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# Bisdiazonium Tetrafluoroborates as Arylating Agents in Anionarylation of Acrylamides and Methacrylamides

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**Abstract**—Bisdiazonium tetrafluoroborates derived from benzidine, 4,4'-diaminodiphenylmethane, and 4,4'-diaminodiphenylsulfone have been used as arylating reagents in the reactions of chloro-, bromo-, and thiocyanatoarylation of acrylamides and methacrylamides. Anionarylation proceeds via two diazo groups to give 3,3'-[4,4'-biphenyl(methane, sulfone)]bis[2-chloro(bromo, thiocyanato)(2-methyl)propionamides].

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Aryldiazonium salts prepared from aniline and its derivatives, complexes of diazonium salts with copper [1, 2], and triazenes [3] are efficient arylating gents in the Meerwein reactions [4] and anionarylation [5].

Development of new arylating agents for anionarylation of unsaturated compounds is an important field of modern organic synthesis. Bisdiazonium salts of benzidine and its derivatives are especially promising; however, to date their behavior has been studied in detail only under conditions of chloroarylation and the Meerwein reactions [4, 6]. For example, bisdiazonium chlorides derived from benzidine and diaminodiphenylmethane(oxide) react with acrylates, methacrylates, and acrylonitrile to form the products of chloroarylation via both diazo groups [7]. In the case of 4,4'-biphenyl(methane, oxide)bisdiazonium tetrafluoroborate in the presence of chloride anions, the reaction regioselectivity does not change except for chloroarylation of styrene and its derivatives. In the latter reactions, formation of the products of arylation via one diazo group and a parallel substitution of the second group with the chlorine atom (the Sandmeyer reaction) have been observed as well [8].

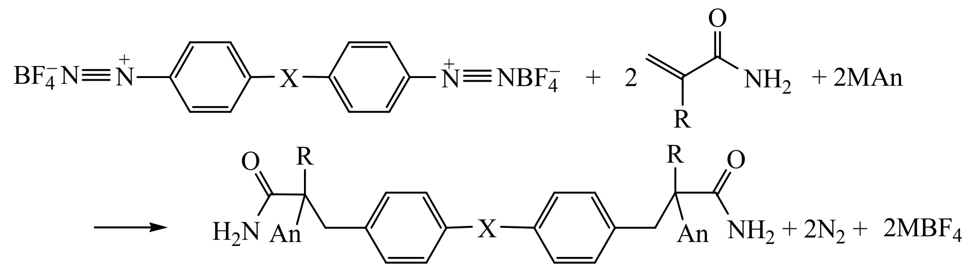
Substituting at the diazonium salt aromatic core does not influence the regioselectivity of chloro-arylation of acrylates, methacrylates and acrylonitrile: with 3,3'-dichloro-4,4'-diphenylmethanebisdiazonium chloride their reactions lead to the bischloroarylated adducts [9].

In order to further extend the synthetic capabilities of anionarylation, we investigated the application of bisdiazonium tetrafluoroborates based on benzidine and its derivatives as arylating reagents. To the very best of our knowledge, the only related reference is [10], describing *O*,*O*-dialkyldithiophosphatoarylation of methyl acrylate and methyl methacrylate with 4,4'-biphenyl(oxide)bisdiazonium tetrafluoroborate to form bisadducts with low yields (about 15%).

In particular, in this work we present the first report on application of bisdiazonium salts derived from benzidine, 4,4'-diaminodiphenylmethane, and 4,4'-diaminodiphenylsulfone in the reactions of chloro-, bromo- and thiocynatoarylation. Acrylamides and methacrylamides, reactive substrates of anionarylation reactions [11, 12], were selected as model compounds.

4,4'-Diphenyl(methane, sulfone)bisdiazonium tetrafluoroborates reacted with acrylamide and methacrylamide in the presence of chloride, bromide, or thiocyanate anions to give 3,3'-[4,4'-diphenyl(methane, sulfone)]bis[2-chloro(bromo, thiocyanato)(2-methyl)propionamides] **I**–**XVIII**, the bisanionarylation products.

Chloro- and bromoarylation of acrylamides and methacrylamides proceeded in water–acetone (1 : 2) medium in the presence of sodium chloride or potassium bromide, respectively, and catalytic amount of copper(II) chloride (bromide) at 15–30°C. Thiocyanatoarylation occurred in water–acetone (1 : 3) medium at –25 to –10°C in the presence of potassium thiocyanate and copper(II) tetrafluoroborate as catalyst. The optimal ratio of bisdiazonium salt/amide/anionoid reagent/catalyst was of 1 : 2.1 : 2.1 : 0.1. The yields of



**I–XVIII**

An = Cl (**I–VI**), Br (**VII–XII**), SCN (**XIII–XVIII**); X = (**I, II, VII, VIII, XIII, XIV**), $CH_2$ (**III, IV, IX, X, XV, XVI**), $SO_2$ (**V, VI, XI, XII, XVII, XVIII**); R = H, $CH_3$; M = Na, K.

**I–XVIII** were of 38–63% depending on the nucleophilicity of the anionoid reagent (Cl < Br < SCN). The presence of sulfonic or methylene group in the molecule of bisdiazonium salt did not alter the product yield and regioselectivity of anionarylation of acrylamides and methacrylamides. The reaction was accompanied by side formation of 4,4'-dichloro(bromo, thiocyanato)diphenyl(methane, sulfone) with 15–30% yield with respect to the diazonium salt. It should be noted that even two-fold decrease in the amide amount did not lead to formation of the monoanionarylated products.

Yields, melting points, elemental analysis and $^1H$ NMR spectral data on 3,3'-[4,4'-diphenyl(methane, sulfone)]bis[2-chloro(bromo, thiocyanato)(2-methyl)propionamides] **I–XVIII** are listed in Tables 1 and 2.

**Table 1.** Yields, melting points and elemental analysis data for 3,3'-[4,4'-diphenyl(methane, sulfone)]bis[2-chloro(bromo, thiocyanato)-(2-methyl)propionamides] (**I–XVIII**)

| Comp. no. | An | X | R | Yield, % | mp, °C[a] | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | N | Cl(Br) | S | | N | Cl(Br) | S |
| **I** | Cl | – | H | 46 | 190 | 7.58 | 19.49 | – | $C_{18}H_{18}Cl_2N_2O_2$ | 7.67 | 19.41 | – |
| **II** | Cl | – | $CH_3$ | 51 | 197 | 7.21 | 17.97 | – | $C_{20}H_{22}Cl_2N_2O_2$ | 7.12 | 18.03 | – |
| **III** | Cl | $CH_2$ | H | 42 | 206 | 7.32 | 18.75 | – | $C_{19}H_{20}Cl_2N_2O_2$ | 7.39 | 18.69 | – |
| **IV** | Cl | $CH_2$ | $CH_3$ | 39 | 223 | 6.94 | 17.50 | – | $C_{21}H_{24}Cl_2N_2O_2$ | 6.88 | 17.41 | – |
| **V** | Cl | $SO_2$ | H | 38 | 208 | 6.59 | 16.47 | 7.52 | $C_{18}H_{18}Cl_2N_2O_4S$ | 6.53 | 16.52 | 7.47 |
| **VI** | Cl | $SO_2$ | $CH_3$ | 43 | 211 | 6.19 | 15.56 | 6.94 | $C_{20}H_{22}Cl_2N_2O_4S$ | 6.12 | 15.50 | 7.01 |
| **VII** | Br | – | H | 55 | 195 | 6.10 | 35.26 | – | $C_{18}H_{18}Br_2N_2O_2$ | 6.17 | 35.19 | – |
| **VIII** | Br | – | $CH_3$ | 58 | 201 | 5.89 | 33.22 | – | $C_{20}H_{22}Br_2N_2O_2$ | 5.81 | 33.14 | – |
| **IX** | Br | $CH_2$ | H | 47 | 205 | 6.04 | 34.22 | – | $C_{19}H_{20}Br_2N_2O_2$ | 5.98 | 34.13 | – |
| **X** | Br | $CH_2$ | $CH_3$ | 52 | 214 | 5.59 | 32.14 | – | $C_{21}H_{24}Br_2N_2O_2$ | 5.65 | 32.20 | – |
| **XI** | Br | $SO_2$ | H | 43 | 212 | 5.49 | 30.77 | 6.12 | $C_{18}H_{18}Br_2N_2O_4S$ | 5.41 | 30.84 | 6.19 |
| **XII** | Br | $SO_2$ | $CH_3$ | 41 | 219 | 5.06 | 29.36 | 5.94 | $C_{20}H_{22}Br_2N_2O_4S$ | 5.13 | 29.25 | 5.87 |
| **XIII** | SCN | – | H | 58 | 138 | 13.73 | – | 15.58 | $C_{20}H_{18}N_4O_2S_2$ | 13.65 | – | 15.62 |
| **XIV** | SCN | – | $CH_3$ | 61 | 155 | 12.69 | – | 14.71 | $C_{22}H_{22}N_4O_2S_2$ | 12.78 | – | 14.62 |
| **XV** | SCN | $CH_2$ | H | 55 | 141 | 13.31 | – | 15.06 | $C_{21}H_{20}N_4O_2S_2$ | 13.20 | – | 15.11 |
| **XVI** | SCN | $CH_2$ | $CH_3$ | 49 | 164 | 12.43 | – | 14.10 | $C_{23}H_{24}N_4O_2S_2$ | 12.38 | – | 14.17 |
| **XVII** | SCN | $SO_2$ | H | 63 | 179 | 11.88 | – | 20.20 | $C_{20}H_{18}N_4O_4S_3$ | 11.81 | – | 20.27 |
| **XVIII** | SCN | $SO_2$ | $CH_3$ | 58 | 196 | 11.07 | – | 19.21 | $C_{22}H_{22}N_4O_4S_3$ | 11.15 | – | 19.14 |

[a] Of the substances recrystallized from methanol.

**Table 2.** $^1$H NMR data of 3,3'-[4,4'-diphenyl(methane, sulfone)]bis[2-chloro(bromo, thiocyanato)(2-methyl)propionamides] (**I**–**XVIII**)

| Comp. no. | Ar | –$NH_2$ | X | C$\underline{H}_2$Ar | R |
|---|---|---|---|---|---|
| **I** | 7.51 d, 7.18 d | 7.91 s, 7.56 s | – | 3.28 d.d, 3.11 d.d | 4.60 t |
| **II** | 7.40 d, 7.10 d | 8.01 s, 7.72 s | – | 3.31 d, 3.16 d | 1.87 s |
| **III** | 7.14 s | 7.65 s, 7.23 s | 3.89 s | 3.24 d.d, 3.01 d.d | 4.54 t |
| **IV** | 7.09 s | 7.72 s, 7.35 s | 3.91 s | 3.27 d, 3.04 d | 1.83 s |
| **V** | 7.84 d, 7.47 d | 7.81 s, 7.53 s | – | 3.33 d.d, 3.15 d.d | 4.62 t |
| **VI** | 7.77 d, 7.36 d | 8.02 s, 7.68 s | – | 3.35 d, 3.14 d | 1.86 s |
| **VII** | 7.56 d, 7.25 d | 7.81 s, 7.50 s | – | 3.34 d.d, 3.18 d.d | 4.52 t |
| **VIII** | 7.46 d, 7.20 d | 7.84 s, 7.61 s | – | 3.35 d, 3.22 d | 1.84 s |
| **IX** | 7.18 s | 7.67 s, 7.32 s | 3.92 s | 3.18 d.d, 2.94 d.d | 4.46 t |
| **X** | 7.11 s | 7.76 s, 7.41 s | 3.88 s | 3.21 d, 2.99 d | 1.86 s |
| **XI** | 7.89 d, 7.49 d | 7.85 s, 7.58 s | – | 3.37 d.d, 3.19 d.d | 4.49 t |
| **XII** | 7.81 d, 7.40 d | 7.99 s, 7.70 s | – | 3.31 d, 3.13 d | 1.87 s |
| **XIII** | 7.53 d, 7.23 d | 7.75 s, 7.48 s | – | 3.25 d.d, 3.07 d.d | 4.23 t |
| **XIV** | 7.44 d, 7.19 d | 8.06 s, 7.78 s | – | 3.43 d, 3.07 d | 1.85 s |
| **XV** | 7.08 s | 7.77 s, 7.45 s | 3.88 s | 3.12 d.d, 2.92 d.d | 4.21 t |
| **XVI** | 7.05 s | 7.84 s, 7.53 s | 3.89 s | 3.17 d, 2.93 d | 1.85 s |
| **XVII** | 7.95 d, 7.53 d | 7.78 s, 7.44 s | – | 3.36 d.d, 3.16 d.d | 4.27 t |
| **XVIII** | 7.83 d, 7.39 d | 7.94 s, 7.67 s | – | 3.34 d, 3.01 d | 1.86 s |

The structure of **I**–**XVIII** was confirmed by IR and $^1$H NMR spectral data. The IR spectra contained absorption bands of carbonyl and amide groups in the ranges of 1660–1676 and 3386–3412 cm$^{-1}$, respectively. The spectra of bisthiocyanatoamides **XIII**–**XVIII** contained the absorption bands of thiocyanate group at 2148–2164 cm$^{-1}$.

In $^1$H NMR spectra of bisanionarylated products, the aromatic protons signals were observed at 7.95–7.40 ppm and 7.53–7.10 ppm, assigned to the *ortho*- and *meta*-protons of diphenyl moieties, respectively. In the case of acrylamide derivatives, the signals of protons of the aromatic methylene groups appeared as two doublets of doublets at 3.37–3.12 and 3.18–2.92 ppm; in the case of methacrylamide the respective protons signals were observed as two doublets in the range of 3.33–2.93 ppm. The proton signal of methine group bonded to chlorine, bromine, or thiocyanate carbon was observed as triplet at 4.62–4.21 ppm. Methyl protons of methacrylate moiety resonated as singlets in the range of 1.87–1.83 ppm.

To conclude, aromatic bisdiazonium salts could be used as efficient arylating reagents in the anionarylation reactions. The studied bisdiazonium salts revealed similar reactivity in reactions of chloro-, bromo- and thiocyanatoarylation. Their application allowed for regioselective anionarylation of unsaturated compounds via both diazo groups.

## EXPERIMENTAL

IR spectra (nujol) were recorded with SPECORD M80 instrument. $^1$H NMR spectra (DMSO-$d_6$ + $CCl_4$) were registered with Varian Mercury (400 MHz) spectrometer relative to external standard TMS. Purity of the prepared compounds was confirmed by TLC

[Silufol UV-254, benzene–methanol (3 : 1), benzene–methanol–acetone (1 : 2 : 1)].

**3,3'-(4,4'-Diphenyl)bis(2-chloropropionamide) (I).** 7.5 g (0.0195 mol) of 4,4'-diphenylbisdiazonium tetrafluoroborate was added during 2 h to a mixture of 2.8 g (0.04 mol) of acrylamide, 0.7 g (0.004 mol) of copper(II) chloride dihydrate, and 2.3 g (0.041 mol) of sodium chloride in 120 mL of water–acetone mixture (1 : 3). At 30–35°C, nitrogen evolution was observed during 120 min. After nitrogen evolution ceased, the reaction mixture was diluted with 50 mL of water and extracted with 100 mL of diethyl ether. The extracts were washed with water, dried over anhydrous calcium chloride, and stripped. The residue was kept at –20°C to complete crystallization. The resulting solid was recrystallized from methanol to obtain 3.3 g (46%) of **I** and 1.3 g (29%) of 4,4'-dichlorobiphenyl, mp 146°C (methanol) (mp 148°C [13]).

**3,3'-(4,4'-Diphenyl)bis(2-bromopropionamide) (VII).** 7.5 g (0.0195 mol) of 4,4'-diphenylbisdiazonium tetrafluoroborate was added during 1 h to a mixture of 2.8 g (0.04 mol) of acrylamide, 1.0 g (0.004 mol) of copper(II) bromide dehydrate, and 4.0 g (0.041 mol) of potassium bromide in 150 mL of water–acetone mixture (1 : 3). At 15–20°C, nitrogen evolution was ob-served during 90 min. After nitrogen evolution ceased, the reaction mixture was diluted with 50 mL of water and extracted with 100 mL of diethyl ether. The extracts were washed with water, dried over anhydrous calcium chloride, and stripped. The solid residue was kept at –20°C to complete crystallization. The resulting solid was recrystallized from methanol to obtain 4.9 g (55%) of **VII** and 1.6 g (26%) of 4,4'-dibrombiphenyl, mp 168°C (methanol) (mp 166.5°C [13]).

**3,3'-(4,4'-Diphenyl)bis(2-thiocyanatopropionamide) (XIII)** was prepared similarly from 2.8 g (0.04 mol) of acrylamide, 1.4 g (0.004 mol) of copper(II) tetrafluoroborate hexahydrate, 4.0 g (0.041 mol) of potassium thiocyanate, and 7.5 g (0.0195 mol) of 4,4'-diphenylbisdiazonium tetrafluoroborate. Yield 4.7 g (58%) of **XIII** and 1.1 g (21%) 4,4'-dithiocyanatobiphenyl, mp 93°C (methanol).

The corresponding bis(chloro, bromo, thiocyanato) propionamides were prepared similarly from bisdiazonium tetrafluoroborates, derived in turn from 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenylsulfone.

## REFERENCES

1. Dombrovski, A.V., *Russ. Chem. Rev.*, 1984, vol. 53, no. 10, p. 943.
2. Grishhchuk, B.D., Gorbovoi, P.M., Ganushchak, N.I., and Dombrovskii, A.V., *Russ. Chem. Rev.*, 1994, vol. 63, no. 3, p. 257.
3. Obushak, M.D., Lyakhovych, M.B., and Ganushchak, M.I., *Tetrahedron Lett.*, 1998, vol. 39, p. 9567.
4. Obushak, N.D., Liakhovich, M.B., Fedorovich, I.S., and Ganushchak, N.I., *Zh. Org. Khim.*, 1996, vol. 32, no. 10, p. 1522.
5. Naidan, V.M. and Smalius, V.V., *Russ. J. Gen. Chem.*, 2005, vol. 75, no. 11, p. 1771.
6. Grishchuk, B.D., Gorbovii, P.M., Baranovskii, V.S., and Ganushchak, M.I., *Zh. Org. Farm. Khim.*, 2008, vol. 6, no. 3(23), p. 16.
7. Ganushchak, N.I., Grishchuk, B.D., Tashchuk, K.G., Nemish, A.Yu., and Dombrovskii, A.V., *Zh. Org. Khim.*, 1972, vol. 8, no. 12, p. 2549.
8. Grishchuk, B.D., *Doctoral (Chem.) Dissertation*, Lviv, 1995.
9. Fedorovich, I.S., Obushak, N.D., Liakhovich, M.B., and Ganushchak, N.I., *Zh. Org. Khim.*, 1996, vol. 32, no. 3, p. 400.
10. Ganushchak, N.I., Obushak, N.D., and Fedorovich, I.S., *Ukr. Khim. Zh.*, 1987, vol. 53, no. 9, p. 970.
11. Grishchuk, B.D., Gorbovoi, P.M., Ganushchak, N.I., and Kudrk, E.Ya., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 10, p. 2335.
12. Baranovskii, V.S., Simchak, R.V., and Grishchuk, B.D., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 2, p. 269.
13. *Svoistva organicheskikh soedinenii* (Properties of Organic Compounds), Potekhin, A.A., Ed., Leningrad: Khimiya, 1984, p. 120.