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The Development and Synthetic Applications of the Meerwein Reaction

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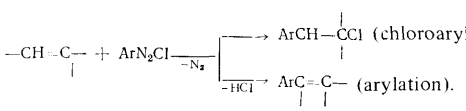
The development of the study of the Meerwein reaction is described and the reactions involving the anion-arylation and arylation of unsaturated compounds by aromatic diazo-compounds and catalysed by transition metal salts are examined and surveyed. The modern ideas about the mechanisms of these reactions and the possibility of their employment in organic synthesis are discussed.
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I. INTRODUCTION

Meerwein[1] described in 1939 the copper(II) chloride-catalysed reaction of unsaturated compounds with arenediazonium chlorides (ADC), which results in the elimination of the nitrogen of the diazo-group and the hydrogen attached to the sp^2-carbon atom is substituted by the aryl group or the aryl group and the chlorine atom add to the multiple bond. Subsequently these reactions were called arylation and chloroarylation respectively:[2]



The Meerwein reaction proved to be an extremely valuable synthetic method whereby it is possible to obtain aliphatic-aromatic olefins and polyfunctional compounds in a single step at low temperatures from a very large number of readily available, cheap, unsaturated compounds and aromatic amines. The olefins can be used in their turn in many reactions in organic synthesis to obtain substances of practical interest.

The subsequent development of this reaction involved the improvement of methods and expansion of the range of saturated and aromatic diazo-compounds employed, containing the anions Cl^-, Br^-, CN^-, HO^-, BF_4^-, $MeCOO^-$, SO_4H^-, NO_3^-, etc. Chloroarylation can be regarded as a special (albeit the commonest) case of the general reaction involving the anion-arylation of unsaturated compounds by aromatic diazo-compounds. Subsequently, it was found that, apart from $CuCl_2$, the reaction is catalysed by CuCl and other salts, mainly transition metal halides.

Since the discovery of the Meerwein reaction, several hundreds of publications, both experimental and theoretical, concerning chloroarylation and arylation of unsaturated compounds have appeared, mainly in the Soviety Union. The first survey of the reactions of unsaturated compounds with aromatic diazo-compounds was published by the present author.[3] Subsequently other reviews appeared,[4-6] covering the literature mainly up to 1970, in which the results obtained were not fully described. This review suggests and surveys the literature data up to 1983. The results of earlier studies are quoted only in so far as it is necessary.

II. THE REACTION MECHANISM

The mechanism of the Meerwein reaction has been discussed for a long time. It was not clear whether the reaction is of the ionic or radical type. The question of what is in actual fact the catalyst, $CuCl_2$ or CuCl, has been controversial; in the absence of these salts, neither chloroarylation nor arylation occurs in most cases. There was a need for theoretical and experimental explanations of a number of side reactions and products accompanying the chloroarylation and arylation reactions. Different versions of the mechanism of this reaction, based on theoretical and experimental studies performed with different degrees of scientific expertise, have been proposed at different times. The polar mechanism proposed by Meerwein[1] and other investigators[2-4] proved unacceptable for a number of reasons. In both early and later studies the majority of investigators of this reaction concluded that, like the Sandmeyer reaction, the Meerwein reaction is catalysed by copper(I) halides and has a radical mechanism.[7,8]

The Meerwein reaction should probably be regarded as an extended version of the Sandmeyer reaction, which in this case occurs in the presence of an unsaturated compound. In the Sandmeyer reaction the aryl radicals and halogen atoms combine to form aryl halides. On the other hand, in the presence of an unsaturated compound, these species interact with the multiple bonds to form chloroarylation and arylation products. The involvement of the molecules of the unsaturated compound, interacting with the arenediazonium ion and the catalyst, apparently leads to the appearance of a ternary reaction complex in the simplest case,[9] which in its turn modifies the mechanism of the entire process.

It is known that transition metal halides, including copper-halides, react with arenediazonium chlorides to form complexes (double salts),[10-14] which are relatively stable in aqueous organic solutions in the cold and at room temperature but begin to decompose after the addition of an unsaturated compound. It has been demonstrated by ultraviolet and infrared spectroscopy[15] that there is a chemical bond between the metal ions and the nitrogen of the diazo-group in double salts of this kind. On the other hand, it is known that copper(I) halides form π-complexes with many olefins even in an aqueous medium. Such complexes react with the ADC to form the product of the Meerwein reaction. The stability of the complexes diminishes in the sequence CuCl > CuBr > CuI; the cyanide CuCN does not form complexes and does not catalyse the Meerwein reaction.[16] The Meerwein reaction and

the catalytic effect of copper halide on the latter should therefore be regarded as radical oxidation-reduction addition to olefins[17] whose mechanism includes a series of consecutive elementary reactions leading to the main and side products. The most logical and experimentally demonstrated mechanism of the interaction of the ADC–copper chloride–unsaturated compound system has been proposed by Schrauzer[18] [reactions (1)–(8)].

Under the classical conditions of the Meerwein reaction, an aqueous acetone solution of $CuCl_2$, whose reduction by acetone to CuCl is well known[19] [reaction (1)], is used. The CuCl generated at the instant of reaction is apparently more reactive than the preparation obtained beforehand. The CuCl formed during the reaction or introduced as such forms a double salt with the ADC [reaction (2)], in which the diazo-group is coordinated to the complex anion $CuCl_2^-$; such complexes are known for transition metal chlorides.[20] The double salt then forms a ternary reaction complex with the olefin (–CH=C<), in which the diazo-group and the olefin are linked to the copper ion in conformity with the coordination number, which is two [reaction (3)]. The details of the binding and of the geometry of the species within the ternary complex are so far unknown.

The onset of reaction is signalled by the evolution of nitrogen (as a result of its elimination from the diazo-group), which begins only after the addition of the olefin. Under the influence of the polarising action of the copper ion and the olefin, the arenediazonium cation is reduced to the radical Ar·. The electrochemical reduction of arenediazonium salts at copper, iron, and other metal cathodes in the presence of unsaturated compounds has demonstrated[21] that this involves the generation of aryl radicals, which interact with the π-bond of the olefin. In this case the diazonium cation is initially reduced via a one-electron mechanism to the arenediazonium radical, which then decomposes to the radical Ar· and free nitrogen:[21–23]

$$[PhN_2]^+ + e \rightarrow PhN_2^{\cdot} \rightarrow Ph^{\cdot} + N_2 .$$

Without being released into the bulk of the medium, the radical Ar· reacts with the olefin to form an aliphatic-aromatic radical [reaction (4)] whose interaction with $CuCl_2$ entails the formation of the chloroarylation product as a consequence of the transfer of the radical species Cl· [reaction (5)]. If there is a hydrogen atom at the α-carbon atom in the aliphatic component of the aliphatic-aromatic radicals, the latter can be eliminated together with a chlorine atom in the form of HCl [reaction (5a)], which constitutes one of the interpretations of the arylation mechanism.[6] One cannot rule out the possibility that the hydrogen atom in the olefin or another ligand can be substituted by the radical Ar· directly:

$$2CuCl_2 + Me_2CO \rightarrow 2CuCl + MeCOCH_2Cl + HCl , \quad (1)$$

$$ArN_2^+Cl^- + CuCl \rightleftarrows ArN_2^+CuCl_2^- , \quad (2)$$

$$ArN_2^+CuCl_2^- \underset{\leftarrow}{\overset{-HC\equiv C<}{\rightarrow}} \left[ArN_2^+CuCl_2^- \cdot \begin{matrix} -C- \\ \| \\ -CH \end{matrix} \right] , \quad (3)$$

$$\left[ArN_2^+CuCl_2^- \cdot \begin{matrix} -C- \\ \| \\ -CH \end{matrix} \right] \xrightarrow{-N_2} [ArCH-\dot{C}-\cdots Cu^{\cdot}Cl_2] , \quad (4)$$

$$[ArCH-\dot{C}-\cdots Cu^{\cdot}Cl_2] \xrightarrow{-CuCl} \begin{cases} \rightarrow ArCH-C(Cl)- , & (5) \\ \xrightarrow{-HCl} ArC(=)C- , & (5a) \end{cases}$$

$$Ar^{\cdot} + Cu^{\cdot}Cl_2 \rightarrow ArCl + CuCl , \quad (6)$$

$$Ar^{\cdot} + Me_2CO \rightarrow ArH + MeCO\dot{C}H_2 , \quad (7)$$

$$ArN_2Cl + H_2O \rightarrow ArOH + HCl + N_2 , \quad (8)$$

$$ArCH-\dot{C}H-\cdots CuCl_2 \xrightarrow[-CuCl]{-HC\equiv C-} Ar(CH=\dot{C}-)_2Cl , \quad (9)$$

$$2ArC(H)-\dot{C}- \rightarrow \left(ArC(H)-C- \right)_2 . \quad (10)$$

Thus, under the conditions of "cuprocatalysis", the chloroarylation proceeds as a redox-initiated free radical addition via stage involving the formation of intermediate complexes of the catalyst with the diazo-compound and with the unsaturated compound.

If for any reason the radical species Ar· and Cl· leave the inner sphere of the reaction complex, side reactions take place, in the first place the formation of ArCl (the Sandmeyer reaction), aromatic hydrocarbons and phenols reaction (6)–(8). The Meerwein reaction is also accompanied by the formation of resins, telomers, and additive dimers. The telomers are formed if the aliphatic-aromatic radical reacts with the next molecule of the monomeric olefin and then the $CuCl_2$ radical [reaction (9)]. As in the polymerisation of unsaturated compounds in the presence of variable-valence catalysts, telomers appear in this instance and under certain conditions can be the main reaction products.[24–29] Additive dimers arise as a consequence of the recombination of the same aliphatic-aromatic radicals [reaction (10)].[30,31]

Arylation formally involves the substitution of a hydrogen atom at a carbon atom involved in the multiple bond by the aryl group of the diazo-compound. Arylation should apparently be regarded in most cases as an addition–elimination process, which can be demonstrated by purely chemical means. It has been shown[32] that, on interaction with the ADC, α-chlorostyrene gives rise smoothly and in satisfactory yields to the α-chlorostilbenes PhCCl=CHAr (Ar = Ph, 4-MeC_6H_4, or 4-$O_2NC_6H_4$). If α-bromostyrene is used in the reaction, then the same α-chlorostilbenes are obtained in virtually quantitative yields:[33]

$$PhCBr=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} [PhCBrCl-CH_2Ar] \xrightarrow{-HBr} PhCCl=CHAr .$$

Consequently, the arylation of α-halogenostyrenes proceeds via a stage involving the addition of the Ar group and the Cl atom of the arenediazonium cation to the ethylenic bond. Since the C–Cl bond in the adduct obtained from α-bromostyrene is stronger than the C–Br bond, HBr and HCl are split off on spontaneous decomposition of the unstable intermediate adduct and α-chlorostilbene is obtained as a result.

III. FACTORS DETERMINING THE EFFECTIVENESS OF THE REACTION

The effectiveness of the reaction, i.e. the yields of the chloroarylation and arylation products, depends on a series of factors, the most important of which are as follows.

The unsaturated component (olefin). The vinyl monomers $H_2C=CH-X$ and $H_2C=CX_2$, in which the ethylenic bond has been activated by one or two electron-accepting groups (X = Cl, CN, Ar, $-C=CH_2$, COR, COOH, COOAlk, etc.) usually react satisfactorily. Because copper halides are capable of transferring radical chains very effectively, such monomers do not give rise to high-molecular-weight compounds. Ethylene, acetylene, and their substituted derivatives, containing electron-donating groups, react poorly. The unsaturated compounds RHC=CHR in which the double bond has been blocked also react with difficulty.

The arenediazonium component. ADC (concentrated or even saturated aqueous solutions are used for the reaction), which are capable of forming complexes with copper halides,

give the best results in most cases. Arenediazonium salts containing other anions usually give rise to lower yields of chloroarylation and arylation products.

The best yields of products are obtained when the *para*-position in the aromatic ring contains a substituent, regardless of the electronic effect which it exhibits; *ortho*- and *meta*-substituted derivatives give rise to lower yields.

Apart from arenediazonium salts (including tetrafluoroborates[34,35]), other compounds forming aryl radicals, for example, benzoyl peroxide, arylhydrazone peroxides, 1-aryl-3,3-dimethyltriazenes, *N*-nitrosoacetanilides, diazoaminobenzene, and diaryliodonium salts, have been proposed for the arylation of olefins;[6] aryl radicals generated by the electrochemical reduction of diazonium salts have also been used.[21] However, with the exception of arylpalladium reagents,[36,37] such sources of aryl radicals have given lower yields of arylation products and in most cases initiated the polymerisation of the olefins.[6]

Catalysts. Apart from copper halides, the salts $FeCl_2$,[30,31,38] $HgCl_2$,[39] $LiPdCl_3$,[40] and Pd(0) (obtained *in situ*)[41] and the $CuSO_4 + FeSO_4$, $Cu(NO_3)_2 + Cu$, and $Cu(NO_3)_2 + Fe$ systems[30] have been used for chloroarylation and arylation. However, $CuCl_2$ and CuCl, used in an amount equivalent to 10–20 mole % per mole of the ADC, still remain the best catalysts. An increase of the catalyst concentration promotes the occurrence of the Sandmeyer reaction, while at lower concentrations ArH is formed.[2,6]

The catalytic capacity of copper halides, iron(II) salts, and certain other redox initiators, can be explained by the comparatively low oxidation-reduction potentials E of the ions of these metals; for example, $E = 0.16$ eV for the $Cu^+ \rightarrow Cu^{2+}$ system and $E = 0.77$ eV for $Fe^{2+} \rightarrow Fe^{3+}$.

The potentials E for the metal ions in the salts $FeCl_3$, $AlCl_3$, $ZnCl_2$, $CdCl_2$, $CoCl_2$, $MnCl_2$, and $NiCl_2$, which do not catalyse or only weakly catalyse chloroarylation and arylation, are significantly higher.[31] Cases are known where arylation takes place in the absence of catalysts, for example, in the reactions of arenediazonium salts with coumarin,[1] quinones, and ferrocene,[2] which can be accounted for by the fairly low oxidation-reduction potentials of these compounds.[31]

Solvents. The chloroarylation and arylation reactions usually take place in aqueous organic media with vigorous stirring. In the absence of water, the reactions hardly begin. In those cases where the arenediazonium and olefinic components dissolve in water, the reactions have been achieved successfully in aqueous media.[2,6] The nature of the organic solvent has a significant influence on the effectiveness of the reaction. The most important requirement which this organic solvent must meet is that it is miscible with water without binding the catalyst chemically at the same time. Solvents such as tetrahydrofuran (THF), 1,4-dioxan, ether, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and pyridine, which apparently bind copper halides and other catalysts in complexes removing them from the reaction sphere thereby, proved to be ineffective.[2,6,42]

Acetone, acetonitrile, and sulpholan proved to be the most suitable solvents. A water–acetone mixture, the volume ratios of the components of which are varied in the range 3 : 1–7 : 10, is usually employed for the reactions.

The pH of the medium. Media close to neutrality (pH 4–6) are optimal in reactions with arenediazonium salts containing electron-donating substituents in the aromatic ring. In the presence of electron-accepting substituents in the ring a high acidity of the medium is required (pH 1–2). It has been suggested that MeCOONa, CaO, $Ca(OH)_2$, and $NaHCO_3$ be added to the reaction mixture in order to maintain and regulate the necessary pH.[2]

Temperature. The chloroarylation and arylation reactions proceed under mild conditions as regards temperature (from −5 to +30 °C). In a few instances the evolution of nitrogen begins at −10 °C. If the temperature is not regulated, then the interaction becomes vigorous, the temperature rises rapidly, and nitrogen is evolved in abundance; in such cases the Sandmeyer reaction and resin formation predominate.

IV. THE LATEST DATA ON THE MEERWEIN REACTION

Studies devoted to the reactions of olefins and their derivatives with arenediazonium salts, which have not been included in previous reviews,[2,3,6] are discussed below. In a number of instances the applications of the products of the anion-arylation and arylation reactions in organic synthesis are indicated.

1. Alkenes, Halogenoalkenes, and Certain Vinyl Monomers

The simplest alkenes, namely ethylene and propene, react with difficulty even with the most reactive ADC. Only under comparatively severe conditions in an autoclave, does ethylene react with diazotised 4-nitroaniline to form 1-chloro-2-(4-nitrophenyl)ethane (45–50%),[43] which is quantitatively converted into 4-nitrostyrene on dehydrochlorination:[2]

$$H_2C{=}CH_2 + 4\text{-}O_2NC_6H_4N_2Cl \xrightarrow[42^\circ C;\ 70\text{–}75\ atm\ N_2]{CuCl_2} \rightarrow 4\text{-}O_2NC_6H_4CH_2CH_2Cl \xrightarrow[-NaCl]{NaOH} 4\text{-}O_2NC_6H_4CH{=}CH_2 .$$

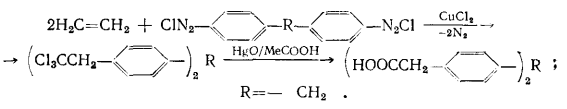
Halogenoalkenes with halogen atoms attached to the sp^2-carbon atom give rise to chloroarylation products on interaction with ADC; the mode of addition to the multiple bond is then consistent with the Markovnikov rule. The vinyl chloride gives rise to 1,1-dichloro-2-arylethanes (60–70%),[44–46] which have served as starting materials for the synthesis of 4-nitrophenylacetaldehyde,[47] β-chlorostyrenes,[48] 1,4-bis-(β-chlorovinyl)benzene, and 1,3-dioxolan-4-ylphenylenediacetaldehyde:[46]

$$H_2C{=}CHCl + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CHCl_2 ;$$
$$Ar{=}Ph,\ 4\text{-}MeC_6H_4,\ 4\text{-}MeOC_6H_4,\ 4\text{-}BrC_6H_4,$$
$$2,4\text{-}Cl_2C_6H_3,\ 4\text{-}O_2NC_6H_4 .$$

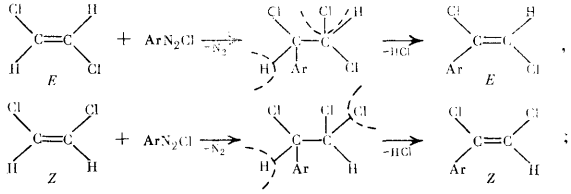
Vinylidene chloride reacts particularly effectively with ADC to form 2,2,2-trichloroarylethanes (~80%),[49] which proved to be convenient starting materials for the synthesis of arylacetic acids[50] and 1,4-bis(ββ-dichlorovinyl)benzene:[51]

$$H_2C{=}CCl_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl_3 ;$$
$$Ar\text{-}4\text{-}MeC_6H_4,\ 4\text{-}ClC_6H_4,\ 4\text{-}MeOC_6H_4,$$
$$4\text{-}O_2NC_6H_4,\ 4\text{-}Cl_3CH_2C_6H_4 .$$

Biphenyl-4,4′-bisdiazonium chloride reacts via both diazo-groups with two molecules of vinylidene chloride to form 4,4′-bis(2,2,2-trichloroethyl)biphenyl (30%), which is converted into biphenyl-4,4′-diacetic acid after hydrolysis. Vinylidene chloride reacts analogously with tetrazonium chloride containing a bridging group between the benzene rings:[52]



The symmetrical dichloroethylene reacts poorly with ADC. The reactivity of the *E*-isomer is twice as high as that of the *Z*-isomer. The reaction results in the formation of 2-aryl-1,1,2-trichloroethanes (two conformers), which are converted into the *E*- and *Z*-aryl-1,2-dichloroethylenes on alkaline dehydrochlorination. HCl is eliminated as a result of the abstraction of the α-hydrogen atom and the chlorine atom from the transoid β-position:[53]



Ar = Ph, 4-ClC_6H_4.

1,3-Dichlorobut-2-ene reacts with benzenediazonium chloride to form $MeCCl_2CH(Ph)CH_2Cl$ in a low yield (~30%),[54] while trichloroethylene gives rise to moderate yields (~50%) of aryl-1,1,1,2-tetrachloroethanes, which are smoothly dehydrochlorinated by an alcoholic solution of alkali to give α,β,β-trichlorostyrenes:[55]

$$ClHC{=}CCl_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCHClCCl_3 \xrightarrow[-HCl]{KOH} ArCCl{=}CCl_2;$$
Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$

Fluorine-containing olefins react with ADC in the usual way, forming adducts, which are converted on dehydrochlorination into the corresponding fluorine-containing aryl derivatives,[56] for example:

$$F_2CHCF_2CH{=}CH_2 + 4\text{-}RC_6H_4N_2Cl \xrightarrow[N_2]{CuCl_2,\ 33^\circ C} \rightarrow$$
$$\rightarrow F_2CHCF_2CHClCH_2C_6H_4R\text{-}4 \xrightarrow[-KCl,\ -H_2O]{KOH/MeOH} F_2CHCF_2CH{=}CHC_6H_4\text{-}R\text{-}4;$$
R = Cl, NO_2, COOH (28—50%).

$F_2CHCF_2C(Me){=}CH_2$, $F_2CH(CF_2)_3CF{=}CF_2$, $CF_3(CF_2)_4CF{=}CF_2$, and $C_4H_9CF{=}CFCl$ react analogously; chlorotrifluoroethylene gives rise to the adducts $ArCF_2CFCl$ (27%) only under comparatively severe conditions (40–50 °C, in an autoclave), while $H_2C{=}CF_2$ and $F_2C{=}CF_2$ hardly react even with the most reactive ADC.[56]

1,1,1-Trifluoropropene reacts with 4-nitrobenzenediazonium halides to form adducts (yield 30–40%), which are also readily dehydrohalogenated and give almost quantitative yields of 2-(4-nitrophenyl)-1-trifluoromethylethylenes:[57]

$$F_3CCH{=}CH_2 + ArN_2X \xrightarrow[MeCOONa]{CaX_2,} F_3CCHXCH_2Ar \xrightarrow[-HCl]{Et_3N} F_3CCH{=}CHAr;$$
Ar = 4-$O_2NC_6H_4$; X = Cl, Br.

The reactions of ADC (catalysed by $CuCl_2$) with vinylsilanes, vinylphosphonate, and vinyl sulphones also involve the addition of chlorine and the aryl groups in the α- and β-positions respectively to the vinyl component. Vinylsilane $Ph_3SiCH{=}CH_2$ gives rise to 15–37% yields of the compounds $Ph_3SiCHClCH_2Ar$ (Ar = 4-ClC_6H_4, 4-BrC_6H_4, 4-$HOCOC_6H_4$, or 3- and 4-$O_2NC_6H_4$);[2] the reactions of $(EtO)_2P(O)CH{=}CH_2$ result in 45% yields of the compounds $(EtO)_2P(O)CHClCH_2Ar$ (Ar = Ph or 4-ClC_6H_4).[58]

Vinyl sulphones react analogously with ADC to form β-aryl-α-halogenoethyl sulphones (yields up to 45%), which are converted on dehydrochlorination into styryl sulphones in high yields:[59–61]

$$RSO_2CH{=}CH_2 \xrightarrow[-N_2]{ArN_2X,\ CuCl_2} RSO_2CHXCH_2Ar \xrightarrow[HX]{base} RSO_2CH{=}CHAr;$$
R = Me, Et, CF_3, 4-MeC_6H_4; X = Cl, Br;
Ar = Ph, 4-FC_6H_4, 4-ClC_6H_4, 3- and 4-$O_2NC_6H_4$, 4-$HOCOC_6H_4$.

2. Acetylenes

The C≡C bond is less reactive in the reactions with ADC than the C=C bond. Like ethylene, acetylene itself undergoes the Meerwein reaction with 4-nitrobenzenediazonium chloride to form a low yield (~20%) of the chloroarylation product, which is wholly dehydrochlorinated by an alcoholic solution of alkali and is converted into 4-nitrophenylacetylene. Substituted acetylenes are more reactive. Thus phenylacetylene is chloroarylated to α-chlorostilbenes in satisfactory yields (46–70%) and the latter have been converted on dehydrochlorination into tolanes (yield 85%):[2]

$$R{-}C{\equiv}CH + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} R{-}CCl{=}CH{-}Ar \xrightarrow[-HCl]{KOH/\ dioxan} R{-}C{\equiv}C{-}Ar;$$
R = H, Ph; Ar = Ph, 4-$O_2NC_6H_4$.

Vinyl- and isopropenyl-acetylenes react with ADC via the ethylenic bond to form chloroarylbutynes, which are converted into arylbutenynes on dehydrochlorination. Allene derivatives have been detected in small amounts together with the chloroaryl derivatives:[62–64]

$$H_2C{=}CR{-}C{\equiv}CH + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl(R){-}C{\equiv}CH \xrightarrow[-HCl]{KOH} \rightarrow$$
$$\rightarrow ArCH{=}CR{-}C{\equiv}CH;$$
R = H, Me; Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$.

Tetrazonium chloridee based on 4,4′-diaminobiphenyl, 4,4′-diamino-3,3′-dimethoxybiphenyl, di(4-aminophenyl) sulphone, and di(4-aminophenyl) ether react via the acetylenic bond with propargyl alcohol, propargylic acid, and phenylacetylene (in the presence of CuCl as the catalyst) with evolution of nitrogen from both diazo-groups, forming bischloroarylation products (46–58%):[65]

$$2HC{\equiv}CR + R''[{-}C_6H_3(R')N_2Cl]_2 \xrightarrow[2N_2]{CuCl_2} [{-}C_6H_3(R')CH{=}CClR]_2R'';$$
R = MeO, COOH, Ph; R′ = H, MeO;
R″ = —, CH_2, SO_2, O.

3. Arylethylenes

Arylethylenes in which the aryl group is conjugated with the ethylenic bond have been widely used in the anion-arylation and arylation reactions. Arylethylenes with a terminal $>C{=}CH_2$ group exhibit an enhanced reactivity. Apart from the electronic effects, steric factors have an effect in this case.

Styrene reacts with ADC at pH ~ 5 ($CuCl_2$, aqueous acetone solution of MeCOONa) to form stilbenes;[2] however, in an acidic medium (pH 1–2) chloroarylation takes place and 2-aryl-1-chloro-1-phenylethanes are formed in satisfactory yields and are readily dehydrochlorinated and converted almost quantitatively into substituted stilbenes:[66–68]

$$PhHC{=}CH_2 + ArN_2Cl \xrightarrow[-N_2]{\begin{cases} \xrightarrow[-HCl]{pH\sim5} PhHC{=}CHAr, & (a) \\ \xrightarrow{pH\ 1\text{-}2} PhHCClCH_2Ar \xrightarrow[-HX]{base} PhHC{=}CHAr; & (b) \end{cases}}$$
(a) Ar-4-ClC_6H_4, 4-$MeOC_6H_4$;
(b) Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 4-$EtOCOC_6H_4$, 4-$Et_2NC_2H_4OCOC_6H_4$, 2-$O_2NC_6H_4$, 3-$O_2NH_6H_4$, 4-$O_2NC_6H_4$.

Arylethylenes containing electron-donating substituents in the aromatic ring or at the ethylenic bond are as a rule readily arylated. The reaction is one of the practically convenient methods of synthesis of substituted stilbenes, frequently in high yields; examples are presented below (the yields expressed as percentages are indicated in brackets):

$$RR^1C{=}CHR^2 + ArN_2Cl \xrightarrow[-N_2]{} RR^1C{-}CR^2Ar + HCl;$$

R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$; R^1 = H, Me, F, Cl, Ph; R^2 = H, Et; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$, 4-$HOCOC_6H_4$, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-$MeCOC_6H_4$, 4-$HOSO_2C_6H_4$, 4-$H_2NSO_2C_6H_4$, 4-$Et_2NC_6H_4C_6H_4$, 4-$Et_2NC_6H_4OCOC_6H_4$ [2, 33, 68, 69]

Styrene enters into the copper salt-catalysed anion-arylation reaction with benzenediazonium salts in the presence of sodium nitrite or sulphide:[70]

$$PhHC{=}CH_2 \xrightarrow[-N_2]{PhN_2Cl,\ CuCl_2} \begin{cases} \xrightarrow{NaNO_2} PhCH(NO_2)CH_2Ph \quad (20\%), \\ \xrightarrow{Na_2S} (PhCH_2CHPh)_2S \quad (25\%). \end{cases}$$

Anion-arylation of styrenes. Styrene reacts with arenediazonium sulphates in an acetic acid–acetone solution saturated with sulphur(IV) oxide in the presence of thiocyanate anions and copper(I) thiocyanate. It is assumed that arenediazonium thiocyanates are formed in the reaction and then generate Ar$^{\cdot}$ radicals. The latter react with SO_2 to form arenesulphonyl radicals, which add together with thiocyanate radicals to the ethyleneic bond of styrene. This results in the formation of 2-(arenesulphonyl)-1-phenyl-1-thiocyanatoethanes (in ~60% yields):[47]

$$ArN_2SO_4H + NH_4SCN \rightleftarrows ArN_2SCN + NH_4HSO_4,$$

$$ArN_2SCN \xrightarrow[-N_2]{SO_2,\ CuSCN} [ArSO_2^{\cdot} + {\cdot}SCN] \xrightarrow{PhHC{=}CH_2} PhHC(SCN)CH_2SO_2Ar;$$

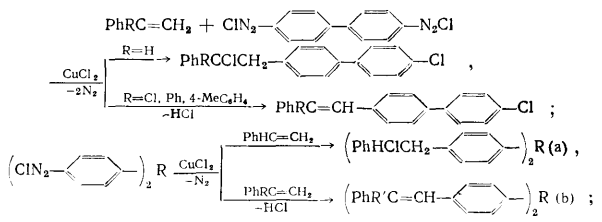
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$.

Under analogous conditions but in the presence of chloride, bromide, *O,O*-diethyl phosphorodithioate, or xanthate anions and catalytic amounts of copper ions, styrene reacts with aromatic diazo-compounds, forming crystalline anion-sulphonylation products (in yields of ~80%): 2-(arenesulphonyl)-1-chloro-1-phenylethanes, 2-(arenesulphonyl)-1-bromo-1-phenylethanes, 2-(arenesulphonyl)-1-(*O,O*-diethylphosphorodithioato)-1-phenylethanes, and 2-(arenesulphonyl)-1-(*O*-ethyl dithiocarbonato)-1-phenylethanes:[48]

$$PhHC{=}CH_2 + ArN_2X + SO_2 + MHal \xrightarrow{CuHal} PhHC(Hal)CH_2SO_2Ar;$$

X = Cl, Br, SO_4H; M = Na, K; Hal = Cl, Br, $(EtO)_2PS_2$, EtOC(S)S; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

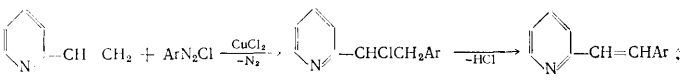
Styrene reacts with biphenyl-4,4′-bisdiazonium chloride with evolution of nitrogen from both diazo-groups, one of which undergoes the Sandmeyer reaction, while the other chloroarylates one styrene molecule to form 4-chloro-4′-(2-chloro-2-phenylethyl)biphenyl in 57% yield. α-Substituted styrenes (R = Ph, Cl or 4-MeC_6H_4) gives rise to products of arylation involving one diazo-group, while the other diazo-group is substituted by chlorine (yields ~50%):[52]



(a) R = S (40), CH_2 (67);
(b) R = S; R′ = Cl (33), Ph (49); R = CH_2; R′ = Cl (54), Ph (49).

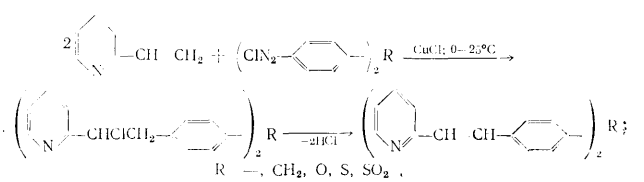
It has been stated[71] that styrene is arylated by bisdiazotised benzidine to form 4,4′-distyrylbiphenyl (yield 14%). Tetrazonium chlorides with a bridging S atom or CH_2 group between the benzene rings react with styrene via both diazo-groups. In reaction (a) the diazo-groups of di(4-diazoniaphenyl)-sulphide chloride and di(4-diazoniaphenyl)methane chloride react with two molecules of styrene to form chloroarylation products. In reaction (b) α-substituted styrenes react with the same tetrazonium chlorides to form arylation products[52] (the yields expressed as percentages are given in brackets). Numerous biphenyl, diphenyl sulphide, and diphenylmethylene derivatives have been synthesised from compounds obtained by chloroarylating and arylating various styrenes by tetrazonium chlorides.[52]

Like styrene, 2-vinylpyridine reacts with ADC to form 2-aryl-1-chloro-1-(2′-pyridyl)ethanes (in 50–60% yields), which are readily converted into 2-stilbazoles on dehydrochlorination (80–96%):[72]



Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 2-$O_2NC_6H_4$, 4-$O_2NC_6H_4$.

2-Vinylpyridine is also readily chloroarylated by tetrazonium chlorides, giving rise to bisadducts, which are converted into bis-stilbazoles (in 80% yield) on treatment with an alcoholic solution of alkali:[73]



R = —, CH_2, O, S, SO_2.

4. Conjugated Dienes

Conjugated dienes react extremely vigorously with aromatic diazo-compounds, evolving nitrogen from the diazo-group and giving rise to arylation, chloroarylation, and anion-arylation products, which are formed readily when the reaction is catalysed by both $CuCl_2$ and CuCl.

In order to explain the mechanism of the chloroarylation of conjugated dienes, it has been assumed,[8] on the basis of data obtained from conductimetric measurements in the ArN_2Cl–CuCl-buta-1,4-diene system, that the chlorine atom in the double salt of arenediazonium and copper(I) chlorides is substituted by the diene. The resulting ternary complex decomposes with evolution of nitrogen from the diazo-group as a consequence of a redox process within the complex and with participation of the copper ion, accompanied by the simultaneous addition of the aryl radicals and chlorine atoms formed to the diene in the 1- and 4-positions. This leads to the formation of 1-aryl-2-chlorobut-2-enes:

$$ArN_2Cl + CuCl \rightleftarrows [ArN_2CuCl]^+Cl^- \xrightarrow{diene} [ArN_2 \cdot diene \cdot Cu^-]^{2+} 2Cl^-;$$

$$[Ar{:}N_2{:}diene{\cdot}Cu]^{2+}2Cl^- \xrightarrow[-N_2]{} ArCH_2CH{-}CHCH_2Cl + CuCl;$$

diene = $CH_2{-}CH{=}CH{-}CH_2$.

The mechanism proposed also makes it possible to account for the chloroarylation of unsaturated monomers and the formation of the products of the side reactions (ArCl, telomers, additive dimers, etc.).[52]

Numerous reactions of buta-1,4-diene with ADC and other anion-substituted arenediazonium compounds have been carried out. In most cases *trans*-chloroarylbutenes are obtained in satisfactory yields (50–80%):[2,8,74,75]

$$CH_2=CH-CH=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CH=CHCH_2Cl\ ;$$

Ar=Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-$HalC_6H_4$ (where Hal=F, Cl, Br, I), 2,4-$Cl_2C_6H_3$, 2,4-$Br_2C_6H_3$, 2-, 3- and 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$, 4-$H_2NSO_2C_6H_4$, 4-$Et_2N(CH_2)_2OCOC_6H_4$,



Divinyl sulphone, in which there is virtually no conjugation between the vinyl groups, reacts with ADC to form adducts involving both one and two vinyl groups (in yields of ~50%):[76]

$$(H_2C=CH)_2SO_2 \xrightarrow[-N_2]{ArN_2Cl,CuCl_2} \begin{cases} \longrightarrow ArCH_2CHClSO_2CH=CH_2 \\ \longrightarrow (ArCH_2CHCl)_2SO_2 \end{cases};$$

Ar=Ph, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

Isoprene is chloroarylated in the 1- and 4-positions with formation of 1-aryl-4-chloro-2-methylbut-2-enes (yields 65–70%):[2,75]

$$H_2C=C(Me)-CH=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2C(Me)=CHCH_2Cl\ ;$$

Ar=Ph, 4-MeC_6H_4; 4-$HalC_6H_4$ (where Hal=F, Br, I), 4-$MeOC_6H_4$, 4-$Et_2N(CH_2)_2OCOC_6H_4$.

Mono- and dichloro-substituted conjugated dienes react analogously with ADC, giving satisfactory yields of 1,4-adducts:[2,77–80]

$$H_2C=CH-CCl=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CH=CClCH_2Cl,$$

$$H_2C=CH-CH=CHCl + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CH=CHCHCl_2,$$

$$H_2C=CCl-CCl=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl=CClCH_2Cl\ ,$$

$$H_2C=CCl-C(Me)=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl=C(Me)CH_2Cl\ .$$

In its reaction with ADC piperylene combines in all cases with the Ar$^{\cdot}$ radical at the methylene group. However, the chlorine atom of the diazo-compound adds in both 2- and 4-positions of the conjugated system, forming a mixture of arylchloropentenes (overall yield 60–70%). The latter are so unstable that they lose HCl already during their isolation or purification; 1-arylpenta-1,3-dienes are obtained on a preparative scale when the above chloro-derivatives interact with bases:[81]

$$H_2C=CH-CH=CHMe + ArN_2Cl \xrightarrow[-N_2]{} \begin{cases} \longrightarrow ArCH_2CHClCH=CHMe \\ \longrightarrow ArCH_2CH=CHCHClMe \end{cases} \xrightarrow[-HCl]{} ArCH=CH-CH=CHMe\ ;$$

Ar=Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

Bi-isopropenyl is chloroarylated to 4-chloro-2,3-dimethylbut-2-enes (in yields of 50–58%):[82]

$$H_2C=C(Me)-C(Me)=CH_2 + ArN_2Cl \xrightarrow[-N_2]{} ArCH_2C(Me)=C(Me)CH_2Cl\ ;$$

Ar=Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$.

The chloroarylation of conjugated dienes catalysed by $FeCl_2$ has been described. The yields of the chloroarylbutenes obtained thereby are somewhat lower (~55%); in this case the reaction is accompanied by the formation of considerable amounts of the products of the Sandmeyer reaction, telomers, and the products formed as a result of the additive dimerisation of the initial monomers.[30,31]

Tetrazonium chloride based on benzidine and diamines containing bridging R^2 groups between the benzene rings chloroarylate conjugated dienes with participation of both diazo-groups (yields 50–60%):[83–85]

$$2H_2C=CR-CH=CH_2 + \left(ClN_2-C_6H_3(R^1)-\right)_2R^2 \xrightarrow[-2N_2]{CuCl_2} \rightarrow \left(ClCH_2CR=CHCH_2-C_6H_3(R^1)-\right)_2R^2\ ;$$

R=H, Me, Cl; R^1=H, Me, MeO; R^2=—, S, CH_2.

Chloroarylbutenes are compounds exhibiting different types of reactivity which have been used as the starting materials for the synthesis of many new substances which are otherwise difficult to obtain. Chloroarylbutenes are readily dehydrochlorinated by bases, being converted thereby into α-arylbutadienes. In particular, a convenient method has been developed for the dehydrochlorination of chloroarylbutenes by heating in dioxan with KOH or NaOH powder, which makes it possible to obtain very satisfactory yields of α-arylbutadienes with various substituents in the benzene ring and in the side chain:[2,77]

$$ArCH_2CR^1=CR^1CH_2Cl \xrightarrow[-HCl]{base} ArCH=CR-CR'=CH_2\ ;$$

R=R′=H; R=Me, R′=H; R=Cl, R′=H; R=R′=Me; R=Ph, R′=H; Ar=Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$ etc.

The reactions involving the substitution of the allyl chlorine atom in chloroallylbutenes are widely used for the synthesis of 1-alkyl-4-arylbut-2-enes,[2] 1-alkoxy- and 1-amino-4-arylbut-2-enes,[79,86] the corresponding quaternary ammonium salts,[74] *N*-arylbutenyldiethanolamines,[87] *N*-arylbutenylsulphonamides,[88] and diethyl 4-arylbut-2-enylphosphonates.[89] The aldehydes $ArCH_2CH=CHCH_2CHO$, which are difficult to obtain, have been synthesised from chloroarylbutenes by the Sommelet reaction.[90] The chloroarylbutenes undergo the Vilsmeier reaction with formation of penta-2,4-dienals.[91] A novel method has been developed recently for the synthesis of diaryloctatetraenes containing substituents in the aromatic rings and in the aliphatic chain.[31]

1,4-Di(4′-chlorostyryl)- and 1,4-di(4′-nitrostyryl)-benzenes were obtained by the interaction of diazotised *p*-chloro- or *p*-nitro-aniline with 4,4′-divinylbenzene followed by the dehydrochlorination of the chloroarylation products (in yields of 14 and 30%):[71]

$$H_2C=CH-C_6H_4-CH=CH_2 + 2(4-RC_6H_4N_2Cl) \xrightarrow[-2N_2]{CuCl_2} \rightarrow 4-RC_6H_4CH_2CHCl-C_6H_4-CHClCH_2C_6H_4R\text{-}4 \rightarrow \xrightarrow[-2HCl]{KOH/C_2H_5OH} 4-RC_6H_4CH=CH-C_6H_4-CH=CHC_6H_4R\text{—}4;$$

R=Cl, NO_2.

The reaction of ADC with conjugated arylbutadienes catalysed by copper chloride is of special interest. In this case arylation takes place, namely substitution of the terminal hydrogen atom in the aliphatic chain by the aryl group of the diazo-compound. This results in the formation of conjugated 1,4-diarylbutadienes:[2,92,93]

$$4\text{-}RC_6H_4CH=CR^1-CR^2=CHR^3 + ArN_2Cl \xrightarrow[-N_2,-HCl]{CuCl_2} 4\text{-}RC_6H_4CH=CR^1-CR^2=CR^3Ar;$$

R=H, Me, Cl, NO_2; R^1=R^2=R^3=H, Me, Cl, Ar=Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

The interaction of α-arylbutadienes with biphenyl-4,4′-bisdiazonium chlorides entails the evolution of nitrogen from both diazo-groups. One diazo-group is involved in arylation and the other in the Sandmeyer reaction (yield ~ 35%):[94,95]

$$4\text{-}RC_6H_4CH=CR'-CH=CH_2 + ClN_2C_6H_4-C_6H_4N_2Cl \xrightarrow[-2N_2,-HCl]{CuCl_2} \rightarrow 4\text{-}RC_6H_4CH=CR'-CH=CH-C_6H_4-C_6H_4Cl\ ;$$

R=H, Me, Cl; R′=H, Me, Cl.

Apart from the reactions with ADC, the interaction of conjugated dienes with arenediazonium salts containing other anions has been described. Buta-1,4-diene reacts with benzenediazonium bromide (in the presence of $CuBr_2$ as the catalyst), giving a low yield (~20%) of $PhCH_2CH=CHCH_2Br$;[2] chloroprene is bromoarylated with satisfactory yields (50 to 58%):[96]

$$H_2C=CCl-CH=CH_2 + 3\text{-}RC_6H_4N_2Br \xrightarrow[-N_2]{} 3\text{-}RC_6H_4CH_2CCl=CHCH_2Br;$$

R=H, Me, MeO.

The interaction of buta-1,4-diene with arenediazonium sulphates and nitrates catalysed by $CuSO_4$ and $Cu(NO_3)_2$ respectively in the presence of added copper or iron powder leads to the formation of a mixture of 1,2- and 1,4-hydroxyarylbut-2-enes (in proportions of 1 : 4 and in an overall yield of ~25%). The same hydroxyarylbutenes (in proportions of 1 : 7 and in an overall yield of ~40%) are also obtained in the reaction of buta-1,4-diene with arenediazonium tetrafluoroborates in the presence of $(MeCOO)_2Cu$ as the catalyst:

$$H_2C=CH-CH=CH_2 + 4\text{-}RC_6H_4N_2X \xrightarrow[-N_2]{pH\ 5-7} \rightarrow 4\text{-}RC_6H_4CH_2CH(OH)-CH=CH_2 + 4\text{-}RC_6H_4CH_2CH=CHCH_2OH;$$
$$X = HSO_4,\ NO_3,\ BF_4;\ R = H,\ Me,\ MeO,\ NO_2.$$

The products of anion-arylation are apparently formed initially and are then hydrolysed to hydroxyarylbutenes under the reaction conditions (in an aqueous acetone medium).[97]

Buta-1,4-diene is anion-arylated by arenediazonium acetates to give 1-acetoxy-4-arylbut-2-enes (25–30%), which are smoothly converted into 1-aryl-4-hydroxybut-2-enes on alkaline hydrolysis:[98]

$$H_2C=CH-CH=CH_2 + 4\text{-}RC_6H_4N_2OCOMe \xrightarrow[-N_2]{(MeCOO)_2Cu} \rightarrow 4\text{-}RC_6H_4CH_2-CHCH_2OCOMe \xrightarrow[-MeCOOH]{H_2O} 4\text{-}RC_6H_4CH_2CH=CHCH_2OH;$$
$$R = H,\ Me,\ MeO.$$

Buta-1,4-diene and isoprene react with arenediazonium tetrafluoroborates in aqueous alcoholic media to form 1-alkoxy-4-arylbut-2-enes (in yields of 30–50% for primary alcohols); secondary alcohols give low yields (~15%), while tertiary alcohols hardly react:[99]

$$H_2C=CR-CH=CH_2 + 4\text{-}R'C_6H_4N_2BF_4 \xrightarrow[-N_2,\ -HF,\ -BF_3]{AlkOH,\ (MeCOO)_2Cu} \rightarrow 4\text{-}RC_6H_4CH_2R'C=CHCH_2OAlk,$$
$$R = H,\ Me;\ R' = H,\ Me,\ Cl;\ Alk = Me,\ Et,\ Pr,\ iso\text{-}Pr,\ Bu,\ PhCH_2.$$

In the presence of ethylene glycol the above dienes are alkoxylated with participation of both hydroxyls and give 35–57% yields of the ethers $(4\text{-}R'C_6H_4CH_2CR=CHCH_2OCH_2)_2$.[99]

On interaction with arenediazonium sulphates, nitrates, and tetrafluoroborates in the presence of sodium nitrate, sodium halides, or sodium salts of carboxylic acids and with catalysis by $(MeCOO)_2Cu$, the same dienes combine with the aryl groups of the diazo-compounds and the anions of the corresponding sodium salts at the ends of the conjugated system to form anion-arylation products (25–45%):[100]

$$H_2C=CR-CH=CH_2 + ArN_2X \xrightarrow[-N_2,\ -NaX]{NaHal} ArCH_2CR=CHCH_2Hal;$$
$$R = H,\ Me;\ X = SO_4H,\ NO_2,\ BF_4;$$
$$Hal = NO_2,\ F,\ Cl,\ Br,\ MeCOO,\ EtCOO,\ PrCOO;$$
$$Ar = Ph,\ 4\text{-}MeC_6H_4,\ 4\text{-}ClC_6H_4.$$

On interaction with arenediazonium tetrafluoroborates or sulphates in the presence of potassium salts of *O,O*-dialkyl or *O,O*-diphenyl phosphorodithioates, buta-1,4-diene and isoprene give rise to 1,4-adducts (in 66–80% yields):[101]

$$H_2C=CR-CH=CH_2 + 4\text{-}R^1C_6H_4N_2X \xrightarrow[-N_2,\ -KX]{(R^2O)_2P(S)SK,\ CuCO_3(OH)_2} \rightarrow 4\text{-}R^1C_6H_4CH_2CR=CHCH_2SP(S)(OR^2)_2;$$
$$R = H,\ Me;\ X = BF_4,\ HSO_4;\ R^2 = Me,\ Et,\ Pr,\ iso\text{-}Pr,\ Bu,\ iso\text{-}Bu,\ Ph.$$

5. Vinyl Ethers and αβ-Unsaturated Aldehydes and Ketones

Vinyl acetate results with ADC[102] (and also with arenediazonium tetrafluoroborates[103]) to form 1-acetoxy-2-aryl-1-chloroethanes (in yields of 30–50%), which readily hydrolyse on steam distillation, giving high yields (~90%) of arylacetaldehydes:[104]

$$MeCOOCH=CH_2 + ArN_2X \xrightarrow[-N_2]{CuCl_2} MeCOOCHClCH_2Ar \xrightarrow[-HCl,\ -MeCOOH]{H_2O} ArCH_2CHO;$$
$$Ar = Ph,\ 4\text{-}MeC_6H_4,\ 4\text{-}MeOC_6H_4,$$
$$2\text{-}\text{ и }4\text{-}ClC_6H_4,\ 4\text{-}BrC_6H_4;\ X = Cl,\ BF_4.$$

A method of synthesis of α-arylketones by the reaction of ADC with enol acetates has been proposed. For this purpose, enol acetate (or enol benzoate or disulphide) is obtained from the initial ketone. On interaction with ADC, the acetate is arylated in the α-position in the ethylene group. After the removal of the acetyl group (by hydrolysis), the α-arylketone is obtained. $ArCH_2COMe$ (from acetone), $ArCH_2COPh$ (from acetophenone), ArPhCHCOPh (from benzyl phenyl ketone), etc. have been obtained in this way:[103,105]

$$RCOMe \xrightarrow[-AcOH]{Ac_2O} RC(OAc)=CH_2 \xrightarrow[-N_2,\ -HCl]{ArN_2Cl,\ CuCl} RC(OAc)=CHAr \xrightarrow[-AcOH]{H_2O+} RCOCH_2Ar,$$
$$R = Me,\ PhCH_2;\ Ar = 4\text{-}ClC_6H_4.$$

Acrolein and crotonaldehyde are chloro- and bromophenylated, combining with the halogen and the $Ph^{\cdot}$ radical at the ethylenic bond in the α- and β-positions respectively. Best results (yields of 20–50%) are achieved when the reaction is carried out at 0–2 °C and pH ~ 7 (Dombrovskii[2]):

$$RHC=CHCHO + PhN_2X \xrightarrow[-N_2]{CuX_2} RCH(Ph)CHXCHO;$$
$$R = H,\ Me;\ X = Cl,\ Br.$$

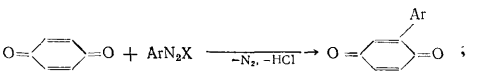
Methyl vinyl ketone is chloroarylated analogously, forming α-chloro-substituted aliphatic-aromatic ketones (yields 20 to 40%):[2]

$$MeCOCH=CH_2 + RC_6H_4N_2Cl \xrightarrow[-N_2]{CuCl_2} MeCOCHClCH_2C_6H_4R;$$
$$R = 4\text{-}Cl,\ 4\text{-}O_2N,\ 4\text{-}COOH.$$

Aryl vinyl and aryl isopropenyl ketones react in the same way, forming unstable aryl β-aryl-α-chloroethyl ketones (yields 25–40%); some of these are dehydrochlorinated even on vacuum distillation and are converted into chalcones:[106]

$$Ar'COCR=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} Ar'COCRClCH_2Ar \xrightarrow{-HCl} Ar'COCR=CHAr;$$
$$R = H,\ Me;\ Ar = Ph,\ 4\text{-}O_2NC_6H_4;$$
$$Ar' = Ph,\ 4\text{-}MeC_6H_4,\ 2,4\text{-}Me_2C_6H_3,$$
$$4\text{-}Cl\text{- and }4\text{-}BrC_6H_4$$

Quinones undergo a vigorous arylation reaction with arenediazonium salts, a distinctive feature of which is that it proceeds in the absence of catalysts owing to the low redox potential of the quinonoid system.[31] The arylation of *p*-benzoquinone has been widely investigated. This reaction constitutes an excellent method of synthesis of numerous monoaryl-*p*-benzoquinones, whose yields frequently reach 80–90%:[2,6]

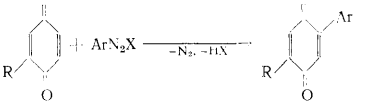


$$+ ArN_2X \xrightarrow[-N_2,\ -HCl]{}$$

;

$$Ar = Ph,\ 2\text{- and }4\text{-}MeC_6H_4,\ 2\text{-, 3- and}$$
$$4\text{-}ClC_6H_4,\ 2,6\text{-}Cl_2C_6H_4,\ 2\text{-}BrC_6H_4,$$
$$2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2,\ 4\text{-}HOC_6H_4,\ 2\text{- and}$$
$$4\text{-}MeOC_6H_4,\ 2,4\text{-}(MeO)_2C_6H_3,\ 2\text{-, 3- and }4\text{-}O_2NC_6H_4,$$
$$4\text{-}MeCOC_6H_4,\ 4\text{-}HOCOC_6H_4,\ 3\text{-}MeOCOC_6H_4,$$
$$2\text{-}PhC_6H_4,\ 4\text{-}PhC_6H_4,\ 4\text{-}H_2NSO_2C_6H_4,$$
$$1\text{- and }2\text{-}C_{10}H_7;\ X = HSO_4^-,\ Cl^-,\ Br^-,\ PO_4^{3-}.$$

Monosubstituted *p*-benzoquinones are arylated predominantly in the 5-position for steric reasons, forming 2-R-5 aryl-*p*-benzoquinones in satisfactory yields:[2,6]



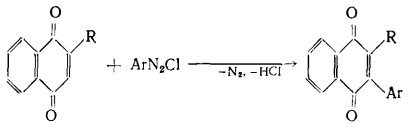
$$+ ArN_2X \xrightarrow[-N_2,\ -HX]{}$$

;

$$R = Me,\ Cl,\ Ph,\ 4\text{-}ClC_6H_4,\ 2\text{-}O_2NC_6H_4,$$
$$4\text{-}MeOCOC_6H_4;\ Ar = Ph,\ 3\text{- and }4\text{-}ClC_6H_4,$$
$$2\text{- and }3\text{-}BrC_6H_4,\ 2,\text{- 3- and }4\text{-}O_2NC_6H_4,\ 4\text{-}MeOC_6H_4,$$
$$4\text{-}MeOCOC_6H_4,\ 1\text{- and }2\text{-}C_{10}H_7;\ X = HSO_4,\ Cl.$$

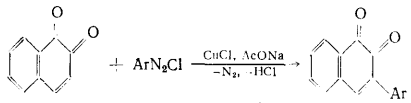
2,3-, 2,5-, and 2,6-Disubstituted *p*-benzoquinones are effectively arylated by diazo-compounds (the 2,3-derivatives in the 5-position and the 2,5- and 2,6-derivatives in the 3-position).[2,6]

1,4-Naphthoquinone and its 2-substituted derivatives are arylated to 2-aryl-1,4-naphthoquinones and 2-R-3-aryl-1,4-naphthoquinones respectively (in moderate yields):[2,6]



R=H, Me, OH, MeO; Ar=Ph, 2- and 4-MeC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$, 3- and 4-$O_2NC_6H_4$, 4-HOC_6H_4, 4-$HOSO_2C_6H_4$, 3-HO-4-$HOCOC_6H_4$, 2-$C_{10}H_7$.

1,2-Naphthoquinone is arylated in the presence of the CuCl catalyst in acetate buffer, giving low yields (5–37%) of 3-aryl-1,2-naphthoquinones:[107]



Ar = 2-, 3- and 4-ClC_6H_4.

6. αβ-Unsaturated Acids and Their Derivatives

The reactions of αβ-unsaturated carboxylic acids their derivatives with ADC have been investigated and described fairly completely. A survey of the available data shows that the reactions of αβ-unsaturated carboxylic acids in which the carboxyl is conjugated with electron-accepting groups proceed with substitution of the vinyl α-hydrogen atom by the Ar· radical derived from the diazo-compound with simultaneous decarboxylation and elimination of HCl.

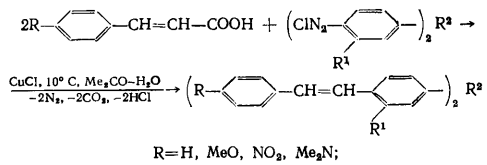
Thus the reactions of β-arylacrylic (cinnamic) acids with ADC proceed via this pathway and constitute the basis of a convenient and simple method of synthesis of numerous stilbenes, whose yields are in most cases good or entirely satisfactory:[2,6]

$$RCX{=}CHCOOH + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2 \text{ or } CuCl} RCX{=}CHAr;$$

X = H, Ph, or other aryl groups;
Ar = Ph or other aryl groups.

Fluorine-containing stilbenes 4-$HOC_6H_4CH{=}CHC_6H_4CF_3$ and 4-$EtOCOC_6H_4CH{=}CHC_6H_4CF_3$-4 have been obtained in this way from diazotised fluoroanilines and cinnamic acid derivatives (yields of 60 and 33%).[108]

On interaction with tetrazonium chlorides, i.e. the chlorides of diphenylbisdiazonium, 3,3'-dinitrobiphenylbisdiazonium, methylenebis(benzenediazonium), oxybis(benzenediazonium), and bis(diazoniaphenyl) sulphone, cinnamic acid give rise to the corresponding bis-stilbenes (in ~50% yield), which exhibit a semiconductor type sensitivity to light:[109]



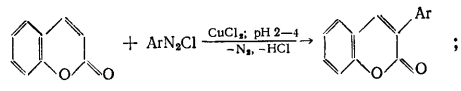
R=H, MeO, NO_2, Me_2N;
R^1=H, NO_2; R^2=—, O, SO_2, CH_2

β-Aroylacrylic acids react analogously with ADC, forming as a rule chalcones in high yields, which constitutes an effective method of synthesis of these compounds:[2,6,110]

$$RCOCH{=}CHCOOH + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2} RCOCH{=}CHAr;$$

R = Ph or other aromatic groups;
Ar=2-, 3- and 4-$HalC_6H_4$ (where Hal=Cl, Br), or 2- 3- and 4-$O_2NC_6H_4$

Coumarin and unbelliferone are arylated in the α-position relative to the carbonyl group, forming 3-arylcoumarins (in yields up to 80%):[2,6,42]



Ar=4-ClC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$ etc.

In the reactions of ADC with maleic acid one of the COOH groups is split off and cinnamic acids are obtained as a result (in yields of ~60%):

$$\begin{matrix} HC{-}COOH \\ \| \\ HC{-}COOH \end{matrix} + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2} ArCH{=}CHCOOH;$$

Ar=2-, 3- and 4-ClC_6H_4, 2.6-$Cl_2C_6H_3$ etc.

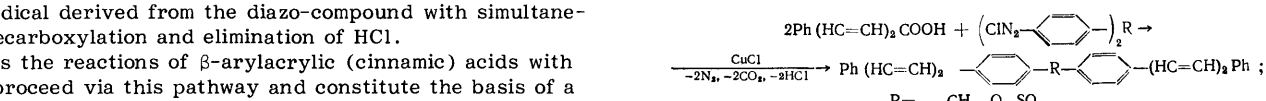
In the arylation of citraconic or bromomaleic acid the COOH group adjoining the methyl group or the bromine atom respectively is split off.[2,6]

Under the conditions of the Meerwein reaction, sorbic and cinnamylideneacetic acids are arylated at the α-carbon atom with simultaneous decarboxylation. This results in the formation of 4-aryl-1-methyl- and 1,4-diaryl-buta-1,3-dienes (for the latter, this reaction is one of the effective methods of synthesis):[2,6]

$$R(CH{=}CH)_2COOH + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2} R(CH{=}CH)_2Ar;$$

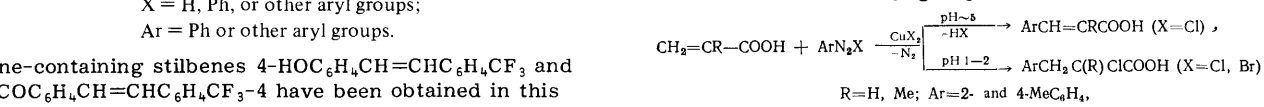
R=Me, Ph; Ar=2-, 3- and 4-ClC_6H_4, 2- and 4-$MeOC_6H_4$, 3- and 4-PhC_6H_4.

Cinnamylideneacetic acid reacts also with aromatic tetrazonium chlorides forming bisbutadienes (in yields up to 64%):[109]



R=—, CH_2, O, SO_2.

In media close to neutrality acrylic and crotonic acids are arylated at the β-carbon atom with retention of the carboxy-group, while in acid media they are halogenoarylated also with retention of the carboxy-group:[2,111]



R=H, Me; Ar=2- and 4-MeC_6H_4, 2-, 3- and 4-ClC_6H_4, 2-, 3- and 4-BrC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$, 2- and 4-$MeOC_6H_4$, 1-$C_{10}H_7$.

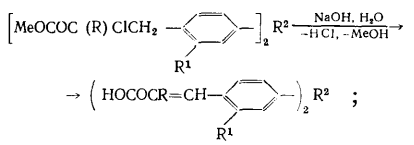
Methyl acrylate and methacrylate react with ADC, combining with a chlorine atom in the α-position and with the aryl radical derived from the diazo-compound in the β-position. This results in the formation of chloroarylation products (the yields reach 70%).[2,112,113] The products obtained from acrylic acid and its derivatives are valuable starting materials for the synthesis of substituted cinnamic acids and their esters and, after aminolysis, they serve as a source of phenylalanines with various substituents in the benzene ring:[2,6]

$$H_2C{=}CRCOOMe + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2C(R)ClCOOMe \xrightarrow[H_2O]{NH_3} \rightarrow ArCH_2CR(NH_2)COOH;$$

R=H, Me, Cl, Br; Ar=Ph etc.

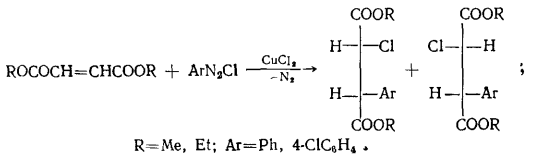
The reactions of methyl acrylate and methacrylate with bisdiazotised 4,4'-diaminobiphenyls, di(4-aminophenyl)-methane, and di(4-aminophenyl) ether proceed via two

pathways: chloroarylation with participation of both diazo-groups (the main reaction with yields of products of 42–62%) and chloroarylation with participation of only one diazo-group and the replacement of the second diazo-group by a chlorine atom via the Sandmeyer reaction (yields 5–21%). The reactions are catalysed by both $CuCl_2$ and $FeCl_2$, but the latter promotes the formation of telomers. The bischloro-arylation products are smoothly dehydrochlorinated and hydrolysed by alkali, being converted into the corresponding biscinnamic acids:[114]



R=H, Me; R^1=H, MeO, NO_2; R^2=O, CH_2.

The reactions of maleate and fumarate esters with ADC proceed mainly as *trans*-addition of the Ar$^{\cdot}$ radical and a chlorine atom to the ethylenic bonds in fumarate esters, to which the maleate esters also isomerise under the reaction conditions.[115] This results in the formation of a mixture of the *erythro*- and *threo*-forms in proportions of 72 : 28:[115,116]



R=Me, Et; Ar=Ph, 4-ClC_6H_4.

Acrylamide undergoes the chloroarylation reaction and gives satisfactory yields (60–70%) of β-aryl-α-chloropropion-amides, whose dehydrochlorination by organic bases results in their smooth conversion into β-arylacrylamides, which is also of synthetic interest:[117]

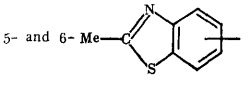
$$H_2C{=}CHCONH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CHClCONH_2 \xrightarrow[-HCl]{Et_3N} ArHC{=}CHCONH_2;$$

Ar=Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$.

Acrylonitrile, the most important derivative of an αβ-unsaturated acid, is widely used in reactions with numerous ADC, which results in good yields (up to 90%) of β-aryl-α-chloropropionitriles. The reactions are catalysed by $CuCl_2$, CuCl, and other catalysts:[2,6,18,19,118,119]

$$H_2C{=}CHCN + ArN_2Cl \xrightarrow[-N_2]{} ArCH_2CHClCN;$$

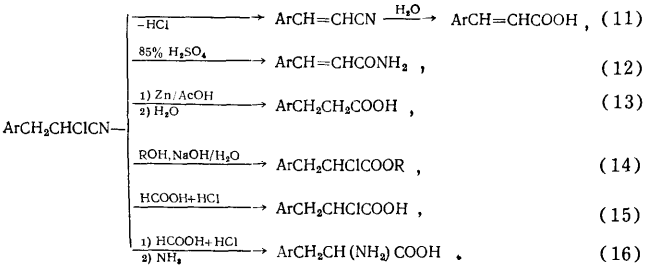
Ar=Ph, 2-, 3- and 4-MeC_6H_4, 2-, 3- and 4-ClC_6H_4, 2.4-$Cl_2C_6H_3$, 2-, 3- and 4-BrC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$, 2.4-$(O_2N)_2C_6H_3$, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-$HOSO_2C_6H_4$, 1- and 2-$C_{10}H_7$,



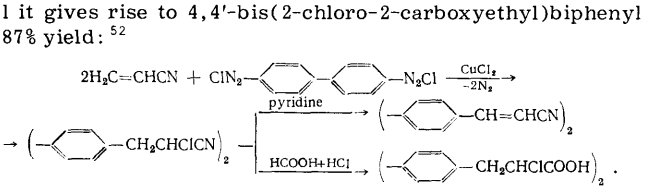
α-Methyl- and α-chloro-acrylonitriles form analogously β-aryl-α-chloroisobutyronitriles $ArCH_2C(Me)ClCN$ [120] and β-aryl-αα-dichloroacrylonitriles $ArCH_2CCl_2CN$ [121] respectively in yields of 50–70%:

(Ar=Ph, 4-MeC_6H_4, 4-Cl and 4-BrC_6H_4, 4-$MeOC_6H_4$, 2-, 3- and 4-$O_2NC_6H_4$).

Arylchloropropionitriles have served as starting materials for the synthesis of new compounds which are otherwise difficult to obtain. Thus they are readily dehydrochlorinated by bases, being converted almost quantitatively into the nitriles of cinnamic acids, whose hydrolysis give rise to the corresponding acids [reaction (11)],[2,118,119] or their amides [reaction (12)].[122] The successive reduction and hydrolysis of chloropropionitriles make it possible to obtain hydro-cinnamic acids [reaction (13)],[2] while alkaline hydrolysis in aqueous alcohol gives rise to esters of α-chlorohydrocinnamic acids [R = Me or Et; reaction (14)].[2] It has been suggested that the ester 4-$ClC_6H_4CH_2CHClCOOMe$ be used to eradicate wild oats in wheat fields.[123,124] The hydrolysis of chloro-propionitriles with a mixture of concentrated formic and hydrochloric acids gives rise to β-aryl-α-chloropropionic acids in ~95% yields [reaction (15)];[2] hydrolysis with the same mixture of acids followed by treatment with ammonia or urotropine results in the formation of D,L-arylalanines and their derivatives from arylchloropropionitriles [reaction (16)]:[2,125]

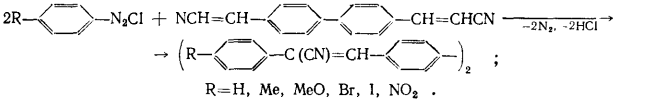


Biphenyl-4,4′-bisdiazonium chloride reacts with acrylo-nitrile with evolution of nitrogen from both diazo-groups and produces 4,4′-bis(2-chloro-2-cyanoethyl)biphenyl in 78% yield. The latter is readily dehydrochlorinated and con-verted into 4,4′-bis(2-cyanoethylene)biphenyl in 71% yield and on heating with a mixture of concentrated HCOOH and HCl it gives rise to 4,4′-bis(2-chloro-2-carboxyethyl)biphenyl in 87% yield:[52]



Acrylonitrile gives rise analogously to the chloroarylation products $X(C_6H_4CH_2CHClCN)_2$, where X = CH_2 or S, on reaction with methylenebis(benzenediazonium) and thiobis-(benzenediazonium)chlorides (yields 44 and 66% respec-tively).[52]

In reactions with ADC, 4,4′-bis(2-cyanovinyl)biphenyl is arylated in the α-position relative to the CN group (reactant ratio 1 : 2, catalyst CuCl, pH 2–4, aqueous acetone medium), giving rise to bisarylation products–4,4′-di(cyanostyryl)-biphenyls (yields 33–52%):[126]



R=H, Me, MeO, Br, I, NO_2.

The anion-arylation of acrylonitrile by the diazonium salts $ArN_2^+A^-$ also proceeds with addition of the anion A^- and the radical derived from the diazo-compound in the α- and β-positions of the ethylenic bond respectively. It has been shown that the interaction of acrylonitrile with arenediazonium sulphates in the presence of thiocyanate ions and catalytic amounts of copper(I) thiocyanate leads to β-aryl-α-thio-cyanatopropionitriles (in yields of ~60%).[47] In this case considerable amounts of ArSCN (up to 35%) are also obtained.[127] Arenediazonium thiocyanates are apparently

formed initially in the exchange reaction and then react further with acrylonitrile in accordance with a familiar mechanism:

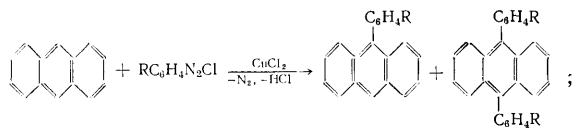
$$ArN_2HSO_4 + NH_4SCN \rightleftarrows ArN_2SCN + NH_4HSO_4,$$
$$H_2C{=}CHCN + ArN_2SCN \xrightarrow[-N_2]{CuSCN} ArCH_2CH(SCN)CN;$$
Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-$O_2NC_6H_4$.

β-Aryl-α-(*O*-ethyl dithiocarbonato)propionitriles have been obtained analogously in the presence of potassium and copper(I) ethylxanthates,[128] while in the presence of sodium and copper(I) diethyl phosphorodithioates the products are β-aryl-α-(*O*,*O*-diethyl phosphorodithioato)propionitriles (in yields of 40–72%):[129]

$$H_2C{=}CHCN + 4\text{-}RC_6H_4N_2HSO_4 \xrightarrow{-N_2}$$
$$\rightarrow \begin{cases} \xrightarrow[EtOC(S)SCu]{EtOC(S)SK} 4\text{-}RC_6H_4CH_2CH[SC(S)OEt]CN, & (a) \\ \xrightarrow[(EtO)_2P(S)SCu]{(EtO)_2P(S)SNa} 4\text{-}RC_6H_4CH_2CH[SP(S)(EtO)_2]CN; & (b) \end{cases}$$
(a) R = H, NO_2; (b) R = NO_2.

7. Aromatic Systems

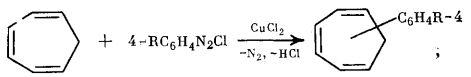
In conclusion we shall consider data on the arylation of aromatic systems under the conditions of the Meerwein reaction or similar conditions. Benzene, toluene, xylenes, halogenobenzenes, and nitrobenzenes are apparently hardly arylated under the conditions of this reaction. However, certain polycyclic aromatic systems enter into the arylation reaction. Thus anthracene is arylated by ADC, forming mixtures of 9-aryl- and 9,10-diarylanthracenes, whose yields vary from 7 to 54%:[130]



$$+ RC_6H_4N_2Cl \xrightarrow[-N_2, -HCl]{CuCl_2} \quad ;$$

R = H, 4-Cl, 4-MeO, 2-NO_2, 4-NO_2.

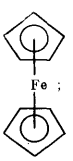
Cyclohepta-1,3,5-triene is also arylated, giving low yields (7–29%) of arylcycloheptatrienes (the position of the Ar group has not been established):[131]



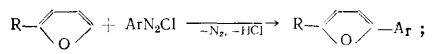
R = H, Cl, NO_2.

It has been shown in the studies of Nesmeyanov, Perevalova, and co-workers[132–134] that ferrocene is arylated by arenediazonium salts in the absence of catalysts, giving satisfactory yields (~60%) of arylferrocenes:

$$FcH + ArN_2X \xrightarrow[-N_2, -HCl]{0^\circ C;\ AcOH} Fc{-}Ar;$$

Fc =  ; X = Cl, HSO_4; Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 3 and 4-$O_2NC_6H_4$.

Among heteroaromatic compounds, substituted furans proved to be the most reactive in relation to ADC. Furan itself is arylated in the α-position with low yields.[135,136] α-Substituted furans, namely furfural, 2-acetylfuran, furan-2-carboxylic acid, and furyl-2-nitroethylene, are arylated in the 5-position on interaction with various ADC (in the presence of $CuCl_2$ or CuCl as the catalysts), giving rise to 5-aryl-2-substituted furans, whose yields vary from 6 to 80%:



R = CHO, Ar = 3-$O_2NC_6H_4$, 4-HOC_6H_4, 4-PhC_6H_4, 4-(4-$MeOC_6H_4$)C_6H_4 137—139; R = COMe, Ar = 4-ClC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$ 140; R = COOH, Ar = 3- and 4-ClC_6H_4, 4-BrC_6H_4, 3- and 4-$O_2NC_6H_4$ 141, 142; R = COOAlk (Alk = Me, Et, Pr), Ar-2-, 3- and 4-ClC_6H_4, 2- and 3-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$ 136, 142; R = COCOOH, Ar = 4-BrC_6H_4 143; R = CH=$CHNO_2$, Ar = 4-ClC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$ 144.

The data described show that the scope of the reactions of unsaturated compounds with aromatic diazo-compounds has not been exhausted. There is apparently no doubt about the radical mechanism of the reactions catalysed by transition metal salts and in the first place by copper chlorides. There is a need for further studies in order to elucidate the details of the mechanism of the conversion of the olefin–catalyst–aromatic diazo-compound complex, which results in the formation of anion-arylation and arylation products. The latter is apparently a process involving the addition-elimination of the elements of arenediazonium at the multiple bond of the unsaturated compound.

Further expansion of the range of unsaturated compounds and aromatic diazo-compounds used in the Meerwein reaction in order to obtain aliphatic-aromatic compounds containing several reaction centres is of undoubted interest for organic synthesis. The improvement of the anion-arylation and arylation methods will make it possible to reduce to a minimum the competing reactions, which will reduce the amount of side products.

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