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Reactions of aromatic diazonium salts with unsaturated compounds in the presence of nucleophiles

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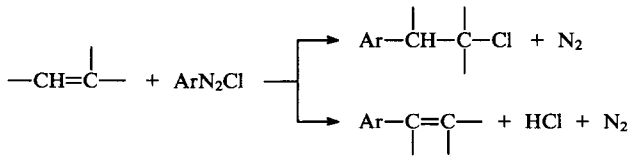
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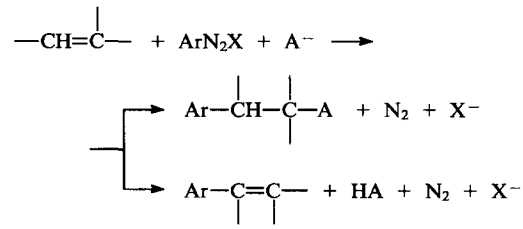
Abstract. The review surveys the reactions of aromatic diazonium salts with diene and monounsaturated compounds in the presence of nucleophiles. Certain further reactions of the reaction products and their applications are considered. The bibliography includes 63 references.

I. Introduction

The reaction of arenediazonium chloride with unsaturated compounds in the presence of copper salts (the Meerwein or Meerwein–Schuster reaction) was described in 1939[1] and immediately found extensive applications in synthetic organic chemistry for the preparation of aryl- and chloroaryl-substituted derivatives.[2–19]



The view that the reaction is catalysed solely by copper halides while diazonium sulfates and nitrates as well as other diazonium salts do not interact with unsaturated compounds was held for a long time. The explanation is that acid and not neutral diazonium salts plus divalent copper salts were used in the reaction, whereas it is univalent copper salts that are the catalysts of the decomposition of diazonium salts. Ethylene derivatives are known to be able to reduce divalent copper halides to the univalent state under certain conditions. However, divalent copper sulfates and nitrates are apparently difficult to reduce in an acid medium, since acids inhibit the reduction of divalent copper salts.[19] It was not until the beginning of the 1980s that conditions were found under which arenediazonium sulfates, nitrates, and tetrafluoroborates react with unsaturated compounds in the presence of external nucleophiles to form products of the addition of the aryl group and the anion to the double bond.[10–15] We suggested that this type of reaction be called anionarylation.[10,16] If sodium chloride is used as the anionoid reagent, then the Meerwein reaction becomes a special case of the anionarylation reaction.[14]



II. Factors determining the effectiveness of the reaction

The possibility of the anionarylation of dienes by diazonium sulfates and nitrates as well as other diazonium salts was discovered by Ganushchak et al.[10] The factors determining the effectiveness of the anionarylation reaction were elucidated later.

Diazonium salts. Among arenediazonium sulfates, nitrates, acetates, and tetrafluoroborates, arenediazonium tetrafluoroborates proved to be the most convenient in the anionarylation reaction. They are extremely stable compounds which can be stored for a long time.

It was noted that the highest yields of the products of the anionarylation reaction are obtained if there are no substituents at all in the aromatic ring or the substituents are in the *para*- or *ortho*-position regardless of their nature. *Meta*-substituted compounds afford significantly lower yields.[20]

Unsaturated compounds. Both monounsaturated and diene derivatives have been investigated in the anionarylation reaction. If the reaction system contains the same anionoid reagent, the yields of the anionarylation products (buta-1,3-diene, isoprene, and chloroprene) are comparable.[11–13]

The vinyl monomers $CH_2=CH-X$ and $CH_2=CX_2$, in which the double bond is activated by one or two electron-accepting groups (X = Cl, CN, Ar, COR, COOH, COOAlk, $P^V=O$, etc.) enter most readily into the anionarylation reaction.[20–22] Owing to the high capacity of copper or iron salts for the transfer of radical chains, such monomers do not produce high-molecular-mass compounds under the reaction conditions.

Catalysts. Various compounds, in particular copper acetate, thiocyanate, hydroxycarbonate [bicarbonate?], tetrafluoroborate, *O,O*-diethyl phosphorodithioate, and ethylxanthate as

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well as the $CuSO_4 + FeSO_4$, $Cu(NO_3)_2 + Cu$, and $Cu(NO_3)_2 + Fe$ systems have been tested as catalysts of the anionarylation reaction. The optimum molar ratio of the diazo-salt to the catalyst is in the range from 0.1 to 0.01–0.025. It is essential to note that the anion of the copper salt hardly affects the reaction. Furthermore, under these conditions as exchange reaction takes place between the copper salts and the anionoid reagents with formation of CuA_2. In most cases, the presence of the catalyst—copper or iron salts—is an obligatory condition, but sometimes the anionarylation reaction can occur also in the absence of the catalyst.[17,18,20,22]

Anionoid reagents. Alkali metal or ammonium salts have been most often used as anionoid reagents. Anionoid reagents such as chlorides, bromides, iodides, fluorides, sulfides, nitrites, thiocyanates, *O,O*-diethyl phosphorodithioates, xanthates, *N,N*-diethyldithiocarbamates, and carboxylates have been investigated in the reaction. Apart from the salts, water, methyl, ethyl, isopropyl, n-butyl, isobutyl, *sec*-butyl, *tert*-butyl, and benzyl alcohols, ethylene glycol, and formic acid have been used successfully as the anionoid reagents.

Solvents. The anionarylation reaction has been carried out in various solvents: water, acetone, acetonitrile, diethyl ether, dimethyl sulfoxide, dimethylformamide, and alcohol. If the unsaturated compound dissolves in water, the reaction can be carried out in an aqueous medium,[23] but, in view of the fact that the majority of unsaturated compounds are insoluble in water, the reaction is usually carried out in an aqueous organic medium. The optimum reaction media are water–acetone or water–acetonitrile mixtures in 1:(1–4) proportions.[14,20–22] In many instances, the reaction takes place only in an organic solvent. When water–acetone or alcohol–acetone systems are used as the organic medium in the absence of other anionoid reagents, the alcohol or water functions as an external nucleophile, whereupon hydroxyarylation and alkoxyarylation reactions occur.

Acidity of the medium. The optimum pH of the reaction medium is in the range from 4 to 6; in order to maintain and regulate the necessary pH, the following additives are introduced: CH_3COONa, CaO, $Ca(OH)_2$, $NaHCO_3$.

Temperature conditions. The anionarylation reaction takes place at temperatures from −65 to +25 °C depending on the nucleophilicity of the anion introduced and the order in which the reagents are added. If the temperature is not regulated, the reaction becomes uncontrolled, the temperature rises rapidly, and nitrogen is evolved abundantly; in such cases, the process involving the substitution of the diazo-group by the anions present in the mixture predominates.

Reaction procedure. The following order of the introduction of reagents into the reaction mixture is optimal: catalyst, solvent, unsaturated compound, diazonium salt. If the anionoid reagent is introduced last, the reaction proceeds as a rule very rapidly, which is indicated by the vigorous evolution of nitrogen. When the last reagent is the diazonium salt, the reaction proceeds quietly even at a higher temperature. The most successful diazonium salt: unsaturated compound: anionoid reagent reactant ratios are 1:(1–1.5):(1.25–2).

III. Anionarylation of 1,3-dienes

The influence of the nature of the aromatic diazonium salt, the catalyst and its amount, and the pH of the medium on the yields of the final products of the hydroxyarylation of buta-1,3-diene (hydroxyarylbutenes) and on the ratio of the 1,2- and 1,4-adducts have been studied.[24] A more detailed investigation established[11] that arenediazonium sulfates and nitrates react with buta-1,3-diene in the presence of a catalyst in a water–acetone medium at pH 5–7 with vigorous evolution of nitrogen and the formation of hydroxyphenylbutenes.[11] The best yields of the products of the hydroxyphenylation of buta-1,3-diene are obtained when mixtures of copper and iron(II) sulfates and of copper nitrate and copper powder or iron filings are used as the catalyst. The hydroxyphenylation of buta-1,3-diene proceeds in both the 1,2- and 1,4-positions with the preferential formation of the 1,4-adduct. 4-Hydroxy-1-phenylbut-2-ene (28%) and 2-hydroxy-1-phenylbut-3-ene (7%) were isolated and their structures were confirmed by chemical reactions.

$$ArN_2X + CH_2{=}CH{-}CH{=}CH_2 + HOH \xrightarrow[Cu(NO_3)_2 + Cu(Fe)]{CuSO_4 + FeSO_4} \begin{cases} \rightarrow ArCH_2{-}CH{=}CH{-}CH_2OH \\ \rightarrow ArCH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH{=}CH_2 \end{cases}$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$NO_2C_6H_4$.
X = HSO_4, NO_3.

Under analogous conditions, arenediazonium tetrafluoroborates interact with buta-1,3-diene in the presence of copper acetate or bicarbonate to form hydroxyarylbutenes.

In the anionarylation of isoprene, the aryl group adds to the isoprene molecule in the 1-position while the hydroxy-group adds in the 2- and 4-positions of the diene chain (the yield of the corresponding products is 30%–42%).[13]

$$ArN_2X + CH_2{=}C(CH_3){-}CH{=}CH_2 + HOH \xrightarrow{Cat.} \begin{cases} \rightarrow ArCH_2{-}C(CH_3){=}CH{-}CH_2OH \\ \rightarrow ArCH_2{-}\underset{\displaystyle OH}{\underset{|}{C}}(CH_3){-}CH{=}CH_2 \end{cases}$$

Treatment of 4-hydroxy-2-methyl-1-phenylbut-2-ene and 2-hydroxy-2-methyl-1-phenylbut-3-ene with thionyl chloride afforded in both cases only 4-chloro-2-methyl-1-phenylbut-2-ene.[25] γ-Benzyl-β-methylacrolein, identified by the melting point of the semicarbazone, was obtained by the reaction of 4-hydroxy-2-methyl-1-phenylbut-2-ene with oxygen in dimethyl sulfoxide (DMSO) and also by the reaction of 4-chloro-2-methyl-1-phenylbut-2-ene, obtained from 4-hydroxy-2-methyl-1-phenylbut-2-ene, with a secondary nitropropane in an alkaline medium.[26] Furthermore, treatment of 4-chloro-2-methyl-1-phenylbut-2-ene with potassium hydroxide in dioxane led to the synthesis of 2-methyl-1-phenylbuta-1,3-diene.[25]

$$C_6H_5CH_2{-}C(CH_3){=}CH{-}CH_2OH \xrightarrow{SO_2Cl} C_6H_5CH_2{-}C(CH_3){=}CH{-}CH_2Cl$$

$$C_6H_5CH_2{-}C(CH_3){=}CH{-}CH_2OH \xrightarrow[DMSO]{O_2} C_6H_5CH_2{-}C(CH_3){=}CH{-}CHO$$

$$C_6H_5CH_2{-}C(CH_3){=}CH{-}CHO \xleftarrow{CH_3CH(NO_2)CH_3} C_6H_5CH_2{-}C(CH_3){=}CH{-}CH_2Cl \xrightarrow{KOH} C_6H_5CH{=}C(CH_3){-}CH{=}CH_2$$

The reactions of arenediazonium tetrafluoroborates with buta-1,3-diene and isoprene both in acetone and in a water–acetone mixture in the presence of copper fluoride or acetate and various added alcohols take place with evolution of nitrogen and the formation of 4-alkoxy-1-arylbut-2-enes.[27]

$$ArN_2X + CH_2{=}CR{-}CH{=}CH_2 + AlkOH \xrightarrow{-N_2} ArCH_2{-}CR{=}CH{-}CH_2{-}OAlk$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4.
X = BF_4, HSO_4, NO_3.
R = H, CH_3.

Similar products have been obtained by the interaction of arenediazonium sulfates and nitrates with dienes in the anionarylation reaction with the corresponding alcohols. Methyl, ethyl, isopropyl, n-butyl, isobutyl, *tert*-butyl, and benzyl alcohols as well

as ethylene glycol were used. In the presence of ethylene glycol, the alkoxyarylation takes place with participation of both hydroxy-groups.

$$2\,CH_2{=}CR{-}CH{=}CH_2 + 2\,ArN_2BF_4 \xrightarrow[-N_2]{HOCH_2CH_2OH} \longrightarrow [ArCH_2CR{=}CHCH_2OCH_2]_2$$

15%–20%

The best yields of the alkoxyarylation products are attained when primary alcohols are used (31%–57%). In the presence of secondary alcohols, the yields of the products fall (14%–23%), whilst tertiary alcohols do not react, which can probably be accounted for by steric factors.

Grishchuk showed for the first time[28] that the anionarylation and arylation reactions can take place simultaneously. Thus the interaction of arenediazonium tetrafluoroborates with buta-1,3-diene in the 1 : 2 water–acetone mixture in the presence of formic acid or its salts proceeds with formation of a mixture of compounds via the following mechanism:

$$C_6H_5N_2BF_4 + CH_2{=}CH{-}CH{=}CH_2 + X{-}O{-}\overset{\overset{O}{\|}}{C}{-}H \longrightarrow$$

X = H, Na.

$$\longrightarrow C_6H_6 + C_6H_5OH + C_6H_5CH_2{-}CH{=}CH{-}CH_2O{-}\overset{\overset{O}{\|}}{C}{-}H$$

1.8% 11.2% 4.3%

$$+ C_6H_5CH_2{-}CH{=}CH{-}CH_2OH + C_6H_5CH_2{-}\underset{\underset{OC(O)H}{|}}{CH}{-}CH{=}CH_2$$

26.3% 7.8%

$$+ C_6H_5CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH{=}CH_2 .$$

48.6%

Gas–liquid chromatography is used to separate and identify the reaction products.

It has been found that arenediazonium tetrafluoroborates interact vigorously with buta-1,3-diene and isoprene under the conditions of oxidation-reduction catalysis in the presence of added sodium nitrite, chloride, bromide, fluoride, propionate, butyrate, and acetate with formation of anionarylation products (in 32%–47% yield).[14] The aryl group and the anionic residue add regioselectively in the 1,4-positions in the diene fragment.

$$ArN_2X + CH_2{=}CR{-}CH{=}CH_2 \xrightarrow[-MX,\,-N_2]{MA} \longrightarrow ArCH_2{-}CR{=}CH{-}CH_2{-}A$$

X = BF_4, HSO_4, NO_3.
R = H, CH_3.
A = NO_2, F, Cl, Br, Ac.

Nitro-, fluoro-, chloro-, bromo-, and carboxy-arylbutenes have been obtained in this way.

Ganushchak et al.[14] were the first to find that arenediazonium tetrafluoroborates interact with isoprene in the presence of an excess of sodium sulfide in anhydrous acetone to form sulfidearylation products [arylalkenyl sulfides] in 25% yield.

$$2\,ArN_2BF_4 + 2\,CH_2{=}C(CH_3){-}CH{=}CH_2 + Na_2S \xrightarrow[-N_2]{} \longrightarrow [ArCH_2{-}C(CH_3){=}CH{-}CH_2]_2S$$

Ar = C_6H_5, p-$CH_3C_6H_4$.

Arenediazonium tetrafluoroborates were introduced into the reaction in the form of dry salts in acetone, whilst the sulfates and nitrates were introduced in solution in aqueous acetone (pH 5–7). The catalysts employed were copper acetate in the case of the tetrafluoroborates and copper and iron(II) sulfates or copper nitrate and iron and copper powders respectively in the case of the sulfates and nitrates.

In order to investigate the influence of the nature of the anion of the diazonium salts further, a study has been made[12] of the interaction of buta-1,3-diene, isoprene, and chloroprene with arenediazonium acetates in aqueous acetone in the presence of copper acetate. It was established that arenediazonium acetates react under the above conditions with dienes, the process involving the evolution of nitrogen and the addition of the aryl residue and of the acetoxy-group preferentially in the 1,4-positions in the diene chain respectively. Only in a few individual instances were the products of 1,2-acetoxyarylation isolated in small amounts. The corresponding aromatic hydrocarbons (10% to 15%) and esters $ArOCOCX_3$ (5%–7%) are formed as side products.

The familiar 1-acetoxy-4-phenylbut-2-ene and the isomeric 2-acetoxy-1-phenylbut-3-ene were synthesised in proportions of 6 : 1 by the interaction of benzenediazonium acetate with buta-1,3-diene. The reactions of benzene- and toluene-p-diazonium acetates with isoprene afforded the 2-acetoxy-1-phenyl and 4-acetoxy-1-phenyl derivatives. After the reaction of ring-substituted benzenediazonium acetates with buta-1,3-diene and isoprene, only the products of 1,4-acetoxyarylation were isolated.

$$ArN_2O\overset{\overset{O}{\|}}{C}CX_3 + CH_2{=}CR{-}CH{=}CH_2 \xrightarrow[-N_2]{Cu(CH_3COO)_2}$$

$$\longrightarrow ArCH_2CR{=}CHCH_2O\overset{\overset{O}{\|}}{C}CX_3$$

$$\longrightarrow ArCH_2{-}\underset{\underset{OC(O)CX_3}{|}}{CR}{-}CH{=}CH_2$$

Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4.
X = H, Cl, F.
R = H, CH_3.

Arenediazonium trichloroacetates and trifluoroacetates were also tested in the anionarylation reactions of 1,3-dienes, which led to the corresponding acetoxy(aryl)butenes. The yields of 1-acetoxy-4-arylbutenes were 25%–40%.

A number of studies have been devoted to the interaction of diazonium salts with dienes under both catalytic and non-catalytic conditions with participation of thiocyanates.[29–31] It was established that arenediazonium tetrafluoroborates interact vigorously with buta-1,3-diene and isoprene in the presence of catalytic amounts of copper salts and alkali metal thiocyanates. This entails the coupled addition of the aryl group in the 1-position and of the isothiocyanate group predominantly in the 2-position in the diene chain. The reaction was carried out in acetone or aqueous acetone at temperatures between –30 and –15 °C.

$$ArN_2BF_4 + CH_2{=}CR{-}CH{=}CH_2 + MSCN \longrightarrow$$

$$\longrightarrow ArCH_2{-}\underset{\underset{N{=}C{=}S}{|}}{CR}{-}CH{=}CH_2 + N_2 + MBF_4$$

Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$.
R = H, CH_3.

Table 1. Conditions in the reactions of aromatic diazonium salts with 1,3-dienes in the presence of nucleophiles.

Anionarylation reaction	Diazonium salt	Diene	Anionoid reagent	Catalyst	Diazonium salt : diene : catalyst	Reaction medium	Yield[a] (%)	Ref.
Hydroxyarylation	ArN_2HSO_4	Buta-1,3-diene	HOH	$CuSO_4 + FeSO_4$	1 : 1.25 : (0.2 + 0.4)	Acetone – water (2 : 1)	30 – 40[b]	11
	ArN_2NO_3	"	HOH	$Cu(NO_3)_2 + Cu(Fe)$	1 : 1.25 : [0.125 + + 0.125 (0.125)]	"	30 – 40[b]	11
	ArN_2BF_4	"	HOH	$Cu(CH_3COO)_2$	1 : 1.25 : 0.05	"	40[b]	11
	ArN_2BF_4	Isoprene	HOH	$Cu(CH_3COO)_2$	1 : 1.25 : 0.05	"	30 – 42[b]	13
Alkoxyarylation	ArN_2BF_4	Buta-1,3-diene, isoprene	CH_3OH, C_2H_5OH, C_3H_7OH	$Cu(CH_3COO)_2$	1 : 2 : 0.1	Acetone – alcohol (4 : 1)	30 – 57	15
	ArN_2BF_4	Isoprene	$C_6H_5CH_2OH$	$Cu(CH_3COO)_2$	1 : 2 : 0.1	"	30	15
	ArN_2BF_4	"	$HOCH_2CH_2OH$	$Cu(CH_3COO)_2$	1 : 2 : 0.1	"	15 – 20	15
Nitroarylation	ArN_2BF_4	Buta-1,3-diene, isoprene	$NaNO_2$	$Cu(CH_3COO)_2$	1 : 1.5 : 0.1	Acetone	32 – 42	14
Carboxyarylation	ArN_2BF_4	"	CH_3COONa, C_2H_5COONa, C_3H_7COONa	$Cu(CH_3COO)_2$	1 : 1.5 : 0.1	"	30 – 47	14
Sulfidoarylation	ArN_2BF_4	"	Na_2S	$Cu(CH_3COO)_2$	1 : 1.5 : 0.1	"	25	14
Acetoxyarylation	$ArN_2OC(O)CH_3$	Buta-1,3-diene, isoprene, chloroprene	–	$Cu(CH_3COO)_2$	1 : 1.5 : 0.1	Acetone – water (1 : 1)	25 – 42[b]	12
Trifluoroacetoxyarylation	$ArN_2OC(O)CF_3$	Isoprene	–	$Cu(CH_3COO)_2$	1 : 1.5 : 0.1	"	25 – 32	12
Trichloroacetoxyarylation	$ArN_2OC(O)CCl_3$	"	–	$Cu(CH_3COO)_2$	1 : 1.5 : 0.1	"	8	12
Isothiocyanatoarylation	ArN_2BF_4	Buta-1,3-diene, isoprene	NaSCN	$Cu(BF_4)_2$	1 : 1.5 : 0.05	"	47 – 63[c]	30, 31
Thiocyanatosulfoarylation	ArN_2HSO_4	Buta-1,3-diene, isoprene, 2,3-dimethylbutadiene	NaSCN	$Cu(SCN)_2$	0.5 : 1 : 0.1	Acetone – acetic acid (1 : 1)	60 – 72	32
(*O,O*-Diethyl phosphoro-dithioato)sulfonylarylation	ArN_2HSO_4	Buta-1,3-diene, isoprene	$NaSP(S)(OC_2H_5)_2$	$Cu[SP(S)(OC_2H_5)_2]_2$	0.5 : 1 : 0.1	"	40 – 42	32
(*O*-Ethyl dithiocarbonato)-sulfoarylation	ArN_2HSO_4	Isoprene	$NaSC(S)OC_2H_5$	$Cu[SC(S)OC_2H_5]_2$	0.5 : 1 : 0.1	"	53	32
Iodoarylation	ArN_2Cl, ArN_2Br, ArN_2HSO_4	"	NaI	–	1 : 2	Water – alcohol (1 : 4)	29 – 44	33

[a] The yield of 1,4-adducts is quoted.
[b] The overall yield of 1,2- and 1,4-adducts.
[c] The yield of the 1,2-adducts is quoted.

It was established that, together with copper acetate and bicarbonate, copper(II) tetrafluoroborate is an effective catalyst of the isothiocyanatoarylation of dienes. The yields of 1-aryl-2-isothiocyanatobut-3-enes are almost the same when the above catalysts are employed and amount to 45% – 63%. It was shown that the reaction can occur also in the absence of copper(II) salts, but the yields of 1-aryl-2-isothiocyanatobut-3-enes are then lower by 17% – 24%. Small amounts of side products (~ 10%) resulting from the reduction of the diazonium salts and substituted isothiocyanatobenzenes were isolated.

1-Aryl-2-isothiocyanatobut-3-enes proved to be fairly convenient starting reagents for the synthesis of previously unknown mono-1,3-di- and 1,1,3-tri-substituted thioureas, namely *N*-(1-arylbut-3-en-2-yl)thioureas, by reaction with ammonia and aliphatic amines.[31]

$$ArCH_2-\underset{\underset{N=C=S}{|}}{CR^1}-CH=CH_2 + HNR^2R^3 \longrightarrow$$

$$\longrightarrow ArCH_2-\underset{\underset{\underset{\underset{NR^2R^3}{|}}{C=S}}{|}}{\overset{\overset{HN}{|}}{CR^1}}-CH=CH_2$$

80% – 90%

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$.
R^1 = H, CH_3; R^2, R^3 = H, CH_3, C_2H_5.

The antibacterial and antifungal properties of 1-aryl-2-isothiocyanatobut-3-enes have been described.[30]

The interaction of aromatic diazonium salts with butadiene, 2,3-dimethylbutadiene, and isoprene in solution in a sulfur dioxide-saturated acetic acid – acetone mixture in the presence of sodium chloride, bromide, thiocyanate, *O,O*-diethyl phosphorodithioate, and xanthate in such a way that the arenesulfonyl group adds to the diene chain in the 1-position while the anion adds in the 4-position with formation of 4-anion-1-arenesulfonylbut-2-enes has been demonstrated.[32]

$$ArN_2X + CH_2=CR^1-CR^2=CH_2 + MA \xrightarrow[SO_2]{CuA_2}$$

$$\longrightarrow ArSO_2CH_2CR^1=CR^2-CH_2A + N_2 + MX$$

41% – 80%

The absence, until recently, of data on the iodoarylation of unsaturated compounds can be explained, in our view by the fact that copper salts and arenediazonium iodides were used as the catalyst by analogy with the Meerwein reaction. Arenediazonium iodides are known to be extremely unstable and, in addition, the iodide anion is readily oxidised to molecular iodine under the experimental conditions.

$$ArN_2X + CH_2=C(CH_3)-CH=CH_2 + MI \longrightarrow$$

$$\longrightarrow ArCH_2C(CH_3)=CHCH_2I$$

29% – 44%

Ar = C_6H_5, *p*(*m*)-$CH_3C_6H_4$.
X = Cl, BF_4, HSO_4.

Ganushchak et al.[33] achieved for the first time the iodoarylation of isoprene. They used ethyl alcohol, acetone, DMSO, dimethylformamide (DMF), and water as the solvents. The best yields of the iodo-derivatives are obtained when DMF and arenediazonium tetrafluoroborates are used. The conditions in the reactions of aromatic diazonium salts with 1,3-dienes in the presence of nucleophiles are presented in Table 1.

IV. Anionarylation of monounsaturated compounds

The possibility of the anionarylation of monounsaturated compounds was first described by Grishchuk.[34] It was shown that arenediazonium tetrafluoroborates interact with acrylonitrile, methyl methacrylate, vinyl chloride, and vinylidene chloride in the presence of sodium nitrite, chloride, and bromide and catalytic amounts of copper salts in such a way that coupled addition of the aryl group and the anion takes place at the point of rupture of the double bond and arylchloro(bromo)ethanes are formed in 25% – 75% yield.

$$ArN_2BF_4 + CH_2=CX^1X^2 + NaA \xrightarrow[-N_2]{}$$

$$\longrightarrow ArCH_2CX^1X^2A + NaBF_4$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$.
X^1 = H, CH_3; X^2 = Cl, Br, CH_3COO, CN, C_6H_5.

The reaction of benzenediazonium tetrafluoroborate with styrene in the presence of sodium nitrite leads to the formation of 1-nitro-1,2-diphenylethane and *trans*-stilbene,[34] while the reaction of acrylonitrile, methyl methacrylate, and vinylidene chloride in the presence of an excess of sodium sulfide affords the corresponding sulfide in 25% yield under catalytic conditions.[34]

$$C_6H_5N_2BF_4 + CH_2=CX^1X^2 + Na_2S \xrightarrow[-N_2]{}$$

$$\longrightarrow [C_6H_5CH_2CX^1X^2]_2S$$

X^1 = H, CH_3, Cl; X^2 = CN, CH_3COO, Cl.

It has been established[35] that *p*-nitrobenzenediazonium sulfates react vigorously with acrylonitrile at 5 – 10 °C in aqueous acetone in the presence of copper and potassium thiocyanate to form β-(*p*-nitrophenyl)-α-thiocyanatopropionitrile in 50% yield.

It was later established[21] that, regardless of the anion of the diazonium salt, arenediazonium sulfates, nitrates, and tetrafluoroborates form the same anionarylethanes on interaction with acrylonitrile, methyl methacrylate, vinyl acetate, styrene, and vinylidene chloride in the presence of sodium chloride, bromide, thiocyanate, and nitrite as well as the catalyst (copper acetate).

$$p\text{-}NO_2C_6H_4N_2HSO_4 + CH_2=CHCN + KSCN \longrightarrow$$

$$\longrightarrow p\text{-}NO_2C_6H_4CH_2-\underset{\underset{SCN}{|}}{CHCN} + N_2 + KHSO_4$$

Under the same conditions, the corresponding sulfides are formed in the presence of sodium sulfide.[21]

$$ArN_2X + CH_2=C\begin{matrix}R^1\\R^2\end{matrix} \xrightarrow{NaA} ArCH_2-\underset{\underset{A}{|}}{\overset{\overset{R^1}{|}}{C}}-R^2 + N_2 + NaX$$

30% – 35%

Naidan et al.[36] investigated the thiocyanatoarylation of acrylonitrile, methyl methacrylate, and styrene. They showed that benzenediazonium sulfates interact with the above monounsaturated compounds in aqueous acetone in the presence of thiocyanate ions.

$$CH_2=CR^1R^2 + ArN_2HSO_4 + NH_4SCN \longrightarrow$$

$$\longrightarrow ArCH_2C(SCN)R^1R^2 + N_2 + (NH_4)_2SO_4$$

R^1 = H, CH_3; R^2 = CN, $COOCH_3$, C_6H_5.

The thiocyanatoarylation reaction in a sulfur dioxide-saturated acetic acid–acetone mixture at temperatures between −16 and −20 °C results in the addition of the thiocyanato- and arenesulfonyl groups to the unsaturated compound. For example, the thiocyanato-group adds in the α-position of styrene, while the arenesulfonyl group adds in the β-position. The yield of 2-arene-sulfonyl-1-phenyl-1-thiocyanatoethane is 53%–58%.

$$ArN_2HSO_4 + SO_2 + C_6H_5CH{=}CH_2 + NH_4SCN \xrightarrow{Cu(SCN)_2} C_6H_5CH(SCN)CH_2SO_2Ar + N_2 + (NH_4)_2SO_4$$

It has also been noted[36] that the earlier hypothesis[35] that copper(II) thiocyanate is the reaction catalyst is incorrect; in fact the catalyst is copper(I) thiocyanate, which is formed readily under the reaction conditions.

In aqueous acetone at 5–10 °C in the presence of copper(I) ethylxanthate and potassium xanthate, acrylonitrile reacts with benzene- and *p*-nitrobenzene-diazonium sulfates.[37] The reaction proceeds with evolution of nitrogen and leads to α-(ethoxythiocarbonylthio)-β-phenylpropionitrile (51%) and α-(ethoxythiocarbonylthio)-β-(*p*-nitrophenyl)propionitrile (40%).

$$CH_2{=}CHCN + ArN_2HSO_4 + C_2H_5OC(S)SK \longrightarrow ArCH_2CH(SC(S)OC_2H_5)CN + N_2 + KHSO_4$$

Ar = C_6H_5, *p*-$NO_2C_6H_4$.

It has been established[38] that in the anionarylation reaction *p*-nitrobenzene-diazonium sulfate interacts with acrylonitrile in the presence of sodium diethyl phosphorodithioate to form α-(diethoxythiophosphorylthio)-β-(*p*-nitrophenyl)-propionitrile in 72% yield.

$$p\text{-}NO_2C_6H_4N_2HSO_4 + CH_2{=}CHCN + (C_2H_5O)_2P(S)SNa \longrightarrow p\text{-}NO_2C_6H_4CH_2CH(CN)SP(S)(OC_2H_5)_2 + N_2 + NaHSO_4$$

The reaction takes place at room temperature and the catalyst is copper *O,O*-diethyl phosphorodithioate.

Interesting data have been published on the anionarylation of acrylic and methacrylic acid esters.[20,39] It was shown that arenediazonium tetrafluoroborates react with acrylic and methacrylic acid esters in acetone or the 1 : 2 water–acetone mixture in the presence of potassium thiocyanate with evolution of nitrogen and the addition of the aryl and thiocyanato-groups at the site of rupture of the double bond in the monounsaturated compound to form 1-alkoxycarbonyl-2-aryl-1-thiocyanatoethanes.

$$R^1C_6H_4N_2BF_4 + CH_2{=}CR^2COOR^3 + KSCN \longrightarrow R^1C_6H_4CH_2{-}\underset{SCN}{CR^2}COOR^3 + KBF_4 + N_2$$

R^1 = H, *m*(*p*)-CH_3, *p*-CH_3O.
R^2 = H, CH_3; R^3 = CH_3, C_2H_5, C_4H_9, *iso*-C_4H_9.

Thiocyanatoarylation takes place at temperatures from −30 to −15 °C. The structure of the diazonium salt and of the monounsaturated compound as well as the nature of the reaction medium (acetone or aqueous acetone) hardly affect the yields of 1-alkoxycarbonyl-2-aryl-1-thiocyanatoethanes, which are ~50%–70%. When toluene-*m*-diazonium tetrafluoroborate is introduced into the reaction, the yields of 1-alkoxycarbonyl-1-thiocyanato-2-(*m*-tolyl)ethanes are somewhat lower (~40%). Isothiocyanatobenzenes are formed in ~20% yield together with the thiocyanatoarylation reaction.

Copper(II) salts were tested as the catalysts: the acetate, bicarbonate, and tetrafluoroborate. It was established that the catalysts ensure comparable yields of 1-alkoxycarbonyl-2-aryl-1-thiocyanatoethanes, i.e. the anion of the copper salt does not affect the anionarylation process.

The study of the thiocyanatoarylation of acrylic and methacrylic acid esters in the absence of copper salts is of definite interest. In this case, the yield of isothiocyanatobenzenes predominates over that of thiocyanatobenzenes [the yield of the corresponding 1-alkoxycarbonyl-2-aryl-1-thiocyanatoethanes in the absence of copper(II) salts is lower by 40%–50%].

It has been shown[40] that arenediazonium tetrafluoroborates interact with α,β,β′-trifluorostyrene and potassium thiocyanate in acetone, forming the thiocyanatoarylation products—2-aryl-1,2,2-trifluoro-1-phenyl-1-thiocyanatoethanes (yield 36% to 46%).

$$ArN_2BF_4 + C_6H_5CF{=}CF_2 + KSCN \longrightarrow ArCF_2CF(SCN)C_6H_5 + KBF_4 + N_2$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$.

This reaction proceeds also in the absence of catalysts—copper or iron salts. Apparently, depending on the degree of electron saturation of the double bond and the nature of the anion, the reaction proceeds via different mechanisms.

$$C_6H_5CHal{=}CH_2 + ArN_2BF_4 + KSCN \xrightarrow{(CH_3)_2CO} \begin{cases} C_6H_5C(SCN){=}CHAr \\ 19\% \\ C_6H_5CH{=}CHAr \\ 22\% \end{cases}$$

The interaction of α-bromo- and α-chloro-styrenes[41] with potassium thiocyanate and arenediazonium salts in acetone in the presence of copper(II) salts leads to *trans*-α-thiocyanatostilbenes and *trans*-stilbenes. The ratio of the reaction products depends on the nature of the solvent: both compounds are formed in acetone whereas *trans*-stilbenes are formed predominantly in aqueous acetone.

It has been established that[22,42] arenediazonium tetrafluoroborates actively interact with vinyl chloride and vinylidene chloride in acetone or the 1 : 4 water–acetone mixture in the presence of copper or iron thiocyanate and potassium (sodium or ammonium) thiocyanate at temperatures between −15 and −5 °C with evolution of nitrogen, affording the products of the addition of the aryl and thiocyanato-groups at the site of the dissociation of the double bond of the monounsaturated compound—2-aryl-1-chloro-1-thiocyanatoethanes and 2-aryl-1,1-dichloro-1-thiocyanatoethanes (yield 73%–82%).

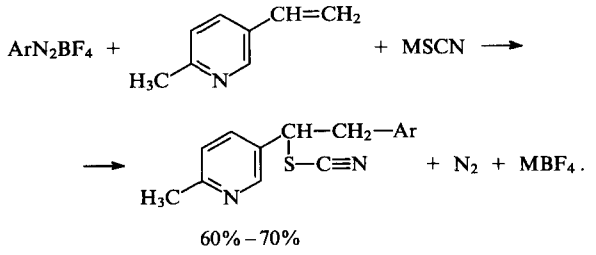
$$ArN_2BF_4 + CH_2{=}CR^1Cl + MSCN \longrightarrow ArCH_2{-}\underset{SCN}{CR^1Cl} + N_2 + MBF_4$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$.
R^1 = H, Cl; M = K, Na, NH_4.

The optimum diazonium salt : unsaturated compound : thiocyanate reactant ratios are 1 : 2 : 1.5. Isothiocyanatobenzenes are formed as side products (10%–15%). The excess of the olefin in the reaction system promotes the main reaction and is also necessary to compensate for the amount of the olefin carried away by the evolved nitrogen.[22]

Arenediazonium tetrafluoroborates interact with allyl chloride and bromide between −15 and −5 °C in the presence of alkali metal thiocyanates to form 1-aryl-3-chloro(bromo)-2-thiocyanatopropanes.[43] The reaction takes place only with participation of copper or iron salts. The yields of the thiocyanatoarylation products are 35%−40%.

2-Methyl-5-vinylpyridine reacts with arenediazonium tetrafluoroborates in the 1:4 water−acetone mixture in the presence of thiocyanates[44] to form 5-(2-aryl-1-thiocyanatoethyl)-2-methylpyridines in accordance with the following mechanism:



60%−70%

The reaction proceeds at a temperature between −65 and −50 °C both in the presence and absence of the catalyst−copper or iron salts. Isothiocyanatobenzenes are formed as side products in a yield of ~7%−10%.

It has been shown[45] that a sulfur-dioxide-saturated solution of benzenediazonium chloride containing copper chloride reacts with styrene at room temperature. The chlorine atom and the benzenesulfonyl group then add at the site of the dissociation of the carbon−carbon double bond, forming 2-benzenesulfonyl-1-chloro-1-phenylethane in 42% yield. Apparently, when benzenediazonium chloride is saturated with sulfur dioxide, benzenesulfonyldiazonium chloride is formed and subsequently reacts with styrene after splitting off nitrogen.

$$C_6H_5N_2Cl + SO_2 + C_6H_5CH{=}CH_2 \xrightarrow{CuCl_2}$$
$$\longrightarrow C_6H_5CHClCH_2SO_2C_6H_5 + N_2$$

In a sulfur-dioxide-saturated mixture of acetic acid and acetone, styrene reacts with aromatic diazonium salts in the presence of chloride and bromide anions, *O,O*-diethyl phosphorodithioates, xanthates, and catalytic amounts of copper ions, affording respectively 1-chloro-, 1-bromo-, 1-(diethoxythiophosphorylthio)-, and 1-(ethoxythiocarbonylthio)-derivatives of 2-arenesulfonyl-1-phenylethanes in 28%−83% yields.[46]

$$ArN_2X + SO_2 + C_6H_5CH{=}CH_2 + MA \xrightarrow{CuA_2}$$
$$\longrightarrow C_6H_5CH(A)CH_2SO_2Ar + N_2 + MX$$

X = Cl, Br, HSO_4.

It has been suggested[41] that an important factor promoting the anionarylation reaction in the absence of a catalyst is an increase in the nucleophilicity of the anion in the added anionoid reagent. In order to confirm this hypothesis, a study has been made[47,48] of the interaction of diazonium salts with acrylic and methacrylic acid esters in the presence of the *N,N*-diethyldithiocarbamate anion, which is more nucleophilic than the thiocyanate anion.

Arenediazonium tetrafluoroborates, sulfates, and nitrates react vigorously with acrylic and methacrylic acid esters, evolving nitrogen and forming 2-aryl-1-(*N,N*-diethylthiocarbamoylthio)-1-methoxycarbonylethanes. The reaction takes place at a temperature between −50 and −20 °C in acetone or aqueous acetone for a 1:1.5 molar ratio of the diazonium salt and the salts of *N,N*-diethyldithiocarbamic acid. The presence of a catalyst — copper(II) or iron(II) salts — hardly affects the *N,N*-diethyldithiocarbamatoarylation of acrylates. The yields of the products are 51%−62%. Those of the target products are independent of the order in which the reagents are introduced into the reaction medium. When arenediazonium sulfates and nitrates are used, the yields of aryl(*N,N*-diethylthiocarbamoylthio)ethanes are lower by 25%−30% than in the case where tetrafluoroborates are used. This can be explained by the fact that aqueous solutions of diazonium salts have pH 3−4 and *N,N*-diethyldithiocarbamic acid is formed under these conditions. The acid is unstable and immediately decomposes.

$$ArN_2X + CH_2{=}CR^1C(O)OCH_3 + MS(S)CN(C_2H_5)_2 \longrightarrow$$
$$\longrightarrow ArCH_2CR^1(COCH_3)SCN(C_2H_5)_2 + N_2 + MX$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$.
X = BF_4, HSO_4, NO_3; R^1 = H, CH_3; M = Na, K, NH_4.

The considerable difference between the nucleophilicities of the thiocyanate and *N,N*-diethyldithiocarbamate groups as well as the presence in the second case of unshared electrons at the second sulfur atom (α-atom) joined to the nucleophilic centre can apparently explain why the dithiocarbamatoarylation process proceeds also in the absence of a catalyst.

It has been shown[47,48] that diazonium salts interact with salts of *N,N*-diethyldithiocarbamic acid in acetone or aqueous acetone at temperatures between −50 and −10 °C, forming *N,N*-diethylthiocarbamoylthiobenzenes in 60%−70% yields.

The iodoarylation of methyl acrylate and methacrylate was described for the first time by Ganushchak et al.[49]

$$ArN_2X + CH_2{=}CR^1R^2 \xrightarrow{MI} ArCH_2{-}\overset{I}{C}R^1R^2$$

X = Cl, BF_4, HSO_4; R^1 = H, CH_3; R^2 = $COOCH_3$.

Alcohol, acetone, dimethyl sulfoxide, dimethylformamide, and water were used as solvents.

The iodoarylation of acrylic ar ylic acid esters and acrylonitrile has been investiga· ·ɑıc fully.[50] It has been established that these compounds interact with aromatic diazonium salts and iodide ions, the aryl group and the iodide ion being added to the double bond. The aryl group adds to the extreme methylene group.

$$ArN_2X + CH_2{=}CR^1R^2 + MI \longrightarrow$$
$$\longrightarrow ArCH_2{-}\overset{I}{C}R^1R^2 + MX + N_2$$
22%−60%

R^1 = H, CH_3, C_3H_7; R^2 = $COOC_4H_9$, CN; X = Cl, BF_4, HSO_4.
R^2 = $C(O)OCH_3$; M = K, Na, NH_4.

The optimum diazonium salt:monomer:iodide reactant ratios are 5:3:5. The reaction takes place in an aqueous medium and in various organic solvents (alcohol, benzene, dioxane, dimethyl sulfoxide, dimethylformamide). The yields of aryliodoethanes are influenced by the structure of the substrate and also by the nature and position of the substituent in the aromatic ring of the diazonium salt. The iodoarylation of acrylonitrile proceeds more vigorously than that of the acrylic acid esters. The yields of the aryliodo-derivatives increase on passing from methyl esters of acrylic acids to the butyl esters and following the introduction of alkyl substituents in the α-position, which may be accounted for by the stability of the intermediate $Ar{-}CH_2\dot{C}(R^1)C(O)OAlk$. Arenediazonium salts containing electron-donating substituents in the *para*-position afford higher yields of the target products compared with the *ortho*- and *meta*-isomers.

Table 2. Conditions in the reactions of aromatic diazonium salts with alkenes in the presence of nucleophiles.

Anionarylation reaction	Diazonium salt	Alkene	Anionoid reagent	Catalyst	Diazonium salt : diene : catalyst	Reaction medium	Yield (%)	Ref.
Nitroarylation	ArN_2BF_4	Acrylonitrile, styrene, methyl methacrylate	$NaNO_2$	$Cu(CH_3COO)_2$	1 : 1 : 0.1	Acetone – water (4 : 1)	20 – 30	21
Sulfidoarylation	ArN_2BF_4	"	Na_2S	$Cu(CH_3COO)_2$	1 : 1 : 0.1	"	20 – 32	21
Thiocyanatoarylation	ArN_2HSO_4	Acrylonitrile, styrene	NaSCN	$Cu(SCN)_2$	1 : 1 : 0.25	Acetone – water (2 : 1)	41 – 72	36
	ArN_2BF_4	Acrylic and methacrylic acid esters	NaSCN	$Cu(CH_3COO)_2$, $(CuOH)_2CO_3$, $Cu(BF_4)_2$	1 : 1.12 : 0.05	"	41 – 72	20
	ArN_2BF_4	Vinyl chloride, vinylidene chloride	NaSCN	$Cu(SCN)_2$	1 : 2 : 0.05	Acetone or acetone – water (4 : 1)	79 – 82	22
	ArN_2BF_4	Allyl chloride, allyl bromide	NaSCN	$Cu(SCN)_2$	1 : 1.25 : 0.1	Acetone – water (3 : 1)	34 – 54	43
(*O*-Ethyl dithiocarbonato)arylation	ArN_2HSO_4	Acrylonitrile	$KS(S)COC_2H_5$	$Cu[S(S)COC_2H_5]_2$	1 : 1 : 0.25	"	40 – 51	37
(Diethyl phosphorodithioato)arylation	ArN_2HSO_4	"	$KS(S)P(OC_2H_5)_2$	$[(C_2H_5O)_2P(S)S]_2Cu$	1 : 1 : 0.25	"	72	38
Chloroarylation	ArN_2BF_4	Allyl chloride	NaCl	$CuCl_2$	1 : 1.25 : 0.1	"	51 – 60	43
Chlorosulfoarylation	ArN_2Cl	Styrene	–	$CuCl_2$	1 : 3 : 0.3	Acetic acid	42	45
Thiocyanatosulfoarylation	ArN_2HSO_4	"	SO_2, NH_4SCN	$Cu(SCN)_2$	1 : 3 : 0.3	Acetone – acetic acid (4 : 3)	40 – 69	36
Bromosulfoarylation	ArN_2HSO_4	"	SO_2, KBr	$CuBr_2$	1 : 3 : 0.3	"	59 – 83	46
(*O,O*-Diethyl phosphorodithioato)arylation	ArN_2HSO_4	"	SO_2, $KS(S)P(OC_2H_5)_2$	$Cu[S(S)P(OC_2H_5)_2]_2$	1 : 3 : 0.3	"	44 – 58	46
(*O*-Ethyl dithiocarbonato)arylation	ArN_2HSO_4	"	SO_2, $KS(S)OC_2H_5$	$Cu[S(S)OC_2H_5]_2$	1 : 3 : 0.3	"	45 – 81	46
N,N-Diethyldithiocarbamatoarylation	ArN_2BF_4	Acrylic and methacrylic acid esters	$NaS(S)CN(C_2H_5)_2$	–	1 : 1.5	Acetone – water (2 : 1)	51 – 62	18
Iodoarylation	ArN_2BF_4	"	NaI	–	5 : 3	Acetone or DMSO	22 – 60	50
(*O,O*-Diethyl phosphorodithioato)arylation	$(BF_4N_2-C_6H_4-)_2X$	"	$KS(S)P(O)_2R^1$	$Cu(CH_3COO)_2$, Cu	2.5 : 5 : 0.75	Acetone	14, 15, 5	52

Together with the iodoarylation products, the products of the iodination of the aromatic ring are formed in all cases. Both reactions apparently begin with the reduction of the diazonium cation by the iodide anion to give the aryl group, which forms an iodoarene or an aliphatic-aromatic radical. The radical reaction mechanism has been confirmed by the formation of aryliodo-derivatives in the presence of other anions.

When 2-aryl-1-iodo-1-methoxycarbonyl(cyano)alkanes are treated with alcoholic alkali, the compound is dehydroiodinated and the ester group is hydrolysed; derivatives of cinnamic acid, containing substituents in the α-position and in the aromatic ring, are then formed in high yields (48%–90%).[50]

In order to extend the limits of the iodoarylation reaction, a study has been made[51] of the interaction of arenediazonium tetrafluoroborates with phenyl-acetylene and lithium iodide in aqueous dimethyl sulfoxide at pH 5–7 and at a temperature of 20–37 °C.

$$ArN_2X + HC{\equiv}C{-}C_6H_5 + LiI \longrightarrow \underset{H\ \ I}{\overset{Ar\ \ C_6H_5}{C{=}C}} + LiBF_4 + N_2$$

Ar = C_6H_5, *o*(*m*,*p*)-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$.

The yields of *cis*-(*E*)-α-iodostilbenes are 36%–48%.

The influence of heteroatomic substituents on the possibility of the involvement of the double bond in the iodoarylation reaction has also been investigated[51] in relation to vinyl derivatives of phosphorus containing the $\geq P(O)-CR{=}CH_2$ fragment. The ethyl esters of vinylphosphonic and 2-propenylphosphonic acids were chosen as the objects of study.

It was established that arenediazonium tetrafluoroborates react with the above phosphorus-containing olefins in the presence of lithium fluoride in the same way as with acrylic acid esters and acrylonitrile.

$$ArN_2BF_4 + CH_2{=}C(R^1)P(O)(OC_2H_5)_2 + LiI \longrightarrow$$

$$\longrightarrow \underset{21\%-49\%}{ArCH_2{-}\overset{I}{\overset{|}{C}}(R^1)P(O)(OC_2H_5)_2} + LiBF_4 + N_2$$

Ar = C_6H_5, *o*(*m*,*p*)-$CH_3C_6H_4$; R^1 = H, CH_3.

The direct iodoarylation of unsaturated compounds has not so far been achieved because arenediazonium iodides have not been obtained and, furthermore, Cu_2I_2 is sparingly soluble under the reaction conditions.

Ganushchak et al.[52] investigated anionarylation reactions with the aid of diazonium salts synthesised from benzidine and di(4-aminophenyl) ether. It was shown that the tetrafluoroborates of the diazonium salts derived from benzidine and di(4-aminophenyl) ether react with acrylic and methacrylic acid esters and potassium *O*,*O*-dialkyl phosphorodithioates in the presence of copper acetate and copper powder, forming 4,4′-bis[2-(dialkoxythiophosphorylthio)-2-methoxycarbonylethyl(propyl)]-biphenyls and 4,4-bis[2-(dialkoxythiophosphorylthio)-2-methoxycarbonylethyl(propyl)]-diphenyl ethers.

$$2\,CH_2{=}C(R)COOCH_3 + BF_4N_2{-}C_6H_4{-}X{-}C_6H_4{-}N_2BF_4$$

$$+\ 2\,(R^1O)_2P(S)SK \xrightarrow[-N_2,\ -KBF_4]{Cu(CH_3COO)_2/Cu}$$

$$\longrightarrow H_3COOC(R)CH_2{-}C_6H_4{-}X{-}C_6H_4{-}CH_2C(R)COOCH_3$$

$$\underset{SP(S)(OR^1)_2}{\overset{|}{\ }} \qquad \underset{SP(S)(OR^1)_2}{\overset{|}{\ }}$$

14%–15%

X = bond, O; R^1 = n-C_3H_7, *iso*-C_3H_7.

The majority of the olefin anionarylation products, for example, 1-chloro-1-thiocyanato-, 1,1-dichloro-1-thiocyanato-, and 1-alkoxycarbonyl-1-thiocyanato-derivatives of 2-arylethanes exhibit antifungal and antibacterial properties.[39,42]

The conditions in the reactions of aromatic diazonium salts with alkenes in the presence of nucleophiles are presented in Table 2.

V. The mechanism of the anionarylation reaction

A necessary condition for the occurrence of the anionarylation reaction is in many cases the presence of a catalyst — copper or iron salts — in the reaction mixture. The reaction occurs in the absence of a catalyst only occasionally. This depends on the structure of the unsaturated compound and the nucleophilicity of the anion introduced.

The data available at present concerning different aspects of the reaction of diazonium salts with unsaturated compounds suggest that it proceeds via a radical-anion mechanism in the presence of a catalyst and via a radical mechanism in its absence.

We shall now consider the mechanism of the anionarylation reaction catalysed by copper and iron compounds, which is presented in Scheme 1. The principal stages of this reaction have been described in detail.[8] In stage (1), arenediazonium tetrafluoroborates interact with anionoid reagents to form the anion-arenediazonium. Under the reaction conditions, copper(II) is readily reduced to copper(I).[3,4,22] Next, the copper(I) salt formed in stage (2) forms a double bond with the anionarenediazonium in which the diazo-group is coordinated to the complex anion $(CuA_2)^-$. In individual instances, such salts have been isolated in a pure form[53] or their existence has been demonstrated conductometrically.[4,55] Next, the double salt forms with the unsaturated compounds a ternary reaction complex A [stage (3)] in which the diazo-group and the olefin are bound to the copper ion.[3,34,54]

Scheme 1

$$ArN_2X + MA \longrightarrow ArN_2A + MX \qquad (1)$$

$$ArN_2A + CuA \longrightarrow ArN_2^+(CuA_2)^- \qquad (2)$$

$$ArN_2^+(CuA_2)^- + CH_2{=}CR^1R^2 \rightleftharpoons$$

$$\rightleftharpoons \underset{(A)}{\left[ArN_2^+(CuA_2)^- \overset{CH_2}{\overset{\|}{CR^1R^2}}\right]} \qquad (3)$$

$$\left[ArN_2^+(CuA_2)^- \overset{CH_2}{\overset{\|}{CR^1R^2}}\right] \xrightarrow[-N_2]{} \left[Ar{-}CH_2{-}\dot{C}R^1R^2{\cdots}CuA_2\right] \qquad (4)$$

$$\left[Ar{-}CH_2{-}\dot{C}R^1R^2{\cdots}CuA_2\right] \xrightarrow[-CuA]{} Ar{-}CH_2{-}CR^1R^2A \qquad (5)$$

The formation of transition metal, including copper and iron, complexes with arenediazonium salts has been demonstrated.[34,53–55] Such complexes are relatively stable in aqueous organic, organic, and aqueous solutions in the cold and at room temperature, but begin to decompose after the addition of the unsaturated compound.

It has long been known that copper(I) salts form π-complexes with diene and monounsaturated compounds in organic and aqueous media[54,56] (this factor constitutes the basis of the industrial chemisorption separation of hydrocarbons[57]). The evolution of nitrogen, which occurs only after the addition of the unsaturated compound, is a sign of the onset of the reaction.

Electron transfer from copper(I) to the diazonium cation in complex A (see Scheme 1) leads to the evolution of nitrogen from the diazo-group and the formation of the radical Ar$^\cdot$ and copper(II). It has been shown[58] that, on exposure to the polarising action of the copper ion, the arenediazonium cation is reduced to the radical Ar$^\cdot$ via a one-electron mechanism.

$$C_6H_5N_2^+ + e \longrightarrow C_6H_5N_2^{\cdot} \longrightarrow C_6H_5^{\cdot} + N_2$$

Next, the radical Ar$^{\cdot}$ forms an aliphatic–aromatic radical with the unsaturated compound without passing to the bulk of the solution [stage (4)]. On interaction with CuA_2, the aliphatic–aromatic radical then affords anionarylation products as a result of the transfer of the radical-anion [stage (5)]. The formation of such radicals has been detected by EPR with the aid of spin-trapping agents.[59]

When iron(II) salts are used, the reaction proceeds in accordance with the following scheme in our view.

Scheme 2

$$ArN_2A \longrightarrow A\dot{r} + N_2 + A^{\cdot} \quad (6)$$

$$A\dot{r} + CH_2{=}CR^1R^2 \longrightarrow Ar{-}CH_2{-}\dot{C}R^1R^2 \quad (7)$$
(B)

$$Ar{-}CH_2{-}\dot{C}R^1R^2 + A^{\cdot} \longrightarrow Ar{-}CH_2{-}\underset{\displaystyle A}{\underset{|}{C}}R^1R^2 \quad (8)$$

$$A\dot{r} + A^{\cdot} \longrightarrow ArA \quad (9)$$

$$Ar{-}CH_2{-}\dot{C}R^1R^2 + CH_2{=}CR^1R^2 \longrightarrow$$
$$\longrightarrow Ar{-}CH_2{-}CR^1R^2{-}CH_2{-}\dot{C}R^1R^2$$
$$\longrightarrow \text{tarry polymeric substances.} \quad (10)$$

Apart from copper and iron salts, the salts of other variable-valence metals with similar oxidation–reduction potentials can also play the role of catalysts.

We shall now proceed to the consideration of the anionarylation of olefins in the absence of a catalyst (Scheme 2). In this case, the diazonium salts interact in the first stage with the anionoid reagents to form the anionarenediazonium, which then readily decomposes via reaction (6).[60,61] The aryl radical formed interacts with the olefin, affording the aliphatic–aromatic radical **B** [stage (7)].[58,62] The subsequent mode of reaction is determined by the stability of this radical. If radical **B** is sufficiently stable, the anionarylation of unsaturated compounds [stage (8)] takes place, but if radical **B** is unstable, reaction (10), leading mainly to tarry polymeric substances, occurs.

The presence of anionoid reagents in systems containing a diazonium salt is known to lead to its decomposition via a radical mechanism. The aryl radicals formed have been detected by EPR.[63]

* * *

In conclusion we may note that the expansion of the range of unsaturated compounds and aromatic diazonium salts used in the anionarylation reaction in order to obtain aliphatic-aromatic synthons containing several reaction centres, which are otherwise difficult to obtain, is of undoubted interest for organic synthesis. The improvement of methods used in anionarylation reactions is an important aspect. It will make it possible to reduce competing reactions to a minimum.

References

1. H Meerwein, E Büchner, K Emster *J. Prakt. Chem.* **152** 237 (1939)
2. E Müller *Angew. Chem.* **61** 179 (1949)
3. S C Dickerman, D J DeSouza, N Jacobson *J. Org. Chem.* **34** 710 (1969)
4. M Allard *Bull. Soc. Chim. Fr.* **5** 1921 (1972)
5. A Krutosikova *Collect. Czech. Chem. Commun.* **39** 1892 (1974)
6. A V Dombrovskii *Usp. Khim.* **26** 695 (1957)
7. A V Dombrovskii, in *Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii* (Reactions and Methods of Investigation of Organic Compounds) (Moscow: GNTIKhL, 1962) p. 285
8. A V Dombrovskii *Usp. Khim.* **53** 1625 (1984) [*Russ. Chem. Rev.* **53** 956 (1984)]
9. C S Rondestvedt, in *Organic Reactions* Vol. 2 (Translated into Russian: Moscow: Mir, 1965) p. 199
10. N I Ganushchak, N F Stadniichuk, B D Grishchuk, A V Dombrovskii, in *II Ukrainskaya Respublikanskaya Konferentsiya po Organicheskoi Khimii (Tezisy Dokladov)* [The 2nd Ukrainian Republic Conference on Organic Chemistry (Abstracts of Reports)] (Dnepropetrovsk: Dnepropetrov. Univ., 1971) p. 85
11. N I Ganushchak, B D Grishchuk, A V Dombrovskii *Zh. Org. Khim.* **9** 1004 (1973)
12. N I Ganushchak, B D Grishchuk, V A Baranov, A V Dombrovskii *Zh. Org. Khim.* **9** 2142 (1973)
13. N I Ganushchak, B D Grishchuk *Zh. Vses. Khim. Ova im D I Mendeleeva* **18** 357 (1973)
14. N I Ganushchak, B D Grishchuk, V A Baranov, A V Dombrovskii *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **18** 1381 (1975)
15. N I Ganushchak, B D Grishchuk, A V Dombrovskii *Ukr. Khim. Zh.* **41** 499 (1975)
16. B D Grishchuk, P M Gorbovoi, N I Ganushchak, in *16 Ukrainskaya Konferentsiya po Organicheskoi Khimii (Tezisy Dokladov)* [The 16th Ukrainian Conference on Organic Chemistry (Abstracts of Reports)] (Ternopol': Pedagogicheskii Inst., 1992) p. 244
17. E E Bilaya, N I Ganushchak, N D Obushak, B D Grishchuk, Yu A Pozderskii, A L Bel'ferman *Zh. Obshch. Khim.* **56** 1916 (1986)
18. B D Grishchuk, P M Gorbovoi, L P Sviderskaya, A A Dyachuk, V P Tikhonov, N I Ganushchak *Zh. Obshch. Khim.* **60** 432 (1990)
19. J K Kochi *J. Am. Chem. Soc.* **78** 4815 (1956)
20. B D Grishchuk, P M Gorbovoi, N I Ganushchak *Zh. Obshch. Khim.* **59** 1868 (1989)
21. N I Ganushchak, B D Grishchuk, V A Baranov, T A Shilo, V G Nemesh *Ukr. Khim. Zh.* **43** 130 (1977)
22. B D Grishchuk, P M Gorbovoi, E Ya Kudrik, N I Ganushchak *Zh. Obshch. Khim.* **61** 2583 (1991)
23. B D Grishchuk, P M Gorbovoi *Tiotsianato-, Brom- i Khlorarilirovanie Akrilamida* (Thiocyanato-, Bromo- and Chloroarylation of Acrylamide) (Kiev, 1993) article deposited at the GNTB of Ukraine No 1057-Uk 93
24. N I Ganushchak, B D Grishchuk, V S Buryak, V I Mogil'nikov, N F Stadniichuk, A V Dombrovskii, in *12 Ukrainskaya Respublikanskaya Konferentsiya po Organicheskoi Khimii (Tezisy Dokladov)* [The 12th Ukrainian Republic Conference on Organic Chemistry) (Abstracts of Reports)] (Uzhgorod: Uzhgorod. Univ., 1974) p. 63
25. A V Dombrovskii, N I Ganushchak *Ukr. Khim. Zh.* **24** 217 (1958)
26. M M Yukhomenko, A V Dombrovskii *Ukr. Khim. Zh.* **33** 76 (1967)
27. N I Ganushchak, B D Grishchuk, A V Dombrovskii *Ukr. Khim. Zh.* **41** 499 (1975)
28. B D Grishchuk, P M Gorbovoi, N I Ganushchak, E Ya Kudrik, V B Grishchuk, O G Tikhonchuk, O V Mikhal'chuk, in *16 Ukrainskaya Konferentsiya po Organicheskoi Khimii (Tezisy Dokladov)* [The 16th Ukrainian Conference on Organic Chemistry (Abstracts of Reports)] (Ternopol': Pedagogicheskii Inst., 1992) p. 242
29. B D Grishchuk, P M Gorbovoi, N I Ganushchak *Zh. Obshch. Khim.* **58** 616 (1988)
30. B D Grishchuk, N G Prodanchuk, P M Gorbovoi *Khim.-Farm. Zh.* **11** 25 (1990)
31. B D Grishchuk, P M Gorbovoi, M V Vovk, A A Dyachuk, I A Martynyak, N I Ganushchak *Ukr. Khim. Zh.* **57** 89 (1991)
32. V M Naidan, G D Naidan, S G Drozdova, V M Musienko *Zh. Obshch. Khim.* **55** 391 (1985)
33. N I Ganushchak, N D Obushak, O P Polishchuk *Zh. Org. Khim.* **20** 654 (1984)
34. B D Grishchuk, Author's abstract of Candidate's Thesis in Chemical Sciences, Chernov. Univ., Chernovtsy, 1974
35. V M Naidan, G D Naidan *Zh. Org. Khim.* **10** 664 (1974)
36. V M Naidan, G D Naidan, A V Dombrovskii *Zh. Obshch. Khim.* **49** 1829 (1979)
37. V M Naidan, G D Naidan, G V Litvin *Zh. Org. Khim.* **14** 2010 (1978)
38. V M Naidan, G D Naidan *Zh. Obshch. Khim.* **48** 2787 (1978)

39. B D Grishchuk, N G Prodanchuk, P M Gorbovoi, V N Nivalov, V G Sinchenko *Khim.-Farm. Zh.* **2** 139 (1990)
40. E E Bilaya, N I Ganushchak, N D Obushak, B D Grishchuk, Yu A Pozderskii, A L Bel'ferman *Zh. Obshch. Khim.* **56** 1916 (1986)
41. N D Obushak, N I Ganushchak, E E Bilaya, B D Grishchuk, in *15 Ukrainskaya Respublikanskaya Konferentsiya po Organicheskoi Khimii (Tezisy Dokladov)* [The 15th Ukrainian Republic Conference on Organic Chemistry) (Abstracts of Reports)] (Uzhgorod: Uzhgorod. Univ., 1986) p. 270
42. B D Grishchuk, N G Prodanchuk, V G Sinchenko, P M Gorbovoi, E Ya Kudrik *Khim.-Farm. Zh.* **12** 47 (1991)
43. B D Grishchuk, P M Gorbovoi, N I Ganushchak, D M Brush, E Ya Kudrik *Zh. Obshch. Khim.* **63** 1655 (1993)
44. B D Grishchuk, P M Gorbovoi, E Ya Kudrik, V B Grishchuk, M V Volk, L P Sviderskaya, in *16 Ukrainskaya Konferentsiya po Organicheskoi Khimii (Tezisy Dokladov)* [The 16th Ukrainian Conference on Organic Chemistry (Abstracts of Reports)] (Ternopol': Pedagogicheskii Inst., 1992) p. 243
45. V M Naidan, G D Naidan, G V Litvin *Zh. Org. Khim.* **14** 2622 (1978)
46. V M Naidan, G D Naidan *Zh. Obshch. Khim.* **50** 2611 (1980)
47. B D Grishchuk, P M Gorbovoi, L P Sviderskaya, A A Dyachuk, V P Tikhonov, N I Ganushchak *Zh. Obshch. Khim.* **60** 432 (1990)
48. P M Gorbovoi, B D Grishchuk, Yu P Filinov *Neftepererabotka i Neftekhim.* **40** 63 (1991)
49. N I Ganushchak, N D Obushak, O P Polishchuk *Zh. Org. Khim.* **20** 654 (1984)
50. N I Ganushchak, N D Obushak, O P Polishchuk *Zh. Org. Khim.* 2554 (1986)
51. O P Polishchuk, Author's abstract of Candidate's Thesis in Chemical Sciences, L'vov, Polytechnical Inst., 1987
52. N I Ganushchak, N D Obushak, N S Fedorovich *Ukr. Khim. Zh.* **53** 970 (1987)
53. N D Obushak, N I Ganushchak, M B Lyakhovich *Zh. Org. Khim.* **27** 1757 (1991)
54. N I Ganushchak, V D Golik, I V Migaichuk *Zh. Org. Khim.* **8** 2356 (1972)
55. O Sulton *Chem. Rev.* **3** 443 (1975)
56. A Wells, in *Structural Inorganic Chemistry* Vol. 3 (Translated into Russian; Moscow: Mir, 1988) p. 239
57. S Yu Pavlov, in *Vydelenie i Ochistka Monomerov dlya Sinteticheskogo Kauchuka* (Isolation and Purification of Monomers for Synthetic Rubber) (Leningrad: Khimiya, 1987) p. 115
58. E P Koval'chuk, N I Ganushchak, N D Obushak, I N Krupak *Ukr. Khim. Zh.* **49** 161 (1983)
59. M B Lyakhovich, R G Gasanov, N D Obushak, N I Ganushchak, Z V Todres *Izv. Akad. Nauk SSSR, Ser. Khim.* **5** 1214 (1991)
60. D C Nonhebel, J C Walton, in *Free Radical Chemistry* (Translated into Russian; Moscow: Mir, 1977) p. 445
61. G Tsolinger *Khimiya Azokrasitelei* (Chemistry of Azo Dyes) (Leningrad: GNTIKhL, 1960)
62. N I Ganushchak, N D Obushak, E P Koval'chuk, G V Trifonova *Zh. Obshch. Khim.* **54** 2334 (1984)
63. L A Kiprianova, A F Levit, I P Gragerov *Teor. Eksp. Khim.* **12** 219 (1976)