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Reaction of Arenediazonium Tetrafluroborates with *N,N*-Methylenediacryalmide in the Presence of Thiocyanate Anions

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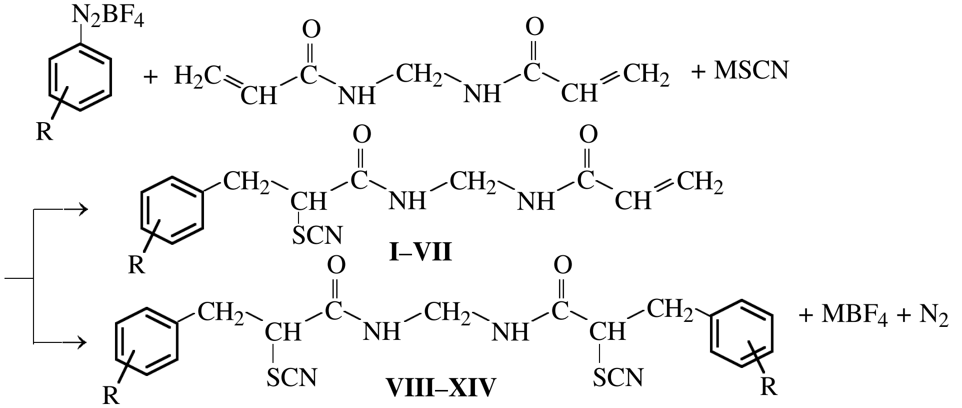
Abstract—The reactions of arenediazonium tetrafluoroborates with *N,N*-methylenediacrylamide in H_2O–DMF (1 : 3) and H_2O–DMSO (1 : 4) in the presence of thiocyanate anions involve thiocyanatoarylation by one or two multiple bonds to give [(3-aryl-2-thiocyanatopropionylamino)methyl]-2-acryalmides and *N,N*-methylenebis(2-thiocyanato-3-arylpropionamides).

At present we have studied thiocyanatoarylation of various monounsaturated compounds like $CHR^1=CR^2R^3$ and effects of various factors on this reaction [1, 2]. In [3], we have found that arenediazonium tetrafluoroborates react with acrylamide in the presence of alkali metal or ammonium thiocyanates with elimination of diazo nitrogen and formation of α-thiocyanato-β-arylpropionamides which may present interest as antimicrobials. The reactions occur in aqueous acetone (1 : 2) and only in the presence of a catalyst, copper or iron salt.

Proceeding with the studies in [2] and aiming at revealing unknown regularities of reaction of aromatic diazonium salts with unsaturated compounds containing two isolated multiple bonds, we brought into thiocyanatoarylation *N,N*-methylenediacrylamide.

It was found that arenediazonium tetrafluoroborates react with *N,N*-methylenediacrylamide in the presence of thiocyanate ions. The reaction involves evolution of diazo nitrogen and addition of the aryl and thiocyanato groups by the site of cleavage of one or two multiple bonds: [(3-aryl-2-thiocyanatopropionylamino)methyl]-2-acrylamides **I**–**VII** or *N,N*-methylenebis(2-thiocyanato-3-arylpropionamides) **VIII**–**XIV**.



(1)

(2)

R = H (**I, VIII**), 2-CH_3 (**II, IX**), 3-CH_3 (**III, X**), 4-CH_3 (**IV, XI**), 4-CH_3O (**V, XII**), 4-NO_2 (**VI, XIII**), 2,5-Cl_2 (**VII, XIV**);
M = Na, K, NH_4.

The reaction occurs in aqueous dimethylformamide (1 : 3) or aqueous dimethyl sulfoxide (1 : 4) in the presence of thiocyanate anions and catalytic amounts of copper(II) tetrafluoroborate at 10–15°C. At the arenediazonium salt : *N,N*-methylenediacrylamide : thiocyanate : copper(II) tetrafluoroborate ratio of 1.1 : 1 : 1.1 : 0.1, monoadducts **I**–**VII** are formed, and at double the quantities of diazonim salt, thiocyanate,

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Table 1. Yields, constants and elemental analyses of [(3-aryl-2-thiocyanatopropionylamino)methyl]-2-acrylamides **I–VII** and *N,N*-methylenebis(2-thiocyanato-3-arylpropionamides) **VIII–XIV**

Comp. no.	Yield, %	mp, °C[a]	Found, %		Formula	Calculated, %	
			N	S		N	S
I	91	218	14.29	10.99	$C_{14}H_{15}N_3O_2S$	14.52	11.08
II	82	191	13.77	10.41	$C_{15}H_{17}N_3O_2S$	13.85	10.57
III	55	194	13.84	10.48	$C_{15}H_{17}N_3O_2S$	13.85	10.57
IV	85	199	13.65	10.34	$C_{15}H_{17}N_3O_2S$	13.85	10.57
V	85	188	13.02	9.89	$C_{15}H_{17}N_3O_3S$	13.16	10.04
VI	63	164	16.67	9.62	$C_{14}H_{14}N_4O_4S$	16.76	9.59
VII	90	186	11.58	8.85	$C_{14}H_{13}Cl_2N_3O_2S$	11.73	8.95
VIII	86	205	13.09	15.00	$C_{21}H_{20}N_4O_2S_2$	13.20	15.10
IX	74	184	12.14	14.10	$C_{23}H_{24}N_4O_2S_2$	12.38	14.17
X	42	188	12.21	14.12	$C_{23}H_{24}N_4O_2S_2$	12.38	14.17
XI	79	193	12.11	13.99	$C_{23}H_{24}N_4O_2S_2$	12.38	14.17
XII	74	176	11.41	13.01	$C_{23}H_{24}N_4O_4S_2$	11.56	13.23
XII	46	160	16.19	12.27	$C_{21}H_{18}N_6O_6S_2$	16.33	12.46
XIV	81	179	9.77	11.24	$C_{21}H_{16}Cl_4N_4O_2S_2$	9.96	11.40

[a] From ethanol.

and catalyst, bisadducts **VIII–XIV**.

Bisadducts **VIII–XIV** were also obtained by thiocyanatoarylation of monoadducts **I–VII**.

$$\mathbf{I–VII} + ArN_2BF_4 + MSCN \xrightarrow[-N_2,\ -MBF_4]{Cu(BF_4)_2} \mathbf{VIII–XIV}. \quad (3)$$

Bisadducts **VIII–XIV** obtained by schemes (2) and (3) have the same physicochemical constants.

The obtained experimental evidence gives us grounds to state that the thiocyanatoarylation of *N,N*-methylenebisacrylamide occurs stepwise: first by one multiple bond and then by the second, which is consistent with the earlier proposed mechanism of anionarylation [4].

The yields, constants, elemental analyses, and ^1H NMR and IR spectra of monoadducts **I–VII** and bisadducts **VIII–XIV** are given in Tables 1 and 2.

The structures of adducts **I–XIV** are confirmed by their ^1H NMR and IR spectra. The IR spectra of these compounds contain absorption bands of the carbonyl, thiocyanato, and amido groups at 1720–1728, 2152–2160, and 3412–3420 cm^{-1}.

The ^1H NMR spectra of compounds **I–XIV** contain multiplets of aromatic protons at 7.7–6.8 ppm. The CH_2–Ar methylene protons and the asymmetric CH–CSN protons form an *ABX* system and appear as two doublets of doublets and a triplet at 3.40–3.30, 3.05–3.27, and 4.23–4.32 ppm, respectively (J_{AX} 6.6, J_{BX} 7.2, and J_{AB} 14 Hz). The respective coupling constants for monoadducts are 7.2, 7.8, and 14.4 Hz. In addition, the spectra of monoadducts **I–VII** show signals of the methylene [doublets of doublets at 5.65–5.60 (*cis*-H) and 6.15–6.10 ppm (*trans*-H), coupling constants 10 and 17 Hz, respectively] and methine protons (multiplet at 6.22–6.17 ppm) of the terminal vinyl groups.

EXPERIMENTAL

The IR spectra of compounds **I–XIV** were recorded in mineral oil on a Specord M-80 instrument. The ^1H NMR spectra were measured in DMSO-d_6 on a Varian VXR-300 instrument (300 MHz), external reference HMDS. The purity of the synthesized compounds was established by TLC on Silufol UV-254 plates (eluent ethanol–acetone, 4:1).

[(3-Phenyl-2-thiocyanatopropionylamino)methyl]-2-acrylamide (I). Benzenediazonium tetrafluoroborate, 5.5 g, was added for 30 min to 4.0 g of *N,N*-methylenediacrylamide, 0.9 g of copper(II) tetrafluoroborate hexahydrate, and 2.2 g of ammonium thiocyanate in 150 ml of H_2O–DMF (1:3). Nitrogen evolution was observed at 10–15°C for 45 min. When nitrogen no longer evolved, 150 ml of water was added to the reaction mixture, and the precipitate that formed was filtered off, dried, and twice recrystallized from ethanol to obtain 6.8 g (91%) of compound **I**.

Compounds **II–VII** were prepared in a similar way.

Table 2. IR and ^{1}H NMR spectra of [(3-aryl-2-thiocyanatopropionylamino)methyl]-2-acrylamides **I–VII** and *N,N*-methylenebis(2-thiocyanato-3-arylpropionamides) **VIII–XIV**

Comp. no.	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm
	SCN	C=O	
I	2152	1720	9.05–8.89 m (2H, 2NH); 7.53–7.36 m (5H, Ph); 6.20 m (1H, CH=); 6.13 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.64 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.48 t (2H, N–CH_2–N); 4.31 t (J_{AB} 14.4 Hz) (1H, CH); 3.38 d.d (J_{AX} 7.8 Hz), 3.25 d.d (J_{BX} 7.2 Hz) (2H, CH_2Ph)
II	2152	1720	8.99–8.81 m (2H, 2NH); 7.22-7.01 m (4H, C_6H_4); 6.22 m (1H, CH=); 6.15 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.65 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.45 t (2H, N–CH_2–N); 4.29 t (J_{AB} 14.4 Hz) (1H, CH); 3.39 d.d (J_{AX} 7.8 Hz), 3.26 d.d (J_{BX} 7.2 Hz) (2H, $CH_2C_6H_4$); 2.24 s (3H, $CH_3C_6H_4$)
III	2156	1720	8.99–8.84 m (2H, 2NH); 7.14–6.91 m (4H, C_6H_4); 6.19 m (1H, CH=); 6.15 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.63 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.44 t [2H, N–CH_2–N); 4.29 t (J_{AB} 14.4 Hz) (1H, CH); 3.38 d.d (J_{AX} 7.8 Hz), 3.26 d.d (J_{BX} 7.2 Hz) (2H, $CH_2C_6H_4$); 2.28 s (3H, $CH_3C_6H_4$)
IV	2156	1720	9.04–8.82 m (2H, 2NH); 7.17–7.00 m (4H, C_6H_4); 6.21 m (1H, CH=); 6.15 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.65 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.44 t (2H, N–CH_2–N); 4.27 t (J_{AB} 14.4 Hz) (1H, CH); 3.40 d.d (J_{AX} 7.8 Hz), 3.27 d.d (J_{BX} 7.2 Hz) (2H, $CH_2C_6H_4$); 2.28 s (3H, $CH_3C_6H_4$)
V	2156	1724	9.08–8.91 m (2H, 2NH); 7.04–6.88 m (4H, C_6H_4); 6.20 m (1H, CH=); 6.12 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.63 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.44 t (2H, N–CH_2–N); 4.27 t (J_{AB} 14.4 Hz) (1H, CH); 3.71 s (3H, $CH_3OC_6H_4$); 3.36 d.d (J_{AX} 7.8 Hz), 3.25 d.d (J_{BX} 7.2 Hz) (2H, $CH_2C_6H_4$)
VI	2152	1724	9.07–8.91 m (2H, 2NH); 7.66–7.41 m (4H, C_6H_4); 6.17 m (1H, CH=); 6.10 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.60 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.45 t (2H, N–CH_2–N); 4.29 t (J_{AB} 14.4 Hz) (1H, CH); 3.40 d.d (J_{AX} 7.8 Hz), 3.27 d.d (J_{BX} 7.2 Hz) (2H, $CH_2C_6H_4$)
VII	2152	1720	8.98–8.84 m (2H, 2NH); 7.64–7.52 m (5H, C_6H_3); 6.22 m (1H, CH=); 6.14 d.d (J_{HH} 17 Hz) (H-*trans*, CH_2=); 5.62 d.d (J_{HH} 10 Hz) (H-*cis*, CH_2=); 4.46 t (2H, N–CH_2–N); 4.32 t (J_{AB} 14.4 Hz) (1H, CH); 3.38 d.d (J_{AX} 7.8 Hz), 3.25 d.d (J_{BX} 7.2 Hz) (2H, $CH_2C_6H_3$)
VIII	2156	1724	9.06 br.s (2H, 2NH); 7.35–7.24 m (10H, 2Ph); 4.43 t (2H, N–CH_2–N); 4.23 t (J_{AB} 14 Hz) (2H, 2CH); 3.30 d.d (J_{AX} 7.2 Hz), 3.05 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2Ph$)
IX	2160	1724	9.02 br.s (2H, 2NH); 7.15–7.04 m (8H, $2C_6H_4$); 4.45 t (2H, N–CH_2–N); 4.21 t (J_{AB} 14 Hz) (2H, 2CH); 3.32 d.d (J_{AX} 7.2 Hz), 3.03 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2C_6H_4$); 2.24 s [6H, $2(CH_3C_6H_4)$]
X	2160	1728	9.08 br.s (2H, 2NH); 7.11–6.97 m (8H, $2C_6H_4$); 4.44 t (2H, N–CH_2–N); 4.22 t (J_{AB} 14 Hz) (2H, 2CH); 3.30 d.d (J_{AX} 7.2 Hz), 3.04 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2C_6H_4$); 2.27 s [6H, $2(CH_3C_6H_4)$]
XI	2160	1724	9.02 br.s (2H, 2NH); 7.14–7.07 m (8H, $2C_6H_4$); 4.44 t (2H, N–CH_2–N); 4.23 t (J_{AB} 14 Hz) (2H, 2CH); 3.31 d.d (J_{AX} 7.2 Hz), 3.06 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2C_6H_4$); 2.28 s [6H, $2(CH_3C_6H_4)$]
XII	2168	1724	9.02 br.s (2H, 2NH); 7.09–6.85 m (8H, $2C_6H_4$); 4.44 t (2H, N–CH_2–N); 4.22 t (J_{AB} 14 Hz) (2H, 2CH); 3.72 s [6H, $2(CH_3OC_6H_4)$]; 3.34 d.d (J_{AX} 7.2 Hz), 3.06 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2C_6H_4$)
XIII	2152	1720	9.08 br.s (2H, 2NH); 7.42–7.18 m (8H, $2C_6H_4$); 4.41 t (2H, N–CH_2–N); 4.23 t (J_{AB} 14 Hz) (2H, 2CH); 3.35 d.d (J_{AX} 7.2 Hz), 3.09 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2C_6H_4$)
XIV	2160	1724	9.04 br.s (2H, 2NH); 7.45–7.29 m (6H, $2C_6H_3$); 4.43 t (2H, N–CH_2–N); 4.23 t (J_{AB} 14 Hz) (2H, 2CH); 3.31 d.d (J_{AX} 7.2 Hz), 3.05 d.d (J_{BX} 6.6 Hz) (4H, $2CH_2C_6H_3$)

***N,N*-Methylenebis(3-phenyl-2-thiocyanatopropionamide) (VIII).** *a.* Benzenediazonium tetraflurorborate, 8.1 g, was added for 45 min to 3.1 g of *N,N*-methylenediacrylamide, 1.4 g of copper(II) tetrafluoroborate hexahydrate, and 3.2 g of potassium thiocyanate in 150 ml of H_2O–DMF (1 : 3). Nitrogen evolution was observed at 10–15°C for 1 h. When nitrogen no longer evolved, 200 ml of water was added to the reaction mixture, and the precipitate that formed was filtered off, dried, and crystallized from ethanol to obtain 7.3 g (86%) of compound **VIII**.

b. Benzenediazonium tetrafluoroborate, 0.72 g, was added for 20 min to 1.0 g of [(3-phenyl-2-thiocyanatopropionylamino)methyl]-2-acrylamide, 0.12 g of copper(II) tetrafluoroborate hexahydrate, and 0.37 g of potassium thiocyanate in 100 ml of H_2O–DMF (1 : 3). Nitrogen evolution was observed at 15–20°C for 45 min. The precipitate was treated as described in procedure *a* to obtain 1.9 g (80%) of compound **VIII**.

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