

## Arenediazonium Tetrachlorocuprates(II). Modified Versions of the Meerwein and Sandmeyer Reactions

N. D. Obushak, M. B. Lyakhovich, and E. E. Bilaya

Ivan Franko Lviv National University, ul. Universitetskaya 1, Lviv, 79000 Ukraine  
e-mail: obushak@pancha.lviv.ua

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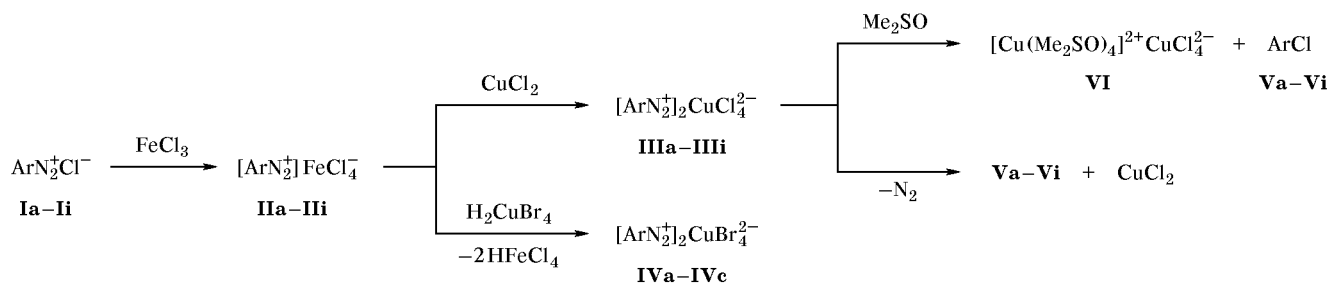
**Abstract**—Chloroarylation of unsaturated compounds with arenediazonium chlorides in the presence of  $\text{CuCl}_2$  as catalyst involves intermediate formation of arenediazonium tetrachlorocuprates(II)  $[\text{ArN}_2^+]_2 \text{CuCl}_4^{2-}$ . A procedure for preparative isolation of these intermediates was developed, and they were shown to be efficient arylating agents. Reactions of  $[\text{ArN}_2^+]_2 \text{CuCl}_4^{2-}$  with unsaturated compounds gave the corresponding Meerwein products; a mechanism was proposed for these reactions. In polar solvents arenediazonium tetrachlorocuprates(II) are converted into chloroarenes, presumably through a cyclic transition state.

Analysis of published data on decomposition of arenediazonium salts in the presence of copper(I) or copper(II) salts as catalyst shows that such reactions involve intermediate formation of copper complexes [1–6]. We previously found [6–10] that arenediazonium salts react with unsaturated compounds in the presence of copper(II) chloride to give  $\text{CuCl}_2$  complexes with arenediazonium salts as primary products. In some cases such complexes can be isolated from the reaction mixture. They were identified as arenediazonium tetrachlorocuprates(II)  $[\text{ArN}_2^+]_2 \text{CuCl}_4^{2-}$ . Structurally related binary complexes of many metals are well known; they are used in the synthesis of organometallic compounds by the Nesmeyanov reaction [11]. Binary complex salts of copper(II) and arenediazonium chlorides have been studied poorly, mainly by spectral methods [12–14]. The reason is

that the procedure for preparation of coordination compounds from arenediazonium salts and cobalt(II), mercury(II), zinc, cadmium(II), iron(III), manganese(II), and other metal chlorides takes advantage of the poor solubility of these complexes in water in the presence of excess chloride ions [14]. By contrast, arenediazonium tetrachlorocuprates(II) are readily soluble in water, and the procedure proposed in [12] for synthesizing such complexes in nonaqueous medium gives the target products as finely crystalline substances with reduced stability.

We have developed a convenient preparative method for synthesizing arenediazonium tetrachlorocuprates(II). Initially, arenediazonium chlorides **Ia–Ii** were treated with iron(III) chloride in aqueous solution to obtain arenediazonium tetrachloroferrates(III) **IIa–IIi**. The subsequent exchange reaction of **IIa–IIi**

Scheme 1.



**I–III, V, Ar** = Ph (**a**), 3-MeC<sub>6</sub>H<sub>4</sub> (**b**), 4-MeC<sub>6</sub>H<sub>4</sub> (**c**), 2-MeOC<sub>6</sub>H<sub>4</sub> (**d**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**e**), 3-BrC<sub>6</sub>H<sub>4</sub> (**f**), 4-BrC<sub>6</sub>H<sub>4</sub> (**g**), 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**h**), 2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**i**); **IV**, Ar = Ph (**a**), 4-MeC<sub>6</sub>H<sub>4</sub> (**b**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**c**).

with  $\text{CuCl}_2$  in acetone or ethanol gave arenediazonium tetrachlorocuprates(II) **IIIa–IIIi** (Scheme 1).

The use of less polar solvents is less efficient because of the lower solubility of salts **IIa–IIIi**. Crystalline compounds **IIIa–IIIi** are stable on storage; they are readily soluble in water, sparingly soluble in polar organic solvents, and insoluble in nonpolar solvents (Tables 1, 2). It should be noted that 1-naphthalenediazonium tetrachlorocuprate(II) [7] and analogous complexes of unsubstituted and substituted 4,4'-biphenylbisdiazonium salts [8] were synthesized by us previously in aqueous acetone or aqueous alcohol.

The developed procedure was also used to prepare arenediazonium tetrabromocuprates(II). The corresponding arenediazonium tetrabromoferrates(III), unlike their chlorine-containing analogs, did not separate from solutions containing excess halide ions. Compounds **IVa–IVc** were obtained by reaction of arenediazonium tetrachloroferrates(III) **IIa**, **IIc**, and **IIe** with copper(II) bromide (as anionic complex; Scheme 1). Salts **IVa–IVc** were isolated as dark green crystalline substances; their yields were considerably lower than the yields of chlorine-containing analogs **III** (Table 1). In addition, salts **IV** turned out to be less stable than **III**, which makes it difficult to use them as reagents.

Although salts **IIIa–IIIi** are stable in the crystalline state, in strongly polar media (DMF, DMSO, aqueous acetone, or aqueous acetonitrile) they decompose under mild conditions with liberation of nitrogen and formation of chloroarenes **Va–Vi** in 84–97% yield (see Experimental). Dimethyl sulfoxide appeared to be the most appropriate solvent ensuring specific decomposition of salts **IIIa–IIIi**. Copper(II) chloride released from salts **IIIa–IIIi** reacts with DMSO to form insoluble complex **VI** [15]. Its formation favors decomposition of **IIIa–IIIi** under mild conditions (Scheme 1). In such a way chloroarenes **Va–Vi** were obtained in high yields (see Experimental); thus decomposition of arenediazonium tetrachlorocuprates(II)

**Table 1.** Yields, decomposition points, and  $\nu_{\text{N}\equiv\text{N}}$  frequencies of arenediazonium tetrahalocuprates(II) **IIIa–IIIi** and **IVa–IVc**

| Compound no. | Yield, % | Decomposition point, °C | $\nu_{\text{N}\equiv\text{N}}$ , $\text{cm}^{-1}$ |
|--------------|----------|-------------------------|---|
| <b>IIIa</b>  | 83       | 86–87                   | 2268  |
| <b>IIIb</b>  | 88       | 92–93                   | 2251  |
| <b>IIIc</b>  | 93       | 100–101                 | 2244  |
| <b>III d</b> | 91       | 121–122 <sup>a</sup>    | 2244  |
| <b>IIIe</b>  | 97       | 126–127                 | 2236  |
| <b>III f</b> | 84       | 121–122                 | 2253  |
| <b>III g</b> | 94       | 117–118                 | 2246  |
| <b>III h</b> | 79       | 109–110                 | 2242  |
| <b>III i</b> | 81       | 103–104                 | 2254  |
| <b>IVa</b>   | 26       | 70–71                   | 2262  |
| <b>IVb</b>   | 58       | 75–76                   | 2240  |
| <b>IVc</b>   | 50       | 82–83                   | 2235  |

<sup>a</sup> Published data [14]: mp 119–120°C.

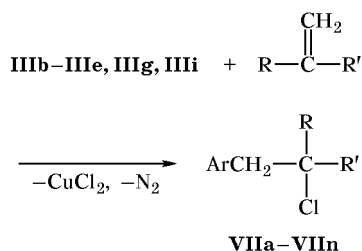
**IIIa–IIIi** can be regarded as an efficient version of the Sandmeyer reaction.

We also examined decomposition of salts **IIIa–IIIi** in the presence of unsaturated compounds, namely acrylic acid derivatives. Methyl, ethyl, and butyl acrylates, methyl methacrylate, and acrylonitrile were found to react with compounds **IIIa–IIIi** at room temperature, yielding chloroarylation products **VIIa–VII n** (Scheme 2, Table 3).

The yields of adducts **VIIa–VII n** according to Scheme 2 were higher than under usual conditions of the Meerwein reaction (aqueous solution of arenediazonium halide, aqueous acetone, catalytic amount of  $\text{CuCl}_2$ ) [16]. The properties of compounds **VIIa**, **VII g–VII i**, and **VII n** were consistent with published data [17–19]; Table 4 contains boiling points, refractive indices, and elemental analyses of newly synthesized compounds **VII b–VII f**, and **VII m**. The  $^1\text{H}$  NMR spectra of such compounds were reported previously [18, 20].

Salts **IIIa–IIIi** are identical to intermediate complexes isolated by us in the reactions of arenediazonium chlorides with unsaturated compounds, catalyzed by copper(II) halides (Meerwein reaction). ESR study of the reactions of arenediazonium tetrachlorocuprates(II) with styrene and acrylonitrile with the aid of spin traps revealed formation of aralkyl radicals  $\text{ArCH}_2\dot{\text{C}}\text{HPh}$  and  $\text{ArCH}_2\dot{\text{C}}\text{HCN}$  (as spin adducts with nitrosodurene); however, no spin adducts derived from aryl radicals were detected [21]. Obviously, aryl

**Scheme 2.**



For Ar, R, and R' in **VIIa–VII n**, see Table 2.

**Table 2.** Elemental analyses of arenediazonium tetrahalocuprates(II) **IIIa–IIIi** and **IVa–IVc**

| Comp. no.    | Found, % |      |       |       |       | Formula   | Calculated, % |      |       |       |       |
|--------------|----------|------|-------|-------|-------|---|---------------|------|-------|-------|-------|
|              | C        | H    | Cu    | Hlg   | N     |   | C             | H    | Cu    | Hlg   | N     |
| <b>IIIa</b>  | 34.94    | 2.20 | 15.38 | 33.87 | 13.16 | C <sub>12</sub> H <sub>10</sub> Cl <sub>4</sub> CuN <sub>4</sub>                | 34.68         | 2.42 | 15.29 | 34.13 | 13.48 |
| <b>IIIb</b>  | 38.25    | 3.36 | 14.44 | 31.87 | 12.35 | C <sub>14</sub> H <sub>14</sub> Cl <sub>4</sub> CuN <sub>4</sub>                | 37.90         | 3.18 | 14.32 | 31.97 | 12.63 |
| <b>IIIc</b>  | 38.07    | 3.42 | 14.52 | 32.17 | 12.41 | C <sub>14</sub> H <sub>14</sub> Cl <sub>4</sub> CuN <sub>4</sub>                | 37.90         | 3.18 | 14.32 | 31.97 | 12.63 |
| <b>III d</b> | 35.70    | 3.15 | 13.57 | 30.16 | 11.42 | C <sub>14</sub> H <sub>14</sub> Cl <sub>4</sub> CuN <sub>4</sub> O <sub>2</sub> | 35.35         | 2.96 | 13.36 | 29.82 | 11.78 |
| <b>III e</b> | 35.48    | 2.75 | 13.20 | 30.05 | 11.54 | C <sub>14</sub> H <sub>14</sub> Cl <sub>4</sub> CuN <sub>4</sub> O <sub>2</sub> | 35.35         | 2.96 | 13.36 | 29.82 | 11.78 |
| <b>III f</b> | 25.42    | 1.56 | 10.84 | 52.90 | 9.43  | C <sub>12</sub> H <sub>8</sub> Br <sub>2</sub> Cl <sub>4</sub> CuN <sub>4</sub> | 25.13         | 1.41 | 11.08 | 52.60 | 9.77  |
| <b>III g</b> | 25.18    | 1.31 | 10.92 | 52.49 | 9.70  | C <sub>12</sub> H <sub>8</sub> Br <sub>2</sub> Cl <sub>4</sub> CuN <sub>4</sub> | 25.13         | 1.41 | 11.08 | 52.60 | 9.77  |
| <b>III h</b> | 26.35    | 0.87 | 11.57 | 51.43 | 9.78  | C <sub>12</sub> H <sub>6</sub> Cl <sub>8</sub> CuN <sub>4</sub>                 | 26.05         | 1.09 | 11.48 | 51.26 | 10.12 |
| <b>III i</b> | 26.48    | 0.96 | 11.74 | 51.56 | 9.90  | C <sub>12</sub> H <sub>6</sub> Cl <sub>8</sub> CuN <sub>4</sub>                 | 26.05         | 1.09 | 11.48 | 51.26 | 10.12 |
| <b>IV a</b>  | 24.18    | 1.81 | 10.60 | 53.65 | 9.35  | C <sub>12</sub> H <sub>10</sub> Br <sub>4</sub> CuN <sub>4</sub>                | 24.29         | 1.70 | 10.71 | 53.86 | 9.44  |
| <b>IV b</b>  | 26.91    | 2.38 | 10.37 | 51.57 | 8.89  | C <sub>14</sub> H <sub>14</sub> Br <sub>4</sub> CuN <sub>4</sub>                | 27.05         | 2.27 | 10.22 | 51.43 | 9.01  |
| <b>IV c</b>  | 26.03    | 2.20 | 9.66  | 49.28 | 8.68  | C <sub>14</sub> H <sub>14</sub> Br <sub>4</sub> CuN <sub>4</sub> O <sub>2</sub> | 25.73         | 2.16 | 9.72  | 48.91 | 8.57  |

radical reacts with the double bond inside the activated triple complex without leaving the solvent cage [2, 3]. Copper(II) salt was also used by us in a modified version of the Meerwein reaction in DMF and DMSO. These solvents are incapable of reducing copper(II) to copper(I). On the other hand, the possibility for the reaction  $\text{CuCl}_2 + \text{Me}_2\text{CO} \rightarrow \text{CuCl} + \text{MeC(O)CH}_2\text{Cl}$  to occur in acetone was important while interpreting the Meerwein reaction mechanism [2, 16, 22], taking into account that just copper(I) ions

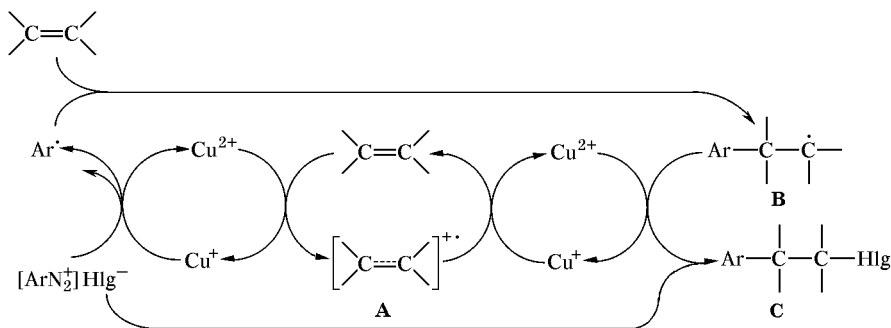
**Table 3.** Yields of alkyl 3-aryl-2-chloropropionates **VIIa–VIIi** and 3-aryl-2-chloropropionitriles **VIIj–VII n**

| Comp. no.    | Ar  | R  | R'                 | Yield, % |
|--------------|---|----|--------------------|----------|
| <b>VII a</b> | 3-MeC <sub>6</sub> H <sub>4</sub>                 | H  | CO <sub>2</sub> Me | 41       |
| <b>VII b</b> | 4-MeC <sub>6</sub> H <sub>4</sub>                 | H  | CO <sub>2</sub> Me | 56       |
| <b>VII c</b> | 2-MeOC <sub>6</sub> H <sub>4</sub>                | H  | CO <sub>2</sub> Me | 42       |
| <b>VII d</b> | 4-MeOC <sub>6</sub> H <sub>4</sub>                | H  | CO <sub>2</sub> Me | 70       |
| <b>VII e</b> | 2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | H  | CO <sub>2</sub> Me | 69       |
| <b>VII f</b> | 2-MeOC <sub>6</sub> H <sub>4</sub>                | H  | CO <sub>2</sub> Et | 44       |
| <b>VII g</b> | 3-MeC <sub>6</sub> H <sub>4</sub>                 | H  | CO <sub>2</sub> Bu | 42       |
| <b>VII h</b> | 4-MeC <sub>6</sub> H <sub>4</sub>                 | Me | CO <sub>2</sub> Me | 59       |
| <b>VII i</b> | 4-MeOC <sub>6</sub> H <sub>4</sub>                | Me | CO <sub>2</sub> Me | 60       |
| <b>VII j</b> | 3-MeC <sub>6</sub> H <sub>4</sub>                 | H  | CN                 | 42       |
| <b>VII k</b> | 4-MeC <sub>6</sub> H <sub>4</sub>                 | H  | CN                 | 72       |
| <b>VII l</b> | 2-MeOC <sub>6</sub> H <sub>4</sub>                | H  | CN                 | 40       |
| <b>VII m</b> | 2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | H  | CN                 | 66       |
| <b>VII n</b> | 4-BrC <sub>6</sub> H <sub>4</sub>                 | H  | CN                 | 61       |

could generate aryl radicals by the reaction  $\text{ArN}_2^+ + \text{Cu}^+ \rightarrow \text{Ar}^\cdot + \text{N}_2 + \text{Cu}^{2+}$ .

We believe that the catalytic activity of copper(II) can be interpreted in terms of a radical ion mechanism [10, 23–25]. It is supported by unusual pathways of the Meerwein reactions, e.g., replacement of the halogen atom in halostyrenes by aryl group [25–27]. Radical cations were detected by UV spectroscopy in the system  $\text{>C=C<} + \text{Cu}^{2+}$  [25]. Thus, previously described examples of partial *cis*–*trans* isomerization of unreacted substrates, such as benzylideneacetone [28] and maleic acid esters [29], may be explained by rotation about the double bond in the corresponding radical cation. *cis*–*trans* Isomerizations due to loosening of the double bond in radical cations have been well documented [30], and they can be regarded as a criterion of radical ion mechanism [31]. With the above in mind, Scheme 3 shows a possible general mechanism of decomposition of arenediazonium salts in the presence of unsaturated compounds, catalyzed by Cu(II) halides. The catalytic system  $\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$  mediates electron transfer from olefin to diazonium ion. The aryl radical thus formed reacts with the double bond without leaving the activated complex [arenediazonium tetrachlorocuprate(II)–olefin or arenediazonium salt–catalyst–olefin] to give aryl-substituted alkyl radical **B**; just the latter is detected by the ESR method [21]. Electron transfer from radical **B** through copper(II) ion to radical cation **A** (formed in the first cycle) results in formation of product **C**. According to Scheme 3, some olefin molecules exist as the corresponding radical cations which are capable of changing their configuration.

Scheme 3.



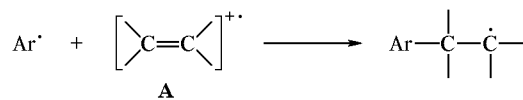
Hlg = Cl, Br.

A question arises so as to whether our results and the proposed reaction mechanism are consistent with the data of [1, 2, 22, 32–34] where the catalytic activity of copper(I) chloride was substantiated. In most of these publications copper(I) salts *in statu nascendi* were noted to better catalyze the reaction; in other words, copper(I) ions generated *in situ* are more effective than those added to the reaction mixture. Here, one should keep in mind that most copper(I) salts in aqueous solution give rise to a very low concentration of  $\text{Cu}^+$  ions, for the latter undergo fast oxidation to  $\text{Cu}^{2+}$  ( $K = [\text{Cu}^{2+}]/[\text{Cu}^+] \approx 10^6$ ) [35]. Primarily, this concerns anionarylation of unsaturated compounds [16, 33], catalyzed by copper salts other than copper chlorides. Copper(I) chloride is stable in water; moreover, the solubility of  $\text{CuCl}$  in acid solutions of arenediazonium chlorides (excess  $\text{HCl}$ ) increases due to formation of the complex ion  $[\text{CuCl}_2]^-$  [36]. On the other hand,  $\text{CuCl}$  undergoes oxidation to  $\text{CuCl}_2$  in  $\text{HCl}$ -containing media:  $2\text{CuCl} + 1/2\text{O}_2 + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O}$  [37].

Copper(II) salts in aqueous solution form hexaaqua ions  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  in which water molecules can readily be replaced by other ligands [35]. As a rule, no more than four water molecules are replaced (inner coordination sphere). In particular, addition of  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{LiCl}$ , or  $\text{LiBr}$  to an aqueous solution of copper(II) salt leads to formation of halide complexes where redox interaction between copper(II) and halide ions is possible. Provided that the other ligands, such as acetone or olefins, are present, this interaction is accompanied by halogenation of the organic ligand [38, 39]. Presumably, ligand exchange and their interactions play an important role in the chloroarylation process [2, 33].

Thus the catalytic activity of copper(I) and copper(II) salts in the Meerwein reaction can be explained in terms of two  $\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$  catalytic cycles and

formation of mixed-ligand complex ion. Both catalytic species participate in one-electron transfer process (Scheme 3):  $\text{Cu(II)}$  oxidizes the substrate molecule, while  $\text{Cu(I)}$  reduces diazonium ion. The formation of radical cations **A** and radicals **B** indicates that two catalytic cycles are operative, otherwise the formation of radical **B** cannot be explained. In this case, the following process would occur:



Salts **IIIa–IIIi** turned out to be effective arylating agents. This fact indirectly supports the active role of tetrachlorocuprate ions in the chloroarylation, in keeping with published data. According to [38, 40],  $\text{CuCl}_4^{2-}$  ion is more active than other copper(II) species in reactions involving electron transfer. For example, reactions of alkyl radicals with ligand transfer (inner-sphere oxidation) in the presence of tetrachlorocuprate ions are faster by an order of magnitude than the same reactions catalyzed by  $\text{Cu}^{2+}$  [40, 41]. Aryl-substituted alkyl radicals **B** (Scheme 3) are likely to react with  $\text{CuCl}_4^{2-}$  more effectively in the final stage. Olefins containing electron-acceptor groups at the double bond are known to be more reactive in the Meerwein reactions. Radicals derived from such olefins are oxidized with ligand transfer, following the inner-sphere mechanism [40, 42]. Presumably, adduct **C** is formed by oxidation of radical **B** with ligand transfer. An alternative path, outer-sphere oxidation with electron transfer and formation of carbocation, is less probable. The same also applies to other catalytic addition processes [43], in particular to those catalyzed by metal complexes and involving ligand exchange [44]. In reactions of arenediazonium

**Table 4.** Boiling points, refractive indices, and elemental analyses of compounds **VIIb–VIIf** and **VIIIm**

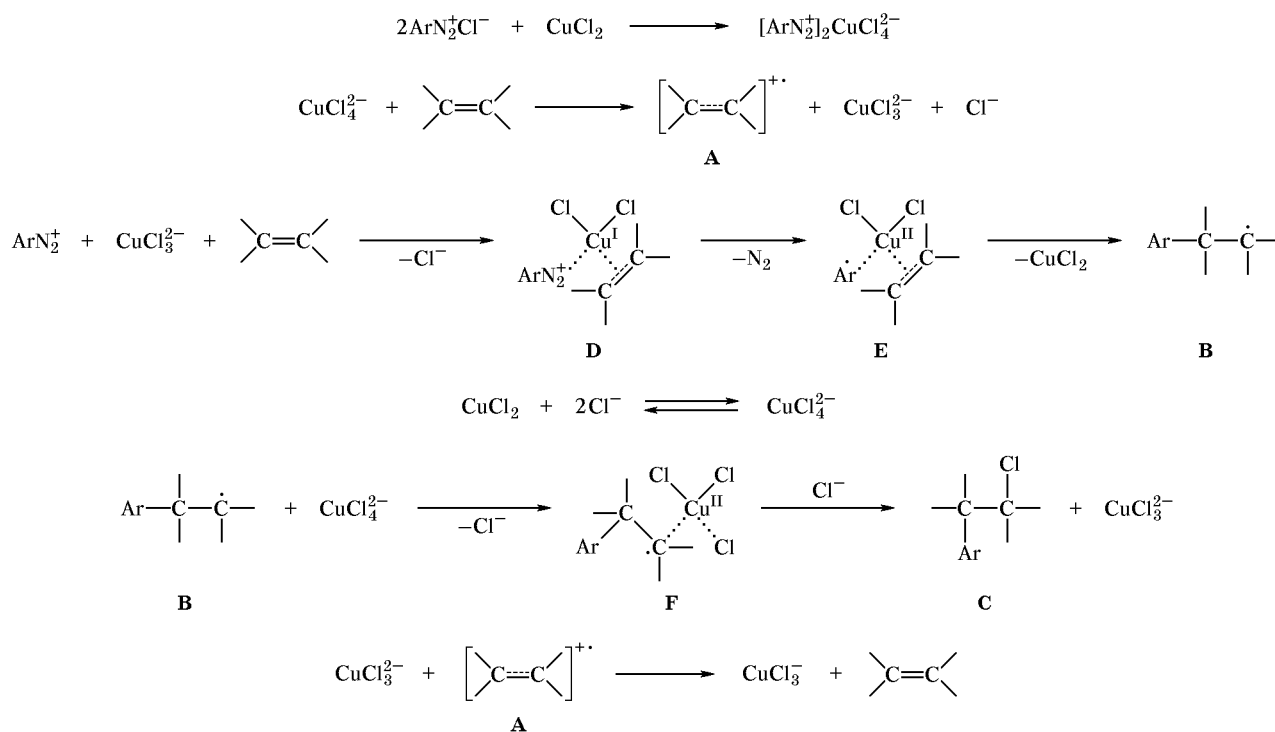
| Comp. no.    | bp, °C (2 mm) | $n_D^{20}$ | Found, % |      | Formula   | Calculated, % |      |
|--------------|---------------|------------|----------|------|---|---------------|------|
|              |               |            | C        | H    |   | C             | H    |
| <b>VIIb</b>  | 109–110       | 1.5234     | 61.93    | 6.22 | C <sub>11</sub> H <sub>13</sub> ClO <sub>2</sub>              | 62.12         | 6.16 |
| <b>VIIc</b>  | 117–118       | 1.5259     | 57.79    | 5.62 | C <sub>11</sub> H <sub>13</sub> ClO <sub>3</sub>              | 57.77         | 5.73 |
| <b>VIIId</b> | 117–118       | 1.5254     | 57.53    | 5.90 | C <sub>11</sub> H <sub>13</sub> ClO <sub>3</sub>              | 57.77         | 5.73 |
| <b>VIIe</b>  | 127–128       | 1.5490     | 45.03    | 3.50 | C <sub>10</sub> H <sub>9</sub> Cl <sub>3</sub> O <sub>2</sub> | 44.89         | 3.39 |
| <b>VIIIf</b> | 124–125       | 1.5239     | 59.17    | 6.12 | C <sub>12</sub> H <sub>15</sub> ClO <sub>3</sub>              | 59.38         | 6.23 |
| <b>VIIIm</b> | 114–116       | 1.5650     | 45.90    | 2.61 | C <sub>9</sub> H <sub>6</sub> Cl <sub>3</sub> N               | 46.09         | 2.58 |

salts with styrene derivatives radicals **B** can be oxidized, which is consistent with the data of [45]. The resulting carbocation reacts with external nucleophile or eliminates a proton [46].

Taking into account the above stated, we propose a mechanism of chloroarylation shown in Scheme 4. In the first catalytic cycle tetrachlorocuprate(II) ion mediates electron transfer from the olefin to diazonium ion, yielding intermediate **E**. The formation of such radical complex (ArSO<sub>2</sub> and CuX<sup>n+</sup>, n = 0, 1) was discussed in [47]. This is strongly supported by the absence of aryl radicals (according to the ESR data [21]) and their dimerization products, the corresponding biaryls. However, in some cases the latter

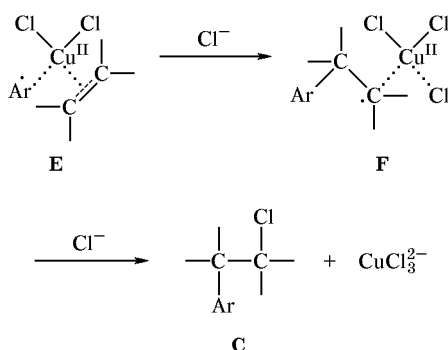
are formed in small amounts [32]. It should be noted that under analogous conditions, which exclude formation of intermediates like **E**, biaryls are among the major products. Here, intermediates are aryl-copper(I) and diarylcopper(II) [48]. Some reagents capable of generating aryl radicals but incapable of forming complexes were ineffective in the reaction under study [49, 50].

Intermediates **D** and **E** are  $\pi$ -complexes of the olefin with copper ion [2, 3, 50, 51]. It is interesting that we succeeded in effecting cyanoarylation only with 1,3-dienes [52]. Copper(I) cyanide does not form  $\pi$ -complexes [51, 53], but in reactions with dienes oxidation of aryl-substituted alkyl radical **B** is possible

**Scheme 4.**

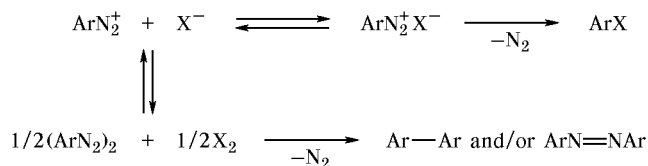
due to electron transfer (rather than due to ligand transfer alone,  $\mathbf{F} \rightarrow \mathbf{C}$ ) [54], which favors cyanoarylation process.

The transformation  $\mathbf{E} \rightarrow \mathbf{F}$  can occur both with liberation of radical  $\mathbf{B}$  and inside the complex. Taking into account that radical  $\mathbf{B}$  was detected by ESR spectroscopy, Scheme 4 shows the first version. However, if elimination of radical  $\mathbf{B}$  from the activated complex is not the main reaction path, the second catalytic cycle should follow a cryptoradical mechanism:



Active intermediate complexes containing different ligands can react with each other [55], especially if these complexes are labile. Apart from the above factors, successful Meerwein reactions under conditions allowing formation of other products are favored by the unique (but not exclusive) role of copper(I) and copper(II) halides which readily undergo redox processes and catalyze not only addition process but also decomposition of diazonium salts. The mechanism of decomposition of salts **IIIa–IIIi** attracts interest. This reaction results in almost quantitative formation of chloroarenes **Va–Vi**, and it can be regarded as a version of the Sandmeyer reaction, although there is a strong difference: The Sandmeyer reaction is catalyzed by copper(I) salts, whereas decomposition of salts **IIIa–IIIi** (which is fast and efficient in various polar solvents) occurs in the presence of copper(II) ions. It should be noted that no free radical species were detected in this reaction by ESR [21]. Taking into account mild reaction condi-

tions and weak effect of substituent in the aromatic ring,  $S_N1$  mechanism of replacement of diazo group by chlorine also seems to be hardly probable. Bagal *et al.* [56] proposed a mechanism of nucleophilic substitution of diazo group, which does not involve one-electron transfer stage. The reaction of diazonium ion with base ( $X^-$ ) is treated as a cycle involving two covalent products,  $ArN_2X$  and  $(ArN_2)_2$  [56]:



Here,  $ArN_2X$  is an intermediate in the nucleophilic substitution process, and  $(ArN_2)_2$  is the main source of aryl radicals. The equilibrium shifts toward formation of one of the above covalent products, depending on their acid–base and redox properties [56]. Copper(II) salts shift the equilibrium toward formation of  $ArN_2X$  via complex formation with the latter, thus reducing the probability of radical decomposition. Salts **IIa–IIIi** can form complexes with two diazonium species (Scheme 5). Stabilization of labile *syn*-diazo compounds through formation of cyclic complexes was reported previously [1, 57]. This mechanism should be favored by polar solvents, as was observed experimentally.

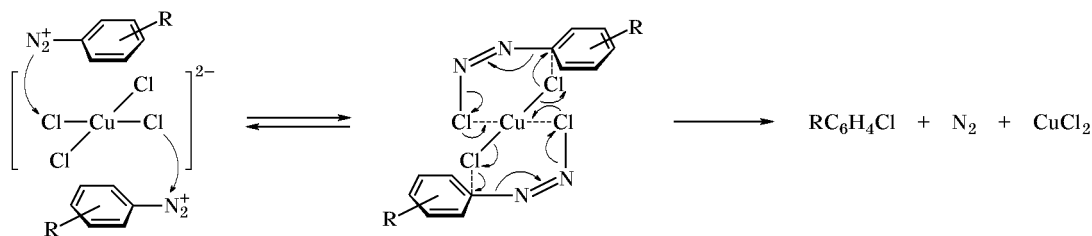
## EXPERIMENTAL

The IR spectra of **IIIa–IIIi** were recorded on a Specord 75IR instrument in mineral oil.

**Arenediazonium tetrachlorocuprates IIIa–IIIi.** Arenediazonium chlorides **Ia–Ii** were obtained by diazotization of 0.1 mol of the corresponding amines, following a standard procedure ( $HCl$ ,  $NaNO_2$ ). A solution of 81.1 g of  $FeCl_3 \cdot 6H_2O$  in a minimal amount of water was added to a solution of diazonium salt **Ia–Ii** in water at  $-5^\circ C$ .

a. Concentrated hydrochloric acid was added dropwise with stirring at  $0-5^\circ C$  to a solution of **IIa–IIIi**

Scheme 5.



(see above). Salts **IIIa–IIIi** quantitatively precipitated from the solution.

*b.* A solution of 5.6 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 75 ml of ethanol and 5 ml of concentrated hydrochloric acid was added at 0°C to a solution of 65 mmol of salt **IIa–IIIi** in 100 ml of acetone. The precipitate of salt **IIIa–IIIi** was filtered off, washed with diethyl ether, and dried in air. An additional amount of **IIIa–IIIi** was precipitated from the filtrate by adding 150 ml of diethyl ether.

**Arenediazonium tetrabromocuprates(II) IVa–IVc.** A solution of 1.1 g of copper(II) bromide in 5 ml of ethanol and 2.5 ml of hydrobromic acid was added at 0°C to a solution of 10 mmol of arenediazonium tetrachloroferrate(III) **IIa**, **IIc**, or **Iie** in 10 ml of acetone. The precipitate of salt **IVa–IVc** was filtered off, washed with diethyl ether, and dried in air. An additional amount of salt **IVa–IVc** was isolated from the filtrate by precipitating with diethyl ether (10 ml).

**Decomposition of arenediazonium tetrachlorocuprates(II) IIIa–IIIi.** Salt **IIIa–IIIi**, 25 mmol, was gradually added in portions to 50 ml of appropriate solvent (DMSO, DMF, aqueous acetone, or aqueous acetonitrile) while stirring at room temperature. A vigorous reaction occurred with evolution of nitrogen. When DMSO was used as solvent, solvate complex of copper(II) chloride with DMSO [15] was formed. The precipitate of product **VI** was filtered off, the filtrate was diluted with 50 ml of water and extracted with diethyl ether, the extract was dried over  $\text{MgSO}_4$ , the solvent was removed, and the residue was distilled under reduced pressure. Below are given product number and yield, %: **Va**, 92; **Vb**, 96; **Vc**, 89; **Vd**, 84; **Ve**, 94; **Vf**, 90; **Vg**, 92; **Vh**, 93; **Vi**, 97.

**Reactions of arenediazonium tetrachlorocuprates(II) IIIa–IIIi with unsaturated compounds.** Salt **IIIa–IIIi**, 40 mmol, was added in portions over a period of 1 h to a mixture of 0.1 mol of unsaturated compound, 40 ml of acetone, and 40 ml of water, while stirring at 20–25°C. The mixture was kept until nitrogen no longer evolved (~2.5 h), diluted with 100 ml of water, and extracted with diethyl ether. The extract was dried over  $\text{MgSO}_4$  and evaporated, and the residue was distilled under reduced pressure to isolate compounds **VIIa–VIIh**.

## REFERENCES

1. Saunders, K.H. and Allen, R.L.M., *Aromatic Diazo Compounds*, London: Edward Arnold, 1985, pp. 594–612, 734–744.
2. Ganushchak, N.I., Golik, V.D., and Migaichuk, I.V., *Zh. Org. Khim.*, 1972, vol. 8, no. 11, pp. 2356–2361.
3. Ganushchak, N.I., Obushak, N.D., Koval'chuk, E.P., and Trifonova, G.V., *Zh. Obshch. Khim.*, 1984, vol. 54, no. 10, pp. 2334–2337.
4. Pfeil, E., *Angew. Chem.*, 1953, vol. 65, no. 1, pp. 155–158.
5. Galli, K., *Chem. Rev.*, 1988, vol. 88, no. 5, pp. 765–792.
6. Obushak, N.D., *Doctoral (Chem.) Dissertation*, Lviv, 1999.
7. Obushak, N.D., Ganushchak, N.I., and Lyakhovich, M.B., *Zh. Org. Khim.*, 1991, vol. 27, no. 8, pp. 1757–1762.
8. Obushak, N.D., Lyakhovich, M.B., Fedorovich, I.S., and Ganushchak, N.I., *Russ. J. Org. Chem.*, 1996, vol. 32, no. 10, pp. 1471–1476.
9. Obushak, N.D., Lyakhovich, M.B., Fedorovich, I.S., and Ganushchak, N.I., *Russ. J. Org. Chem.*, 1997, vol. 33, no. 3, pp. 345–347.
10. Obushak, M.D., Lyakhovich, M.B., and Ganushchak, M.I., *Tetrahedron Lett.*, 1998, no. 39, pp. 9567–9570.
11. Nesmeyanov, A.N., *Ber.*, 1929, vol. 62, no. 7, pp. 1010–1018; Belov, B.I. and Kozlov, V.V., *Usp. Khim.*, 1963, vol. 32, no. 2, pp. 121–153.
12. Kazitsyna, L.A., Reutov, O.A., and Buchkovskii, Z.F., *Zh. Obshch. Khim.*, 1961, vol. 31, no. 9, pp. 2943–2950.
13. Kazitsyna, L.A., Kupletskaya, N.B., Ptitsyna, V.A., and Reutov, O.A., *Zh. Obshch. Khim.*, 1963, vol. 33, no. 10, pp. 3243–3248.
14. Kazitsyna, L.A., Reutov, O.A., and Kikot', B.S., *Zh. Obshch. Khim.*, 1961, vol. 31, no. 9, pp. 2950–2957.
15. Meek, D.W., Straub, D.K., and Drago, R.S., *J. Am. Chem. Soc.*, 1960, vol. 82, no. 23, pp. 6013–6016.
16. Rondstedt, C.S., *Org. React.*, 1976, vol. 24, pp. 225–259.
17. *Beilsteins Handbuch der organischen Chemie*, EIII, vol. 9, p. 2480; *ibid.*, EIII, vol. 10, p. 535; *ibid.*, EIV, vol. 9, pp. 1770–1772; *ibid.*, EIV, vol. 10, p. 702.
18. Obushak, N.D., Matiichuk, V.S., and Ganushchak, N.I., *Russ. J. Org. Chem.*, 1998, vol. 34, no. 2, pp. 239–244.
19. Dickerman, S.C., de Souza, D.J., Fryd, M., Megna, I., and Skoultchi, M.M., *J. Org. Chem.*, 1969, vol. 34, no. 3, pp. 714–719.
20. Obushak, N.D., Ganushchak, N.I., Lesyuk, A.I., Pil'ov, S.G., Demchuk, O.M., and Mazyar, L.P., *Russ. J. Org. Chem.*, 1997, vol. 33, no. 4, pp. 432–435;

- Ganushchak, N.I., Obushak, N.D., and Polishchuk, O.P., *Zh. Org. Khim.*, 1986, vol. 22, no. 12, pp. 2554–2558.
21. Lyakhovich, M.B., Gasanov, R.G., Obushak, N.D., Ganushchak, N.I., and Todres, Z.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, no. 5, pp. 1214–1216.
  22. Kochi, J.K., *J. Am. Chem. Soc.*, 1955, vol. 77, no. 10, pp. 5090–5092.
  23. Obushak, N.D., Lyakhovich, M.B., and Ganushchak, N.I., *Zh. Org. Khim.*, 1993, vol. 29, no. 4, pp. 731–734.
  24. Bila, E.E., Obushak, M.D., and Ganushchak, M.I., *Pol. J. Chem.*, 2000, vol. 74, no. 11, pp. 1567–1573.
  25. Obushak, N.D., Bilaya, E.E., and Ganushchak, N.I., *Zh. Org. Khim.*, 1991, vol. 27, no. 11, pp. 2372–2376; Bilaya, E.E., Obushak, N.D., and Ganushchak, N.I., *Vestn. L'vovsk. Univ., Ser. Khim.*, 1989, no. 30, pp. 74–78; *Ref. Zh., Khim.*, 1989, no. 21 Zh 230.
  26. Obushak, N.D., Lyakhovich, M.B., Ganushchak, N.I., and Bilaya, E.E., *Zh. Org. Khim.*, 1983, vol. 19, no. 7, p. 1545.
  27. Obushak, N.D., Ganushchak, N.I., and Bilaya, E.E., *Zh. Org. Khim.*, 1989, vol. 25, no. 11, pp. 2459–2460.
  28. Allard, M. and Levisalles, J., *Bull. Soc. Chim. Fr.*, 1972, no. 5, pp. 1921–1925.
  29. Isaev, S.D., Yurchenko, A.G., Chernova, Yu.S., and Mramornova, S.A., *Zh. Org. Khim.*, 1972, vol. 8, no. 10, pp. 2054–2057.
  30. Lewis, F.D., Petiske, J.R., Oxman, J.D., and Nepras, M.J., *J. Am. Chem. Soc.*, 1985, vol. 107, no. 1, pp. 203–207; Mlcoch, J. and Steckhan, E., *Angew. Chem.*, 1985, vol. 97, no. 5, pp. 429–431; Bellville, D.J. and Bauld, N.L., *J. Am. Chem. Soc.*, 1982, vol. 104, no. 1, pp. 294–295; Todres, Z.V., *Zh. Fiz. Khim.*, 1980, vol. 54, no. 5, pp. 1097–1110.
  31. Todres, Z.V., *Ion-radikaly v organicheskom sinteze* (Radical Ions in Organic Synthesis), Moscow: Khimiya, 1986.
  32. Rondstvedt, C.S., *Organic Reactions*, Cope, A.C., Ed., New York: Wiley, 1960, vol. 11. Translated under the title *Organicheskie reaktsii*, Moscow: Mir, 1965, vol. 11, pp. 199–266.
  33. Dombrovskii, A.V., *Usp. Khim.*, 1984, vol. 53, no. 10, pp. 1625–1647.
  34. Kochi, J.K., *J. Am. Chem. Soc.*, 1955, vol. 77, no. 10, pp. 5090–5092; Kochi, J.K., *J. Am. Chem. Soc.*, 1957, vol. 79, no. 11, pp. 2942–2948.
  35. Cotton, F.A. and Wilkinson, G., *Advanced Inorganic Chemistry. A Comprehensive Text*, New York: Wiley, 1966, 2nd ed.
  36. Keefer, R.M., Andrews, L.J., and Kepner, R.E., *J. Am. Chem. Soc.*, 1949, vol. 71, no. 11, pp. 3906–3909.
  37. Candlin, J.P., Taylor, K.A., and Thompson, D.T., *Reactions of Transition-Metal Complexes*, Amsterdam: Elsevier, 1968; Volkova, L.G., Levitin, I.Ya., and Vol'pin, M.E., *Usp. Khim.*, 1975, vol. 44, no. 7, pp. 1217–1235.
  38. Becker, H.G.O. and Israel, G., *Z. Phys. Chem.*, 1975, vol. 256, no. 3, pp. 436–452.
  39. Ondrejovic, G., Čislovova, J., and Gažo, J., *Chem. Zvesti*, 1966, vol. 20, no. 10, pp. 729–737.
  40. Jenkins, C.L., and Kochi, J.K., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 3, pp. 856–865.
  41. Jenkins, C.L. and Kochi, J.K., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 3, pp. 843–855.
  42. Jenkins, C.L. and Kochi, J.K., *J. Org. Chem.*, 1971, vol. 36, no. 21, pp. 3103–3111.
  43. Zvezdin, V.L., Domrachev, G.A., Sangalov, Yu.A., and Semchikov, Yu.D., *Dokl. Akad. Nauk SSSR*, 1971, vol. 198, no. 1, pp. 102–105; Tanaskov, M.M. and Stadnichuk, M.D., *Zh. Obshch. Khim.*, 1978, vol. 48, no. 5, pp. 1140–1146.
  44. Zubritskii, L.M., Fomina, T.N., and Bal'yan, Kh.V., *Zh. Org. Khim.*, 1982, vol. 18, no. 7, pp. 1391–1401; Zubritskii, L.M., Romashchenkova, N.D., and Petrov, A.A., *Zh. Org. Khim.*, 1983, vol. 19, no. 12, pp. 2465–2477; Masters, C., *Homogeneous Catalysis by Metal Complexes*, Taqui Khan, M.M. and Martell, A.E., Eds., New York: Academic, 1974.
  45. Kochi, J.K. and Bemis, A., *J. Am. Chem. Soc.*, 1968, vol. 90, no. 15, pp. 4038–4051.
  46. Obushak, N.D., Buchinskii, A.M., Bilaya, E.E., and Ganushchak, N.I., *Russ. J. Gen. Chem.*, 1997, vol. 67, no. 8, p. 1317; Bilaya, E.E., Obushak, N.D., and Ganushchak, N.I., *Russ. J. Org. Chem.*, 1999, vol. 35, no. 4, pp. 632–633.
  47. Tanaskov, M.M. and Stadnichuk, M.D., *Zh. Obshch. Khim.*, 1978, vol. 48, no. 5, pp. 1140–1146.
  48. Cohen, T., Lewarchik, R.J., and Tarino, J.Z., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 25, pp. 7753–7760.
  49. Vogl, O. and Rondstvedt, C.S., *J. Am. Chem. Soc.*, 1955, vol. 77, no. 11, pp. 3067–3069.
  50. Ganushchak, N.I., Obushak, N.D., Koval'chuk, E.P., and Fedorov, B.S., *Ukr. Khim. Zh.*, 1985, vol. 51, no. 10, pp. 1081–1083.
  51. Herberhold, M., *Metal  $\pi$ -Complexes*, Amsterdam: Elsevier, 1972.
  52. Obushak, N.D., Ganushchak, N.I., and Matii-chuk, V.S., *Russ. J. Org. Chem.*, 1996, vol. 32, no. 5, p. 766.



53. Schrauzer, G.N., *Chem. Ber.*, 1961, vol. 94, no. 7, pp. 1891–1898.
54. Nonhebel, D., Tedder, J., and Walton, J., *Radicals*, Cambridge: Cambridge Univ., 1979.
55. Vorob'eva, T.P., Kachanova, Zh.P., Berdnikov, V.M., and Purmal', A.P., *Kompleksoobrazovanie v katalize. Seriya Problemy kinetiki i kataliza* (Complex Formation in Catalysis. Problems of Kinetics and Catalysis Series), Moscow: Nauka, 1968, p. 109; Lipatova, T.E. and Nizel'skii, Yu.N., *Dokl. Akad. Nauk SSSR*, 1967, vol. 175, no. 1, pp. 128–131; Lipatova, T.E. and Nizel'skii, Yu.N., *Dokl. Akad. Nauk SSSR*, 1970, vol. 190, no. 4, pp. 880–883.
56. Bagal, I.L., El'tsov, A.V., and Stepanov, N.D., *Zh. Org. Khim.*, 1977, vol. 13, no. 1, pp. 22–30.
57. Efros, L.S. and Gorelik, M.V., *Khimiya i tekhnologiya promezhutochnykh produktov* (Chemistry and Technology of Intermediate Products), Leningrad: Khimiya, 1980.