

THE OXIDATIVE CROSS-COUPLING OF SUBSTITUTED
2-NAPHTHOLS, PART II: SELECTIVITY AS A MECHANISTIC PROBE^{1,2}

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ABSTRACT: Mechanistic study of Cu(II)-mediated coupling revealed that the model reaction between 2-naphthol and 3-carbomethoxy 2-naphthol can be controlled to give either the cross-coupled product (4) or a non-selective /approximately 1:1/ mixture of the cross- and homo-coupled products (4) and (5), respectively, the alternative homo-product (3) being virtually absent in both instances. The copper/ligand ratio has been found to be the main controlling factor and operation of two active copper species differing greatly in selectivity as well as reactivity has been suggested. Plausible model of a binuclear Cu(II) complex explaining the preferential cross-coupling has been devised and possible relevance to the oxidative polymerization of 2,6-dimethylphenol has been considered.

In spite of its broad synthetic significance³⁻⁷ and a considerable effort expedited, the mechanism of transition metal ion-mediated oxidative coupling of phenols remains far from being understood.⁷⁻¹² There is a general consent that the first step in the oxidation is generation of the phenoxy-radical from the corresponding phenolate or phenol. The subsequent fate of the radical depends presumably on the nature of oxidant and also on the substitution pattern; in any case, however, three alternative mechanisms⁷ must be considered, namely *homolytic coupling*, *heterolytic coupling* and *radical insertion*. Lack of mechanistic tools renders distinction among the alternatives difficult. Uncertain remains also the coordinating role of the transition metal ion in the coupling reaction.

Prevailing part of the available evidence rests so far on the coupling of a single substrate (*self-* or *homo-coupling*). Our recent discovery^{1,13,14} that two different phenolic substrates may participate simultaneously in a Cu(II)-mediated oxidation and give rise to *cross-coupled* products, in some instances with a remarkably high selectivity, prompted us to seek mechanistic explanation. In this paper we wish to report that selectivity of the *cross-coupling* may serve as a valuable probe providing a new insight into mechanism

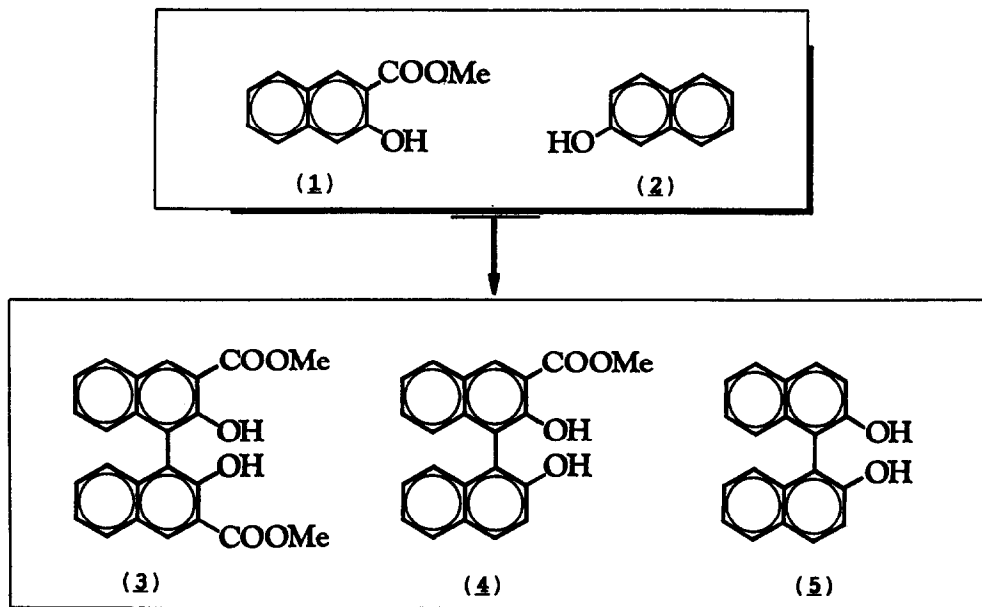
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of the coupling reactions.

**EFFECT OF LIGANDS ON SELECTIVITY IN Cu(II)-MEDIATED
CROSS-COUPLING REACTIONS**

There are numerous reports in the literature⁹⁻¹³ concerning the effect of amine ligand in the Cu(II)-mediated *homo*-coupling of phenolic compounds indicating that not only structure¹¹ but also stoichiometry of the ligands may affect strongly and sometimes fundamentally yields, rates and regioselectivity in the reaction. In the preceding preparative study¹ we have already inspected the effect of ligand structure in the Cu(II)-mediated *cross*-coupling of 2-naphthols. Examining various amines differing in their steric requirements and basicity, we have noted only minor selectivity variations. In actual fact, we have found that the amine ligand can be completely omitted from the reaction and replaced by a single equivalent of a stronger, e.g. methoxide, base. As a continuation of the study, we have now investigated the effect of ligand stoichiometry employing the *cross*-coupling of 3-carbomethoxy-2-naphthol (**1**) and 2-naphthol (**2**) as the model reaction (*Scheme 1*).

Scheme 1



In the first series of experiments the oxidizing reagent was prepared by mixing cupric chloride and *tert*-butylamine in various molar ratios in methanol. An equimolar mixture of the two investigated naphthols (**1**) and (**2**) was added to a twofold excess of the reagent and the coupling course was monitored by GC. It was found (*Table 1*) that stoichiometry of the Cu(II)/amine complex does not affect perceptibly the reaction selectivity, the *cross*-

coupled product (4) prevailing always greatly over the homo-coupled products (3) and (5) regardless of the copper/amine ratio.

Table 1

Entry	Cu(II)/Amine ^a	Yield(%) ^b	Time (min)	% (3)	% (4)	% (5)
I	1/2	95	60	5	90	5
II	1/4	97	30	5	91	4
III	1/8	94	25	6	89	5

^a(1)/(2)/Cu(II) was kept at 1/1/4 molar ratio, reactions were run at 50°C under anaerobic conditions; ^bisolated mixture of products (3)-(5), see ref.1.

In the second series of experiments the amine ligand was replaced by the methoxide anion, the reagent being preformed by mixing MeONa and CuCl₂ in various ratios and treated again in a twofold excess with equimolar mixture of naphthols (1) and (2) (Table 2). In the absence of methoxide base [Entry I], the oxidative coupling did not take place, at least under the investigated conditions. At 1:1 CuCl₂/NaOMe ratio the reaction proceeded rapidly, giving rise almost exclusively to the cross-coupled product (4) [Entry II]. A gradual slowing-down of the overall reaction occurred on increasing further the proportion of the methoxide ion [Entries III and IV], accompanied by a very pronounced decrease of the cross-coupling selectivity. Nearly equal proportions of the cross-coupled (4) and the homo-coupled product (5) were produced at 1:2 Cu(II)/NaOMe ratio, the other homo-coupled product (3) being practically absent in the reaction mixture.

Table 2

Entry	Cu(II)/NaOMe ^a	Yield(%)	Time(min)	% (3)	% (4)	% (5)
I	1/0	0	600	-	-	-
II	1/1	75	50	5	95	0
III	1/2	30 ^b	840	2	55	43
IV	1/3	<1	900	-	-	-

^a(1)/(2)/Cu(II) was kept at 1/1/4 molar ratio, reactions were run at 50°C under anaerobic conditions. ^b60% of (1) and 40% of (2) were recovered.

In the third series of experiments, amine was added to the CuCl₂/NaOMe reagent preformed at two different ratios [Table 3]. No effect of amine has been found with the reagent preformed at 1:1 molar ratio, the prevailing and very fast formation of the cross-coupled product being observed in the absence as well as in the presence of the amine ligand [Entries I and II]. In contrast, a marked acceleration and increased cross-coupling selectivity was induced by the added amine at 1:2 Cu(II)/NaOMe ratio [Entries III-V].

In the fourth experimental series we have modified preparation of the oxidizing reagent. Instead of preforming the Cu(II)/amine or Cu(II)/NaOMe

Table 3

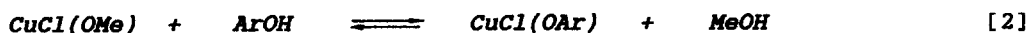
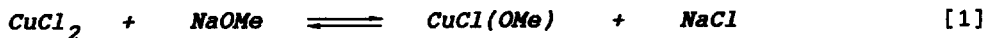
Entry	Cu(II)/NaOMe ^a	amine [eq.]	Yield [%]	Temp. [°C]	Time [h]	% (3)	% (4)	% (5)
I	1/1	none	75	22	5	5	95	0
II	1/1	Pyridine [1]	84	22	4	4	96	0
III	1/2	none	b	50	14	2	55	43
IV	1/2	Pyridine [2]	c	50	8	6	79	15
V	1/2	tBuNH ₂ [4]	d	50	8	15	73	12

^a(1)/(2)/Cu(II) was kept at 1/1/4 molar ratio; ^b(4) isolated in 14% yield; ^c(4) isolated in 44% yield; ^d(4) isolated in 43% yield.

complex, the amine or sodium methoxide has been treated first with the mixture of naphthols (1) and (2), followed by the addition of cupric chloride in various molar ratios. A significant acceleration has been attained in this arrangement, however, the *cross-coupling* selectivity remained essentially unaffected.

Summing up, it has been found that two different patterns of reactivity/selectivity behaviour may arise in the investigated reaction. In one extreme, the overall reaction is fast and leads almost exclusively to the *cross-coupled* product (4). In the other extreme, the overall reaction is slow and affords the *cross-* and *homo-coupled* products (4) and (5) in nearly equal proportions. A gradual transition between the two extreme situations can be attained by varying the proportion of the methoxide and, to some extent, also the amine ligand in the reaction. It strongly suggests that two different Cu(II) complexes with different composition may take part in the reaction.

Information concerning composition of the alternative Cu(II) complexes can be drawn simply from the above experiments. The first information comes from the observation that the Cu(II)-mediated coupling of the naphthols (1) and (2) does not occur in the absence of base. It shows that deprotonation of the participating naphthol is indispensable in the reaction. The second information can be inferred from the observation that one equivalent of sodium methoxide added to CuCl₂ promotes a fast and highly selective *cross-coupling*. It suggests that equilibria [1] and [2] are involved in the reaction leading to incorporation of one naphtholate into the Cu(II) coordi-



nation sphere. The observation that prior treatment of sodium methoxide with naphthols accelerates the coupling lends a further credence to this suggestion. In the absence of methoxide ion, the deprotonation of naphthol can be induced also by amine base. Owing to a lower amine basicity, more than

one equivalent of amine is however required (eq.[3a],[b]):



In this way, similar if not identical Cu(II) complex species may arise from naphthol and CuCl_2 in the presence of amine as well as one equivalent of methoxide base, with the overall composition corresponding to a formula $[\text{L}_x\text{Cu}^{(\text{II})}(\text{OAr})]_n$ where L_x summarizes "weak" ligands (methanol, amine, chloride ion) and n is an integer equal or greater than 1 (*vide infra*).

A distinctly different Cu(II) complex species is expected to arise from CuCl_2 and naphthol (1:1) upon treatment with two equivalents of sodium methoxide. From the equilibria¹⁵:



it can be inferred that the resulting active complex contains both the naphtholate ($\text{ArO}^{(-)}$) as well as methoxide ion in the coordination sphere of Cu(II).

Interconversion of the two alternative complex species $[\text{L}_x\text{Cu}^{(\text{II})}(\text{OAr})]_n$ and $\text{L}_x\text{Cu(OMe)(OAr)}$ appears possible on basis of the obtained evidence. Results from the third experimental series suggest (*Table 3*) that external amine ligand L_{ext} may be instrumental in such an interconversion, as shown in eq.[6]:



POSSIBLE MODES OF SELECTIVITY IN CROSS-COUPLING REACTIONS

As it has been pointed out already in the Introduction, three different mechanisms may operate in the oxidative coupling of phenols. Before attempting to discuss their role in the investigated reaction, some features of the individual mechanisms which may bear upon cross-coupling selectivity will be considered.

In the *homolytic coupling* (radical recombination), the oxidation potential (E_{ox}) which determines easiness of radical formation from the starting phenol (phenolate) is assumed to be main controlling factor in the reaction. When the oxidation potentials of the two competing phenolic substrates (X and Y) differ significantly, the product of *homo*-coupling of the substrate possessing a lower oxidation potential (Y) will prevail in the early (fast) stage of the reaction (eqs.[7],[8]) followed later by a slower





homo-coupling of the other (less easily oxidizable) substrate (*X*) (eqs. [9], [10]). The *cross*-coupled product is expected to be practically absent under



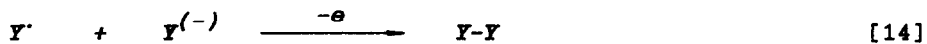
such circumstances in the reaction mixture.¹⁶

In the *heterolytic coupling*, the more easily oxidizable phenol (phenolate) *Y* is oxidized (in one two-electron or two one-electron steps)^{17a} to phenoxonium ion Y^{\dagger} which subsequently undergoes recombination with the unreacted phenol or phenolate (*Y* or *X*) (eqs. [11]-[13]):



Since the intermediary cation Y^{\dagger} is a strong electrophile, a more or less pronounced preference for the phenol *Y* which is assumedly a stronger¹⁸ nucleophile than the less easily oxidizable phenol *X* could be expected.^{17b}

In the *radical insertion* mechanism¹⁹ (eqs. [14] and [15]), the situation is more complex, since in addition to oxidation potentials of



starting phenols also intrinsic insertion selectivity²⁰ of the individual radicals may participate in the product control. In dependence on the insertion selectivity, very different results may be obtained in the reaction. If, in one extreme, the phenoxy-radical Y^{\cdot} behaves as an electrophile,²⁰ the more easily oxidizable phenolate $Y^{(-)}$ which is a stronger nucleophile would be attacked preferentially giving rise to the *homo*-coupled product *Y-Y*. If, however, in the other extreme, the phenoxy-radical Y^{\cdot} behaves as a nucleophile,²⁰ the less easily oxidizable phenol *X* which is a better electrophile could be a more convenient partner and the *cross*-coupled product *Y-X* would be preferentially obtained.

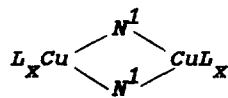
Formally, in this way, results of the present study might appear to be in best accord with the *radical insertion* mechanism. However, one has to keep in mind that the outlined mechanistic scheme represents an oversimplification of the actual situation. As it will be pointed out in the following section, also the coordinating role of the central copper atom has to be taken into account.

ON THE DIFFERENT CROSS-COUPLING SELECTIVITY OF THE TWO
ALTERNATIVE Cu(II) COMPLEXES PARTICIPATING IN THE REACTION

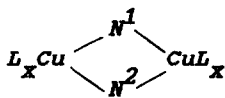
As it already followed from our experimental findings, two distinct Cu(II) complex species differing greatly in reactivity as well as selectivity may take part in the oxidative coupling of naphthols (1) and (2). The composition $L_xCu^{(II)}(OMe)(OAr)$ has been assessed to the less reactive complex affording the *cross*- and *homo*-coupled products (4) and (5), respectively, in nearly equal proportions. In a contrast, the structure $[L_xCu^{(II)}(OAr)]_n$ has been attributed to the more reactive complex species leading almost exclusively to the *cross*-coupled product (4). An explanation of so marked differences between the two similar species now gets on the agenda of our discussion.

The selectivity pattern found for the less reactive complex $L_xCu^{(II)}(OMe)(OAr)$ does not require any specific role for the coordinated metal ion. It is proposed that the complex involving the more easily oxidizable naphtholate (2) preferentially undergoes intramolecular electron transfer [Cu(II)→Cu(I)] yielding the corresponding naphthoxy radical which either directly (eqs. [14],[15]) or following further one-electron oxidation (eqs.[11]-[13]) reacts with both the available naphtholates (1) and (2) in a non-selective fashion.²¹

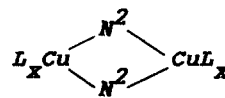
On the other hand, a reasonable explanation for the high *cross*-coupling selectivity of the more reactive complex $[L_xCu^{(II)}(OAr)]_n$ may be given only when the well known propensity of some Cu(II) salts to binuclear complexes formation is taken into account. In accord with available evidence that phenoxides may serve as bridges in such complexes,²²⁻²⁴ three alternative binuclear structures (6)-(8) can be postulated to arise in the presence of two different naphtholates (N^1, N^2).



(6)



(7)



(8)

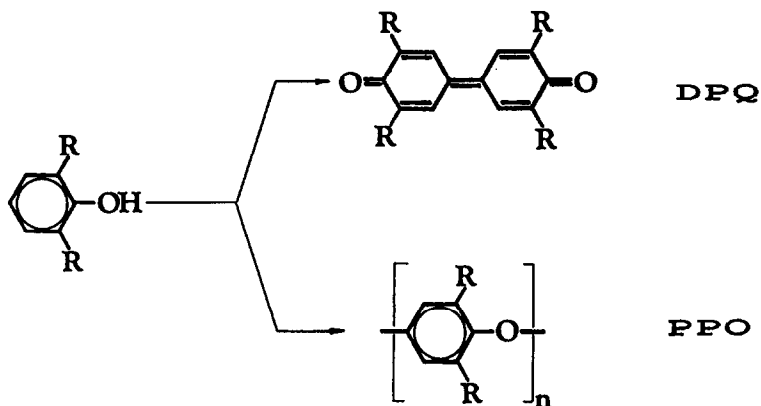
Two complementary factors are proposed to participate in control of the redox processes proceeding in the binuclear complexes. The first factor concerns oxidation potentials E_{Ox} of the bridged naphtholates N^1 and N^2 . It is assumed that the oxidation potential depends on substitution, the naphtholate (1) [designed as N^1] bearing the electron-withdrawing carbomethoxy-substituent being less prone to the oxidation than the unsubstituted naphthol (2) [designed as N^2]. A preferential oxidation of the naphtholate (2) via the complexes (7) and (8) can be accordingly expected.

The other factor concerns redox potential of Cu(II) ion in the binuclear complexes. It is assumed that the redox potentials in the individual complexes (6)-(8) are different. All the available experience indicates that redox potential of any metal ion becomes more negative on ligand coordination, the effect being the stronger, the greater is the ligand electron-donating ability. Since the ligand N^1 is a weaker electron donor

RESEMBLANCE BETWEEN OXIDATIVE CROSS-COUPLING AND OXIDATIVE POLYMERIZATION OF PHENOLS

Endres and Hay¹⁰ discovered that the oxidative polymerization of 2,6-dimethylphenol [DMP] catalyzed by Cu(II)/amine complexes provides an excellent approach to the production of poly(2,6-dimethyl-1,4-phenylene oxide) [PPO], accompanied, however, by an undesired side product, diphenoquinone [DPQ], resulting from C-C coupling instead of C-O coupling (Scheme 3). Because of the outstanding properties of polymer and its commercial im-

Scheme 3



portance many workers investigated the factors controlling the C-O/C-C coupling ratio.^{10,12,25-27}

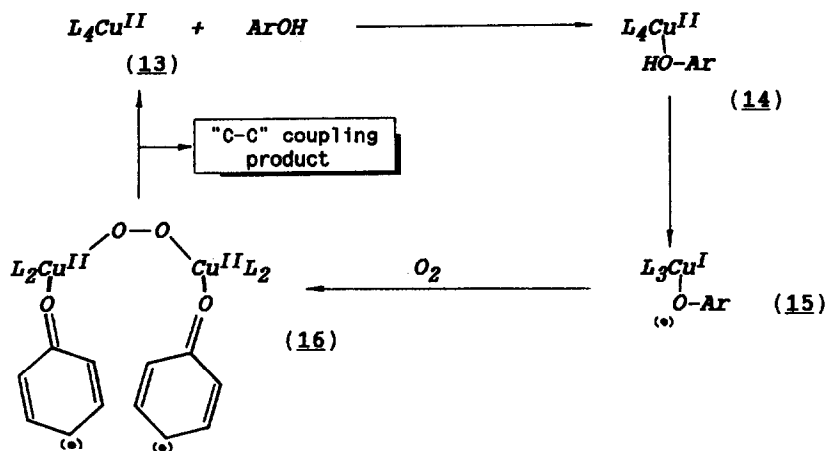
The Cu(II)/amine and also Cu(II)/hydroxide ratios have been found to have a strong effect on product distribution in the reaction, PPO prevailing always greatly at high amine and/or hydroxide/copper ratios, whereas DPQ at low amine and/or hydroxide/copper ratios. Under the conditions used in the polymerization, it has been also found that changing the base/copper ratio changes also the composition of the copper complexes. Therefore, various mechanistic explanations for the product variation based on two different complexes yielding C-O and C-C coupling, respectively, have been suggested.

One explanation, which rests on a *homolytic coupling* mechanism,²⁸⁻³⁰ postulates coupling of copper-ion-coordinated radicals. Since phenoxy radicals coordinated in two different complexes are bound to have different orientations, one complex should give C-O coupling while the other the undesired C-C coupling.

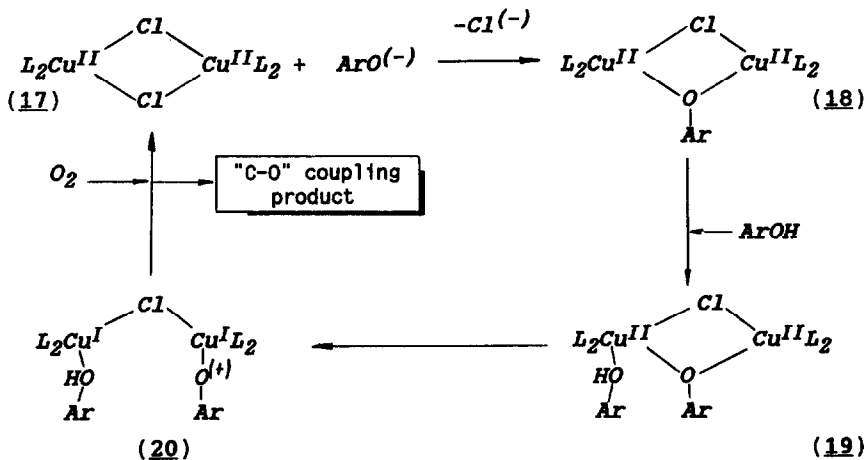
Another explanation is based on hypothesis assuming a concurrent operation of *homolytic* and *heterolytic coupling* mechanisms in the reaction. Revillon³¹⁻³² and Waters³³ proposed that the *homolytic* mechanism operates at high amine and/or hydroxide/copper ratios accounting for the prevailing C-O coupling whereas the *heterolytic* mechanism is responsible for the C-C coupling at low amine and/or hydroxide/copper ratios. Challa and cowor-

kers,^{12,27} on the other hand, recently proposed a reversed scenario, in which the *homolytic* mechanism operates at low and the *heterolytic* mechanism at high amine and/or hydroxide/copper ratios, a mononuclear²⁷ complex species being involved under the former whereas a binuclear¹² complex species under the latter conditions. A catalytic cycle involving the two alternative complex species is sketched in *Schemes 4* and 5.

Scheme 4



Scheme 5



In *Scheme 4*, DMP coordinates at the axial position of the mononuclear complex (13) [L=amine] yielding complex (14). Subsequent proton transfer to

amine ligand and electron transfer from phenoxide to copper(II) give the structure (15). In the presence of oxygen, two of these copper(I) phenoxy radical complexes (15) are combined through a dioxygen bridge to give a binuclear intermediate (16) in which the *para*-positions of both phenoxy radicals are in close proximity allowing combination to DPQ.

According to *Scheme 5*, the starting binuclear chloro-bridged copper(II) complex (17) reacts with phenoxide anion yielding the phenoxo-bridged complex (18). The axial coordination of a free phenol to (18) gives the active complex species (19). Intramolecular two-electron transfer from the bridged phenoxide anion to the adjacent Cu(II) ions in the (19) gives rise to the Cu(I)-coordinated phenoxonium ion (20) which is liable to leave its coordination site and react with the neighbouring ArOH unit. Taking the high electronegativity of oxygen into consideration, the transition state involving ArOH with a negative charge at the oxygen is the most favoured (C-O coupling).

In this way, some striking analogies concerning the observed effects of the base/copper ratios on selectivity and also their explanation become apparent between the cross-coupling and the coupling polymerization reaction. It may be noted, in particular, that binuclear and mononuclear complex species have been proposed to compete in both the compared reactions, the former species accounting always for the more selective whereas the latter for the less selective mode of coupling.

On the other hand, it can be seen that the actual structures of the active complex species as well as the mechanisms proposed in the two reactions are markedly different. It should not come as a surprise since also experimental conditions employed in the two reactions markedly differ. In the cross-coupling reaction, the Cu(II) complexes are employed under anaerobic conditions in stoichiometric amounts. In the coupling polymerization, on the other hand, the copper complexes are present only in catalytic amounts being regenerated by O₂ in the course of the reaction.

Notwithstanding the differences, it may appear on a closer analysis that the generalized explanation we have now proposed for the selective cross-coupling in *Scheme 2* is valid also for the C-O coupling in the polymerization reaction.

Experimental

All the products appearing in following experiments were isolated and fully characterized as described in the preceding paper [see ref.1], here only general procedures are therefore given.

THE EFFECT OF Cu(II)/AMINE STOICHIOMETRY (Table 1)

A solution of (1) [202mg, 1mmol], (2) [144mg, 1mmol] and CuCl₂ [538mg, 4mmol] in MeOH (80mL) was deoxygenated²⁷ and a given amount of *tert*-butylamine was added to the vigorously stirred solution at room temperature. The resulting heterogeneous mixture was stirred at 50°C for the time indicated and then cooled down and quenched with 6M HCl to pH~3. After removal of solvent the residue was extracted with chloroform, the extracts were washed

with water, 10%aq. NaHCO₃ and dried with MgSO₄. Evaporation of chloroform left the crude product which was analyzed by GC [naphthalene as internal standard].

THE EFFECT OF Cu(II)/NaOMe STOICHIOMETRY (Table 2)

A given amount of NaOMe (1.26M solution in MeOH) was added to a vigorously stirred solution of anhydrous copper(II) chloride [538mg, 4mmol] in dry MeOH (20mL) and the mixture was stirred at room temperature for 5 minutes, deoxygenated and a solution of (1) [202mg, 1mmol] and (2) [144mg, 1mmol] was added in one portion. The work-up and the analysis of the product mixture were performed as described above.

THE EFFECT OF THE AMINE LIGAND ON Cu(II)/NaOMe-MEDIATED COUPLINGS (Table 3)

The reactions were performed in the same way as those given in Table 2 except that a given amount of the amine ligand [Entry II and IV: 0.64mL (632mg, 8mmol) of pyridine; Entry V: 1.68mL (1.17g, 16mmol) of *tert*-butylamine] was added to the preformed Cu(II)/NaOMe system prior to addition of the naphthols (1) and (2).

Acknowledgment

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(b) Reported examples of a *bona fide heterolytic cross-coupling* (refs.35,36) are in a reasonable accord with the selectivity prediction.
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