

**Arenediazonium Tetrachlorocuprates(II). Modification of the Meerwein and Sandmeyer Reactions**

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Received 19 June 1998; accepted 12 October 1998

Abstract: In the copper-catalysed reactions of arenediazonium chlorides with unsaturated compounds arenediazonium tetrachlorocuprates(II) are formed as intermediates. A general method of preparation of these complexed diazonium salts is described. In polar solvents these salts undergo chlorinative dediazonation to give chloroarenes in high yield. The reaction of an arenediazonium tetrachlorocuprate(II) with an activated alkene results in the same products as the Meerwein reaction. A radical cation mechanism for this reaction is proposed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

The analysis of the literature on the copper-catalyzed decomposition of arenediazonium salts shows that in these reactions copper-containing complex intermediates are formed.^{1–4} Previously we found that complex arenediazonium salts with CuCl₂ are formed during the initial steps of the interaction of diazonium chlorides and unsaturated compounds using copper(II) chloride as the catalyst.⁵ In many cases we isolated them from the reaction medium and identified them as arenediazonium tetrachlorocuprates(II) (ArN≡N⁺)₂CuCl₄²⁻.

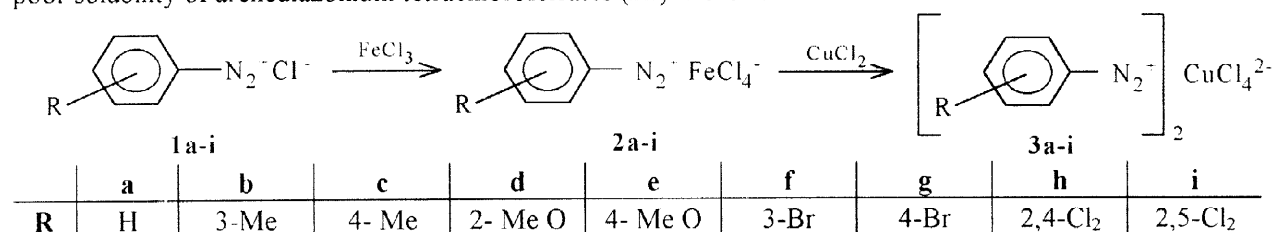
These diazonium metal double salts with diazonium cations in the outer coordination sphere are well known for many metals and are often used in the synthesis of organometallic compounds by means of the Nesmeyanov reaction.⁶

Complex cupric salts with arenediazonium chlorides have been studied by spectroscopic methods,⁷ but their synthetical potential has not been studied properly. It can be explained by the fact, that the general method of preparation of complex arenediazonium salts with cobalt, mercury, zinc, cadmium, iron, manganese chloride is based on poor solubility of these coordination salts in water when chloride ions are in excess.⁸ Arenediazonium tetrachlorocuprates(II) possess high solubility in water. At the same time the method of their preparation in non-aqueous media⁷ is not preparatively useful because the salts are formed as very unstable fine-crystalline precipitates.

1-Naphthalenediazonium tetrachlorocuprate(II) has been obtained by us from a water-alcohol medium,⁵ and for other salts the following general method of preparations was developed:

As the first step - arenediazonium tetrachloroferrates(III) **2 a-i** are obtained by the interaction of aqueous solution of diazotized aromatic amines **1 a-i** with an iron(III) chloride solution.

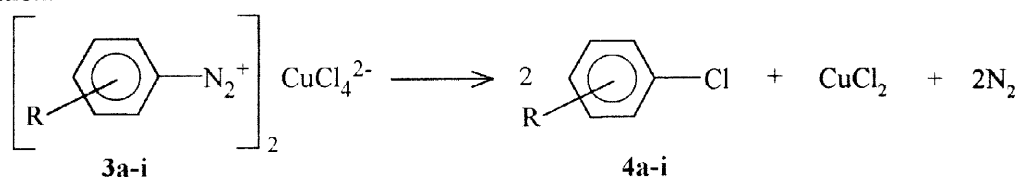
As the second step - arenediazonium tetrachlorocuprates(II) **3 a-i** are obtained by the metathesis reaction from salts **2 a-i** in acetone or in ethanol. The use of other, less polar solvents is not so effective because of the poor solubility of arenediazonium tetrachloroferrates (III) in them.



Salts **3 a-i** (table 1) are identical with the coordination intermediates isolated from the initial steps of the reaction between arenediazonium chlorides and unsaturated compounds in the presence of CuCl₂ as the catalyst.

Compounds **3a-i** are yellow crystalline substances well soluble in water, moderately soluble in polar solvents and insoluble in non-polar organic solvents.

Some dediazonation reactions of synthesized diazonium salts have been studied. It has been ascertained that these salts are stable in solid state, but in high-polar solvents (dimethylformamide, dimethylsulfoxide, water-acetone, water-acetonitrile) under mild conditions they decompose with evolution of nitrogen and chloroarene formation.⁹



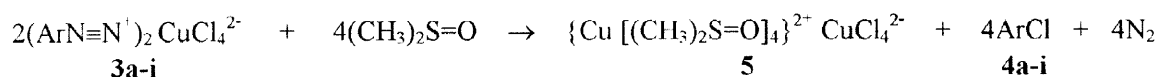
The presence of the diazonium group and redox catalyst - CuCl₂ in one molecule evidently promotes the chloro-dediazonation reaction.

Table1. Arenediazonium tetrachlorocuprates(II) **3 a-i** and chloroarenes **4 a-i**

	3			4
	Yields, %	M. p. ^a , °C	$\nu(\text{N}\equiv\text{N})$, cm ⁻¹	Yields, %
a	83	86-7	2268	92
b	88	92-3	2251	96
c	93	100-1	2244	89
d	91	121-2 ^b	2244	84
e	97	126-7	2236	94
f	84	121-2	2253	90
g	94	117-8	2246	92
h	79	109-10	2242	93
i	81	103-4	2254	97

^aDecomposition. ^bLit.⁸ 119-120 °C

The decomposition of arenediazonium tetrachlorocuprates(II) in DMSO is carried out specifically. This solvent proved to be the most suitable one. It was ascertained that CuCl₂ released in the reaction forms an insoluble complex, compound **5**, with DMSO.¹⁰ It seems probable that its formation promotes the process of arenediazonium tetrachlorocuprate(II) decomposition under mild conditions.



Chloroarenes **4a-i** are obtained by the described method in high yields, so the arenediazonium tetrachlorocuprates(II) decomposition may be considered as an effective modification of the Sandmeyer reaction.

Dediazonation of the salts **3a-i** has also been studied in the presence of activated alkenes, such as acrylic acid derivatives. It has found that methyl, ethyl, butyl acrylate, methyl methacrylate and acrylonitrile in the polar solvent reacted with complex salts **3a-i**. Chloroarylation products are obtained as a result of the reaction.¹¹

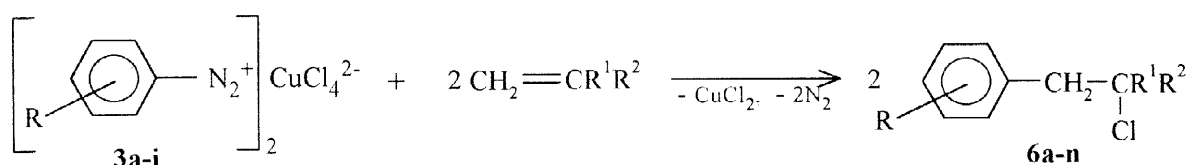


Table 2. Products of chloroarylation 6 a-n

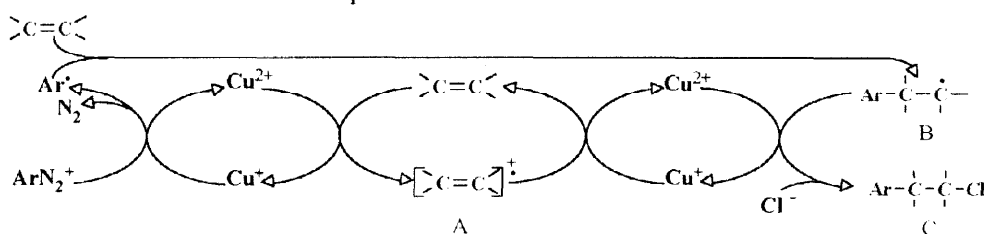
6	R	R ¹	R ²	Yields %	6	R	R ¹	R ²	Yields %
a	3-Me	H	COOMe	41	h	4-Me	Me	COOMe	59
b	4-Me	H	COOMe	56	i	4-MeO	Me	COOMe	60
c	2-MeO	H	COOMe	42	j	3-Me	H	CN	42
d	4-MeO	H	COOMe	70	k	4-Me	H	CN	72
e	2,5-Cl ₂	H	COOMe	69	l	2-MeO	H	CN	40
f	2-MeO	H	COOEt	44	m	2,5-Cl ₂	H	CN	66
g	3-Me	H	COOBu	42	n	4-Br	H	CN	61

Adducts **6a-n** were obtained with better yields than when using the traditional Meerwein reaction conditions (the use of the arenediazonium chloride aqueous solution, water-acetone medium and cupric chloride catalyst)¹²

The interaction of arenediazonium tetrachlorocuprates(II) with olefins has been studied by ESR spectroscopy using the spin trapping technique.¹³ The radicals $\text{ArCH}_2\dot{\text{C}}\text{HPh}$ and $\text{ArCH}_2\dot{\text{C}}\text{HCN}$ have been detected in mixtures of the arenediazonium tetrachlorocuprates(II) with styrene and acrylonitrile as spin adducts with nitrosodurene.¹⁴ However, aryl radicals signals are not detected under these conditions. Obviously aryl radicals react with the nearby double bond within the activated triple complex without leaving the solvent cage.^{2,3} Note that copper(II) salts in our modification of Meerwein reaction are not reduced to Cu(I) by solvents used in the reaction. At the same time reduction of CuCl_2 by acetone¹⁵ ($\text{CuCl}_2 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{COCH}_2\text{Cl} + \text{CuCl}$) plays an important role in the mechanistic description of Meerwein arylation because the resulting Cu(I) is able to generate aromatic radicals ($\text{ArN}_2^+ + \text{Cu(I)} \rightarrow \text{Ar}^\bullet + \text{Cu(II)} + \text{N}_2$)

We explain the catalytic activity of copper(II) in terms of a radical cation mechanism.^{16,17} This mechanism is confirmed by unusual direction of the Meerwein reaction in some cases, for example: when the replacement of halogen by an aryl radical occurs in the reaction of halogenostyrenes with arenediazonium salts.^{16,18,19} A radical cation in the system olefin - Cu^{2+} has been detected by UV spectroscopy.¹⁶ The above cases of partial *cis trans*-isomerization under the conditions of the reaction of non-reacted substrates - benzylideneacetone²⁰ and maleic esters,²¹ which were not interpreted before, may be explained by the rotation about the carbon-carbon double bond in the radical cation state.²²

Taking into consideration all the data we offer a general mechanism for the copper(II) catalytic dediazonation of arenediazonium salts in the presence of an alkene.



The cupric ion transfers an electron from the unsaturated substrate to the diazonium cation and the newly formed diazonium radical quickly loses nitrogen. The resulting aryl radical attacks the double bond within the active complex (arenediazonium tetrachlorocuprate^(II) - olefin or diazonium salt - catalyst - olefin²³) and yields an radical (B). It was detected by ESR spectroscopy. The formation both cation radical (A) and radical (B) as intermediates indicates that the reaction involves two catalytic cycles, in the other case radical (B) is not formed ($\text{Ar}^\bullet + [>\text{C}=\text{C}<]^{++} \rightarrow \text{Ar}-\dot{\text{C}}-\text{C}^+-$). The latter radical is oxidized by ligand transfer.^{2,24} As a result the electron transfers to the cation radical (A) obtained in the first cycle. The scheme shows that the part of the monomer is in a cation radical state (A) and the change of its geometry is possible just at this stage.²²

Acknowledgments. This work was supported, in part, by the International Soros Science Education Program (ISSEP) through grants NN **APU 053075** and **STU 050217**.

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