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Anionarylation of Acrylic and Methacrylic Acids Derivatives with *p*- and *m*-Phenylenebisdiazonium Tetrafluoroborates

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Abstract—Chloro-, bromo- and thiocyanatoarylation of amides and nitriles of acrylic and methacrylic acids with bisdiazonium salts based on *m*- and *p*-phenylenediamines have been studied. 3,3'-[1,4(3)-phenylene]bis[2-halopropanamides(nitriles)] and 2-thiocyanato-(2-methyl)-3-[4(3)-thiocyanatophenyl]propinamides have been obtained as bishaloarylation and monothiocyanatoarylation products, respectively.

Keywords: anionarylation, phenylenebisdiazonium tetrafluoroborate, amide, nitrile of unsaturated acid

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The Meerwein arylation and anionarylation with bisdiazonium salts acting as arylation agent is a convenient method of regioselective modification of unsaturated compounds with one or two diazo groups [1–5].

Chloro-, bromo- and thiocyanatoarylation of amides of acrylic and methacrylic acids with bisdiazonium tetrafluoroborates derived from benzidine, diaminodiphenylmethane, or diaminodiphenylsulfone involved the both diazo groups due to their spatial accessibility [6].

In this work we further studied chloro-, bromo- and thiocyanatoarylation of amides and nitriles of acrylic and methacrylic acids with *p*- and *m*-phenylenebisdiazonium tetrafluoroborates. We expected that using those diazonium salts could significantly enhance the anionarylation regioselectivity due to interaction between the diazo groups via the conjugated molecule fragment.

Reactions of phenylenebisdiazonium tetrafluoroborates with unsaturated compounds have been scarcely reported in the literature. For instance, *m*-phenylenebisdiazonium tetrafluoroborate is known to react with acrylonitrile, styrene, acrylates, and methacrylates in the presence of NaCl and $CuCl_2$. The major reaction products correspond to chloroarylation of one of the diazo groups accompanied by simultaneous Sandmeyer substitution of the other group by chlorine.

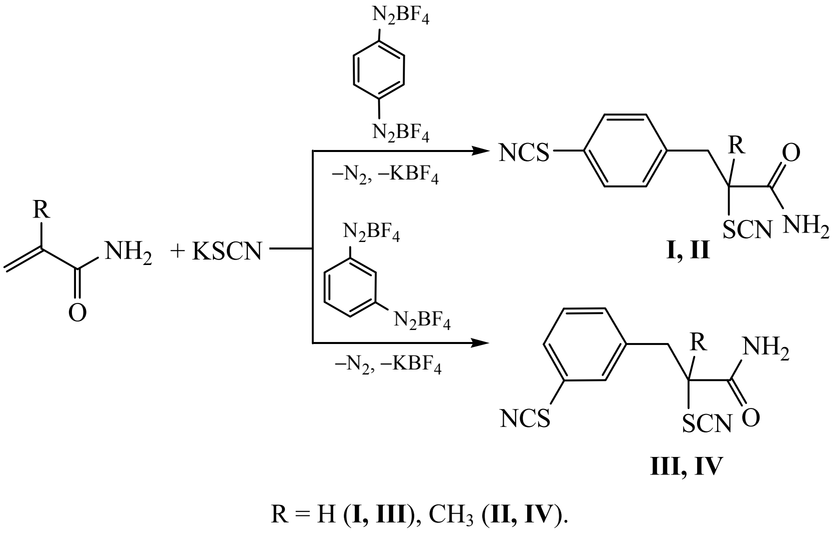
We found that reactions of *p*- and *m*-phenylenebisdiazonium tetrafluoroborates with acrylamide and methacrylamide in the presence of thiocyanate anions involved thiocyanatoarylation of one diazonium group and nucleophilic substitution of the second one with SCN to give compounds **I**–**IV** with yields of 44–63% (Scheme 1).

Thiocyanatoarylation occurred in the 1 : 2.5 water–acetone medium in the presence of catalytic amounts of copper(II) tetrafluoroborate at –30 to –25°C. The optimal ratio of phenylenebisdiazonium:amide:anion reagent : catalyst was of 1.0 : 2.2 : 2.2 : 0.03. The reaction was accompanied by formation of *p*- and *m*-dithiocyanatobenzenes in yields of 20–25% (with respect to the diazonium salt) and resinous products of unknown structure.

Changing the solvent nature (acetone, dimethylformamide, acetonitrile, or their binary mixtures with water), the reagents ratio (increasing amount of the unsaturated substrate), and the sequence of the reagents mixing did not allow for thiocyanatoarylation at the both diazonium groups.

In order to elucidate the effect of the anion nucleophilicity on the anionarylation regioselectivity, we studied chloro- and bromoarylation of amides and nitriles of acrylic and methacrylic acids with phenylenebisdiazonium tetrafluoroborates. The major reaction direction was haloarylation of the both diazonium moieties to form **V**–**XVI** (Scheme 2).

Scheme 1.

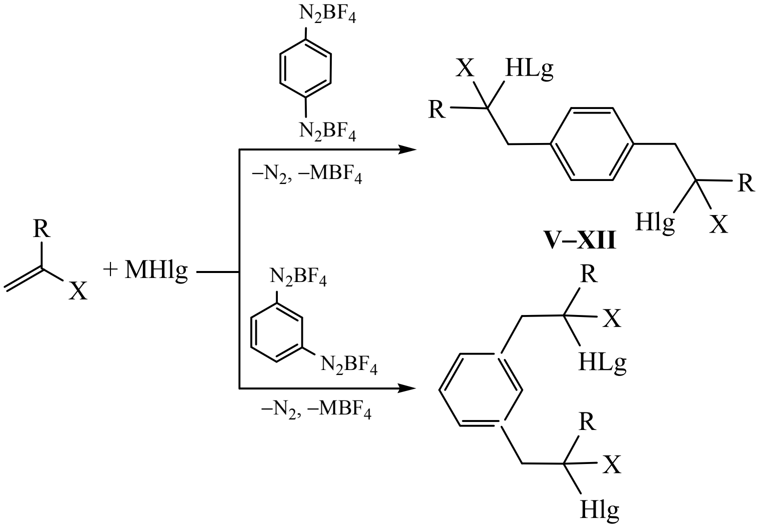


I, II

III, IV

R = H (**I, III**), CH$_3$ (**II, IV**).

Scheme 2.



V–XII

XIII–XVI

Hlg = Cl (**V**–**VIII**, **XIII**, **XIV**), Br (**IX**–**XII**, **XV**, **XVI**); X = C(O)NH$_2$ (**V**, **VI**, **IX**, **X**, **XIII**–**XVI**), CN (**VII**, **VIII**, **XI**, **XII**); R = H (**V**, **VII**, **IX**, **XI**, **XIII**, **XV**), CH$_3$ (**VI**, **VIII**, **X**, **XII**, **XIV**, **XVI**).

The reactions occurred in the 1 : 2.5 water–acetone medium at 0–25°C in the presence of sodium chloride or potassium bromide, with copper(II) tetrafluoroborate as the catalyst. Yield of the bishaloamides and -nitrites were of 20–63%. Further reaction products were *p*- and *m*-dichloro(bromo)benzenes with yield of up to 40%.

The reactions of *m*-phenylenebisdiazonium tetrafluoroborate with acrylonitrile and methacrylonitrile yielded only traces of the target bishalonitriles (less than 5%, ^{1}H NMR), nucleophilic substitution of the diazonium group with chlorine or bromine being the main reaction pathway. Under the conditions tested, substantial resinification was observed, caused apparently by polymerization of the unsaturated nitriles.

Yield of the chloro-, bromo-, and thiocyanatoarylation products **I**–**XVI** increased as the anion nucleophilicity increased in the Cl < Br < SCN series. Yields, melting points, and ^{1}H NMR features of compounds **I**–**XVI** are collected in Tables 1 and 2.

Table 1. Yield, melting point, and elemental analysis data of compounds **I**–**XVI**

Comp. no.	An	X	Ar	R	Yield, %	mp, °C[a]	Found, %			Formula	Calculated, %		
							N	Cl(Br)	S		N	Cl(Br)	S
I	SCN	$CONH_2$	*p*-C_6H_4	H	51	148	16.07	–	24.41	$C_{11}H_9N_3OS_2$	15.96	–	24.35
II	SCN	$CONH_2$	*p*-C_6H_4	CH_3	63	151	15.23	–	23.07	$C_{12}H_{11}N_3OS_2$	15.15	–	23.12
III	SCN	$CONH_2$	*m*-C_6H_4	H	40	119	15.86	–	24.28	$C_{11}H_9N_3OS_2$	15.96	–	24.35
IV	SCN	$CONH_2$	*m*-C_6H_4	CH_3	44	128	15.21	–	23.19	$C_{12}H_{11}N_3OS_2$	15.15	–	23.12
V	Cl	$CONH_2$	*p*-C_6H_4	H	24	185	9.60	24.60	–	$C_{12}H_{14}Cl_2N_2O_2$	9.69	24.52	–
VI	Cl	$CONH_2$	*p*-C_6H_4	CH_3	29	194	8.92	22.47	–	$C_{14}H_{18}Cl_2N_2O_2$	8.83	22.35	–
VII	Cl	CN	*p*-C_6H_4	H	25	180	11.00	28.12	–	$C_{12}H_{10}Cl_2N_2$	11.07	28.01	–
VIII	Cl	CN	*p*-C_6H_4	CH_3	20	172	10.01	25.13	–	$C_{14}H_{14}Cl_2N_2$	9.96	25.22	–
IX	Br	$CONH_2$	*p*-C_6H_4	H	43	198	7.49	42.36	–	$C_{12}H_{14}Br_2N_2O_2$	7.41	42.27	–
X	Br	$CONH_2$	*p*-C_6H_4	CH_3	51	205	6.93	39.47	–	$C_{14}H_{18}Br_2N_2O_2$	6.90	39.35	–
XI	Br	CN	*p*-C_6H_4	H	38	178	8.14	46.77	–	$C_{12}H_{10}Br_2N_2$	8.19	46.72	–
XII	Br	CN	*p*-C_6H_4	CH_3	43	169	7.64	43.12	–	$C_{14}H_{14}Br_2N_2$	7.57	43.18	–
XIII	Cl	$CONH_2$	*m*-C_6H_4	H	23	177	9.62	24.59	–	$C_{12}H_{14}Cl_2N_2O_2$	9.69	24.52	–
XIV	Cl	$CONH_2$	*m*-C_6H_4	CH_3	27	161	8.80	22.36	–	$C_{14}H_{18}Cl_2N_2O_2$	8.83	22.35	–
XV	Br	$CONH_2$	*m*-C_6H_4	H	35	153	7.34	42.36	–	$C_{12}H_{14}Br_2N_2O_2$	7.41	42.27	–
XVI	Br	$CONH_2$	*m*-C_6H_4	CH_3	42	163	6.95	39.30	–	$C_{14}H_{18}Br_2N_2O_2$	6.90	39.35	–

[a] Recrystallized from methanol.

Structures of **I**–**XVI** were confirmed by IR and NMR spectroscopy data. IR spectra of halo(thiocyanato)amides **I**–**VI**, **IX**, **X**, and **XIII**–**XVI** contained characteristic absorption bands of carbonyl (1652–1688 cm^{-1}) and amide (3374–3404 cm^{-1}) groups. In the spectra of thiocyanatoamides **I**–**IV,** absorption band of thiocyanate stretching was observed as well at 2152–2168 cm^{-1}. Absorbance bands at 2224–2236 cm^{-1} observed in the spectra of **VII**, **VIII**, **XI**, and **XII** were assigned to nitrile group.

^1H NMR spectra of adducts **I**–**XVI** contained signals of the aromatic protons (7.63–7.04 ppm). In the cases of derivatives of acrylamide and acrylonitrile, protons of methylene groups adjacent to aromatic rings resonated at 3.40–3.13 and 3.29–2.99 ppm as two doublets of doublets. In the spectra of methacrylamide and methacrylonitrile derivatives, two doublets of methylene protons appeared in the range of 3.50–3.16 ppm. Protons of methine groups adjacent to chlorine, bromine, or thiocyanate group were observed as triplets at 4.57–4.19 ppm (5.54–5.37 ppm in the cases of acrylonitrile derivatives). Singlets at 1.91–1.72 ppm were assigned to methyl protons of methacrylate fragment.

To conclude, bisdiazonium salts prepared from *p*- and *m*-phenylenediamines are highly reactive in the studied anionarylation reactions. In contrast to diphenylbisdiazonium tetrafluoroborates, they are more reactive towards nucleophilic substitution of the diazonium group, especially in the case of strong nucleophiles, such as thiocyanate anion. Furthermore, the Sandmeyer reaction and anionarylation occur under similar conditions, and it is possible to combine these processes using one and the same arylating agent.

EXPERIMENTAL

IR spectra (Vaseline oil) were recorded using the Specord M80 instrument. ^1H NMR spectra (DMSO-d_6 or $CDCl_3$; TMS as internal reference) were registered

Table 2. ^{1}H NMR spectral data (δ, ppm, *J*, Hz) of compounds **I**–**XVI**

Comp. no.	Ar	N$\underline{H}_2$	C$\underline{H}_2$Ar	R
I	7.59 d (*J* 8), 7.35 d (*J* 8)	8.00 s, 7.76 c	3.39 d.d (*J* 12.4), 3.07 d.d (*J* 14.2)	4.25 t (*J* 11.6)
II	7.63 d (*J* 8), 7.38 d (*J* 8)	8.18 s, 7.93 s	3.50 d (*J* 14.8), 3.16 d (*J* 14.4)	1.84 s
III	7.44 d (*J* 8), 7.39–7.34 m, 7.27 d (*J* 8)	6.01 s, 5.78 s	3.23 d.d (*J* 12.8), 2.99 d.d (*J* 14.0)	4.19 t (*J* 12.2)
IV	7.48 d (*J* 8), 7.44–7.38 m, 7.32 d (*J* 7.6)	6.07 s, 5.88 s	3.38 d (*J* 14.0), 3.31 d (*J* 14.4)	1.80 s
V	7.54 d (*J* 8.2), 7.29 d (*J* 8)	7.73 s, 7.36 s	3.18 d.d (*J* 12.2), 3.10 d.d (*J* 14.4)	4.57 t (*J* 11.8)
VI	7.18 s	7.52 s, 7.45 s	3.27 d (*J* 14.2), 3.20 d (*J* 14.0)	1.90 s
VII	7.43 d (*J* 8.4), 7.37 d (*J* 8)	–	3.37 d.d (*J* 14.4), 3.20 d.d (*J* 12.6)	5.54 t (*J* 11.2)
VIII	7.36 s	–	3.34 d (*J* 14.2), 3.25 d (*J* 13.8)	1.91 s
IX	7.50 d (*J* 8), 7.22 d (*J* 8)	7.66 s, 7.24 s	3.13 d.d (*J* 14.0), 3.06 d.d (*J* 13.8)	4.51 t (*J* 11.4)
X	7.60 d (*J* 8.2), 7.36 d (*J* 7.8)	8.16 s, 7.93 s	3.50 d (*J* 13.0), 3.18 d (*J* 13.4)	1.84 s
XI	7.36 s	–	3.40 d.d (*J* 14.2), 3.29 d.d (*J* 13.8)	5.37 t (*J* 12.2)
XII	7.49 d (*J* 7.6), 7.25 d (*J* 8)	–	3.45 d (*J* 14.0), 3.36 d (*J* 14.0)	1.78 s
XIII	7.29–7.09 m	7.49 s, 7.36 s	3.30 d.d (*J* 13.2), 3.21 d.d (*J* 14.0)	4.52 t (*J* 11.8)
XIV	7.31–7.18 m	7.66 s, 7.52 s	3.50 d (*J* 14.0), 3.35 d (*J* 14.4)	1.86 s
XV	7.22–7.04 m	7.52 s, 7.27 s	3.24 d.d (*J* 14.2), 3.17 d.d (*J* 14.2)	4.48 t (*J* 12.2)
XVI	7.27–7.11 m	7.60 s, 7.42 s	3.47 d (*J* 13.8), 3.33 d (*J* 14.0)	1.72 s

with the Varian Mercury (400 MHz) spectrometer. TLC was performed on Silufol UV-254 plates eluting with benzene–methanol (4 : 1) or methanol–benzene–acetone (1: 3: 1) mixture.

2-Thiocyanato-3-(4-thiocyanatophenyl)propionamide (I). *p*-Phenylenebisdiazonium tetrafluoroborate (5.6 g, 0.018 mol) was added to a mixture of 2.85 g (0.04 mol) of acrylamide, 0.2 g (0.0005 mol) of copper (II) tetrafluoroborate hexahydrate and 3.9 g (0.04 mol) of potassium thiocyanate in 100 mL of the 1 : 2.5 water–acetone mixture over 1.5 h. Nitrogen evolution was observed at –20 to –23°C for 60 min. After nitrogen evolution ceased, 30 mL of water was added to the reaction mixture, and the mixture was extracted with 50 mL of diethyl ether. The extracts were washed with water, dried with anhydrous calcium chloride, and evaporated. The residue was incubated at –20°C until its complete solidification. The resulting solid was recrystallized from methanol. Yield 2.4 g (51%). Additionally, 1.1 g (21%) of *p*-dithiocyanatobenzene (mp 93°C) was isolated.

Thiocyanatoamides **II**–**IV** were prepared similarly.

3,3'-(1,4-Phenylene)bis(2-chloropropanamide) (V). *p*-Phenylenebisdiazonium tetrafluoroborate (5.6 g, 0.018 mol) was added to a mixture of 2.85 g (0.04 mol) of acrylamide, 0.2 g (0.0005 mol) of copper(II) tetrafluoroborate hexahydrate, and 2.35 g (0.04 mol) of sodium chloride in 100 mL of the 1 : 2.5 water–acetone mixture over 2 h. Nitrogen evolution was observed at 20–25°C during 3 h. After nitrogen evolution ceased, 50 mL of water was added to the reaction mixture, and the mixture was extracted with 75 mL of diethyl ether. The extracts were washed with water, dried with anhydrous calcium chloride, and evaporated. The residue was incubated at –20°C until its complete solidification. The resulting solid was recrystallized from methanol. Yield 1.0 g (24%). Additionally, 0.7 g (27%) of *p*-dichlorobenzene {mp 53°C (mp 54°C [8])} was isolated.

3,3'-(1,4-Phenylene)bis(2-bromopropanamide) (IX). *p*-Phenylenebisdiazonium tetrafluoroborate (5.6 g, 0.018 mol) was added to a mixture of 2.85 g (0.04 mol) of acrylamide, 0.2 g (0.0005 mol) of copper(II) tetrafluoroborate hexahydrate, and 4.75 g (0.04 mol) of potassium bromide in 100 mL of the 1 : 2.5 water–acetone (1 : 2.5) mixture over 2 h. Nitrogen evolution was observed at 0–10°C during 2 h. After nitrogen evolution ceased, 50 mL of water was added to the reaction mixture, and the mixture was extracted with 50 mL of diethyl ether. The extracts were washed with water, dried with anhydrous calcium chloride, and evaporated. The residue was incubated at –20°C until its complete solidification. The resulting solid was recrystallized from methanol. Yield 2.9 g (43%). Additionally, 1.4 g (32%) of *p*-dibromobenzene {mp 87°C (mp 87.5°C [8])} was isolated.

Bishaloamides **VI**, **X**, **XIII–XVI** and bishalonitriles **VII**, **VIII**, **XI**, **XII** were prepared similarly.

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