'-dimethoxy-2,2'-binaphthylidene-1,1'-dione (19) was assigned,[107] is decolorized with triphenylmethyl radical. It was later observed[115] that 4-methoxy-1-naphthol was transformed in alkaline medium through exposure to air to a blue compound which showed paramagnetic properties[116] and again structure 19 was accepted. The same compound was also obtained by anodic oxidation of naphthalene in methanol,

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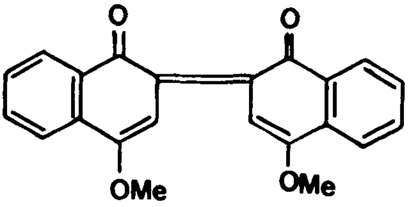
saturated with calcium oxide, in particular in the presence of oxygen. On the basis of its oxidation to the biquinone and of other data, the structure 20 has been proposed.[117] The blue radical is stable in solid state at temperatures above 100°C, but it is decolorized by sunlight in few minutes.



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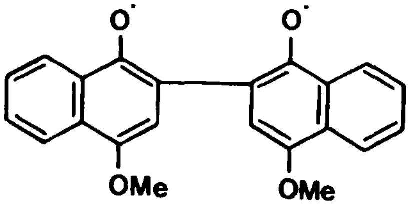

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e) Other Oxidants

A variety of reagents have been used for oxidative dimerization of substituted naphthalenes, naphthols or naphthylamines. These products are presented in Table VII. Promising results have been obtained with thallium(III) trifluoroacetate as oxidant under various conditions, in particular with electron rich substrates. Yields are usually better when compared to those with other reagents.[118,119]

TABLE VII. Oxidative Coupling with Various Reagents

Starting Naphthalene	Reagent	1,1'-Binaphthalene	% Yield	Ref.
1(OH)	$VOCl_3$ or VCl_4	4,4'(OH)	56,40	120
1(OMe)	$VOCl_3$	4,4'(OMe)	84	121
	TTFA[a,b]		51-88	118,119
	HCO_3H		70	122
1(OEt)	isatin,H^+	4,4'(OEt)	-	123
1(Me)	TTFA[a,b]	4,4'(Me)	32-93	118,119
1(i-Pr)	TTFA[b]	4,4'(i-Pr)	34-70	118
1(CH_2COOMe)	TTFA[c]	4,4'(CH_2COOMe)	53	118
1(Ph)	TTFA[b]	4,4'(Ph)	55-98	118
1(NH_2)	$Fe_2(SO_4)_3$	4,4'(MeCONH)	-	35

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TABLE VII (continued)

Starting Naphthalene	Reagent	1,1′-Binaphthalene	% Yield	Ref.
1(Br)	TTFA[d]	4,4′(Br)	25-87	118,119
1(I)	TTFA[d]	4,4′(I)	25-94	118,119
2(OH)	V_2O_5,300°C	2,2′(OH)	20	124
	Cu-acetate, formiate or chloride		-	125
	O_2,CaO,300°		-	59
	$VOCl_3$ or VCl_4		65,38	120
	MTA[g]		60	126
	Cu-amine complex		62	127
	Cu-pyridine complex		70	127
	O_2/NaOH		20	128
2(OMe)	$VOCl_3$(TFA)	2,2′(OMe)	7(47)	121
2(PhNH)	$KMnO_4$	2,2′(PhNH)	44	129
2(R-Ph-NH)	$KMnO_4$[e,f]	2,2′(R-Ph-NH)	22-44	130
5(NO_2) 1,2,3,4(H)	$(COOEt)_2KOEt$	8,8′(NO_2) 1,1′,2,2′,3,3′,4,4′(H)	10	131
1,2(OH)	H_2O_2	3,3′,4,4′(OH)	28	132
	O_2/OH^-		-	133
2,7(OH)	Cu-amine complex	2,2′,7,7′(OH)	27	127
1,7(OMe)	TTFA[b]	4,4′,6,6′(OMe)	41-74	118
2,7(OMe)	$VOCl_3$	2,2′,7,7′(OMe)	68	121
1,2(Me)	TTFA	3,3′,4,4′(Me)	74	118
1(NH_2) 2(Me)	$FeCl_3$ or H_2SO_4	3,3′(Me) 4,4′(NH_2)	74	134
	H_2O_2/AcOH or $FeCl_3$		50	135
2(OH) 5(NH_2)	MTA[g]	2,2′(OH) 5,5′(NH_2)	13	136
1(OMe) 2(Me)	TTFA[b]	3,3′(Me) 4,4′(OMe)	24-97	118,119
1(OMe) 2(Cl)	TTFA[b]	3,3′(Cl) 4,4′(OMe)	8-94	118,119
1(OMe) 2(Br)	TTFA[b]	3,3′(Br) 4,4′(OMe)	11-86	118,119
1(Br) 2(Me)	TTFA	3,3′(Me) 4,4′(Br)	42	118
6(OH) 7(t-Bu) 1,2,3,4(H)	MnO_2	2,2′(OH)3,3′(t-Bu) 5,5′,6,6′,7,7′,8,8′(H)	48	78
1(OH) 2,3(COOMe) 1,4(H)	MnO_2	4,4′(OH)2,2′,3,3′ (COOMe)	13	137

TABLE VII (continued)

Starting Naphthalene	Reagent	1,1-Binaphthalene	% Yield	Ref.
2(OH)3,4,8(Me) 5,6,7,8 (H)	Cu-amine complex	2,2'(OH)3,3',4,4' 8,8'(Me)5,5',6,6', 7,7',8,8'(H)	46	127
1,3(OH)6,7(OMe) 2(COOEt)	I_2	2,2',4,4'(OH)3,3' (COOEt)6,6',7,7'(OMe)	-	138
1(PhNH)8(SO_3H)	HNO_2[h]	4,4'(PhNH)5,5'(SO_3H)	1-30	139-142

a. TTFA = thallium (III)trifluoroacetate. Yields vary depending on reaction conditions (in the presence of BF_3.O$(Et)_2$or TFA).

b. Or with Hg$(OCOCF_3)_2$, Pb$(OCOMe)_4$, $FeCl_3$, CoF_3.

c. 95% yield with Pb$(OCOMe)_4$.

d. Or with Pb$(OCOMe)_4$, $FeCl_3$, CoF_3.

e. R = m-MeO, p-MeO, p-Me, m-Cl, m-Me.

f. The p-Me derivative was also dimerized with $FeCl_3$,$NaNO_2/H^+$ or in the presence of *p*-nitrosodimethylaniline and $ZnCl_2$.[143,144]

g. MTA = manganese(III) tris(acetylacetonate).

h. Yields of 1-31% were obtained with $K_2Cr_2O_7$, CrO_3, CoF_3, Pb$(OCOMe)_4$, $KMnO_4$ or TTFA.

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In several cases oxidation of naphthalene derivatives yields the corresponding binaphthalene quinones (Table VIII). For example, 2,3-dihydroxynaphthalene is oxidized in the presence of Fremy's salt and the formed 3-hydroxy-1,2-naphthoquinone is dimerized in low yield to 2. Upon heating in water the latter is transformed in 30% yield into the binaphthalenequinone 3 together with other products.[32]

Binaphthylidene quinones were obtained from various naphthols or 1,2-naphthoquinone (Table IX) and naphthols or 1,4-naphthoquinones can be transformed into the corresponding binaphthoquinones (Table X). The binaphthalenebiquinone 21 is obtainable by several methods. It is formed from 2-methoxynaphthalene and lead tetraacetate at room temperature (2.3% yield) or from 1-acetoxy-2-methoxynaphthalene and lead tetra-

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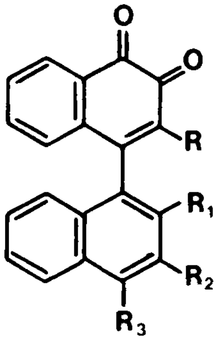
TABLE VIII. Oxidative Coupling to Quinones by Various Oxidants



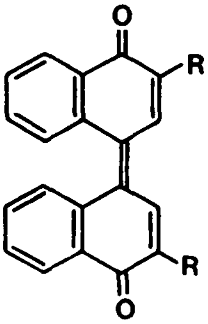
Starting Naphthalene	Reagent	R	R_1	R_2	R_3	% Yield	Ref.
Naphthalene	CrO_3,Mn(II)	-	-	-	-[a]	-	145
	Periodic acid	-	-	-	I	10	146
2(OMe)	HCO_3H	-	OMe	-	-	64	122
2(OH)	H_2O_2,Mo(VI)	-	OH	-	-	67	147,148
	Cu(II)/collidine complex					-	36
1,2(OH)	H_2O_2/OH^-	-	-	OH	OH	83	132
	O_2/OH^-					-	133
3(OH) 2(COOH)	Fremy's salt	COOH	OH	COOH	-	60	38

a.Together with 1,2'-binaphthalene-1',4'-dione.

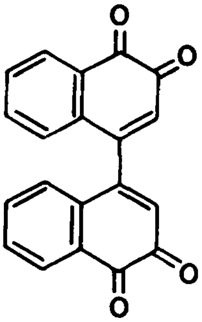
acetate at room temperature (6.2% yield).[98] It is formed also from 1,2'-naphthoquinone in the presence of acid,[33] with PbO_2 [41] or in a reaction with ethyl azidoformate among other products.[151]

1,2-Naphthoquinone is otherwise oxidized with $FeCl_3$ to 3-hydroxy-2,2'-binaphthalene-1,3',4,4'- tetrone.[87] A particular case represents the reaction of 2,3-dimethyl-5,7-diethoxy-1,4-naphthoquinone with BBr_3 to give 2,2'-diethoxy-4,4'-dihydroxy-6,6',7,7'-tetramethyl-1,1'-binaphthalene-5,5',8,8'-tetrone in 17% yield.[157] 4,4'-Dichloro-2,2'-binaphthylidene-1,1'dione

TABLE IX. Oxidative Coupling to 1,1′-Binaphthylidene-4,4′-diones by Various Oxidants



Starting Naphthalene	Oxidant	R	% Yield	Ref.
1(OH) 2(Me)	Azobenzene	Me	85	149
	CrO_3 or $K_3Fe(CN)_6$		20	34,150
1(OH) 2(Et)	$Cu(NO_3)_2,O_2$ collidine	Et	38	36



21

is obtained in quantitative yield from CrO_3 oxidation of 4-chloro-1-naphthol.[83] Solutions of some binaphthoquinones are extremely sensitive to light (mamegaquinone dimethyl ether, bijuglone dimethyl ether) and are quickly transformed into the corresponding pentacyclic compounds.[106]

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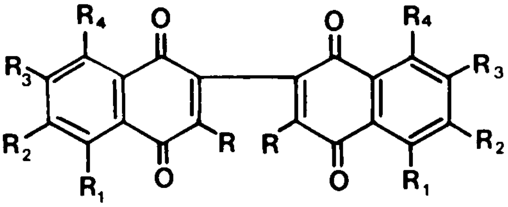
TABLE X. 2,2'-Binaphthoquinones



Starting compound	Oxidant	R	R_1	R_2	R_3	R_4	% Yield	Ref.
Naphthalene								
1(OH) 2,4(Br)	HNO_3	-	-	-	-	-	low	152
1(OH) 4(MeCONH)	$Na_2Cr_2O_7$ or HNO_3 or $FeCl_3$	-	-	-	-	-	60-75	153
1,4-Naphthoquinone								
	$PdCl_2$	-	-	-	-	-	>5	39
	N_3COOEt	-	-	-	-	-	-	151
2(OH)	$K_2S_2O_8$	OH	-	-	-	-	61	154
2(NH_2)	$K_2S_2O_8$	NH_2	-	-	-	-	70	155
2(MeNH)	$K_2S_2O_8$	NHMe	-	-	-	-	10-42	155
2(EtNH)	$K_2S_2O_8$	NHEt	-	-	-	-	10	155
2,5(OH)	$K_2S_2O_8$	OH	-	-	-	OH	25	156
2,8(OH)	$K_2S_2O_8$	OH	OH	-	-	-	13	156
2(OH) 5(OMe)	$K_2S_2O_8$	OH	-	-	-	OMe	75	154
2(OH) 6(OMe)	$K_2S_2O_8$	OH	-	-	OMe	-	48	154
2(OH) 7(OMe)	$K_2S_2O_8$	OH	-	OMe	-	-	44	154
2(OH) 6(Br)	$K_2S_2O_8$	OH	-	-	Br	-	82	154
3(NH_2) 5(OMe)	$K_2S_2O_8$	NH_2	OMe	-	-	-	47	155

4. Reductive Coupling

It has been observed that reductive coupling occurred during attempted reduction of naphthalenes or naphthoquinones. Naphthalene, when reduced with sodium and amines yields numerous products, among them also dimers. The product distribution varies considerably depending on reactions and the selected

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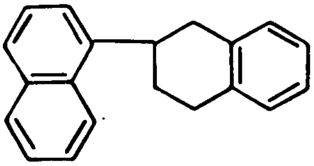
amine.[158] If steric effects are present in the added amine, reductive amination diminished and reductive dimerization may increase. For example, with sodium in dipropylamine a remarkable selective formation of 1,2'-dimer results and at room temperature the dimers 22, 23 and 24 were formed in a ratio of 73:11:16; at higher temperatures (40-80°C) the dimer 22 was formed almost exclusively.[159]



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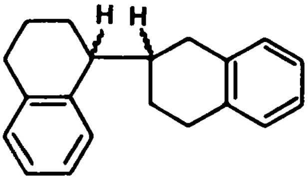

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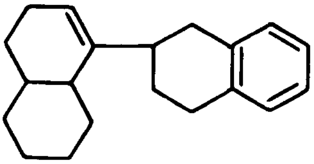

24

On the other hand, it is reported that reductive amination of naphthalene with sodium and in the presence of amines yielded also 1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthalene in 14-44% yield.[158] Other examples of reductive coupling with hydrazines and other reagents are given in Table XI.

There are also several cases of dimer formation resulting from reduction of 1,2-naphthoquinones. From 1,2-naphthoquinone upon reductive acetylation also 3,3',4,4'-tetraacetoxy-1,1'-binaphthalene was obtained as a minor product.[169] 3-Chloro-1,2-naphthoquinone when treated with diethyl zinc and thereafter with diazoethane was transformed into 2,2'-dichloro-3,3',4,4'-tetraethoxy-1,1'-binaphthalene.[170] 7,7'-Dibromo-3,3',4,4'-tetraacetoxy-1,1'-binaphthalene was obtained from 6-bromo-1,2-naphthoquinone and phenyl azide followed by reductive acetylation, or simply by reductive acetylation of the above quinone.[171] Also 4,4-dichloro-1,2,3,4-tetrahydronaphthalene-1,2,3-trione dihydrate when reduced with stannous chloride afforded 1,1'-binaphthalene-2,2', 3,3', 4,4'-hexol[172] to which previously the structure of 1,2,3-trihydroxynaphthalene was assigned.

A variety of new complex reducing agents of the type NaH-RONa-MX_n, prepared from activated sodium hydride (NaH-RONa)

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TABLE XI. Binaphthalene from Reductive Coupling

Starting Naphthalene	Reagent	1,1-Binaphthalene	% Yield	Ref.
Naphthalene	i) Na, ii) i-BuCl, NH_3	4,4'(i-Bu)	-	160
1(Br)	$PhNHNH_2$/Pd-Hg	1,1'-Binaphthalene	50	161,162
	complex of Ni or Zr salts		60,27	163
	NH_2NH_2, Pd/C		14	164
2(OH)	NH_2NH_2	2,2'(NH_2)	45	165
1(COOMe)	Na-Hg, H_3BO_3	4,4'(COOMe) 1,1',4,4'(H)	20	166
1(COOMe) 2(OH)	Na-Hg, H_3BO_3	4,4'(COOMe) 3,3'(OH) 1,1', 2,2'(H)	-	167
		2,2'-Binaphthalene		
2(Br)	$PhNHNH_2$/Pd-Hg	2,2'-Binaphthalene	71	161,162
	NH_2NH_2, Pd/C		50	164
2(OMe) 6(Br)	NH_2NH_2, Pd	6,6'(OMe)	7	168

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and various metal salts were examined for reduction of 1-bromonaphthalene. Complexes containing Ti, Cr, Mn, Fe, Ni, Cu, Cd or Zr salts yielded in addition to naphthalene, also 1,1'-binaphthalene in yields up to 60%.[173]

5. Coupling of Halonaphthalenes in the Presence of Metals

The Ullmann reaction remains one of the most important synthetic methods for the preparation of binaphthalene derivatives although reaction conditions of this coupling are quite severe. Therefore, this reaction is not suitable for highly functionalized and sensitive naphthalene derivatives. Examples

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of the Ullmann reaction for 1,1'-, 1,2'- and 2,2'-binaphthalenes are presented in Tables XII-XIV and the use of other metals or salts is given in Table XV.

TABLE XII. 1,1'-Binaphthalenes from the Ullmann Reaction

Starting Naphthalene	Reaction Temp. (°C)	1,1'-Binaphthalene	% Yield	Ref.
1(Br)			50	174
1(I)	280-285		92,74	175,176
1(Br) 2(OH)	230,280	2,2'(OH)	-	124,177
1(Cl) 2(COOMe)	290	2,2'(COOH)[a]	46	178
1(Br) 2(COOMe)	190,	2,2'(COOMe)	72	179,180
	270-280		78,81	181,182
1(I) 2(NO_2)	120-130(DMF)	2,2'(NO_2)	-	183,184
1(I) 3(NO_2)	260	3,3'(NO_2)	low	183
1(I) 4(NO_2)	220-230	4,4'(NO_2)	-	174
1(I) 5(NO_2)	220-230	5,5'(NO_2)	-	185
1(I) 8(NO_2)	in $PhNO_2$	8,8'(NO_2)	43	186
1(I) 4(MeO)	220-230	4,4'(OMe)	15-20	62
5(I) 1(COOMe)	220-240	5,5'(COOMe)	75	187
8(Cl) 1(COOEt)	290	8,8'(COOEt)	-	188
1(I) 8(SO_3K)		8,8'(SO_3H)	-	189
1(I) 4,8(NO_2)	in $PhNO_2$	4,4',8,8'(NO_2)	36	186
1(I) 4(Br) 8(NO_2)	in $PhNO_2$	4,4'(Br)8,8'(NO_2)	-	186
1(Br) 3(Me) 4(NH_2)	in tetralin	3,3'(Me) 4,4'(NH_2)	39	134
1(I) 2(NO_2) 4(Br)	150-160	2,2'(NO_2) 4,4'(Br)	low	184
5,8(Br)1(COOMe)	210-230	4,4'(Br 8,8'(COOMe)	55	190
1(I) 2(COOMe) 3(OMe) 4(Pht)[b]	220-230	2,2'(COOMe) 3,3'(OMe)[c] 4,4'(NH_2)	42	38
5(I) 6,7,8(OMe) 1(COOMe)	260-275	2,2',3,3',4,4'(OMe) 5,5'(COOMe)	-	191

a. Subsequent saponification of the diester

b. Pht = phthalimido

c. After hydrazinolysis

TABLE XIII. 1,2'-Binaphthalenes from the Ullmann Reaction

Starting Naphthalene	Reaction Temp. (°C)	1,2'-Binaphthalene	% Yield	Ref.
1(I) 2(NO_2) and 2(I) 1(NO_2)	175	1',2(NO_2)	4	192
1(I) 4(OMe) and 2(I) 1(OMe)	230-240	1',4(OMe)	low	62
2(Br) and 8(Cl) 1(COOEt)	290	8(COOH)	-	193
1(I) 4(OMe) and 3(Br) 2(COOH)	290	4(OMe) 3'(COOH)	low	194

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If 1-bromo-2-naphthoates of chiral alcohol of R- and S-configuration were used in the Ullmann synthesis, axial dissymmetry or R- and S-chirality was induced. The optical yields amounted up to 13% when the chiral alcohol was l-menthol.[213] In a similar manner chiral diol esters were used in the Ullmann synthesis, followed by cleavage of the ester likage and lithium aluminium hydride reduction. The induced chirality (S or R) depends on the starting chiral diol and may be relatively high.[214]

A mixed coupling was successful when 6-bromo-1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene was converted to the arylzinc reagent and coupled to ethyl 6-bromo-2-naphthalenecarboxylate in the presence of tetrakis(triphenylphosphine) nickel(O) as catalyst (yield 48%).[215] In other cases, cross-coupling was less successful, except for the preparation of 1,2'-binaphthalenes (Table XIII). For example, the Ullmann reaction of a mixture of 1-bromonaphthalene and ethyl 8-chloronaphthalene-1- carboxylate at 290°C afforded 1,1'-binaphthalene in low yield.[193] If 1-iodonaphthalene was used,in addition of the parent binaphthalene methyl 1,1'-binaphthalene-8-carboxylate at 290°C afforded 1,1'-binaphthalene in low yield.[193] If 1-iodonaphthalene was used, in addition of the parent binaphthalene methyl 1,1'-binaphthalene-8-carboxylate was also obtained in 14% yield.[216]

TABLE XIV. 2,2'-Binaphthalenes from the Ullmann Reaction

Starting Naphthalene	Reaction Temp. (°C)	2,2'-Binaphthalene	% Yield	Ref.
2(Br)	280-285	2,2'-Binaphthalene	low	174
2(I)	230-260		67	195
2(I) and 2-iodomesitylene			low	196
2(I) 1(Me)	260	1,1'(Me)	-	197
2(I) 1(MeO)	200-210	1,1'(MeO)	-	59
2(I) 1(NO_2)	in $PhNO_2$ or DMF	1,1'(NO_2)	40	184,198
	120-130		44	183
2(I) 3(NO_2)	130-135	3,3'(NO_2)	low	199
2(I) 1(SO_3Na)	100	1,1'(SO_3Na)	-	189
3(I) 1(NO_2)	in $PhNO_2$	4,4'(NO_2)	31	200
3(Br) 2(COOMe)	190-200	3,3'(COOMe)	50	180
6(I) 5(NO_2)	190	1,1'(NO_2)	low	183
1,2,3,4(H)	140	5,5',6,6',7,7',8,8'(H)	73	201
7(I) 6(NO_2)	110-120 or	3,3'(NO_2)	-	183,184
1,2,3,4(H)	in DMF	5,5',6,6',7,7',8,8'(H)	-	199

TABLE XV. Coupling of Halonaphthalenes in the Presence of Various Metals and Salts

Starting Naphthalene	Promotor	1,1'-Binaphthalene	% Yield	Ref.
1(Cl)	Li (260°C)	1,1'-Binaphthalene	-	202
	Na + Michlers ketone		by-product	203
5(Br) 6,7(Me) 1,2,3,4 (H)	i) Li ii) CoBr	2,2',3,3'(Me) 5,5',6,6',7,7',8,8'(H)	36	204
		1,2'-Binaphthalene		
1(Br) 2(F)	BuLi	1'(Br) 2(F)	-	205

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TABLE XV. (continued)

Starting Naphthalene	Promotor	2,2'-Binaphthalene	% Yield	Ref.
		2,2'-Binaphthalene		
1(Br)	$AlCl_3$		-	206
2(Cl)	Na		low	203,207
2(Br or I)	Li		good	208
2(Br) 6(OMe)	TlBr	6,6'(OMe)	72	209
2(Br) 1(F)	BuLi	1(F)	low	205
6(Br) 2(OH)	Pd, NH_2NH_2	6,6'(OH)	10	168
6(Br) 2(OMe)	Mg	6,6'(OMe)	low	210
2(Br) 3(Me) 1,6,7 (OMe)	i) BuLi ii) $CoBr_2$	1,1',6,6',7,7'(OMe) 3,3'(Me)	10	211
1,3(Br) 2(OH) 4(OCOMe)	$SnCl_2/OH^-$	4,4'(Br) 1,1',3,3'(OH)	40	212

6. Binaphthalenes *via* Grignard and Organolithium Compounds

Grignard reagents prepared from halonaphthalenes have been used in homo and hetero coupling reactions leading to binaphtalenes. Various reaction conditions have been employed (Table XVI , XVII).

1,1'-Binaphthalene results in variable yields (up to 65%) from the action of various metal acetylacetonates on magnesium or lithium derivatives of naphthalene.[233] 2-Methoxy-1-naphthyl lithium when oxidized with t-butyl hydroperoxide gave 4,4'-dihydroxy-3,3'-dimethoxy-1,1'-binaphthalene in 7% yield.[234] From heptafluoronaphthyllithium tridecafluoro-1,2'-binaphthalene was obtained as minor product *via* the corresponding naphthalyne.[235]

α-Naphthoylmesitylene reacted with phenylmagnesium bromide to give 3,3'-diphenyl-1,1'-binaphthalene-4,4'-diol and also 3,3'-diphenyl-1,1'-binaphthylidene-4,4'-dione.[236] To the

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former product the structure of 2-phenyl-1-naphthol was assigned previously.[237]

TABLE XVI. 1,1′- and 1,2′-Binaphthalenes *via* Grignard Compounds

Starting Naphthalene R 1(MgBr)	Second Component	1,1′-Binaphthalene	% Yield	Ref.
H	t-BuBr	1,1′-Binaphthalene	-	217
	$CrCl_3$		-	218
	$CuCl_2$		80	34,219
	AuCl.CO		71	220
	1,4-dichloro-2-butyne		88	221
2(Me)	$CuCl_2$	2,2′(Me)	32	222
4(Me)	$CrCl_3$	4,4′(Me)	-	218
2(OMe)	$B(OMe)_3, H_2O_2$	3,3′(OMe) 4,4′(OH)	-	223
5(i-propenyl)	-	5,5′(i-propenyl)	low	224
4(F)	phthalic anhydride	4,4′(F)	by-product	225
		1,2′-Binaphthalene		
H	phenyl 2-OMe 1-naphthoate	1′(COOPh)	78	226

Although dissymmetric binaphthalenes have been utilized in asymmetric recognition, only recently synthetic routes to chiral binaphthalenes were developed. 2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane has been used in an asymmetric synthesis of 2,2′-dimethyl-1,1′-binaphthalene from 1-bromo-2-methylnaphthalene *via* its Grignard reagent. The (S)(+)dimer was obtained in 32% yield and 1.9% optical purity but in the presence of a nickel complex the dimer was obtained with 12.5% ee.[238,239] A new approach used nucleophylic aromatic displacement of an o-methoxy group activated by an achiral or chiral oxazoline substituent in the naphthalene

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TABLE XVII. 2,2'-Binaphthalenes *via* Grignard Compounds

Starting Naphthalene R 2(MgBr)	Second Component	2,2'-Binaphthalene	% Yield	Ref.
H	CO_2	2,2'-Binaphthalene	28	227
	$FeCl_3$		low	228
	TlBr		84	209
	MeI		28	229
	2-bromonaphthalene		-	87
	phenyl 2(OMe) 1-naphthoate	1(COOH)[a]	59	226
1(Me)[b]	CO_2	1,1'(Me)	low	230
5(Me) 8(i-Pr)	Me_2SO_4	5,5'(Me) 8,8'(i-Pr)	by-prod.	231
1(OEt) 1,2,3,4(H)	$EtOH/H_2SO_4$	3,3',4,4'(H)	-	232

a. Together with some 2,2'-binaphthalene

b. As 2(MgI).

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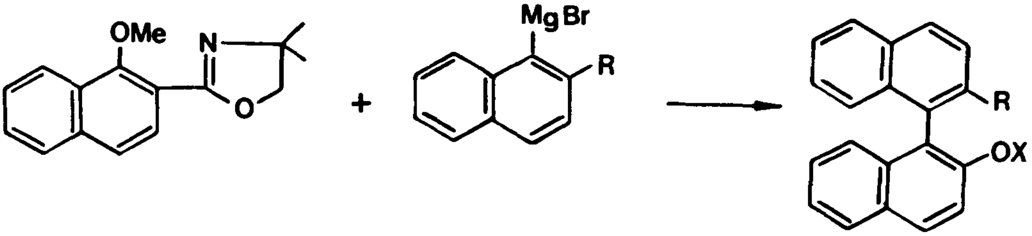
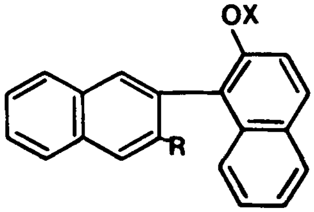
ring. In this manner 2-(4,4'-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)-1-methoxynaphthalene (or with a chiral oxazoline at position 2) when treated with 1-naphthylmagnesium bromide afforded after hydrolysis and reduction 2-hydroxymethyl-1,1'-binaphthalene in about 80% yield and 90% ee of (R)-isomer.[240,241] In a similar manner the 2'-methyl derivative (68% yield, 87.4% ee of (R)-isomer) and the 2'-methoxy analog (71% yield, 96% ee of (R)-isomer) were prepared.[240,241]

Similar results were obtained from the reaction between <u>25</u> and <u>26</u> (R = OMe) to give the 1,1'-binaphthalene <u>27</u> (R = OMe, OX = oxazoline group). In the presence of dichlorobis(triphenylphosphine) nickel as catalyst, the yield was over 90%, without added catalyst yields were 54% or 65%.[242] Compound <u>27</u> (R = H) was obtained in the presence of catalyst in 75% yield. On the other hand, the lithio compound prepared from 1-bromo-2-methoxynaphthalene reacted with <u>25</u> to give <u>28</u> (R = OMe) in 71% yield in the absence of catalyst and the



25 26 27

lithio compound prepared from 3-bromo-2-methoxynaphthalene afforded the same product in 79% yield. The lithio compound prepared from 2-bromonaphthalene reacted with 25 to give 29 (R = H) in 98% yield and compound 27 (R = Me) was prepared from 25 and 1-bromo-2-methylnaphthalene via its Grignard reagent in 80% yield.[242] From 29 and optically active alkoxides chiral ethers 30 were prepared. The 1-menthoxy, quininoxy, quinidinoxy, α-fenchoxy and bornoxy groups served as leaving groups. The 1,1′-binaphthalene 31 (R = H) was obtained in 12-83% yield with optical yields of 10-80% ee, whereas 31 (R = OMe) was obtained in 7-65% yield and optical yields were 48-94% ee.[242,243]



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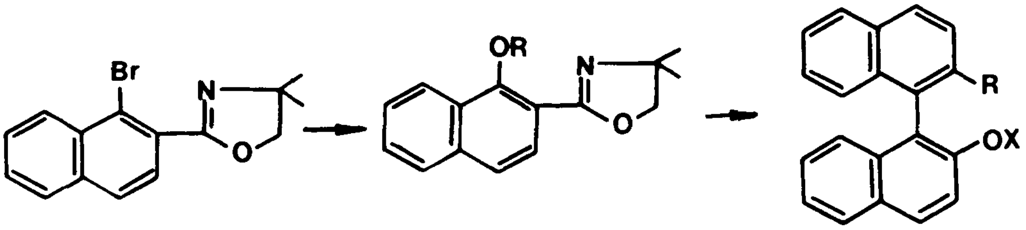

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7. Binaphthalene from Diazonium Salts, Nitro, Azo, Azoxy or Hydrazo Compounds

Binaphthalenes with amino groups have been prepared in general from the corresponding nitro, azo, azoxy or hydrazo compounds with various reducing agents (Table XVIII).

TABLE XVIII. Aminobinaphthalenes from Nitro, Azo, Azoxy or Hydrazonaphthalenes

Starting Naphthalene	Reagent	1,1'-Binaphthalene	% Yield	Ref.
2(NO_2)	Zn/AcOH, O_2 Zn/NH_4Cl	2,2'(NH_2)	-	244 245
1,1'-azo	$SnCl_2$/AcOH Zn/KOH	4,4'(NH_2)	33 -	246,247 248
2,2'-azo	$SnCl_2$/HCl Zn/AcOH	2,2'(NH_2)	87,36 -	249-251 58
1,1'-hydrazo	HCl	4,4'(NH_2)	low[a]	246
2,2'-hydrazo	Zn/AcOH HCl or NaOH	2,2'(NH_2)	- -	252 44
1,1'-azo	Zn/NH_4Cl or KOH	1,1'(NH_2)	-	248,253
	$SnCl_2$		10	254
1,1'-azoxy	Zn/NaOH	1,1'(NH_2)	-	253
1,1'(Br)-2,2'-azo	$SnCl_2$	3,3'(NH_2) 4,4'(Br)	-	255

a. 1,1'-Diamino-2,2'-binaphthalene is the main product.

Another useful method, although giving products in rather low yields is the decomposition of diazonium salts, prepared from naphthylamines, in the presence of various promotors (Table XIX).

Several binaphthalenes were prepared from derivatives of 8-amino-1-naphthoic acid lactams (naphthostyryls) which were first hydrolyzed and subsequently diazotized and treated with either Cu_2O and aqueous ammonia or with Cu_2Cl_2. Various 1,1'-binaphthalene-8,8'-dicarboxylic acids were prepared by this method.[256,260]

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TABLE XIX. Binaphthalenes from Decomposition of Diazonium Salts

Starting Naphthalene	Promotor	1,1'-Binaphthalene	% Yield	Ref.
1(NH_2) 2(Me)	H_2SO_4	3,3'(Me) 4,4'(OH)[a]	-	150
1(NH_2) 4(Br) 8(NO_2)	-	4,4'(Br) 8,8'(NO_2)	-	186
1(COOH)5(Cl)8(NH_2)	Cu_2O/NH_3	4,4'(Cl) 8,8'(COOH)	-	256
1(COOH)5(Br)8(NH_2)	Cu_2O/NH_3	4,4'(Br) 8,8'(COOH)	-	256
		2,2'-Binaphthalene		
2(NH_2)	$Zn/CuSO_4$		-	257
2(NH_2) 3(COOH)	Cu_2O	3,3'(COOH)	71	258
2(NH_2) 1(NO_2)	Cu_2O	1,1'(NO_2)	-	259

a. Together with 2-methyl-1-naphthol.

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The 1,2'-binaphthalenes were prepared as follows. Treatment of 2-(nitrosoacetylamino)naphthalene with excess of amyl 2-naphthoate and subsequent heating the product with alkali gave besides an isomeric acid 1,2'-binaphthalene-2-carboxylic acid.[261] This was the first example of a Hey reaction in the naphthalene series. It has been found that the second component of the reaction should be in liquid state at normal temperature and it must be present in considerable excess. Another example is 3'-hydroxy-1,2'-binaphthalene-1',4'-dione which was obtained from the reaction between the diazonium salt, prepared from 1-naphthylamine, and 2-hydroxy-1,4-naphthoquinone.[262] Also 1,2'-hydrazonaphthalene when decomposed with acid is transformed into 1,2'-diamino-1,2'-binaphthalene in 95% yield.[192] Diazotized 2-naphthylamine is transformed in the presence of 2-hydroxy-1,4-naphthoquinone into 3-hydroxy-2,2'-binaphthalene-1,4-dione in 17-22% yield.[262,263]

Recently, it has been found that 2,2'-hydrazonaphthalene is rearranged in an enantioselective way in the presence of

(+)camphor-10-sulfonic acid into 2,2'-diamino-1,1'-binaphthalene with optical yields up to 15% in the (-)-enantiomer. It has been observed that enantioselectivity depends on solvent and temperature.[264]

II. FORMATION OF BINAPHTHALENES FROM TETRALONES AND OTHER REDUCED NAPHTHALENES

Tetralones were converted into binaphthalenes mainly with Grignard reagents. For the most part 1-tetralones have been used as starting materials (Table XX). So far, only two cases of conversion of 2-tetralone have been reported. 2-Tetralone, when treated with 4-methoxy-1-naphthylmagnesium bromide was transformed after dehydrogenation with sulfur into 4-methoxy-1,2'-binaphthalene,[275] whereas 3-methyloctahydro-2-naphthalenone when treated with aluminium and mercuric chloride yielded 3,3'-dimethyl-hexadecahydro-2,2'-binaphthalene. Dehydrogenation of the latter in the presence of palladized carbon yielded 3,3'-dimethyl-2,2'-binaphthalene.[276] In addition, various reagents have been used for the dimerization of tetralones and these products are presented in Table XXI.

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TABLE XX. Binapthtalenes from Tetralones and Grignard Reagents

1-Tetralone	Naphthyl-MgBr		1,1'-Binaphthalene	% Yield	Ref.
	R	Position of MgBr			
	H	1	3,4(H)[a]	20	265
			[b]	17	34,266
				25	267
6(OMe)	H	1	6(OH)[b]	-	268
5,8(Me)	H	1	5,8(Me) 3,4(H)[c]	20	269
	2(OMe)	1	2(OMe)	51	270
	4(OMe)	1	4(OMe)[d]	12	268

TABLE XX. (continued)

1-Tetralone	Naphthyl-MgBr		1,2'-Binaphthalene	% Yield	Ref.
	R	Position of MgBr			
			1,2'-Binaphthalene		
	H	2	[d,e]	48	87
				-	271,272
	6(MeO)	2	6'(OMe) 3,4(H)	-	268
	3,4(H)	2	3,3',4,4'(H)	-	273
6(MeO)	6(MeO)	2	6,6'(OMe) 3,4(H)	27	274

a. Followed by heating the product in vacuo.

b. After subsequent dehydrogenation with sulfur and demethylation with HBr.

c. Followed by hydrolysis and heating with AcOH.

d. Dehydrogenation with sulfur.

e. Dehydrogenation with Pd/C.

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From 1-tetralone and Ti(II) salt, 1,1',2,2',3,3',4,4'-octahydro-1,1'-binaphthylidene was obtained, the ratio of E:Z forms being 7:3. In a similar manner the 2,2'-dimethyl derivative was obtained in 60% yield, but only the E isomer was formed.[292]

It has been known that dilute solutions of 2-tetralone in the presence of little alkali and air become deep indigo blue colored. This "tetralone blue test"[293] is used to recognize the presence of 2-tetralone or its derivatives. The structure of this compound (32) was elucidated and the compound is obtained either from 2-tetralone itself in alkaline solution and in the presence of air, or from 2-tetralone and 1,2-naphthoquinone in the presence of alkali (yield 1.6, or 13.4%). In a similar manner from 6-bromo-1,2-naphthoquinone and 2-tetralone the 7-bromo analog of 32 was obtained in 19% yield.[66]

TABLE XXI. Binaphthalenes from Tetralones and Various Reagents

1-Tetralone	Reagent	1,1'-Binaphthalene	%Yield	Ref.
1-Tetralone	Al/Hg	3,3',4,4'(OH)	34	277
	2-methyl-1-naphthyl lithium	2'(Me) 3,4(H)	9	278
	$BrCH_2COOEt$,Mg	3,3',4,4'(H)	-	279
2(OH)	O_2	3,4(OH) 3,4'(oxo)	-	133
2(OCOMe)	O_2	3,4(OH) 3',4'(oxo)	-	133
7(Me)	Al/Hg	7,7'(Me) 3,3',4,4'(H)	86	280
7(OMe)	Al/Hg	1,1'(OH) 7,7'(OMe)[a] 1,1',2,2',3,3',4,4'(H)	44	281
2(Br)	piperidine,O_2	3,3'(piperidino)4,4'(OH)	-	282
2(Br)	morpholine,O_2	3,3'(morpholino)4,4'(OH)	-	282
7(Br)	Al/Hg	7,7'(Br) 3,3',4,4'(H)	48	283
5,7(Me)	Al/Hg	5,5',7,7'(Me) 3,3',4,4'(H)	44	269
2(OH) 3,3(Me)	Pd/C	2,2'(Me) 3',4'(OH) 3,4(oxo)	-	284
		1,2'-Binaphthalene		
1-Tetralone	SeO_2	3(OH) 1',3,4,4'(oxo)	low	285
	HCl	1'(oxo) 1',2',3,3' 4,4'(H)[b]	-	286 287
	ethyl polyphosphate		-	288
	Amberlyst-15		91	289
	$TiCl_4/Et_3N$		70	290
6(OMe)	$TiCl_4/Et_3N$	6,6'(OMe) 1'(oxo) 1',2',3,3',4,4'(H)	78	290
7(OMe)	$TiCl_4/Et_3N$	7,7'(OMe) 1'(oxo) 1',2',3,3',4,4'(H)	70	290

a. Not isolated pure.

b. Previously, the structure of this product was erroneously assigned as 1',2,3,3',4,4'-hexahydro-1,2'-binaphthylidene-1'-one.[291]

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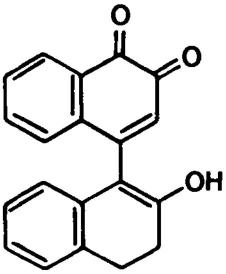

32,Blue

Ultrasonic vibration, when applied to a mixture of 1-tetralone in refluxing cyclohexane and in the presence of basic alumina yields 1',2',3,3',4,4'-hexahydro-1,2'-binaphthalene-1'-one in 77% yield.[294] The yield is more than doubled as compared to the acid catalyzed dimerization of 1-tetralone.[291] For the product from the last mentioned reaction an erroneous structure with an exo double bond was assigned on the basis of the previously tentatively proposed structure.[295]

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III. FORMATION OF BINAPHTHALENES BY ADDITION OF NAPHTHOLS TO NAPHTHOQUINONES

Naphthols add to naphthoquinones either in a neutral, alkaline or acid solution, sometimes with preferential subsequent oxidation to quinones. The addition may be complicated by the formation of complex mixtures containing trimeric or polymeric products.

Condensation of 1,2-naphthoquinone and 1-naphthol in the presence of sulfuric acid gives 4'-hydroxy-1,1'-binaphthalene-3,4-dione in 25% yield.[34] A similar reaction between 3,7-dimethyl-1,2-naphthoquinone and 1,2-dihydroxy-3,7-dimethylnaphthalene, but folowed by oxidation with nitric acid yielded 2,2',6,6'-tetramethyl-1,1'-binaphthalene-3,3',4,4'-tetrone in 64% yield.[35] 3-Hydroxy-2-naphthoic acid and 1,2-naphthoquinone-3-carboxylic acid are transformed under neutral conditions into 2',3,4-trihydroxy-1,1'-binaphthalene-2,3'-dicarboxylic acid in 64% yield.[38]

There are only two examples of 1,2′-binaphthalene formation. 1,4-Naphthoquinone and 1-naphthol are transformed in an acid-catalyzed reaction into 1,2′-binaphthalene-1′,4,4′-triol.[296] Similarly, plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) in admixture with its hydroquinone is transformed in buffered phosphate into a mixture of compounds and one compound, after isolation and methylation, was identified as 4,8′-dimethoxy-3′,7-dimethyl-1,2′-binaphthalene-1′,4′,5,8-tetrone.[297]

More examples are in the 2,2′-series. Naphthazarin, being a naphthol and a quinone, when dissolved in ammonia, is present in the form of an radical anion as judged from the ESR spectrum. Also under anaerobic conditions and in the presence of pyridine and triethanolamine the same radical anion is formed.[298] For its further transformation into 2,2′-binaphthazarin, trimers and polymers several mechanistic possibilities have been discussed.[298] Also under other reaction conditions binaphthazarin has been formed.[299-301] It is of interest to note that binaphthazarin is cleaved by diazomethane to give a naphthindazolequinone.[301,302]

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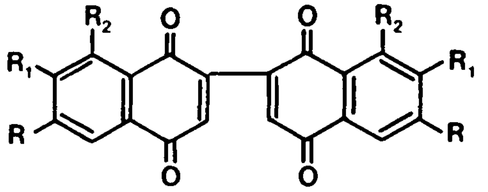
In Table XXII are presented other examples of binaphthoquinones prepared from mixtures of quinones and the corresponding naphthols. Besides this symmetrical dimerization also a dimerization through "C_2-C_3" positions was found in the case when 5-hydroxy-7-methyl-1,4-naphthoquinone (7-methyljuglone) and 1,4,5-trihydroxy-7-methylnaphthalene were treated in pyridine- methanol at room temperature and in absence of air to give 5,8′-dihydroxy-7,6′-dimethyl-2,2′-binaphthalene-1,1′,4,4′-tetrone in 29% yield together with a trimer.[305] On the other hand when 1,4-naphthoquinone and 1,4-dihydroxynaphthalene were heated in acetic acid in the presence of air 2,2′-binaphthalene-1,1′,4,4′-tetrole was obtained.[40] The same binaphthalene derivative, but acetylated, was obtained together with triphthaloylbenzene and 1,4-diacetoxynaphthalene when the above quinone and dihydroxynaphthalene were treated with pyridine and acetic acid at room temperature. The ratio of products is dependent on the ratio of starting compounds.[299]

TABLE XXII. 2,2′-Binaphthalene-1,1′;4,4′-tetrones from Naphthoquinones and Naphthols



Reaction Conditions	R	R_1	R_2	% Yield	Ref.
Pyridine, MeOH, then	-	-	OH	22-30	303
chloranil or Ag_2O				47,62	304
Pyridine, EtOH, Ag_2O	Me	-	OH[a]	33-66	303
				30-40	304
Pyridine/EtOH, Ag_2O	Me	MeCO	OH[b]	85-94	303

a. Mamegaquinone. Isolated from roots of Diospyros lotus together with other compounds.[103,105]
b. Dianellinone.

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IV. CYCLIZATIONS AND CYCLOADDITIONS

There are two main synthetic approaches for binaphthalenes in which naphthalene units are formed with cyclization. One of them used biphenyl derivatives as precursors and the other appropriately substituted naphthalenes where the side chain is used to form the second naphthalene ring.

(R)(-)-6,6′-Dimethyl-1,1′-biphenyl-2,2′-bis(butyric acid) when treated with $SOCl_2$ and subsequently with $AlCl_3$ is transformed into (R)-(-)-2,2′-dimethyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene-5,5′-dione in 64% yield.[306] In a similar manner, 2,2′- or 4,4′-dimethoxy-1,1′-biphenyl-3,3′-bis(butyric acid) obtained by Friedel-Crafts succinoylation of the corresponding biphenyls and subsequent Clemmensen reduction, were cyclized with polyphosphoric acid into 7,7'- or 5,5'-dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene-8,8'-dione.[307] Binaphthazarin was obtained in 1% yield by Friedel-Crafts condensation of 2,2',5,5'-tetramethoxybiphenyl and maleic anhydride[308] or in a better yield (8%) by cyclization of 2,2',5,5'-tetramethoxy-4,4'-bis(β-carboxypropionyl)biphenyl under Friedel-Crafts conditions.[301] A precursor of diospyrol, 8,8'-diacetoxy-4,4'-dibromo-6,6'-diethoxycarbonyl-1,1'-dimethoxy-2,2'-binaphthalene was obtained in moderate yield from 5,5'-dibromo-4,4'-diformyl-2,2'-dimethoxybiphenyl in a Stobbe condensation with diethyl succinate and subsequent cyclization with acetic anhydride.[309] On the other hand, 3,3'-dimethyl-6,6',7,7'-tetramethoxy-2,2'-binaphthalene-1,1',4,4'-tetrone was obtained in low yield in a cycloaddition reaction between 2,3-dimethoxy-1,3-butadiene and the corresponding bis-benzoquinone.[310]

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Aroylnaphthalenes were used as starting material for the preparation of several binaphthalenes. They were submitted to Stobbe condensation with diethyl succinate to give the corresponding half-esters, usually as a mixture of the E and Z isomers. These were cyclized with acetic anhydride to give a mixture of the corresponding phenanthrene derivative and binaphthalene. Examples are given in Table XXIII.

Similarly, α-(2-naphthyl)-γ-phenylbutyric acid, after being converted into the acid chloride, was cyclized in the presence of $AlCl_3$ into 1,2,3,4-tetrahydro-2,2'-binaphthalene 1-one.[313] A mixture of α- and β-benzylnaphthylketones, obtained from naphthalene and phenylacetyl chloride, when treated with ethyl cyanoacetate, gave a mixture of products, which upon separation and cyclization gave 3-cyano-2,2'-binaphthalen-4-ol.[314] 1'-Carboxy-1',2',3',4'-tetrahydro-1,2'-binaphthalene-4'-one was prepared from diethyl α-(o-carbethoxyphenyl)-β-(1-naphthyl)glutarate (obtained from β-(1-naphthyl)acrylate and diethyl homophthalate) after treatment with sodium and subsequent saponification.[315] An interesting synthesis is the cycloaddition of benzyne to triphenyl-naphthyl-2'-cyclopentadienone to give 6,7-dimethyl-1,3,4-triphenyl-2,2'-binaphthalene in 75% yield.[316]

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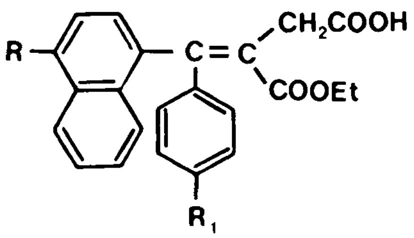
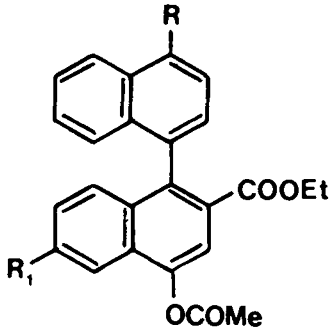
TABLE XXIII. Binaphthalenes by Cyclization

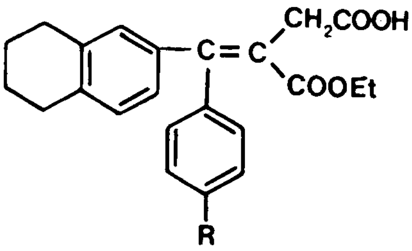
Precursor 1,1'-Binaphthalene

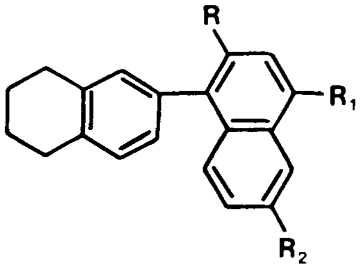




R	R_1		R	R_1	R_2	% Yield	Ref.
H	H	(Z + E)	H	H	-	13	311
OMe	H	(Z + E)	OMe	H	-	13	311
OMe	OMe	(Z + E)	OMe	OMe[a]	-	-	311
OMe	Cl	(Z + E)	OMe	Cl	-	19	311

Precursor 1,2'-Binaphthalene





Me		(E)	COOEt	OCOMe	Me	100	312
Cl		(E + Z)	COOEt	OCOMe	Cl	92	312
Br		(E + Z)	COOEt	OCOMe	Br	96	312
H		(E + Z)	COOEt	OCOMe	H	60	194

a. Isolated as the phenol-acid after hydrolysis.

Preparation of binaphthalenes with the use of the Diels-Alder reaction has been achieved only in few cases. 7-Nitro-1,2,3,4-tetrahydro-1,1′-binaphthalene-3,4-dicarboxylic acid was prepared in 28% yield from p-nitrophenylmaleic anhydride and 1-vinylnaphthalene.[317] A similar reaction with phenylmaleic anhydride afforded 1,2,3,4-tetrahydro-1,1′-binaphthalene-3,4-dicarboxylic acid in 36% yield.[267] 1,1′-Naphthylbutadiene and p-benzoquinone are transformed at room temperature after 3 days into cis-syn-1,4,9,10-tetrahydro-1,1′-binaphthalene-5,8-dione in 63% yield.[318] In a similar manner 6,6′-dimethylbiphenyl-2,2′,5,5′-diquinone when heated with excess of 2,3-dimethoxy-1,3-butadiene is transformed upon oxidation into 6,6′,7,7′-tetramethoxy-3,3′-dimethyl-2,2′-binaphthalene-1,1′,4,4′-tetrone in 52% yield.[310] Moreover, decahydro-2-naphthyl-1,4-benzoquinone when heated with 1,3-butadiene, followed by oxydation, afforded dodecahydro-2,2′-binaphthalene-1′,4′-dione.[319]

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V. BINAPHTHALENES BY RING OPENING OF POLYCYCLIC SYSTEMS

Polycyclic aromatic or heterocyclic compounds have been used for the preparation of few binaphthalene derivatives. From pentaphene upon ozonolysis and reductive work-up 2,2′-binaphthalene-3,3′-dicarboxaldehyde was obtained in 25% yield. The same compound was also obtained via OsO_4 oxidation, followed by sodium periodate oxidation. When chromium trioxide was used as oxidant the corresponding diacid was obtained in 14% yield.[258] By reductive cleavage of octahydrodibenzo /a.i./ biphenylene with lithium 1,1′,2,2′,3,3′,4,4′-octahydro-2,2′-binaphthalene was obtained.[320]

The isomeric dibenzofluorenones, when heated with potassium hydroxide at 240°C and above were transformed into 1,1′-binaphthalene-2-carboxylic acid,[180] 1,2′-binaphthalene-2-carboxylic acid,[321] 2,2′-binaphthalene-1-carboxylic acid[180] or 2,2′-binaphthalene-3-carboxylic acid.[180]

Fused α-pyrones were used to prepare 1,2′- or 2,2′-binaphthalenes. Ring opening occurred upon heating in the presence of palladized carbon at 260° for 14 h and thus 1,2′-binaphthalene (90% yield) or its 6′-methoxy analog (65% yield) and 2,2′-binaphthalene (90% yield) or its 5-methoxy- (36% yield), 6-methoxy- (80% yield) and 7-methoxy (60% yield) derivatives were obtained.[322] On the other hand hydrolysis of hexamethyltetrahydroaurofusarin (two fused γ-pyrone rings) in 4N NaOH gave 7,7′-diacetyl-1,1′,3,3′,4,4′,8,8′-octamethoxy-2,2′-binaphthalene-6,6′-diol in moderate yield.[323]

VI. MISCELLANEOUS METHODS

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1. Arylation of Ambident Ions

Arylation of naphthols with 2,3-dichloro-1,4-naphthoquinone is in principle an arylation with a reactive halo compound since haloquinones can be regarded as vinylogs of acyl halides.[324] Moreover, naphthols behave in several reactions as ambident ions giving upon alkylation also C-alkylated products and it has been well established that protic solvents favour C-alkylation.[325] Also the added base has a profound effect on the outcome of the reaction since in a further transformation dinaphthofuranquinones can be formed.

Although it was reported that 2-naphthol is O-arylated with 2,3-dichloro-1,4-naphthoquinone,[326] the C-arylated structure was assigned to the product.[327] The O-arylated compound was also synthesized.[121]

Theoretical calculations by the semiempirical MNDO method confirm that in addition to the oxygen atom in 1- or 2-naphtholate positions 2 or 1, respectively, are expected to be attacked preferentially by electrophiles. Although sodium acetate proved to be the most adequate base added in these C-arylations, the reaction gives practically the same result if lithium hydroxide is used.[121] In this manner, 2,3-dichloro-1,4-naphthoquinone reacts with 2-naphthol in the presence of sodium acetate (36% yield) or lithium hydroxide (33% yield) to give 3′-

chloro-2-hydroxy-1,2'-binaphthalene-1',4'-dione[121,327] and from 1-naphthol 3-chloro-1'-hydroxy-2,2'-binaphthalene-1,4-dione was obtained in 70% yield.[121]

2. Decomposition of Sulfides or Disulfides

There are only few examples of binaphthalene formation from sulfur containing naphthalenes. Desulfuration of 2-naphthalenethiol with $NaEt_3BH$ and $CoCl_2$ gives besides naphthalene also 2,2'-binaphthalene in 27% yield.[328] The same compound is also formed from 2,2'-dinaphthyl disulfide after heating with powdered Raney-nickel at 220°C (yield 68-90%) and as by-product naphthalene is formed. In lower yield (50%) the same binaphthalene is formed from 2-naphthyl thiobenzoate at 220°C and in the presence of Raney-nickel.[329] 1,1'-Binaphthalene-2,2'-diol is formed on heating bis(2-hydroxynaphthyl-1)sulfide or disulfide with copper at 230-240°C.[330]

3. Formation of Binaphthalenes in the Presence of Radicals

Organic radicals may be used for dimerization of naphthalenes. In this manner, 3,6-di-t-butyl-2-naphthol when oxidized with 2,4,6-tri-*t*-butylphenoxyl is transformed into 3,3',6,6'-tetra-*t*-butyl-1,1'-binaphthalene-2,2'-diol in 63% yield.[331] A tentative structure of 4,4',7,7'-tetra-*t*-butyl-2,2'-binaphthalene-3,3'-diol was assigned to the product obtained from treatment of 1,6-di-t-butyl-2-naphthol with 2,4,6-tri-*t*-butylphenoxyl (yield 69%).[76] Also from the reaction between 3,4-dihydro-2,4,6-triphenyl-2H-1,2,4,5-tetrazin-1-yl radical and 2-naphthylmagnesium bromide at 0°C 2,2'-binaphthalene was obtained in 86% yield.[332]

4. Dimerization of Naphthols under the Influence of Enzymes

Enzymatic oxidative coupling of naphthols has been tried in few cases. It is well known that several enzymes of higher plants are able to influence the coupling of phenols and amines. A laccase from Polyporus versicolor has been used in the preparation of 2,2',3,3'-tetramethyl-1,1'-dihydro-1,1'-binaphthalene-4,4'-dione from 2,3-dimethyl-1-naphthol (yield 51%).[94]

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The same enzyme tranformed in the presence of oxygen 2-methyl-1-naphthol into 3,3′-dimethyl-1,1′-binaphthylidene-4,4′-dione in 63% yield.[94] With an oxidase and in the presence of oxygen 4-methoxy-1-naphthol was transformed into 4,4′-dimethoxy-2,2′-binaphthylidene-1,1′-dione.[333]

5. Electrochemical Methods

1,1′-Binaphthalene is formed by electrolysis of 1-naphthylmagnesium bromide or of lithium, cadmium and zinc derivatives of naphthalene in 34-48% yield.[334,335] Anodic oxidation of naphthalene in the presence of mesitylene[196] or in the presence of various alkylbenzenes gives 1,1′-binaphthalene in yields up to 36% depending on the particular alkylbenzene and reaction conditions.[336] Anodic oxidation of 1-naphthol yielded 1,1′-binaphthalene-4,4′-diol.[337] In a similar manner 4,4′-diamino-1,1′-binaphthalene is formed from 1-naphthylamine[338] and 1′-(3,4-dimethoxybenzylamino)-6,7-dimethoxynaphthalene or its 6-bromo derivative are transformed into 4,4′-bis(N-3,4-dimethoxyphenylmethylamino)-6,6′,7,7′-tetramethoxy-1,1′-binaphthalene or its bromo analog (yield 42 or 48%).[339] Electrolytic oxidation of 1-methylnaphthalene on lead anode gave 4,4′-dimethyl-1,1′-binaphthalene in 10% yield, together with 39% of unchanged material and polymers.[340] Electrochemical reduction of the Wieland-Miescher ketone yielded a mixture of compounds among them also 2,2′-dihydroxy-1,10′-dimethyl-2,2′,3,3′,4,4′,6,6′,7,7′,8,8′-dodecahydro-2,2′-binaphthalene-5,5′-dione.[341]

In a recent study of electrochemical oxidative dehydrodimerization of naphthylamines this method gave the best result when compared to other selected oxidants. 4,4′-Dianilino-1,1′-binaphthalene-5,5′-disulfonate was obtained from 8-anilino-1-naphthalenesulfonate in 30% yield (50% yield by HPLC). In a similar manner 1- and 2-anilinonaphthalene were converted into 4,4′-dianilino- and 2,2′-dianilino-1,1′-binaphthalene in 35% and 28% yield, respectively.[142]

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6. Photochemical Formation of Binaphthalenes

Photoexcited naphthalene (irradiation of naphthalene in acetonitrile-water and in the presence of triethylamine with a medium pressure mercury lamp) is transformed into 1,1',4,4'-tetrahydro-1,1'-binaphthalene as the major product. Also 1-methoxynaphthalene is photochemically reduced into the 5,5'-dimethoxy analog.[342] Photolysis of 1-nitro-2-phenylnaphthalene gives 3,3'-diphenyl-1,1'-binaphthalene-4,4'-diol in 43% yield.[236]

2-Naphthyllithium in ether gives upon irradiation (high pressure mercury lamp) exclusively 2,2'-binaphthalene,[343] whereas tri-1-naphthylboron is transformed into 1,1'-binaphthalene in poor yield.[344]

Although phenols readily undergo coupling by the action of chemicals and form C-C or C-O bonds, 1- and 2-naphthols do not undergo any photodimerization. It is known that irradiation of phenol gives all five possible o- and p- C-C and C-O coupling dimers. Methoxy, cyano and methoxycarbonyl substituted naphthalenes give cyclodimers formed by 1,4-1,4-coupling. However, it was found that sodium 1-naphtholate when irradiated with a high pressure mercury lamp is transformed into 1',4'-dihydro-1,1'-binaphthalene-4,8'-diol (81% yield), probably via a photoinduced nucleophilic addition. The dimer, after being heated to its decomposition point (184°C) is reverted to 1-naphthol.[345] If the same starting compound, dissolved in benzene-methanol is irradiated, a mixture of a 1,2'-dimer and a pentacycle is formed, whereas in the presence of naphthalene besides other products also 1,1',4,4'-tetrahydro-1,1'-binaphthalene is formed.[346]

It was observed already in 1893 that 2-hydroxy-1,4-naphthoquinone (lawsone) is dimerized on prolonged keeping. This dimerization to 3,3'-dihydroxy-2,2'-binaphthalene-1,1',4,4'-tetrone has been later elaborated photochemically on a preparative scale.[347,348] In a similar manner the 2-methoxy analog has been transformed into the same product.[348] There is also a report that sunlight irradiation of the cyclobutane dimers of 1,4-naphthoquinone and its 2-methyl or 2-

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phenyl derivatives yields the corresponding (3,3'-disubstituted) 2,2'-binaphthalene-1,1',4,4'- tetrones.[349]

2-Methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone reacted photochemically with xanthene to give 3,3'-dihydroxy-3,3'-dimethyl-1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthalene-1,1',4,4'-tetrone in 4% yield.[350] The dimer is most probably formed via the hydrogen abstraction by the excited epoxyquinone from xanthene.

7. Others

It is of interest to note that 4,4'-dimethoxy-2,2'-binaphthylidene-1,1'-dione is obtained in low yield from treatment of 1,4-dihydroxynaphthalene with diazomethane.[100]

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REFERENCES

1. R. H. Thomson, "Naturally Occurring Quinones", Academic Press, London, 1971.
2. R. Adams, T. A. Geissman and J. D. Edwards, Chem. Rev., 60, 555 (1960).
3. H. Jackson. Curr. Top. Reprod. Endocrinol., 2, 145 (1982)
4. M. R. N. Prasad and E. Diczfalusy, Fertil. Steril., Proc. World Congr., 11th, 1983, p.255. Ed. by R. F. Harrison.
5. D. S. Linholter, R. C. Helgeson and D. J. Cram, J. Org. Chem., 46, 393 (1981) and references cited therein.
6. S. Miyano, M. Nawa and H. Hashimoto, Chem. Lett., 729 (1980).
7. R. Noyori, I. Tomino and Y. Tanino, J. Am. Chem. Soc., 101, 3129 (1979).
8. J. P. Mazaleyrat and D. J. Cram, ibid., 103, 4585 (1981).
9. K. Tani, T. Yamagata, S. Otsuka, H. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita and R. Noyori, Chem. Commun., 600 (1982).

10. P. E. Fanta, Synthesis, 9 (1974).

11. P. J. Leake, Chem. Rev., 56, 27 (1956).

12. A. J. Floyd, S. F. Dyke and S. E. Ward, ibid., 76, 509 (1976).

13. W. E. Bachmann, and R. A. Hoffman, Org.React., 2, 224 (1944).

14. O. C. Dermer and M. T. Edmison, Chem. Rev., 57, 77 (1957).

15. D. H. Hey, Quart Rev. (London), 25, 483 (1971).

16. M. Sainsbury, Tetrahedron, 36, 3327 (1980).

17. H. Musso, Angew. Chem., 75, 965 (1963).

18. A. I. Scott, Quart Rev., 19, 1 (1965).

19. A. N. Ssachanen and M. D. Tilitschejew, Ber., 62, 658 (1929).

20. P. G. Copeland, R. E. Dean and D. McNeil, J. Chem. Soc., 1689 (1960).

21. R. B. Kress, E. N. Duesler, M. C. Etter, I. C. Paul, D. Y. Curtin, J. Am. Chem. Soc., 102, 7709 (1980).

22. R. Kuroda and S. F. Mason, J. Chem. Soc. Perkin Trans II., 167 (1981).

23. A. K. Kerr and J. M. Robertson, J. Chem. Soc., B., 1146 (1969).

24. J. D. Edwards and J. L. Cashaw, J. Am. Chem. Soc., 79, 2283 (1957).

25. M. C. Venuti, J. Org. Chem., 46, 3124 (1981).

26. A. Manmade, P. Herlihy, J. Quick, R. P. Duffley, M. Burgos and A. P. Hoffer, Experientia, 39, 1276 (1983).

27. D. W. Cameron, G. I. Feutrill, L. J. H. Lammerts van Bueren, C. L. Raston and A. H. White, Aust. J. Chem., 30, 2313 (1977).

28. D. W. Cameron, G. I. Feutrill and L. J. H. Pannan, ibid., 33, 2531 (1980).

29. D. W. Cameron, G. I. Feutrill and L. J. H. Pannan, C. L. Raston, B. W. Skelton and A. H. White, J. Chem. Soc., Perkin Trans. I, 610 (1981).

30. K. H. Weisgraber and U. Weiss, J. Chem. Soc. Perkin Trans. I, 83 (1972).

31. T. Teitei, D. Wells, P. J. Collin, G. Sugowdz, and W. H. F. Sasse, Aust. J. Chem., 28, 2005 (1975).

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32. H. J. Teuber and G. Steinmetz, Ber., 98, 666 (1965).
33. J. Stenhouse and C. E. Groves, Ann., 194, 202 (1878).
34. H. Cassebaum and W. Langenbeck, Ber., 90, 339 (1957).
35. H. Cassebaum, ibid., 90, 1537 (1957).
36. W. Brackman and E. Havinga, Rec. Trav. Chim. Pays-Bas, 74, 1021 (1955).
37. H. Wittmann and H. Jeller, Monatsh. Chem., 111, 921 (1980).
38. B. Pracejus, Ann., 601, 61 (1956).
39. M. Pardhasaradhi and B. M. Choudary, Indian J. Chem., 17B, 79 (1979).
40. R. Pummerer, A. Pfaff, G. Riegelbauer and E. Rosenhauer, Ber., 72, 1623 (1939).
41. E. Rosenhauer, F. Braun, R. Pummerer and G. Riegelbauer, ibid., 70, 2281 (1937).
42. W. Smith, J. Chem. Soc., 35, 224 (1879).
43. R. Gerstl, Ber., 10, 1597 (1877).
44. H. Meyer and A. Hofmann, Monatsh. Chem., 37, 681 (1916).
45. J. Loevenich and K. Sipmann, J. prakt. Chem., 124, 127 (1929).
46. P. Kovacic and F. D. Koch, J. Org. Chem., 30, 3176 (1965).
47. N. Fröschl and J. Harlass, Monatsh. Chem., 59, 257 (1932).
48. S. R. Bansal, D. C. Nonhebel and J. M. Mancilla, Tetrahedron, 29, 993 (1973).
49. A. Scholl and C. Seer, Ber., 55, 330 (1922).
50. A. Homer, J. Chem. Soc., 91, 1103 (1907).
51. A. Homer, ibid., 97, 1141 (1910).
52. J. Dewar and H. O. Jones, J. Chem. Soc., 85, 212 (1904).
53. H. Inoue and K. Ishimura, Bull. Chem. Soc. Jpn., 9, 431 (1934).
54. J. Bergman and L. Engman, Tetrahedron, 36, 1275 (1980).
55. P. Kovacic and N. O. Brace, J. Am. Chem. Soc., 76, 5491 (1954).
56. R. Hirayama, T. Yamagishi, K. Mita, S. Kitajima and M. Hida, Nippon Kagaku Kaishi, 1684 (1977); Chem.Abstr., 88, 37474 (1978).
57. A. P. Dianin, J. Russ. Phys.-Chem. Ges., 6, 183 (1874).
58. A. Corbellini and E. Debenedetti, Gazz. Ghim. Ital., 59, 391 (1929).

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59. G. R. Clemo, J. G. Cockburn and R. Spence, J. Chem. Soc., 1264 (1931).

60. W. M.Cumming and G. Howie, ibid., 528 (1932).

61. I. S. Ioffe and B. K. Kritschewzow, Zh. Obshch. Khim., 9, 1136 (1939).

62. J. D. Edwards and J. L. Cashaw, J. Am. Chem. Soc., 76, 6141 (1954).

63. H. Walder, Ber., 15, 2166 (1882).

64. A. Rieche and K. Jungholt, ibid., 64, 578 (1931).

65. R. Pummerer, E. Prell and A. Rieche, ibid., 59, 2159 (1926).

66. H. H. Wanzlick, M. Lehmann-Horchler and S. Mohrmann, ibid., 90, 2521 (1957).

67. R. C. Helgeson, T. L. Tarnowski and D. J. Cram, J. Org. Chem., 44, 2538 (1979).

68. I. S. Ioffe and S. G. Kusnetzow, Zh. Obshch.Khim., 5, 877 (1935).

69. K. Brass and R. Patzelt, Ber., 70, 1341 (1937).

70. F. R. Hewgill and B. S. Middleton, J. Chem. Soc. C, 2316 (1967).

71. I. S. Ioffe and I. S. Smoljanitskaja, Zh. Obshch. Khim., 5, 1205 (1935).

72. K. Weil and W. Kuhn, Helv. Chim. Acta, 27, 1648 (1944).

73. D. J. Cram, R. C. Helgeson, S. C. Peacock, L. J. Kaplan, L. A. Domeier, P. Moreau, K. Koga, J. M. Mayer, Y. Chao, M. G. Siegel, D. H. Hoffmann and G. D. Y. Sogah, J. Org. Chem., 43, 1930 (1978).

74. W. M. Stanley and R. Adams, Rec. Trav. Chim. Pays-Bas, 48, 1035 (1929).

75. I. S. Ioffe, Zh. Obshch. Khim., 3, 453 (1933).

76. A. Rieker, N. Zeller, K. Schurr and E. Müller, Ann., 697, 1 (1966).

77. A. Corbellini and A. Pasturini, Gazz. Chim. Ital., 60, 843 (1930).

78. J. W. A. Findlay and A. B. Turner, J. Chem. Soc. C, 23 (1971).

79. H. Laatsch, Ann., 319 (1984).

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80. A. Rieche and W. Rudolph, Ber., 73, 335 (1940).

81. B. Alberti, Ann., 450, 304 (1926).

82. F. Russig, J.prakt. Chem., 62, 53 (1900).

83. D. Schulte-Frohlinde and F. Erhardt, Ber., 93, 2880 (1960).

84. D. Schulte-Frohlinde and F. Erhardt, Ann., 671, 84 (1964).

85. F. R. Hewgill and L. R. Mullings, Aust. J. Chem., 28, 355 (1975).

86. H. Wichelhaus, Ber., 30, 2199 (1897).

87. S. C. Hooker and L. F. Fieser, J. Am. Chem. Soc., 58, 1216 (1936).

88. L. F. Fieser and D. H. Sachs, ibid., 90, 4129 (1968).

89. A. Rieche, B. Elschner and M. Landbeck, Angew. Chem., 72, 385 (1960).

90. B. Feringa and H. Wynberg, J. Am. Chem. Soc., 98, 3372 (1976).

91. R. A. Anderson, D. T. Dalgleish, D. C. Nonhebel and P. L. Pauson, J. Chem. Res., Part S, 16 (1977).

92. D. Schulte-Frohlinde and F. Erhardt, Ann. 671, 92 (1964).

93. A. Rieche, K. Kirschke and M. Schulz, ibid., 711, 103 (1968).

94. B. R. Brown and A. H. Todd, J. Chem. Soc., 5564 (1963).

95. J. L. G. Nilsson, H. Selander, H. Sievertsson and I. Skanberg, Acta Chem.Scand., 24, 580 (1970).

96. H. Laatsch, Ann., 299 (1983).

97. E. R. Cole, G. Crank and B. J. Stapleton, Aust. J. Chem., 32, 1749 (1979).

98. F. Wessely, J. Kotlan and W. Metlesics, Monatsh.Chem., 85, 69 (1954).

99. A. Zeeck, P. Russ, H. Laatsch, W. Loeffler, H. Wehrle, H. Zähner and H. Holst, Ber., 112, 957 (1979).

100. H. Laatsch, Ann., 1367 (1984).

101. R. B. Gupta, R. N. Khanna, and V. P. Manchanda, Indian J. Chem., 18B, 217 (1979).

102. A. V. B. Sankaram and G. S. Sidhu, ibid., 12, 519 (1974).

103. K. Yoshihira, M. Tezuka and S. Natori, Tetrahedron Lett., 7 (1970).

Downloaded At: 11:18 27 January 2011

104. K. Yoshihira, M. Tezuka, P. Kanchanapee and S. Natori, Chem. Pharm. Bull. (Tokyo), 19, 2271 (1971).
105. K. Yoshihira, M. Tezuka and S. Natori, ibid., 19, 2308 (1971).
106. H. Laatsch, Ann., 1321 (1980).
107. S.Goldschmidt and H. Wessbecher, Ber., 61, 372 (1928).
108. H. Laatsch, Z. Naturforsch., B, 39B, 244 (1984).
109. H. Laatsch, Ann., 251 (1985).
110. B. C. Maiti, O. C. Musgrave and D. Skoyles, Chem.Commun., 244 (1976).
111. O. C. Musgrave and D. Skoyles, ibid., 1461 (1970).
112. O. C. Musgrave and D. Skoyles, J. Chem. Soc. Perkin I., 1128 (1974).
113. M. Gates, J. Am. Chem. Soc., 66, 124 (1944).
114. G. T. Morgan and D. C. Vining, J. Chem. Soc., 119, 1707 (1921).
115. N. Kuroki, A. Inoue, T. Kitao and K. Konishi, J. Soc. Org. Synt. Commun. Jpn. 14, 676 (1956).
116. Y. Matsunaga, Can. J. Chem., 37, 1003 (1959).
117. F. Barba, A. Soler and J. Varea, Tetrahedron Lett. 557 (1976).
118. A. McKillop, A.G. Turrell, D. W. Young and E. C. Taylor, J. Am. Chem. Soc., 102, 6504 (1980).
119. A. McKillop, A. G. Turrell and E. C. Taylor, J. Org. Chem., 42, 764 (1977).
120. W. L. Carrick, G. L. Karapinka and G. T. Kwiatkowski, ibid., 34, 2388 (1969).
121. O. Bajt, Z. Medja, S. Polanc, M. Tišler and J. Koller, Croat. Chem. Acta, In print.
122. H. Fernholz and G. Piazolo, Ber., 87, 578 (1954).
123. C. Marschalk, Bull. Soc. Chim. Fr., 124 (1936).
124. G. R. Clemo and R. Spence, J. Chem. Soc., 2811 (1928).
125. O. Eckstein, Ber., 38, 3660 (1905).
126. M. J. S. Dewar and T. Nakaya, J. Am. Chem. Soc., 90, 7134 (1968).
127. B. Feringa and H. Wynberg, Tetrahedron Lett., 4447 (1977).
128. G. Brumstrom, J. Am. Chem. Soc., 77, 2463 (1955).

Downloaded At: 11:18 27 January 2011

129. R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton and K. U. Ingold, J. Org. Chem., 33, 4329 (1968).

130. R. F. Bridger, ibid., 35, 1746 (1970).

131. F. C. Uhle, C. G. Vernick and G. L. Schmit, J. Am. Chem. Soc., 77, 3334 (1955).

132. A. Weissberger and W. Schwarze, Ann., 487, 53 (1931).

133. F. Straus, O. Bernoully and P. Mautner, ibid., 444, 165 (1925).

134. H. E. Fierz-David, L. Blangley and H. Dübendorfer, Helv. Chim. Acta, 29, 1661 (1946).

135. K. Fries and W. Lohmann, Ber., 54, 2912 (1921).

136. Y. Omote, Y. Takizawa and N. Sugiyama, Bull. Chem. Jpn, 45, 2882 (1972).

137. N. J. P. Broom and P. G. Sammes, J. Chem. Soc. Perkin I, 465 (1981).

138. U. Weiss, H. H. Fales and K. H. Weisgraber, Ann., 914 (1979).

139. J. L. Bohnert, D. A. Malencik, S. R. Anderson, D. Teller and E. H. Fischer, Biochemistry, 21, 5570 (1982).

140. F. J. Farris, G. Weber, C. C. Chiang and I. C. Paul, J. Am. Chem. Soc., 100, 4469 (1978).

141. C. G. Rosen and G. Weber, Biochemistry, 8, 3915 (1959).

142. J. M. Hornback and H. E. Gossage, J. Org. Chem., 50, 541 (1985).

143. O. N. Witt, Ber., 21, 726 (1888).

144. H. T. Bucherer and F. Seyde, ibid., 40, 859 (1907).

145. S. Ramesh and M. V. Bhatt, Curr. Sci, 46, 809 (1977).

146. M. V. Bhatt and M. B. Gopinathan, Indian J. Chem., 20, 72 (1981).

147. A. R. Bader, J. Am. Chem. Soc., 73, 3731 (1951).

148. I. D. Raacke-Fels, C. H. Wang, R. K. Robins and B. E. Christensen, J. Org. Chem., 15, 627 (1950).

149. W. Bradley and L. J. Watkinson, J. Chem. Soc., 319 (1956).

150. R. Lesser, Ann., 402, 1 (1914).

151. M. S. Chauhan, D. M. McKinnon and R. G. Cooke, Can. J. Chem., 55, 2363 (1977).

152. C. Liebermann and S. Schlossberg, Ber., 32, 546 (1899).

153. F. Ullmann, Helv. Chim. Acta, 9, 442 (1926).

Downloaded At: 11:18 27 January 2011

154. K. Chandrasenan and R. H. Thomson, Tetrahedron, 27, 2529 (1971).
155. A. R. Forrester, A. S. Ingram, I. L. John and R. H. Thomson, J. Chem. Soc. Perkin I, 1115 (1975).
156. H. Laatsch, Ann., 1886 (1983).
157. H. J. Banks, D. W. Cameron, M. J. Crossley and E. L. Samuel, Aust. J. Chem., 29, 2247 (1976).
158. R. C. Bansal, E. J. Eisenbraun and P. W. Flanagan, J. Am. Chem. Soc., 88, 1837 (1966).
159. L. E. Harris, E. J. Eisenbraun, P. W. Flanagan, M. C. Hamming and G. W. Keen, J. Org. Chem., 37, 336 (1972).
160. M. Lerer, Ann. Off. Nat. Combust. Liq., 8, 681 (1933).
161. R. Nakajima, M. Kinosada, T. Tamura and T. Hara, Bull. Chem. Soc. Jpn., 56, 1113 (1983).
162. R. Nakajima, Rep. Asahi Glass Found. Ind. Technol., 42, 279 (1983).
163. B. Loubinoux, R. Vanderesse and P. Caubere, Tetrahedron Lett., 3951 (1977).
164. M. Busch, W. Weber, C. Darboven, W. Renner, H. J. Hahn, G. Mathauser, F. Strätz, K. Zitzmann and H. Engelhardt, J. prakt. Chem., 146, 1 (1936).
165. G. R. Clemo and E. C. Dawson, J. Chem. Soc., 1114 (1939).
166. G. T. Mondodoev, N. M. Przhiyalgovskaja and V. N. Belov, Zh. Org. Khim. 1, 2008 (1965).
167. N. M. Przhiyalgovskaja, E. N. Sidorenko and A. T. Prudchenko, ibid., 11, 382 (1975).
168. K. W. Bentley, J. Chem. Soc., 2398 (1955).
169. L. F. Fieser and M. A. Peters, J. Am. Chem. Soc., 53, 793 (1931).
170. B. Eistert and L. Klein, Ber., 101,900 (1968).
171. L. F. Fieser and J. L. Hartwell, J. Am. Chem. Soc., 57, 1479 (1935).
172. H. Greenland, J. T. Pinhey and S. Sternhell, Aust. J. Chem., 28, 2655 (1975).
173. J. J. Brunet, R. Vaderesse and P. Caubere, J. Organometal.Chem., 157, 125 (1978).
174. C. S. Schoepfle, J. Am. Chem. Soc., 45, 1566 (1923).

Downloaded At: 11:18 27 January 2011

175. K. Brass and R. Patzelt, Ber., 70, 1349 (1937).
176. F. Ullmann and J. Bielecki, ibid., 34, 2174 (1901).
177. O. Hinsberg, ibid., 48, 2092 (1915).
178. R. Kuhn and O. Albrecht, Ann., 465, 282 (1928).
179. E. D. Bergmann and J. Szmuszkovicz, J. Am. Soc., 73, 5153 (1951).
180. R. H. Martin, J. Chem. Soc., 679 (1941).
181. D. M. Hall and E. E. Turner, ibid., 1242 (1955).
182. E. Weber, I. Csöregh, B. Stensland and M. Czugler, J. Am. Chem. Soc., 106, 3297 (1984).
183. W. M. Cumming and G. Howie, J. Chem. Soc., 3176 (1931).
184. R. S. W. Braithwaite and P. F. Holt, ibid., 3025 (1949).
185. R. Scholl, Monatsh. Chem., 42, 405 (1921).
186. H. H. Hodgson and J. H. Crook, J. Chem. Soc. 571 (1937)
187. C. Seer and R. Scholl, Ann., 398, 82 (1913).
188. L. Kalb, Ber., 47, 1724 (1914).
189. W. M. Cumming and G. D. Muir, J. Roy Tech. Coll., 4, 61, (1937).
190. H. G. Rule and F. R. Smith, J. Chem. Soc., 1096 (1937).
191. R. D. Haworth, B. P. Moore and P. L. Pauson, ibid., 3271 (1949).
192. E. R. Ward and B. D. Pearson, ibid., 3378 (1959).
193. J. Meisenheimer and O. Beisswenger, Ber., 65, 32 (1932).
194. W. I. Awad, F. G. Baddar, F. A. Fouli, S. M. A. Omran and M. I. B. Selim, J. Chem. Soc. C, 507 (1968).
195. F. Ullmann, G. M. Meyer, O. Loewenthal and E. Gilli, Ann., 332, 38 (1904).
196. K. Nyberg, Acta Chem. Scand, 25, 3770 (1971).
197. R. Scholl, Monatsh. Chem., 39, 231 (1918).
198. V. Vesely, Ber., 38, 136 (1905).
199. R. F. Curtis and G. Viswanath, J. Chem. Soc., 1670 (1959).
200. H. H. Hodgson and R. L. Elliott, ibid., 123 (1937).
201. E. R. Ward, and B. D. Pearson, ibid., 1676 (1959).
202. J. F. Spencer and G. M. Price, ibid., 97, 385 (1910).
203. E. H. Rodd and F. W. Linch, ibid., 2174 (1927).
204. E. Marcus, W. M. Lauer and R. T. Arnold, J. Am. Chem. Soc., 80, 3442 (1958).

Downloaded At: 11:18 27 January 2011

205. G. Wittig and E. Benz, Ber., 92, 1999 (1959).
206. R. Weitzenböck and C. Seer, Ber., 46, 1994 (1913).
207. F. D. Chattaway, J. Chem. Soc., 65, 877 (1894).
208. V. Vesely and F. Stursa, Collect. Czech. Chem. Commun., 4, 139 (1932).
209. A. McKillop, L. F. Elsom and E. C. Taylor, Tetrahedron, 26, 4041 (1970).
210. E. Bergmann, Chem. Ind. (London), 465 (1939).
211. D. A. Shirley and W. L. Dean, J. Am. Chem. Soc., 79, 1205 (1957).
212. K. Fries and K. Schimmelsschmidt, Ann., 484, 245 (1930).
213. S. Miyano, M. Tobita, S. Suzuki, Y. Nishikawa and H. Hashimoto, Chem. Lett., 1027 (1980).
214. S. Miyano, S. Handa, K. Shimizu, K. Tagami and H. Hashimoto, Bull. Chem. Soc. Jpn, 57, 1943 (1984).
215. M. I. Dawson, R. L. S. Chan, K. Derdzinski, P. D. Hobbs and W. R. Chao, J. Med. Chem., 26, 1653 (1983).
216. Y. Badar, A. S. Cooke and M. M. Harris, J. Chem. Soc. C, 1315 (1966).
217. E. Späth, Monatsh, Chem., 34, 1965 (1913).
218. G. M. Bennett and E. E. Turner, J. Chem. Soc., 105, 1057 (1914).
219. E. Sakellarios and T. Kyrimis, Ber., 57, 322 (1924).
220. M. S. Kharasch and H. S. Isbell, J. Am. Chem. Soc., 52, 2919 (1930).
221. S. K. Taylor, S. G. Bennett, K. J. Heinz and L. K. Lashley, J. Org. Chem., 46, 2194 (1981).
222. H. J. Bestmann and W. Both, Ber., 107, 2926 (1974).
223. I. G. C. Coutts, D. J. Humphreys and K. Schofield, J. Chem. Soc. C, 1982 (1969).
224. W. F. Short and H. Wang, J. Chem. Soc., 991 (1950).
225. M. S. Newman, D. Mac Dowell and S. Swaminathan, J. Org. Chem., 24, 509 (1959).
226. R. C. Fuson and F. W. Wassmundt, J. Am. Chem. Soc., 78, 5409 (1956).
227. H. Gilman and N. B. St. John, Rec. Trav. Chim., Pays-Bas, 48, 743 (1929).

Downloaded At: 11:18 27 January 2011

228. W. Herz and E. Lewis, J. Org. Chem., 23, 1646 (1958).
229. J. Loevenich and A. Loeser, Ber., 60, 320 (1927).
230. F. Mayer and O. Schnecko, ibid., 56, 1408 (1923).
231. K. Adachi and J. Tanaka, Yuki Gosei Kagaku Kyokai Shi, 31, 322 (1973); Chem. Abstr. 80, 59766 (1974).
232. J. Braun and K. Kirschbaum, Ber., 54, 597 (1921).
233. R. Pallaud and J. L. Zenou, C. R. Acad. Sci., Paris, 266, 1608 (1968).
234. H. S. Chang and T. J. Edward, Can. J. Chem., 41, 1233 (1963).
235. J. Burdon, H. S. Gill, J. W. Parsons and J. C. Tatlow, Chem. Commun., 1147 (1979).
236. J. H. Boyer and J. Patel, Org. Prep. Proced. Int., 14, 418 (1982).
237. R. C. Fuson, M. D. Armstrong and S. B. Speck, J. Org. Chem., 7, 297 (1942).
238. K. Tamao, A. Minato, N. Miyake, T. Matsuda, Y.Kiso and M. Kumada, Chem. Lett., 133 (1975).
239. K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi and M. Kumada, Tetrahedron Lett., 1389 (1977).
240. A. I. Meyers and K. A. Lutomski, J. Am. Chem. Soc., 104, 879 (1982).
241. A. I. Meyers and K. A. Lutomski, Synthesis, 105 (1983).
242. J. M. Wilson and D. J. Cram, J. Org. Chem., 49, 4930 (1984).
243. J. M. Wilson and D. J. Cram, J. Am. Chem.. Soc., 104, 881 (1982).
244. J. Meisenheimer and K. Witte, Ber., 36, 4153 (1903).
245. W. M. Cumming and G. S. Ferrier, J. Chem. Soc., 125, 1108 (1924).
246. R. Nietzki and O. Goll, Ber., 18, 3252 (1885).
247. S. Cohen and R. E. Oesper, Ind.Eng. Chem., Analyt. Ed., 8, 306 (1936).
248. G. D. Parkes and G. N. Walton, J. Chem. Soc., 201 (1940).
249. W. R. Brode and R. E. Brooks, J. Am. Chem. Soc., 63, 923 (1941).
250. P. Jacobson, Ann., 427, 142 (1922).
251. R. Kuhn and P. Goldfinger, ibid., 470, 183 (1929).

Downloaded At: 11:18 27 January 2011

252. H. T. Bucherer and M. Schmidt, J. prakt. Chem., 79, 369 (1909).

253. W. M. Cumming and G. Howie, J. Chem. Soc., 133 (1933).

254. H. H. Hodgson and J. Habeshaw, ibid., 77 (1947).

255. H. H. Hodgson, J. Habeshaw and P. B. R. Murti, J. Chem. Soc., 1390 (1947).

256. A. Corbellini, M. Atti and V. Fossati, Rend. Ist. lomb. Sci. lettere Rend., 69, 287 (1936).

257. F. D. Chattaway, J. Chem. Soc., 67 653 (1895).

258. E. J. Moriconi and L. Salce, J. Org. Chem., 32, 2829 (1967).

259. H. H. Hodgson, E. Leigh and G. Turner, J. Chem. Soc., 744 (1942).

260. A. P. Karishin and Yu. V. Samusenko, Zh. Org. Khim., 7, 150 (1971).

261. G. Swain and A. R. Todd, J. Chem. Soc., 674 (1941).

262. L. F. Fieser, E. Berliner, F. J. Bondhus, F. C. Chang, W. G. Dauben, M. G. Ettlinger, G. Fawaz, M. Fields, C. Heidelberger, H. Heyman, W. R. Vaughan, A. G. Wilson, E. Wilson, M. I. Wu, M. T. Leffler, K. E. Hamlin, E. J. Matson, E. E. Moore, M. P. Moore and H. E. Zaugg, J. Am. Chem. Soc., 70, 3203 (1948).

263. O. Neunhoeffer and J. Weise, Ber., 71, 2703 (1938).

264. F. Sannicolo, Tetrahedron Lett., 26, 119 (1985).

265. C. D. Nenitzescu and M. Avram, J. Am. Chem. Soc., 72, 3486 (1950).

266. E. Buchta, H. Vates and H. Knopp, Ber., 91, 228 (1958).

267. L. E. Miller and D. J. Mann, J. Am. Chem. Soc., 73, 45 (1951).

268. H. Cassebaum, Ber., 90, 2876 (1957).

269. F. Bell and D. H. Waring, J. Chem. Soc., 2689 (1949).

270. J. A. Berson and M. A. Greenbaum, J. Am. Chem. Soc., 80, 653 (1958).

271. M. Orchin and L. Reggel, ibid., 69, 505 (1947).

272. L. H. Klemm, D. Reed, L. A. Miller and B. T. Ho, J. Org. Chem., 24, 1468 (1959).

273. H. A. Weidlich, Ber., 71, 1201 (1938).

Downloaded At: 11:18 27 January 2011

274. R. B. Woodward and R. H. Eastman, J. Am. Chem. Soc., 66, 674 (1944).

275. H. Cassebaum and H. Hofferek, Ber., 92, 1643 (1959).

276. E. D. Bergmann and R. Ikan, J. Am. Chem. Soc., 80, 208 (1958).

277. H. A. Weidlich, Ber., 71, 1203 (1938).

278. A. D. Campbell, R. A. Elder and G. W. Emerson, J. Chem. Soc., 3526 (1959).

279. G. Schroeter, Ber., 58, 713 (1925).

280. M. S. Newman, J. Am. Chem. Soc., 62, 1683 (1940).

281. D. G. Thomas and A. H. Nathan, ibid., 70, 331 (1948).

282. L. B. Volodarski, L. S. Berman, and V. A. Koptyung, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 109 (1967); Chem. Abstr. 70, 3792 (1969).

283. M. Crawford, R. A. M. Mackinnon and V. R. Supanekar, J. Chem. Soc., 2807 (1959).

284. C. Broquet and R. Quelet, Bull. Soc. Chim. Fr., 1882 (1962).

285. F. Weygand and I. Frank, Berl, 84, 591 (1951).

286. H. L. Retcofsky, L. Reggel and R. A. Friedel, Chem. Ind. (London), 617 (1969).

287. J. M. Springer, C. W. Hinman, E. J. Eisenbraun, P. W. K. Flanagan and M. C. Hamming, J. Org. Chem., 35, 1260 (1970).

288. J. Chenault and C. Sainson, C. R. Acad. Sci., Paris, Ser. C, 287, 545 (1978).

289. J. W. Burnham, R. G. Melton, E. J. Eisenbraun, G. W. Keen and M. C. Hamming, J. Org. Chem., 38, 2783 (1973).

290. A. G. Holba, V. Premasager, R. C. Barot, and E. J. Eisenbraun, Tetrahedron Lett., 26, 571 (1985).

291. M. Orchin, L. Reggel and R. A. Friedel, J. Am. Chem. Soc., 71, 2743 (1949).

292. P. Lemmen and D. Lenoir, Ber., 117, 2300 (1984).

293. Org. Syn., Coll. Vol. IV, 906, J. Wiley, New York, 1963.

294. B. C. Barot, D. W. Sullins and E. J. Eisenbraun, Synth. Commun., 14, 397 (1984).

295. J. W. Cook and C. A. Lawrence, J. Chem. Soc., 1431 (1936).

296. R. Pummerer and G. Huppmann, Ber., 60, 1442 (1927).

Downloaded At: 11:18 27 January 2011

297. A. V. B. Sankaram, A. S. Rao and G. S. Sidhu, Tetrahedron Lett., 3627 (1975).

298. H. Brockmann, H. Grewe and K. Hoyermann, ibid., 1493 (1971).

299. H. Brockmann, H. Grewe and W. Waldmüller, Ber., 104, 1436 (1971).

300. H. E. Fierz-David, L. Blangley and W. Kramichfeldt, Helv. Chim. Acta, 30, 816 (1947).

301. H. Brockmann and H. Vorbrüggen, Ber., 95, 810 (1962).

302. H. Brockmann and K. Van der Merwe, Naturwissenschaften, 49, 130 (1962).

303. H. Brockmann and H. Laatsch, Ann., 433 (1983).

304. H. Brockmann and H. Laatsch, Tetrahedron Lett., 453 (1978).

305. H. Brockmann and H. Laatsch, ibid., 3695 (1973).

306. H. Akimoto and S. Yamada, Tetrahedron, 27, 5999 (1971).

307. K. P. Mathai and S. Sethna, J. Indian Chem. Soc., 42, 86 (1965).

308. H. Brockmann and E. Hieronymus, Ber., 88, 1379 (1955).

309. T. R. Govindachari, N. Viswanathan, K. R. Ravindranath and B. Anjaneyulu, Indian J. Chem., 11, 1081 (1973).

310. R. Adams and B. R. Baker, J. Am. Chem. Soc., 63, 535 (1941).

311. V. B. Baghos, F. H. Nasr and M. Gindy, Helv. Chim. Acta, 62, 90 (1979).

312. F. G. Baddar, N. Latif and H. A. A. Pegaila, J. Indian Chem. Soc., 52, 1177 (1975).

313. M. S. Newman, J. Org. Chem., 9, 518 (1944).

314. H. Fiesselmann and W. Ehmann, Ber., 91, 1706 (1958).

315. R. A. Rao and R. R. Rao, Indian J. Chem., 6, 24 (1968).

316. K. Ghosh and A. J. Bhattacharrya, Indian J. Chem., 14B, 793 (1976).

317. L. E. Miller and C. J. Strickler, J. Am. Chem. Soc., 76, 698 (1954).

318. A. S. Bailey and A. J. Shutlleworth, J. Chem. Soc. C, 115 (1968).

319. L. F. Fieser, E. Berliner, F. J. Bondhus, F. C. Chang, W. G. Dauben, M. G. Ettlinger, G. Fawaz, M. Fields, C. Heidelberger, H. Heyman, W. R. Vaughan, A. G. Wilson,

Downloaded At: 11:18 27 January 2011

E. Wilson, M. I. Wu, M. T. Leffler, K. E. Hamlin, E. J. Matson, E. E. Moore, M. P. Moore and H. E. Zaugg, J. Am. Chem. Soc., 70, 3186 (1948).

320. P. H. Ruehle, T. K. Dobbs, L. L. Ansell, D. Van der Helm and E. J. Eisenbraun, J. Org. Chem., 42, 1098 (1977).
321. J. W. Cook, and R. W. G. Preston, J. Chem. Soc., 553 (1944).
322. K. Chebaane and M. Guyot, Tetrahedron, 33, 757 (1977).
323. J. S. Gray, G. C. J. Martin and W. Rigby, J. Chem. Soc. C, 2580 (1967).
324. Houben-Weyl, "Methoden der Organischen Chemie", Band VII/3a, Teil I: Chinone, Teil I., G.Thieme Verlag, Stuttgart, 1977.
325. N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, J. Am. Chem. Soc., 77, 6269 (1955).
326. R. V. Acharya, B. D. Tilak and M. R. Venkiteswaran, J. Sci. Ind. Res., 16B, 400 (1957).
327. F. D. Saeva, J. Org. Chem., 37, 1442 (1972).
328. H. Alper and T. L. Prince, Angew. Chem., 92, 321 (1980).
329. H. Hauptmann, W. F. Watler and C. Marino, J. Am. Chem. Soc., 80, 5832 (1958).
330. S. Onufrowicz, Ber., 21, 3559 (1888).
331. H. P. Schneider, E. Streich, K. Schnurr, N. Pauls, P. Winter and A. Rieker, Ber., 117, 2660 (1984).
332. Y. Miura, Y. Morimoto and M. Kinoshita, Bull. Chem. Soc. Jpn., 49, 253 (1976).
333. G. G. Guilbauld and D. N. Kramer, Anal. Chem., 36, 2494 (1964).
334. J. L. Morgat and R. Pallaud, C. R. Acad. Sci., Paris, 260, 574 (1965).
335. J. L. Morgat and R. Pallaud, C. R. Acad. Sci., Paris, 260, 5579 (1965).
336. K. Nyberg, Acta Chem. Scand., 27, 503 (1973).
337. L. Papouchado, R. W. Sandford, G. Petrie and R. N. Adams, J. Electroanal. Chem., 65, 275 (1975).
338. N. Vettorazzi, J. J. Silber and L. Sereno, ibid., 125, 459 (1981).

Downloaded At: 11:18 27 January 2011

339. J. M. Quante, F. R. Stermitz and L. L. Miller, J. Org. Chem., 44, 293 (1979).

340. F. Fichter and S. Herszbein, Helv. Chim. Acta, 11, 1264 (1928).

341. L. Mandell, H. Hamilton and R. A. Day, J. Org. Chem., 45, 1710 (1980).

342. J. A. Barltrop and R. J. Owers, Chem. Commun., 1462 (1970).

343. E. E. Van Tamelen, J. I. Brauman and L. E. Ellis, J. Am. Chem. Soc., 87, 4964 (1965).

344. G. C. Calhoun and G. B. Schuster, J. Org. Chem., 49, 1925 (1984).

345. T. Kitamura, T. Imagawa and M. Kawanisi, Chem. Commun., 81 (1977).

346. T. Kitamura, T. Imagawa and M. Kawanisi, Tetrahedron, 34, 3261 (1978).

347. S. C. Hooker, J. Am. Chem. Soc., 58, 1212 (1936).

348. S. Hashimoto and Y. Tanaka, Doshisha Daigaku Rikogaku Kenkyu Hokoku, 20, 1 (1979); Chem. Abstr., 91, 184872 (1979).

349. F. J. C. Martins, J. Dekker, A. M. Viljoen and D. P. Venter, S. Afr. J. Chem., 30, 89 (1977).

350. K. Maruyama and S. Arakawa, J. Org. Chem., 42, 3793 (1977).

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