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REACTIONS OF COPPER(II) HALIDES WITH AROMATIC COMPOUNDS—IX[1]

REACTIONS OF 1- AND 2-ALKOXYNAPHTHALENES

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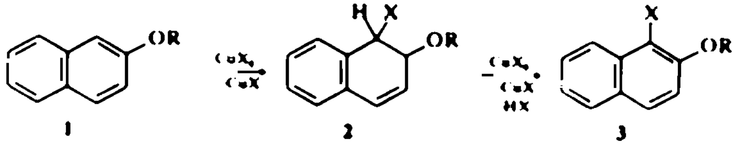
Abstract—2-Alkoxynaphthalenes undergo halogenation with copper(II) halides in the 1-position though 2-benzyloxynaphthalene with copper(II) bromide gives additionally di-β-naphthol, 1-benzyl-2-naphthol, and benzyl bromide. The reaction of 1-alkoxynaphthalenes with copper(II) halides leads to 1-alkoxy-4-halogenonaphthalenes and 4,4'-dialkoxy-1,1'-binaphthyls. 8-Chloro-1-methoxynaphthalene is a further product from the reaction of 1-methoxynaphthalene and copper(II) chloride. The reactions are postulated to proceed *via* the radical cation of the alkoxynaphthalene formed in an electron transfer reaction. This can then either react further with the copper(II) halide or dimerize.

9-Alkoxy- and 9-acyloxyanthracenes undergo reaction with copper(II) halides, under heterogeneous conditions in carbon tetrachloride or chlorobenzene, to give bianthron-9-yl together with smaller amounts of the 10-halogenated product.[2] The formation of bianthron-9-yl arises from coupling of 9-anthryloxy radicals, which are themsevles formed in a concerted 4-centre reaction with the copper(II) halide. The 10-halogenated product results from a halogen atom transfer to the 10-position. The resultant radical on further reaction with the copper(II) halide gives the product. The present work extends this to a study of 1- and 2-alkoxynaphthalenes and also to anisole to see whether the same dual type of behaviour is observed.

2-Methoxy- and 2-ethoxynaphthalene (1, R = Me or Et) undergo halogenation with both copper (II) bromide and chloride in the 1-position (Table 1). Careful examination of the reaction product failed to reveal the presence of any di-β-naphthol which might have been formed by analogy with the behaviour of 9-alkoxyanthracenes. These reactions can be postulated to proceed by halogen atom transfer to the 1-position to give the radical (2), which is subsequently oxidised by copper(II) halide to the halogenated alkoxynaphthalene (3) (Scheme 1). This scheme is strictly analogous to that proposed for the halogenation of 9-alkyl- and 9-arylanthracenes.[3] The absence of any di-β-naphthol would indicate that there is no reaction at the methoxyl group. This is not surprising as the ease of reaction at this position would depend on the stability of the resultant radical and the 9-anthryloxy radical would be expected to be more stable than the 2-naphthoxy radical.

Anisole behaved similarly to 2-methoxynaphthalene and underwent reaction with both copper (II) bromide and chloride to give a mixture of *o*- and *p*-halogenoanisoles. In neither instance was any *m*-halogenoanisole formed. If the reaction were a pure atom-transfer reaction then one might expect halogenation to occur at the *meta*-position as well as at the *ortho*- and *para*-positions by analogy with the behaviour of aromatic compounds toward alkyl and aryl radicals.[4] Kochi has shown that the transition state for ligand transfer is akin to that of an atom transfer in a typical free-radical reaction.[5] The absence of any *m*-halogenoanisole can be taken to indicate that there is a significant component of pure electron transfer in the transition state. Norman *et al.* have established that the reaction of anisole with lead tetra-acetate, which involves the formation of the radical cation of anisole, occurs exclusively at the *ortho*- and *para*-positions.[6] The very much greater reactivity of 2-methoxynaphthalene than 2-methylnaphthalene[7] is also consistent with a significant degree of electron transfer in the transition state.[8] Only a small difference in reactivity would be expected if the reaction proceed-



SCHEME 1

Table 1. Reactions of 2-alkoxy- and 2-acetoxynaphthalenes (2-$ROC_{10}H_7$) with copper(II) halides

R	Halogenating Agent (CuX_2)	Solvent	Rxn time (h)	Product (%) Unchanged 2-$ROC_{10}H_7$	1-X-2-$ROC_{10}H_6$
Me	$CuCl_2$	CCl_4	192	0	> 98
		PhH	46	0	> 98
		PhCl	4½	0	> 98
	$CuBr_2$	CCl_4	5½	0	> 98
		PhH	4½	0	> 98
		PhCl	3	0	> 98
		MeOH	18	5	95
Et	$CuCl_2$	PhCl	5	0	> 98
	$CuBr_2$	PhCl	7	0	> 98
$PhCH_2$	$CuCl_2$	PhCl	120	92	8
	$CuBr_2$	PhH	20	0	17[a]
COMe	$CuCl_2$	PhCl	168	28	72

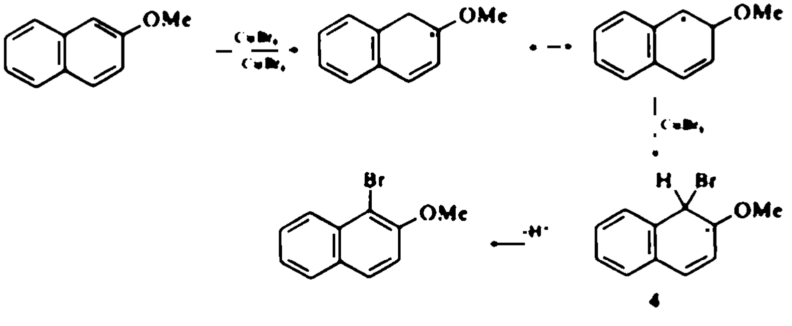
[a] 1-Bromo-2-naphthol (61%), benzyl bromide (10%), and di-β-naphthol (1.4%) were also obtained.

ed by a pure atom-transfer pathway. It is thus arguable that the reaction proceeds *via* the radical cation (4) (Scheme 2), though one cannot be sure whether it is a pure electron-transfer reaction or if there is also some component of atom transfer as well.

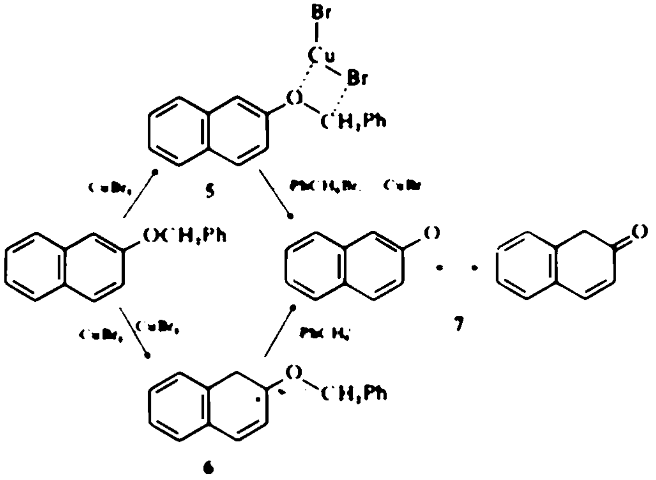
The relatively low reactivity of 2-acetoxynaphthalene and 2-benzoyloxynaphthalene (Table 1) in these reactions is also consistent with an electron-transfer mechanism.

2-Benzyloxynaphthalene reacts with copper(II) chloride to give 1-chloro-2-benzyloxynaphthalene. The reaction is considerably slower than that of 2-methoxynaphthalene possibly due to the intervention of steric effects. In contrast to this reaction, reaction of 2-benzyloxynaphthalene with copper(II) bromide is much more rapid and gives in addition to 2-benzyloxy-1-bromonaphthalene (17%), 1-bromo-2-naphthol (61%), di-β-naphthol (1.4%), and benzyl bromide (10%). The formation of 1-bromo-2-naphthol and di-β-naphthol probably indicates the intermediacy of the 2-naphthoxy radical which can either react with copper(II) bromide to give 1-bromo-2-naphthol or dimerize. The 2-naphthoxy radical (7) can either be formed *via* a four-centre transition state (5) as proposed for the reactions of 9-alkoxyanthracenes or by loss of a benzyl group from the radical cation (6) (cf. Scheme 3). Further studies are in progress to distinguish between these possibilities both of which would also satisfactorily amount for the formation of benzyl bromide. No satisfactory explanation can be advanced to explain the formation of 1-benzyl-2-naphthol. This is formed by heating 2-benzyloxynaphthalene in a sealed tube at 250° for several hours,[8] but it is difficult to see why copper(II) bromide should catalyse this rearrangement at 80° particularly when copper(II) chloride has no effect at 132°.

The reaction of 1-methoxynaphthalene with copper(II) bromide in benzene gave a mixture of 1-bromo-4-methoxynaphthalene (2) and 4,4'-dimethoxy-1,1'-binaphthyl (Table 3). This latter was contaminated by a trace of what appeared, on the basis of its retention time in g.l.c. and elemen-



SCHEME 2



SCHEME 3

tal analysis, to be an isomer of 4,4'-dimethoxy-1,1'-binaphthyl. This reaction is postulated to proceed by electron-transfer to give the radical cation of 1-methoxynaphthalene, which either undergoes reaction with copper(II) bromide or dimerizes. When this reaction is carried out under homogeneous conditions in methanol, 1-bromo-4-methoxynaphthalene is the sole product. In homogeneous conditions a radical cation will not be generated in close proximity to a second radical cation and thus reaction with copper(II) bromide in the solution is favoured.

Anodic oxidation of anisole has been shown to give 4,4'-dimethoxybiphenyl,[10] the reaction involving coupling of the radical cation of anisole. This lends support to the proposed mechanism for the formation of 4,4'-dimethoxy-1,1'-binaphthyl. Reaction of anisole with iron(III) chloride has also been reported to give 4,4'-dimethoxybiphenyl.[11] This reaction can likewise be considered to involve the dimerization of the radical cation of anisole.

The reaction of 1-methoxynaphthalene with copper(II) chloride in chlorobenzene gave in addition to 1-chloro-4-methoxynaphthalene and 4,4'-dimethoxy-1,1'-binaphthyl, 1-chloro-8-methoxynaphthalene and 3-chloro-4,4'-dimethoxy-1,1'-binaphthyl (Table 3). This latter was formed from further reaction of 4,4'-dimethoxy-1,1'-binaphthyl and was only formed in very low yield when the reaction was carried out in benzene. That none of the 3,3'-dichlorinated 4,4'-dimethoxybinaphthyl was produced in the reaction and that reaction of 3-chloro-4,4'-dimethoxy-1,1'-binaphthyl with copper(II) chloride only proceeded very slowly suggests that the chlorination of 4,4'-dimethoxy-1,1'-binaphthyl proceeds by a mechanism which has appreciable electron-transfer character. The formation of 8-methoxy-1-chloronaphthalene is postulated to involve co-ordination of the copper(II) chloride to the ether oxygen: this holds the copper(II) chloride in the correct steric environment for attack at the 8-position. 1-Methoxynaphthalene exists preferentially in the conformation in which the methyl group lies away from the other ring (see later), thus rendering the activation energy for attack at the 8-position less than that for attack at the 2-position.

The structure of 3-chloro-4,4'-dimethoxybinaphthyl was assigned on the basis of its NMR spectrum, which showed the presence of a proton ortho to a methoxyl group, and coupled to an adjacent proton. It was synthesized by chlorination of 4,4'-dimethoxy-1,1'-binaphthyl with one mole of iodo-

Table 2. Reactions of anisole with copper(II) halides

				Products (%)	
Halogenating Agent (CuX_2)	Solvent	Rxn. time (hr)	Unreacted PhOMe	o-BrC_6H_4OMe	p-BrC_6H_4OMe
$CuCl_2$	PhCl	216	21	4	75
$CuBr_2$	PhCl*	68	0	8	92
$CuBr_2$	PhCl	23	0	10	90

*Reaction carried out at 80°

Table 3 Reactions of 1-alkoxynaphthalenes (1-$ROC_{10}H_7$) and 4,4-dialkoxynaphthalenes 4,4'-Di$ROC_{20}H_{12}$ with copper(II) halides

Compound	Copper Halide CuX_2	Solvent	Reaction Time (hr)	Products (%)					
				1-$ROC_{10}H_7$	1-X-4-$ROC_{10}H_6$	1-X-8-$ROC_{10}H_6$	4,4'-DiRO-1,1'-$C_{20}H_{12}$	3-X-4,4'-Di-RO-1,1'-$C_{20}H_{11}$	3,3'-X-4,4'-Di-RO-1,1'-$C_{20}H_{10}$
1-$MeOC_{10}H_7$	$CuBr_2$[a]	PhH	4	8	47	0	45[b]	0	0
1-$MeOC_{10}H_7$	$CuBr_2$[a]	PhCl	5½	10	50	0	40[b]	0	0
1-$MeOC_{10}H_7$	$CuBr_2$[a]	MeOH	18	28	72	0	0[b]	1	0
1-$MeOC_{10}H_7$	$CuCl_2$[a]	PhH	6	1	15	13	70[b]	1	0
		PhCl	10	1	7	5	50[b]	37	0
1-$EtOC_{10}H_7$[c]	$CuBr_2$[a]	PhH	4	1	34	0	60[b]	0	0
1-$EtOC_{10}H_7$	$CuCl_2$[a]	PhH	5	2	14	0	84[b]	0	0
4,4'-Di$MeOC_{20}H_{12}$	$CuCl_2$[a]	PhCl	28		—		5	88	7
4,4'-Di$MeOC_{20}H_{12}$	$CuCl_2$[d]	PhCl	336	-	—		2	61	37
4,4'-Di$EtOC_{20}H_{12}$	$CuCl_2$[a]	PhH	168			—	99	0	0

[a] 2 mol CuX_2/mol organic compound

[b] Contaminated with isomeric material

[c] Unidentified compound of greater retention time also obtained on GLC

[d] 4 mol CuX_2/mol organic compound

Table 4 New halogenated 1- and 2-alkoxynaphthalenes

Compound	M p	Found (%)			Formula	Required (%)		
		C	H	X		C	H	X
4-Bromo-1-methoxynaphthalene	(B p. 159–160°/4 mm)							
2-Chloro-1-methoxynaphthalene	(B p 115°/2 mm)	68·5	4·7	18·8	$C_{11}H_9ClO$	68·6	4·7	18·5
4-Chloro-1-methoxynaphthalene	(B.p 122–124°/7 mm)	68·5	4·8	18·7	$C_{11}H_9ClO$	68·6	4·7	18·5
4-Chloro-1-ethoxynaphthalene	28–29°	70·4	5·3	17·2	$C_{12}H_{11}ClO$	70·0	5·3	17·2
2-Benzyloxy-1-bromonaphthalene	100–101°	64·9	4·1	25·4	$C_{17}H_{13}BrO$	65·1	4·1	25·5
2-Benzyloxy-1-chloronaphthalene	88–89°	76·3	5·1	13·5	$C_{17}H_{13}ClO$	76·0	4·9	13·2

benzene dichloride. Chlorination with two moles gave the corresponding 3,3′-dichloro compound. This latter was also obtained from 4,4′-dimethoxy-3,3′-dinitro-1,1′-binaphthyl thereby establishing the position of chlorination.

The reaction of 1-ethoxynaphthalene with both copper(II) bromide and chloride gave the appropriate 1-ethoxy-4-halogenonaphthalene and 4,4′-diethoxy-1,1′-binaphthyl (Table 3). This latter was accompanied by traces of isomeric compounds. There was no evidence of any reaction in the 8-position possibly due to steric effects with the rather larger alkoxy group.

The NMR spectra of 1-alkoxy-4-halogenonaphthalenes are characterized by a doublet centred at τ 3·26–3·44 with a coupling constant of 8 Hz. This signal is assigned to the proton at the 2-position. The signal due to this proton in 1-alkoxynapthalenes appears as a pair of doublets (J = 6 and 3 Hz) at τ 3·1–3·15 as a result of coupling with the protons at the 3- and 4-positions. In 1-methoxynaphthalene and 1-bromo-4-methoxynaphthalene the methyl of the methoxyl group is close to the proton in the 2-position. This was demonstrated by the observation of a nuclear Overhauser effect between this proton and the protons of the methyl group.

EXPERIMENTAL

Identities of compounds were confirmed by m.p. and m.m.p. determination, comparison of IR and NMR spectra, and GLC analysis. IR spectra were recorded as Nujol mulls on a Perkin Elmer 257 grating spectrometer, NMR spectra in deuterochloroform on a Perkin Elmer R10 spectrometer at 60 MHz using TMS as an internal standard, mass spectra on an A.E.I. MS9 spectrometer. GLC analyses were carried out on benzene solns using a Perkin-Elmer F11 gas-liquid chromatograph using three different columns for various mixtures. Column A was packed with silicone gum rubber E 301 on AW-DMCS 80–100 mesh Chromosorb G, 2·5:97·5, column B with XE 60 2-cyanoethylmethylsilicone on DMCS celite 80–120 mesh 1:9, column C with Carbowax 20 M on the same support.

Materials. Copper(II) bromide and chloride were dried and ground as previously described.[14]

Reactions of 2-alkoxy- and 2-acetoxynaphthalenes with copper(II) halides

(a) *Under heterogeneous conditions*. A vigorously stirred mixture of the substituted naphthalene (0·02 mol) and copper(II) halide (0·4 mol) in solvent (100 ml) was refluxed, generally until evolution of hydrogen halide ceased. The insoluble copper(I) halide was filtered off and the filtrate evaporated to dryness. Crystallization of the residue from MeOH gave the appropriate 2-alkoxy-1-halogenonaphthalene (> 95%) for reactions of 1-methoxy- and 1-ethoxynaphthalenes. In all reactions the product was analysed by GLC using column A operating at 180° (*cf* Table 1).

(b) *in methanol*. The reaction was carried out as above in MeOH (250 ml) in an atmosphere of N_2. The copper(I) bromide was filtered off. Methylene chloride was added to the filtrate, and this was extracted several times with dil HCl, washed with water and dried. The residue, after evaporation of the solvent, was analysed by GLC.

Reaction of anisole with copper(II) halides. The reaction was carried out as in (a) above. The product was analysed by GLC on column C operating at 90° (see Table 2).

Reaction of 1-methoxynaphthalene with copper(II) bromide

(a) *Under heterogeneous conditions*. A stirred mixture of 1-methoxynaphthalene (0·84 g, 0·05 mol) and copper(II) bromide (22·32 g, 0·1 mol) in solvent (250 ml) was refluxed for 4 hr. The hot mixture was filtered and the ppt of copper(I) bromide extracted several times with boiling benzene. Colourless crystals of 4,4′-dimethoxy-1,1′-binaphthyl (2·75 g, 35%), m.p. and mixed m.p. 252–254° (lit.[22] 254°) separated out from the cold filtrate. The filtrate was analysed by GLC using column A at 230° (Table 3). When light petroleum (b.p. 40–60°) was added to the filtrate more 4,4′-dimethoxy-1,1′-binaphthyl was precipitated. This second fraction was contaminated by a trace of material of slightly shorter retention time on GLC and was probably an isomeric dimethoxybinaphthyl. The filtrate after removal of this material and then solvent was distilled under vacuum giving 1-bromo-4-methoxynaphthalene (3·0 g, 26%), b.p. 159–160°/4 mm Hg (lit.[23] 147–153°/3 mm Hg).

(b) *in methanol*. The reaction was carried out as above in MeOH (250 ml) in an atmosphere of N_2 and worked up as described for the reaction of 2-methoxynaphthalene in MeOH.

Reaction of 1-methoxynaphthalene with copper(II) chloride (a) in chlorobenzene

The reaction was carried out as above using 1-methoxynaphthalene (23·8 g, 0·15 mol) and copper(II) chloride (40·33 g, 0·3 mol) in chlorobenzene (600 ml) for 10 hr. The reaction was worked up as before and 4,4′-dimethoxy-1,1′-binaphthyl (10·1 g, 43%), m.p. and mixed m.p. 254°, crystallized out from the filtrate. This was filtered off and the filtrate analysed by GLC (see Table 3). Light petroleum (b.p. 40–60°) was added to the filtrate to precipitate more 4,4′-dimethoxy-1,1′-binaphthyl. GLC analysis of this showed the presence of a second compound of slightly shorter retention time. This could not be separated but elemental analysis of the mixture indicated that it was isomeric with 4,4′-dimethoxy-1,1′-binaphthyl (Found C, 84·4; H, 5·6. $C_{22}H_{18}O_2$ requires C, 84·05; H, 5·8%). The solvent was distilled off from the filtrate and the residue crystallized from light petroleum (b.p. 40–60°) giving colourless needles. This material was purified by chromatography on alumina eluting with light petroleum (b.p. 40–60°) and finally by crystallization from this solvent. This gave colourless needles of *3-chloro-4,4′-dimethoxy-1,1′-binaphthyl*, m.p. and mixed m.p. 135–137° (Found C, 75·7; H, 5·2; Cl, 10·4. $C_{22}H_{17}ClO_2$ requires C, 75·7; H, 4·9; Cl, 10·2%), mass spectrum M^+ 348·09102 ($C_{22}H_{17}{}^{35}ClO_2$ requires 348·09170), τ 1·35–1·75 (2H, m, Ar), 2·2–2·7 (8 H, m, Ar), 3·00 (1 H, d, $H_{2'}$), 5·82 (3 H, s, OMe), 5·87 (3 h, s, OMe). The filtrate after removal of this compound was again evaporated and analysed by GLC using column B at 210°. This showed it to contain 1-methoxynaphthalene, 1-chloro-4-methoxynaphthalene, and a third compound of slightly greater retention time. This residue was distilled and the fraction b.p. 138–141°/3 mm Hg collected. This was dissolved in the minimum of light petroleum (b p 30–40°). After 24 hr at 0° colourless needles of *8-chloro-1-methoxynaphthalene* separated out, m p 61–63° (Found C, 68·9; H, 4·8; Cl, 18·7. $C_{11}H_9ClO$ requires C, 68·6; H, 4·7; Cl, 18·5%). The m p of this material was depressed on a mixture with 2-chloro-1-methoxynaphthalene.

8-Chloro-1-methoxynaphthalene was demethylated using the method of Curphey *et al* with pyridine hydrochloride.[18] A mixture of pyridine (10 ml) and conc HCl (11 ml) was heated in an oil-bath until the temp of the mixture reached 210°. After cooling to 150°, 8-chloro-1-methoxynaphthalene (0·50 g) was added and the temp slowly raised to 180°. The mixture was kept at this temp for 3 hr. After cooling, the mixture was poured into water and the product extracted with methylene chloride. The residue, after removal of the solvent, was crystallized from light petroleum (b p 30–40°) as colourless needles of 8-chloro-1-naphthol (0·258 g, 55%), m p 66° (lit.,[19] 67°). The m p was depressed on admixture with 2-chloro-1-naphthol.

(b) *in benzene*. The reaction was carried out as above in benzene and worked up as described for the reaction with copper(II) bromide. The results are reported in Table 3.

Reaction of 4,4'-dimethoxy-1,1'-binaphthyl with copper(II) chloride

A stirred mixture of 4,4'-dimethoxy-1,1'-binaphthyl (3·14 g, 0·01 mol) and copper(II) chloride (2·68 g, 0·02 mol) in chlorobenzene (200 ml) was refluxed for 28 hr. The mixture was worked up as before and the product analysed by GLC using column A at 230° (Table 3). The residue was chromatographed on alumina. Elution with 1:9 benzene: light petroleum (b p 60–80°) gave 3-chloro-4,4'-dimethoxy-1,1'-binaphthyl, m p and mixed m p 135–137°.

A second experiment using copper(II) chloride (5·36 g, 0·04 mol) and a reaction time of 14 days was carried out and worked up as above (see Table 3).

Reactions of 1-ethoxynaphthalene

(a) *With copper(II) bromide*. The reaction was carried out as described for 1-methoxynaphthalene. Crystals of 4,4'-diethoxy-1,1'-binaphthyl (3 g, 35%), m p and mixed m p 213–214 (lit.,[19] 213°) crystallized out from the filtrate after removal of the copper(I) bromide. The filtrate was then analysed by GLC using column A at 230° (Table 3). Light petroleum (b p 40–60°) was added to the filtrate and more 4,4'-diethoxy-1,1'-binaphthyl was precipitated. GLC analysis showed this was contaminated to the extent of ~10% by material of slightly shorter retention time, which was presumed to be isomeric. This mixture was analysed (Found C, 84·14; H, 6·67. $C_{24}H_{22}O_2$ requires C, 84·17; H, 6·5%).

(b) *With copper(II) chloride*. The reaction was carried out as above and the product analysed by GLC (Table 3).

Preparation of reference materials

2-Alkoxy-1-halogenonaphthalenes and 1-alkoxy-4-halogenonaphthalenes. These were prepared by alkylation of the appropriate halogenonaphthol with the exception of 2-benzyloxy-1-bromonaphthalene and 2-benzyloxy-1-chloronaphthalene which were prepared by halogenation of 2-benzyloxynaphthalene with bromine in AcOH and with sulphuryl chloride respectively. Purification was achieved by distillation or crystallization occasionally after chromatography on alumina. Details of new compounds are recorded in Table 4.

4,4'-Dialkoxy-1,1'-binaphthyls. These were prepared by treatment of the 1-alkoxynaphthalene with aluminium chloride in nitrobenzene at room temp[19] followed by crystallization from benzene. 4,4'-Dimethoxy-1,1'-binaphthyl had m p 252–254° (lit.,[19] 254–255°), τ 1·4–1·65 (2H, m, Ar), 2·4–2·7 (8H, m, Ar), 2·97 (2H, d, J 6 Hz, H_3 and $H_{3'}$), 5·85 (6H, s, OMe). 4,4'-Diethoxy-1,1'-binaphthyl had, m p 213–214° (lit.,[19] 213°).

4,4'-Dimethoxy-3-nitro-1,1'-binaphthyl. 4,4'-Dimethoxy-1,1'-binaphthyl (7·8 g, 0·025 mole) was dissolved in a boiling mixture of AcOH (300 ml) and Ac_2O (300 ml). The soln was cooled to 80° and to this was added dropwise a soln of copper(II) nitrate (3·05 g, 0·0125 mol) in AcOH (200 ml) and Ac_2O (200 ml) over 1 hr without further heating. The mixture was stirred for a further 2 hr and then pured slowly onto crushed ice. The yellow ppt was filtered off, dissolved in methylene chloride, washed with dil NaOHaq and then with water. After drying, the solvent was evaporated off and the residue crystallized from 1:12 benzene-light petroleum (b p 60–80°) giving yellow needles of *4,4'-dimethoxy-3-nitro-1,1'-binaphthyl* (5·8 g, 64%), m p 161–162° (Found C, 73·4; H, 4·7; N, 4·2. $C_{22}H_{17}NO_4$ requires C, 73·5; H, 4·7; N, 3·9%), τ 1·4–1·65 (2H, m, Ar), 2·02 (2H, s, H_2 and H_2), 2·25–2·8 (6H, m, Ar), 3·04 (1H, d, J 8 Hz, $H_{3'}$), 5·75 (3H, s, OMe), 5·90 (3H, s, OMe).

4,4'-Dimethoxy-3,3'-dinitro-1,1'-binaphthyl. This was prepared as above by addition of a soln of copper(II) nitrate (12·1 g, 0·05 mol) in AcOH:Ac_2O (1:1, 50 ml) to 4,4'-dimethoxy-1,1'-binaphthyl (12·5 g, 0·05 mol) in AcOH:Ac_2O (1:1, 1500 ml). The product was worked up as before giving 4,4'-dimethoxy-3,3'-dinitro-1,1'-binaphthyl (12·0 g, 73%), m p 244–246° (lit.,[8] 244°), τ 1·4–1·75 (2H, m, Ar), 2·08 (2H, s, H_2), 2·2–2·8 (6H, m, Ar), 5·74 (6H, s, OMe).

3-Amino-4,4'-dimethoxy-1,1'-binaphthyl. 4,4'-Dimethoxy-3-nitro-1,1'-binaphthyl (1·77 g, 5 mmol) was dissolved in boiling EtOH (200 ml). To this stirred soln, was added conc HCl (5 ml) followed by iron filings (0·9 g) in 4 portions. The vigorously stirred refluxing mixture was heated for a further 2 hr. The soln was neutralized by the addition of a soln of NaOH (5 g) in EtOH (100 ml), and then filtered hot. The ppt was washed with hot EtOH and the combined filtrates were evaporated. The residue, in methylene chloride, was washed with water and dried. The solvent was evaporated off and the residue crystallized from MeOH giving yellow needles of *3-amino-4,4'-dimethoxy-1,1'-binaphthyl* (0·78 g, 48%), m p 140–142° (Found C, 79·7; H, 5·7; N, 4·0. $C_{22}H_{19}NO_2$ requires C, 80·2; H, 5·8; N, 4·25%), τ 1·5–2·95 (9H, m, Ar), 3·03 (1H, s, H_2), 3·19 (1H, d, J 8 Hz, $H_{3'}$), 5·98 (3H, s, OMe), 6·04 (3H, s, OMe), 6·05 br (2H, disappeared on deuteration, NH_2).

3,3'-Diamino-4,4'-dimethoxy-1,1'-binaphthyl. Reduction of 4,4'-dimethoxy-3,3'-dinitro-1,1'-binaphthyl using the above procedure gave pale yellow needles of *3,3'-diamino-4,4'-dimethoxy-1,1'-binaphthyl* from EtOH (2·0 g, 80%) m p 179–180° (lit.,[8] 182°), τ 1·8–2·0 (2H, m, Ar), 2·4–2·95 (6H, m, Ar), 2·99 (2H, s, H_2 and $H_{2'}$), 6·01 (6H, s, OMe), 6·05 br (4H, disappeared on deuteration, NH_2).

3,3'-Dichloro-4,4'-dimethoxy-1,1'-binaphthyl (a) A soln of $NaNO_2$ (0·15 g, 2·2 mmole) was added dropwise to a soln of 3,3'-diamino-4,4'-dimethoxy-1,1'-binaphthyl (0·668 g, 2 mmol) in 6 M HCl (40 ml) maintaining the temp between −5° and 5°. This soln was added dropwise over 1 hr to a soln of copper(I) chloride (0·44 g, 4·4 mmol) in 4 M HCl (45 ml) keeping the temp between −5° and +5°. The mixture was kept at this temp until evolution of N_2 ceased. The ppt was filtered off, washed with water, and dried. It was chromatographed on alumina. Elution with 4:1 light petroleum-benzene gave pale yellow needles of *3,3′-dichloro-4,4′-dimethoxy-1,1′-binaphthyl* (0·40 g, 52%), m.p. 166–167° (Found: C, 68·9; H, 4·3; Cl, 18·9. $C_{22}H_{16}Cl_2O_2$ requires: C, 69·2; H, 4·2; Cl, 18·7%). τ 1·7 (2H, m, Ar), 2·3–2·8 (8H, m, Ar), 5·85 (6H, s, OMe).

(b) To vigorously stirred soln of 4,4′-dimethoxy-1,1′-binaphthyl (1·57 g, 5 mmol) in chloroform (250 ml), was added iodobenzene dichloride (2·74 g, 10 mmol). The mixture was refluxed for 1 week. The solvent was distilled off and the residue analysed by GLC which showed the presence of only one compound. The residue was crystallized from light petroleum giving yellow needles of 3,3′-dichloro-4,4′-dimethoxy-1,1′-binaphthyl (1·44 g, 74%), m.p. and mixed m.p. 166–167°.

3-Chloro-4,4′-dimethoxy-1,1′-binaphthyl. (a) An attempt to prepare this compound from the Sandmeyer reaction with 3-amino-4,4′-dimethoxy-1,1′-binaphthyl using the above conditions failed.

(b) Chlorination of 4,4′-dimethoxy-1,1′-binaphthyl (1·57 g, 5 mmol) using an equimolar amount of iodobenzene dichloride as above. GLC analysis of the crude product showed the presence of only one component. The product was crystallized from light petroleum, b.p. 40–60°, giving yellow needles of 3-chloro-4,4′-dimethoxy-1,1′-binaphthyl (1·20 g, 68%), m.p. 135–137°.

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REFERENCES

[1] Part VIII, D. C. Nonhebel and J. A. Russell, *Tetrahedron* **26**, 2781 (1970)
[2] D. C. Nonhebel and J. A. Russell, *Ibid* **25**, 3493 (1969)
[3] D. Mosnaim, D. C. Nonhebel, and J. A. Russell, *Ibid* **25**, 3485 (1969)
[4] *cf* G. H. Williams, 'Essays in Free-Radical Chemistry', *Chem. Soc. Special Publ.* No. 24, 25 (1970)
[5] J. K. Kochi, *Science* **155**, 415 (1967)
[6] R. A. McClelland, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 562 (1972)
[7] J. M. Mancilla and D. C. Nonhebel, unpublished results
[8] F. M. Elkobaisi and W. J. Hickinbottom, *J. Chem. Soc.* 1873 (1959), 1286 (1960)
[9] H. Cassebaum, *Chem. Ber.* **90**, 1537 (1957)
[10] K. Bechgaard, O. Hammerich, N. S. Moe, A. Ronlan, U. Svanholm, and V. D. Parker, *Tetrahedron Letters* 2271 (1972)
[11] M. Dangjan, *Zh. Obschei Khim.* **8** 1780 (1938)
[12] H. W. Underwood, O. L. Baril, and G. C. Toone, *J. Am. Chem. Soc.* **52**, 4087 (1930)
[13] L. F. Fieser and V. Desreux, *Ibid* **60**, 2255 (1938)
[14] N. P. Buu Hoi, *Liebigs Ann.* **556**, 1 (1944)
[15] E. C. Spaeth, T. A. Geissman, and T. L. Jacobs, *J. Org. Chem.* **11**, 399 (1946)
[16] D. Mosnaim and D. C. Nonhebel, *Tetrahedron* **25**, 1591 (1969)
[17] R. Scholl and C. Seer, *Ber. Dtsch. Chem. Ges.* **55**, 330 (1922)
[18] T. J. Curphey, E. J. Hofman, and C. McDonald, *Chem. Ind.* 1138 (1967)
[19] N. N. Woroschtzow and W. W. Koslow, *Ber. Dtsch. Chem. Ges.* **69**, 412 (1936)