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The Ullmann Ether Condensation

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The review deals with the Ullmann condensation as the most important method for the synthesis of aromatic ethers. The available information about the dependence of the reactivity of the reactants on structure and the reaction mechanism is examined and the experimental condensation conditions are discussed.
The bibliography includes 241 references.

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1. INTRODUCTION

In 1904 Ullmann[1] observed that the presence of metallic copper greatly facilitates the substituion of a halogen atom in an aromatic ring by a phenolic residue:

$$ArX + KOAr' \xrightarrow[Cu]{t^\circ} ArOAr' + KX \ .$$

This catalytic method for the synthesis of aromatic ethers, usually referred to as the Ullmann condensation[2], has become widely used in catalysis and industrial chemistry.

The Ullmann condensation is a method for the synthesis of phenyl ether (used to prepare heat exchangers and in the perfume industry[3-8]), substituted phenyl ethers (monomers for thermostable polymers[9-11]), and polyphenyl ethers, which have found important applications in various branches of modern engineering, for example, as oils for the creation of an ultrahigh vacuum, as high-temperature greases, hydraulic liquids, etc.[12-20]

A wide variety of aryl ethers, including intermediates in the synthesis of complex natural products such as alkaloids[21-36] and also diphenylene dioxides, have been synthesised on a preparative scale by the Ullmann condensation[37-41].

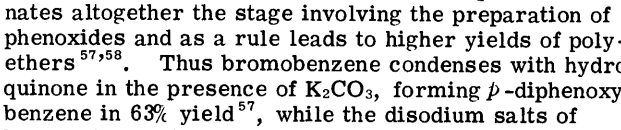
During the last ten years, a number of studies undertaken to determine the principal characteristics of this reaction and to elucidate its mechanism, have been published. Despite the extensive applications of the Ullmann condensation, there is no special review in the literature dealing with the synthetic aspects of this reaction.
The Ullmann ether condensation has been only briefly examined among other reactions in reviews on the synthesis and properties of phenyl[6] and polyphenyl[13,14] ethers, nucleophilic substitution[42], and copper-catalysed processes[43].

2. EXPERIMENTAL CONDENSATION CONDITIONS

The condensation is carried out by heating the initial reactants at 100-300°C in the presence of a copper catalyst in a solvent or without one (in the absence of a solvent, the optimal temperature is usually 180-220°C). To avoid the oxidation of the phenol, the reaction is sometimes performed in an inert atmosphere[44-51].

The phenolic components are frequently introduced in the form of salts, which are obtained by treating phenols with alkalis, alkali metals, and their alkoxides as well as sodamide[52] and sodium hydride[53]. Potassium salts are apparently more reactive. They are employed more frequently than sodium phenoxides[44,45,50,54]. However, a rigorous quantitative estimate of the comparative reactivities of different salts has not been made.

Free phenols can also be introduced into the reaction with aromatic halogeno-derivatives. Potassium carbonate is then added to the mixture and the method of synthesis is greatly simplified without reducing the yield of ethers[50,55]. This version of the condensation has undoubted advantages in the synthesis of aromatic polyethers. The difficulties in the preparation of such ethers are associated with the instability of the alkali metal salts of dihydric phenols which char to a considerable degree[56]. This can be partly avoided by preparing dry phenoxides beforehand under special conditions[53], which, however, complicates the synthesis. The use of K_2CO_3 and of free phenols eliminates altogether the stage involving the preparation of phenoxides and as a rule leads to higher yields of polyethers[57,58]. Thus bromobenzene condenses with hydroquinone in the presence of K_2CO_3, forming *p*-diphenoxybenzene in 63% yield[57], while the disodium salts of hydroquinone gives rise to the same product in a yield of only 0.3%:[53]



It is interesting that other salts, for example $Na_2B_4O_7$, MeCOOLi, MeCOONa, MeCOOK, $(NH_4)_2CO_3$, Na_2CO_3, and $CaCO_3$, are ineffective[57].

The oxides Cu_2O and CuO, which evidently combine the functions of a catalyst and a base, have an unusual effect[45,55,59,60]:

$$2ArX + 2Ar'OH + Cu_2O \rightarrow 2ArOAr' + 2CuX + H_2O \ .$$

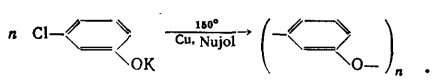
The rate of condensation is in this case lower than in the presence of K_2CO_3 and copper salts [57].

3. THE CATALYST

Metallic copper [1,10,11,15-17,20,21,23-29,35,36,41,47-52,55,56,61-166], the copper salts $CuCl_2$, [15,16,166-170] $Cu(OCOMe)_2$, [46,57,58,61,171-174] $CuSO_4$, [175-179] CuCl, [53,57,180,181] CuBr, [57,182,183] CuI, [57] $CuCO_3$, [7,184,185] and the copper oxides CuO [34,55,186,187] and Cu_2O [45,55,56,62,63,188-190] have been used as catalysts. In addition the copper salts of alkylnaphthalenesulphonic acids [191], alkylbiphenyldisulphonic acids [191], and phenols [192-194] as well as the copper(II) complexes $(C_5H_5N)_2 \cdot CuCl_2$ and $Cu(OCH_3)_2$ [51] have been proposed as catalysts of the Ullmann condensation. Powdered copper is obtained by reducing $CuSO_4$ with zinc [64] or by electrolytic deposition [65,195]. Copper comminuted mechanically, the so called copper bronze [22,66,67,196-211], is also used. Sometimes copper is employed in combination with its salts, for example with $Cu(OCOMe)_2$, [22,39,40,68-70,212-251] CuCl, [222] CuI, [197] and $CuNO_3$. [37,38]

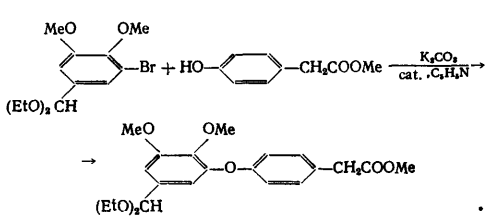
Attempts have been made to replace copper catalysts by other metals, salts, and oxides: titanium [223], iron [224], $Co(OCOMe)_2$, [225] $Ni(NO_3)_2$, [225] and Al_2O_3, [224] but these catalysts have not been widely used, probably owing to their low activity.

Despite the initial view [166], the relative catalytic activities of various forms of copper depend significantly on the method of preparation of the catalyst, the reaction conditions, and many other factors [44,53,55,71,195]. Thus, in a study of the polycondensation of potassium *m*-chlorophenoxide in Nujol in the presence of metallic copper, Brown and Goldman [195] observed that the method of preparation of the catalyst ("chemically" reduced or electrolytically precipitated copper with an admixture of 1% of zinc) and its preliminary treatment have a significant influence on the course of the reaction and the properties of the resulting polymer:



Under these conditions, copper oxides have an insignificant catalytic activity.

On the other hand, in the condensation of phenols and methyl *p*-hydroxyphenylacetate with certain aryl bromides, copper oxides proved to be more active [55]. An appreciable difference between CuO and Cu_2O was not observed and the relative efficiency of the catalyst depended on the nature of the initial compounds and the solvent. For example, in the condensation of the diethyl acetal of 5-bromoveratraldehyde with methyl *p*-hydroxyphenylacetate in boiling pyridine in the presence of copper, Cu_2O, and CuO the yields were 10, 30, and 35% for reaction times of 15, 10, and 9 h respectively:



In a study of the condensation of α-bromonaphthalene with phenols in collidine, Bacon and Stewart [45] also concluded that copper oxides are more active than copper and its salts (Table 1):

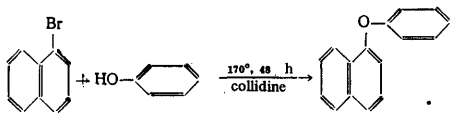


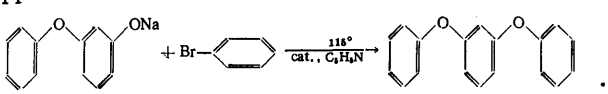
Table 1.

Catalyst	Cu_2O	CuO	Cu	CuCl	CuBr	$CuCl_2$
Yield of α-phenoxynaphthalene, %	50	31	23	traces	traces	0

However, in this case the condensation was carried out in the absence of potassium carbonate and the enhanced activity of copper oxides may have been due to the fact that they are capable of behaving as both catalysts and bases. The presence of oxidised species in finely divided metallic copper also cannot be ruled out.

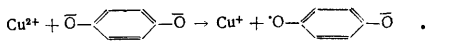
According to Weingarten [44], $CuBr_2$, $CuCl_2$, $Cu(OCOMe)_2 \cdot H_2O$, CuI, CuBr, and CuCl are equally effective as catalysts of the condensation of bromobenzene with potassium phenoxide in diglyme. Metallic copper, Cu_2O, CuO, and $CuSO_4$ are inactive in this reaction.

Copper(I) and copper(II) salts exhibit approximately equal catalytic activities also in the condensation of sodium *m*-phenoxyphenoxide with bromobenzene in pyridine, while copper is ineffective [53]:



The first attempt to discover the catalytically active form of copper [226] did not elucidate the problem appreciably. More convincing results were obtained later [44] in a study of the condensation of bromobenzene with potassium phenoxide in diglyme in the presence of CuBr and $CuBr_2$. These salts showed equal catalytic activities and the ESR spectra and antimagnetic susceptibilities of the catalytic solutions were similar in the two cases. However, a CuBr solution prepared in an atmosphere of nitrogen gave a weaker ESR signal than a $CuBr_2$ solution and its magnetic susceptibility was negligible. On the other hand, when the condensation was carried out in an inert atmosphere, the reaction rate increased. Hence it followed that the active form of the copper catalyst is univalent copper. The catalytic activity of bivalent copper may have been due to its reduction by the phenoxide anion, which was then oxidised to a relatively stable free radical. The latter in fact made the reaction mixture paramagnetic. Indeed, the white precipitate deposited when the solution of $CuBr_2$ and potassium phenoxide in diglyme was poured into water proved to be a copper(I) salt and the addition to the catalytic solution of 2,6-di-t-butyl-4-methylphenol, 2,5-di-t-butylhydroquinone, or phenothiazine—compounds which trap free radicals—resulted in appreciable changes in the ESR spectrum but did not affect the rate of the Ullmann ether condensation.

It has been found[53] that metallic copper does not catalyse the condensation of bromobenzene with sodium *m*-phenoxyphenoxide in boiling pyridine and that, when CuBr is used as a catalyst, the introduction of copper powder into the reaction mixture does not affect the rate of this reaction. Since powdered copper completely reduced bivalent copper to the univalent state under these conditions, the authors[53] concluded that the only possible active form of the catalyst is univalent copper. These workers also believe that bivalent copper may be reduced by phenoxide anions. The low yields of products and the formation of large amounts of resins in the condensation of readily oxidised polyhydric phenols (catechol, hydroquinone, 2,6- and 1,5-dihydroxynaphthalenes and phloroglucinol) were explained by polymerisation processes involving radical-ions of the semiquinone type:



Thus the available literature data show that the active principle of the catalyst is probably univalent copper. On the other hand, bivalent copper compounds and metallic copper are active by virtue of the oxidation-reduction processes occurring in the reaction medium.

However, in the practical selection of the catalyst, one probably should not ignore also the role of factors such as the solubility of copper compounds, the effects of the chemical nature of the solvent and the reactants, etc.

4. THE SOLVENT

An excess of the phenol[7,49,67,72-79,184,185,198,200,220], heavy unsaturated and aromatic hydrocarbons[48,80,172,177-179], alcohols and glycols[22,63,81,82,197,224], diglyme[15,42,44,222], dioxan[22,171,173,174,176], ketones[65,83,169,180], dimethylformamide[11,55,187,189], dimethyl sulphoxide[11,227], nitrobenzene[84,197,204], pyridine and its derivatives[23,26,28,29,34,46,55,57,58,85,86,172,188], quinoline[63], and certain other organic compounds[11,55,63,169] have been used as solvents.

One of the best solvents is pyridine[53,55,57,58]. Thus, in the condensation of bromobenzene with the sodium salt of *m*-resorcinol in pyridine, the yield of *m*-diphenoxybenzene was 74% and the overall yield of this ether and *m*-phenoxyphenol reached 89%. In other solvents the yields were significantly lower[53] (Table 2):

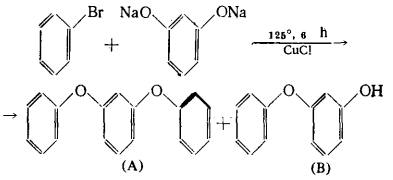


Table 2.

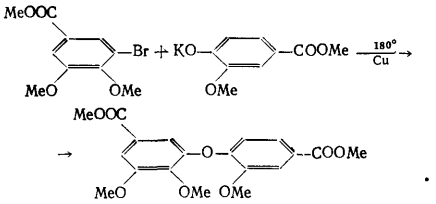
Solvent	Yield, %		Solvent	Yield, %	
	ether (A)	ether (B)		ether (A)	ether (B)
Pyridine (117°C)	74	15	Dimethylformamide	4	34
Pyridine + 2% of water (112°C)	4	22	Hexamethylphosphoramide	5	47
2,4,6-Collidine	17	25	Methyl sulphoxide	14	42
Pyridine *N*-oxide	18	40	n-Propyl sulphone	42	33
Di-n-butylamine	32	19	2-Methoxyethyl ether	21	25
1-Methyl-2-pyrrolidinone	11	46			

Attempts to find rigorous correlations between the effectiveness of the solvent and its characteristics, for example its basicity, have been unsuccessful[45].

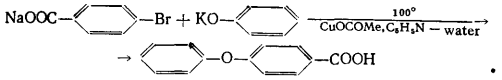
On the other hand, it is significant that the majority of the solvents employed contain in their molecules a heteroatom having a lone electron pair. The dissolution of the copper catalyst is apparently accompanied by complex formation in which the solvent participates via its heteroatom[53]. If it is presumed that the action of the catalyst is also in some way related to the formation of complexes with the reactants, then it is necessary that the copper–solvent complex should be dissociated to a fairly high extent. Indeed, in the above example of the condensation of bromobenzene with the sodium salt of *m*-resorcinol the replacement of 9% pyridine by $\alpha\alpha'$-bipyridyl, which is a more powerful ligand, reduces the yield of *m*-diphenoxybenzene from 74 to 31%. Thus the solvent plays to some extent the role of a cocatalyst[53].

In the light of these findings the promoting effect of the addition of compounds with a tertiary nitrogen atom[87,169,180,211] and the enhanced activity of the complex catalyst $(C_5H_5N)_2CuCl_2Cu(OMe)_2$ [51] become understandable. Admixtures which may be present in the solvent probably also have the same type of effect on the rate of reaction. Thus it has been shown that the reaction of bromobenzene with potassium phenoxide is faster in unpurified diglyme. After the solvent has been purified by distillation from $LiAlH_4$, the rate of reaction falls[44]. The active ingredient was isolated chromatographically; it is suggested[44] that it has the structure of the diester $CH_3OCH_2COOCH_2CH_2.OCHO$. It was observed that the addition of certain other esters, namely ethylene carbonate, the diacetate of propylene glycol, 1,2-diacetoxycyclohexane, etc. to the solvent has a similar activating effect.

The possibility of carrying out the reaction in aqueous media is not altogether clear. An example was quoted above (Table 2) where the addition of 2% of water to pyridine reduced the yield of condensation products almost threefold. Small amounts of water also inhibit the reaction between methyl 5-bromoveratrate and 4-hydroxy-3-methoxybenzoate; however, the process does not require the complete absence of water[71]:



On the other hand, a favourable effect of water on the reaction has also been noted[88,228]. For example, according to Vainshtein et al.[228], sodium *p*-bromobenzoate condensed in aqueous pyridine with potassium phenoxide to give a 90% yield of 4-carboxyphenyl phenyl ether, while in anhydrous pyridine the reaction did not occur at all:



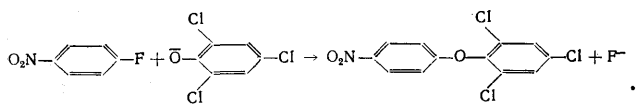
There are data concerning both unsuccessful[173,175] and successful[177] attempts at condensation in aqueous solutions. Instances are also known of its successful achievement in mixtures of organic solvents with water[172,179].

5. THE REACTIVITY OF ARYL HALIDES

As in the majority of copper-catalysed reactions of aryl halides[43,229,230], the case of substitution of halogen atoms in the Ullmann condensation decreases in the sequence I > Br > Cl ≫ F.[45,50,60,65,167,227] Thus, under standard conditions (170°C, 72 h, Cu_2O, collidine), the yields of phenyl ether in the condensation of iodo-, bromo-, and chloro-benzene with phenol were 70, 42, and 10% respectively[60].

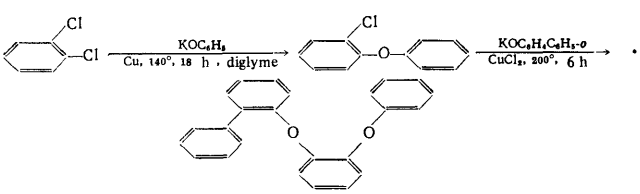
The relative rates of condensation of halogenobenzenes with potassium phenoxide in diglyme at 160°C in the presence of $CuCl_2$ have been determined[167]. For iodo-, bromo-, chloro-, and fluoro-benzenes, they are respectively 40, 40, 1, and 0.001% and more refined kinetic measurements showed that the rate for iodobenzene is approximately threefold higher than for bromobenzene.

On the other hand, there are literature data demonstrating a high reactivity of certain aryl fluorides[89,231]. For example, according to Dahlgard and Brewster[231], *p*-chloronitrobenzene and 2,4,6-trichlorophenol do not condense in an alkaline medium in the presence of a copper catalyst, but the condensation does proceed when *p*-fluoronitrobenzene is used as the halogen-containing component:

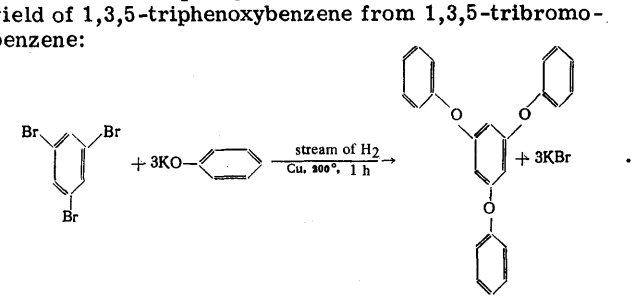


However, one cannot rule out the possibility that in this case the main role is assumed by the non-catalytic halogen-substitution reaction, which fluoro-derivatives in fact tend to undergo to the greatest extent[42,232].

The Ullmann ether condensation usually permits the introduction of several aryloxy-groups into the benzene ring[16,37,50,61,90-92,171]. In this case a stepwise substitution of halogens is possible. Thus 1,2-dichlorobenzene was condensed in succession with phenol and *o*-hydroxybiphenyl; the yield of the intermediate 2-chlorophenyl phenyl ether reached 70% and the yield of the final ether with four benzene rings, formed from the latter, was 62%:[15]

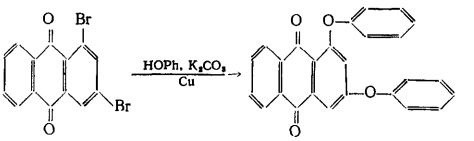


Ullmann and Sponagell[50] succeeded in obtaining a 90% yield of 1,3,5-triphenoxybenzene from 1,3,5-tribromobenzene:



However, the attempt to substitute the four bromine atoms in 1,2,3,5-tetrabromobenzene was unsuccessful. Owing to a dehalogenation side reaction, the initial tetrabromo-compound was reduced to 1,3,5-tribromobenzene and the only condensation product was 1,3,5-triphenoxybenzene (50% yield).

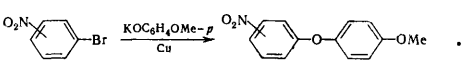
The condensations of various dihalogenoanthraquinones have been described: the yields of the diethers were 64 to 97%.[61,84] For example, 1,3-diphenoxyanthraquinone was synthesised from the corresponding dibromo-derivative by refluxing for 2 h with an excess of phenol in the presence of copper and potassium carbonate, the yield being 97%:[61]



Aryl halides containing a wide variety of substituents in the aromatic ring have been successfully employed in the Ullmann condensation. Even chemically reactive groups such as CHO,[36,85,93-95,211] OH,[15,24,37,49,67,68,78,90] and NH_2[61] do not then require special protection.

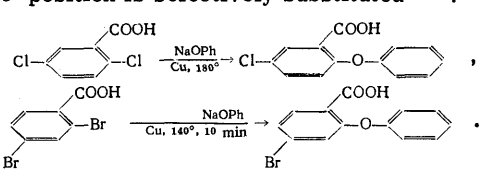
The nature and positions of the substituents have a significant influence on the reactivity of aryl halides. Highly electronegative groups in the *ortho*-position relative to the halogen have a marked activating effect on the latter. Unfortunately, the available literature data are insufficient for a comparison of the activating effects of these groups.

The nitro-group apparently has one of the most powerful activating effects. Its influence is clearly shown when it is present not only in the *ortho*- but also the *para*-position. The *meta*-nitro-group is in this respect less effective. Whereas *p*-bromonitrobenzene condensed with the potassium salt of the monomethyl ether of hydroquinone to give 4-methoxyphenyl 4-nitrophenyl ether in 80% yield, the yield of the corresponding phenyl ether from *m*-bromonitrobenzene under comparable conditions was only 31%:[96]

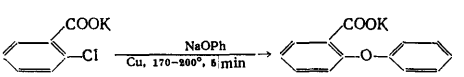


Owing to the enhanced reactivity of *o*- and *p*-halogenonitrobenzenes, the yields of their condensation products as a rule reach 80–90%.[45,64,89,93,96,197]

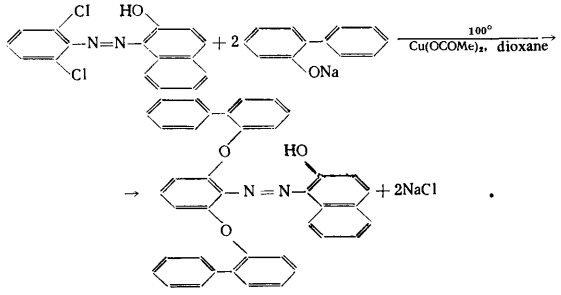
The activating effect of the carboxy-group is shown mainly when it is in the *ortho*-position with respect to the halogen. In dihalogenobenzoic acids the halogen atom in the *ortho*-position is selectively substituted[97,98]:



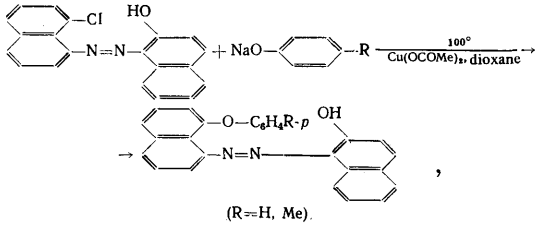
It is also instructive that in preparative syntheses the yields of *o*-aryloxybenzoic acids frequently exceed 80 to 90%.[99,100,166,197] For example, *o*-chlorobenzoic acid (in the form of a salt) condenses with sodium phenoxide on brief heating to 170–200°C in the presence of copper powder to give 90% of *o*-phenoxybenzoic acid[166]:



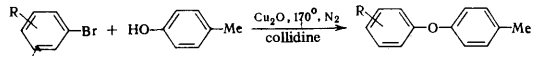
The *ortho*-halogen in azo-compounds exhibits a high reactivity [171-174,176-179]. The condensation of such compounds proceeds at comparatively low temperatures (93° to 110°C) and reaches completion in 4–16 h; the yields of the ethers are invariably high (70–100%). For example the reaction of 2,6-dichlorobenzene(1-azo-1′)-2′-naphthol with the sodium salt of 2-hydroxybiphenyl in boiling dioxan resulted in the quantitative substitution of both chlorine atoms in 4 h: [171]



The azo-group in the *peri*-position of α-chloronaphthalene has a similar effect [173]:



(R=H, Me)



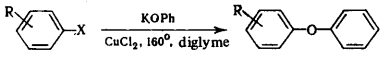
(R=o-Me, p-Me, H, p-OMe)

The presence of electron-donating substituents in the aryl halide molecule does not affect significantly the mobility of the halogen [45,53,101,167,233]. Thus the reaction of *p*-cresol with bromobenzene, *o*- and *p*-bromotoluenes, and *p*-bromoanisole in the presence of Cu_2O in collidine at 170°C in the course of 16 h gave similar yields of ethers: 43, 42, 41, and 54% respectively [45].

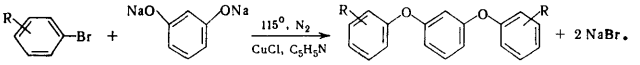
Table 3.

R(X=Cl)	H	*o*-Cl	*m*-Cl	*p*-Cl	*p*-Me	*p*-OMe
Relative rate	1.0	1.4	2.5	1.9	0.78	1.2
R(X=Br)	H	*o*-Me	*m*-Me	*p*-Me		*m*-Br
Relative rate	40	15	31	31		130

Nevertheless in the measurements of the relative rates of condensation of potassium phenoxide in diglyme at 160°C (Table 3) it was possible to observe a weak deactivating effect of the methyl group in various positions of the substituted halogenobenzene, which is typical for nucleophilic aromatic substitution. A slight activating effect of the second halogen atom, which increases in the series of isomers $o < p < m$, was also noted [167]:



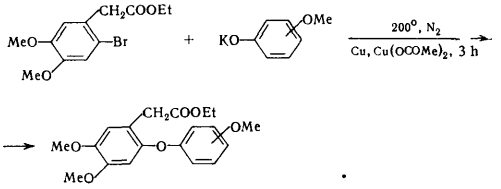
In agreement with this, Williams et al. [53] found that in the condensation of substituted bromobenzenes with the sodium salt of resorcinol the effect of substituents is in general typical for nucleophilic substitution and is described satisfactorily by the Hammett equation with the reaction constant $\rho = +1.4$:



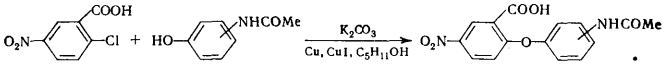
In this reaction the *p*-methoxy-group has a deactivating effect on the halogen and therefore, contrary to other data [45,167], also does not deviate from the general rule. However, one must emphasise that all these quantitative or semiquantitative determinations were made for extremely limited series of substituents.

6. THE PHENOLIC COMPONENT

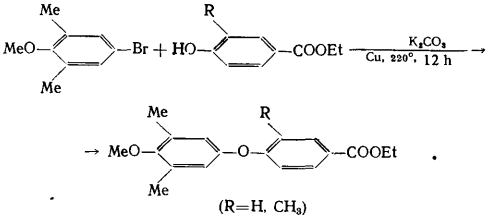
There are almost no literature data on the effect of the structure of the phenolic component on the rate of condensation. Electron-donating groups in the *ortho*-position probably reduce its reactivity. Thus potassium *o*-, *m*-, and *p*-methoxyphenoxides react under identical conditions with ethyl 2-bromo-4,5-dimethoxyphenylacetate, forming the corresponding phenyl ethers in yields of 6, 42, and 46% respectively [212]:



The reaction of *p*-*N*-acetamidophenol with 2-chloro-5-nitrobenzoic acid (boiling pentyl alcohol, potassium carbonate, copper powder, and CuI) resulted in the formation of 2-(*p*-*N*-acetamidophenoxy)-5-nitrobenzoic acid in 79% yield, while only 19% of the ether was obtained from *o*-*N*-acetamidophenol [197]:

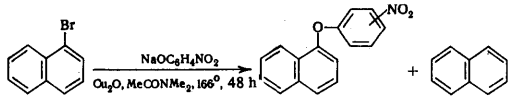


Whereas the introduction of one methyl group in the position adjoining the hydroxyl in ethyl *p*-hydroxybenzoate had only a slight effect on the yield of the product of its condensation with 4-bromo-2,6-dimethylanisole, two *ortho*-methyl-groups completely inhibited this reaction [102]:

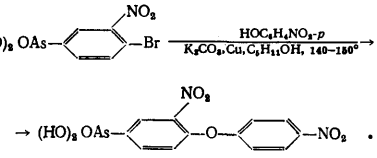


(R=H, CH_3)

Nitrophenols as a rule enter with difficulty into the Ullmann condensation. Thus potassium *p*- and *m*-nitrophenoxides condensed with α-bromonaphthalene in boiling dimethylacetamide in the presence of Cu_2O to give 9 and 38% yields of α-nitrophenoxynaphthalenes after 48 h. The *o*-nitrophenoxide did not condense but the initial bromo-derivative was reduced to naphthalene in all three cases to the extent of 9, 20, and 50% respectively[45]:



A relatively low yield of the ether was obtained also in the condensation of *p*-nitrophenol with 4-arsono-1-bromo-2-nitrobenzene: 10% against 54% for the unsubstituted phenol under the same conditions[82]:



The deactivating effect of the *p*-nitro-group was also noted by McRue et al.[22]

It is very difficult to obtain information concerning the influence of other substituents in phenol on its reactivity by comparing the available data. The differences between the reactivities of phenols based on the results of condensations with α-bromonaphthalene and 4-arsono-1-bromo-2-nitrobenzene under the conditions indicated above for the reactions with nitrophenoxides (in the condensation with α-bromonaphthalene, collidine was employed as the solvent instead of dimethylacetamide) are instructive in this respect, the yields (expressed as percentages) are indicated in brackets:

p-MeO (72) > *p*-Me (62) > *p*-Cl (49) > *o*-COOH (32) > *p*-COOH (11) ≃ ≃ *m*-NO_2 (12) ≃ *p*-NO_2 (12)[45];

o-COOH (82) > *p*-Cl (78) > *p*-COOH (60) > H (54) > *p*-Me (46) > > *o*-Me (25) > *p*-NO_2 (10)[82].

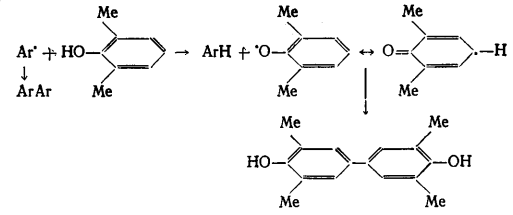
7. SIDE REACTIONS

Typical side reactions accompanying the Ullmann ether condensation are reductive dehalogenation[45,57,65,66,79,103,104,196,234,235], the Ullmann coupling process[45,86,235], and the exchange of halogens between the aryl halide and the copper salt[45].

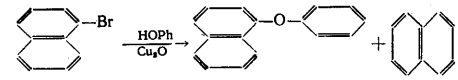
In the reduction process the phenolic component can behave as a hydrogen donor[45,235]. The importance of the side reaction probably increases when the reactivity of the phenol in the condensation is low. For example, the reaction of equimolar amounts of *o*-bromonitrobenzene with *p*-cresol in boiling collidine in the presence of Cu_2O gives a 48% yield of the ether together with 22% of nitrobenzene and 3% of *oo'*-dinitrobiphenyl as by-products. In the reaction with 2,4- and 2,6-dimethylphenols the yield of the ether falls to 0–2%, while that of nitrobenzene increases to 70–80%. At the same time bisphenols were identified in the reaction products, the yield of 4,4'-dihydroxy-3,5,3',5'-tetramethylbiphenyl reaching 20% in the latter case.

Bacon and Stewart[235] proposed the following mechanism for the formation of by-products:

$ArBr + Cu^+ \rightleftharpoons$ complex on the surface of $Cu_2O \rightleftharpoons Ar^\cdot + Cy^{2+} + Br^-$,



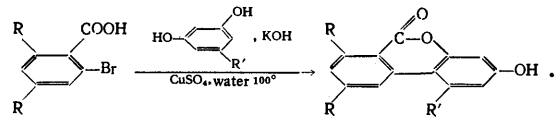
The solvent has an appreciable influence on the relative contributions of the main and side reactions. Thus, the reaction of α-bromonaphthalene with phenol in the presence of Cu_2O gives 61% of α-phenoxynaphthalene in 2,4,6-collidine, 46% in quinoline with 12% of naphthalene as a second product, while in pyridine *N*-oxide the yields are 38% of the ether and 36% of naphthalene[45]:



It is important to note that the characteristics of the structure of the aryl halide, which are responsible for its high reactivity in the Ullmann ether condensation, are probably favourable also for the side reactions.

The reactions enumerated above, occurring under the conditions of the Ullmann ether condensation as side processes, acquire independent synthetic value under special conditions[45,229,230,235,236].

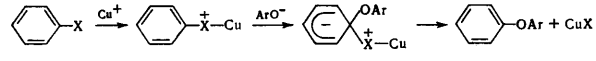
Among other side reactions, mention should be made of condensations involving the mobile hydrogen atoms in the aromatic ring of one of the reactants. An interesting illustration of the possibility of reactions of this kind is provided by the formation of the lactones of substituted 2',4'-dihydroxybiphenyl-2-carboxylic acids in an aqueous alkaline medium in the presence of $CuSO_4$:[175,237,238]



(R=OMe, R'=Me, R=R'=H)

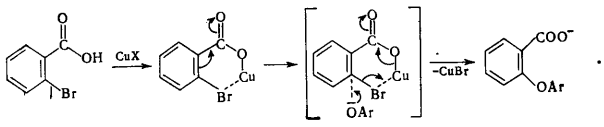
8. THE REACTION MECHANISM

In 1941 Bunnet and Zahler[42] put forward a hypothesis concerning the mechanism of the Ullmann ether condensation according to which the action of the copper catalyst reduces to the formation of a halogenonium compound and a consequent increase in the mobility of the halogen under nucleophilic attack:

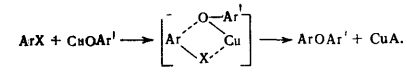


Bunnet and Zahler's mechanism had the importance of a general principle only and, owing to the lack of experimental data, could not specify the valence state of the catalytically active form of copper.

Later this hypothesis was used to account for the high activating effect of the *ortho*-carboxy-group and its almost total absence for the *para*- and *meta*-carboxy-groups[73]:

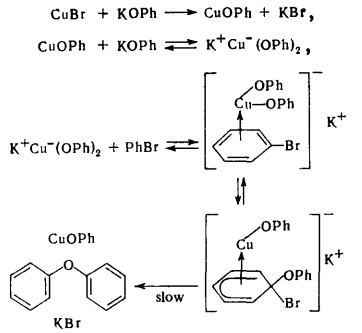


An essentially similar idea constituted the basis of the hypothesis[192] that the condensation proceeds via the usual four-centre mechanism, proposed for the exchange reactions of aryl halides with copper salts[43]:



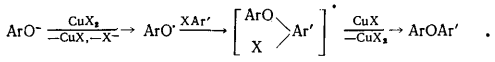
According to this hypothesis, copper(I) phenoxide is formed in the reaction. The possibility of the direct formation of ethers from aryl halides and copper phenoxides has been demonstrated experimentally[192,194].

The condensation mechanism proposed by Weingarten[44] is based on a somewhat different principle. The author begins with the following experimental findings: (1) the catalytically active form of the copper catalyst is univalent copper; (2) the effect of the nature and positions of the substituents in the aryl halide on the mobility of the halogen atom is typical for nucleophilic substitution; (3) the mobility of the halogen decreases in the series I > Br > Cl > F, which is correlated with the ease of dissociation of the carbon–halogen bond. According to Weingarten, the catalytic effect of copper is determined by its interaction (as the phenoxide) with the π electrons of the aromatic system of the aryl halide and not with the halogen atom undergoing substitution. Copper thus plays the role of, as it were, an additional electron-accepting (i.e. activating) substituent:



The main idea of this mechanism is seen to be confirmed by data demonstrating the existence of a copper(I)–benzene complex[239] and the greater ease of substitution of the halogen by the nucleophilic agent in the π-complexes of aryl halides with transition metals, such as the complex of chlorobenzene with chromium tricarbonyl[240]. The proposed mechanism is consistent with kinetic data obtained in a study of the condensation of bromobenzene with potassium phenoxide in diglyme in the presence of CuBr: the reaction is of first order with respect to the aryl halide and the copper salt and of a fractional order with respect to the phenoxide, which increases from a value close to zero at high concentrations to approximately unity at low concentrations. The reaction equation, describing satisfactorily the experimental findings and reflecting the variable order with respect to the phenoxide, may be based either on the hypothesis that at high concentrations the phenoxide is associated but only the monomeric species are reactive or on the hypothesis of a salt effect due to the phenoxide itself. The author was unable to make a choice between these two alternatives.

Kopylov[241] suggested a free-radical mechanism of the Ullmann ether condensation:



This mechanism essentially reflects the tendency to combine within the framework of a fundamentally the same mechanism oxidative polycondensation of phenols[13], oxidative substitution at the halogen in halogenophenols[13], and the Ullmann ether condensation. The validity of this attempt is doubtful and conflicts with experimental data showing that free radicals are not involved in the Ullmann reaction and that the true catalyst of this reaction is univalent and not bivalent copper. Moreover, the first two reactions can occur also under the influence of non-copper oxidants, whereas copper is a specific condensation catalyst. It is more likely that the free radicals, whose formation is indeed possible under the conditions of the Ullmann reaction, are not responsible for the main process but only for the accompanying side reactions.

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