

## Reactions of Arenediazonium Tetrafluoroborates with 1,4-Bis(acryloyloxy)butane in the Presence of Thiocyanate Ion

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**Abstract**—The first thiocyanatoarylation reaction with an unsaturated compound containing two isolated multiple bonds, 1,4-bis(acryloyloxy)butane, was effected. The reactions of 1,4-bis(acryloyloxy)butane with arenediazonium tetrafluoroborates occur in aqueous acetone (1:2) in the presence of copper tetrafluoroborate and thiocyanate ion and involve only one multiple bond to give 1-acryloyloxy-4-(2-thiocyanato-3-arylpropionyloxy)butanes. Irrespective of reactant ratio, the second multiple bond undergoes no thiocyanatoarylation.

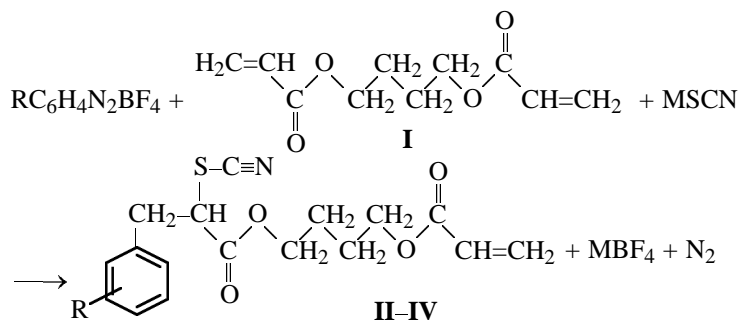
At present thiocyanatoarylation of monounsaturated compounds like  $\text{CH}_2=\text{CR}^1\text{R}^2$ , where  $\text{R}^1 = \text{H}, \text{CH}_3, \text{Cl}$ ;  $\text{R}^2 = \text{COOAlk}, \text{CONH}_2, \text{C}_6\text{H}_5, \text{CN}, \text{Cl}, \text{CH}_2\text{Hg}$ , have been systematically studied under anionarylation conditions [1–3]. Irrespective of the structure of the substrates, the reactions always gave 1-thiocyanato-2-arylethanes.

In [4–6], the examples of *N*-allylacrylamide, diallyl oxide, and diallyl sulfide were used to show that the reactions with unsaturated compounds containing two isolated multiple bonds involve only one of them. Thus, *N*-allylacrylamide underwent thiocyanatoarylation by the double bond of the acrylamide moiety to form *N*-allyl-3-aryl-2-thiocyanatopropion-

amides [4].

Proceeding with these studies, we considered it important to bring into the thiocyanatoarylation reaction new unsaturated compounds containing two identical multiple bonds. For the model compound we chose an ester, 1,4-bis(acryloyloxy)butane (**I**).

It might be expected that arenediazonium tetrafluoroborates would react with compound **I**, involving both multiple bonds. However, we found that only one multiple bond undergoes thiocyanatoethylation, and the reactions give 1-acryloyloxy-4-(2-thiocyanato-3-arylpropionyloxy)butanes **II–IV** by the following scheme.



$\text{R} = \text{H}$  (**II**), *p*- $\text{CH}_3$  (**III**), *p*- $\text{NO}_2$  (**IV**);  $\text{M} = \text{Na}, \text{K}, \text{NH}_4$ .

The reactions of arenediazonium tetrafluoroborates with ester **I** were accomplished in aqueous acetone (1:2) in the presence of alkali metal or ammonium

thiocyanates and catalytic amounts of copper tetrafluoroborate at  $-10$  to  $-5^\circ\text{C}$ . The presence of catalysts is prerequisite for successful reactions.

It should be noted that 1-acryloyloxy-4-(2-isothiocyanato-3-arylpropionyloxy)butanes were not found among the reaction products. The yields of adducts **II–IV** are 41–61%.

The optimal diazonium salt:ester:sodium (potassium, ammonium) thiocyanate:copper tetrafluoroborate ratio was found to be 1:1.2:1.3:0.1. The by-products are aryl isothiocyanates (10–12%).

The reaction temperature is reduced to  $-30$  to  $-25^{\circ}\text{C}$  is reduced if alkali metal or ammonium thiocyanates are introduced last into the reaction medium.

When diazonium salt, sodium (potassium, ammonium) thiocyanate, and copper tetrafluoroborate are used in a 2:2.6:0.2 ratio, neither reaction patterns nor the yields of target products compounds change. Thus, the thiocyanatoarylation of 1,4-bis(acryloyloxy)-butane in the chosen conditions involves one multiple bond, like with diallyl oxide and diallyl sulfide [5, 6].

The observed reaction pattern is consistent with the radical mechanism of catalytic anionarylation we proposed earlier [1].

As follows from our present results, thiocyanate ion exhibits no ambident properties. To explain the fact that in the presence of the thiocyanate group no other products but thiocyanates are formed, we performed MNDO and AM1 semiempirical calculations [7] of certain parameters of the unsaturated substrate in hand, as well as of the adducts 1-acryloyloxy-4-(3-phenyl-2-thiocyanatopropionyloxy)butane and hypothetical analog 1-acryloyloxy-4-(2-isothiocyanato-3-arylpropionyloxy)butane (**V**).

The resulting quantum-chemical data are listed in Table 1.

As seen from Table 1, the enthalpies of formation of the products of thiocyanatoarylation of ester **I** are lower than those of their analogs, the products of isothiocyanatoarylation. Thus, these data point to a possible reason of the reaction result [8].

Upon heating of alcohol solutions of adducts **II–IV**

**Table 1.** Results of quantum-chemical calculations for ester **I** and adducts **II** and **V**

Comp. no.	Standard enthalpy of formation, kcal/mol	Energy, eV	
		HOMO	LUMO
MNDO			
<b>I</b>	-136.3489	-10.7410	-0.0427
<b>II</b>	-85.4787	-9.6202	-0.1084
<b>V</b>	-60.9707	-9.8330	-0.7579
AM1			
<b>I</b>	-147.2436	-11.0740	-0.0246
<b>II</b>	-100.9211	-9.5529	-0.8241
<b>V</b>	-77.0361	-9.1060	-0.7197

we found neither products of isomerization of thiocyanates to isothiocyanates nor heterocyclization products. The control was performed by IR spectroscopy and high-performance liquid chromatography.

The yields, constants, elemental analyses, and  $^1\text{H}$  NMR and IR spectra of compounds **II–IV** are given in Tables 2 and 3.

The structures of adducts **II–IV** were confirmed by  $^1\text{H}$  NMR and IR spectroscopy.

The IR spectra of these compounds contain carbonyl and thiocyanate absorption bands at 1716 and  $2152\text{--}2156\text{ cm}^{-1}$ . The presence in the adducts of a terminal vinyl group is confirmed by the observation of absorption at  $1636\text{--}1640\text{ cm}^{-1}$ , as well as at  $812$  and  $984\text{ cm}^{-1}$  (out-of-plane CH vibrations).

The  $^1\text{H}$  NMR spectra of compounds **II–IV** show a multiplet at 7.44–7.26 ppm from aromatic proton signals. The methylene proton signals of the terminal vinyl group appear as a doublet of doublets at 6.36–6.33 ( $\text{H}_{\text{cis}}$ ) and 5.93–5.98 ppm ( $\text{H}_{\text{trans}}$ ) with coupling constants of 11 and 14 Hz, respectively. The methyl proton signals of the terminal vinyl group give a doublet of doublets at 6.18–6.16 ppm (coupling constant 10 Hz).

**Table 2.** Yields, constants, and elemental analyses of 1-acryloyloxy-4-(2-thiocyanato-3-arylpropionyloxy)butanes **II–IV**

Comp. no.	Yield, %	$n_{\text{D}}^{20}$	$d_4^{20}$	$MR_{\text{D}}$		Found, %		Formula	Calculated, %	
				found	calculated	N	S		N	S
<b>II</b>	61	1.4928	1.1067	87.52	88.07	4.13	9.60	$\text{C}_{17}\text{H}_{19}\text{NO}_4\text{S}$	4.20	9.62
<b>III</b>	56	1.4980	1.0854	93.83	94.38	3.96	9.16	$\text{C}_{18}\text{H}_{21}\text{NO}_4\text{S}$	4.03	9.23
<b>IV</b>	41	1.5112	1.1688	97.02	97.64	7.32	8.40	$\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_6\text{S}$	7.40	8.47

**Table 3.** IR and  $^1\text{H}$  NMR spectra of 1-acryloyloxy-4-(2-thiocyanato-3-arylpropionyloxy)butanes **II–IV**

Comp. no.	IR spectrum, $\nu$ , $\text{cm}^{-1}$		$^1\text{H}$ NMR spectrum, $\delta$ , ppm
	SCN	CH=CH <sub>2</sub>	
<b>II</b>	2156	1636	7.34–7.26 m (5H, Ph), 6.33 d.d ( $\text{H}_{\text{cis}}$ , =CH <sub>2</sub> , $J_{\text{HH}}$ 11 Hz), 6.16 d.d (1H, =CH–, $J_{\text{HH}}$ 10 Hz), 5.93 d.d ( $\text{H}_{\text{trans}}$ , =CH <sub>2</sub> , $J_{\text{HH}}$ 14 Hz), 4.50 d.d (1H, CH, $J_{\text{HH}}$ 7 Hz), 4.11 t [4H, 2(–OCH <sub>2</sub> )], 3.35 d.d ( $J_{\text{HH}}$ 8 Hz), 3.13 d.d (2H, CH <sub>2</sub> Ph, $J_{\text{HH}}$ 8 Hz), 1.48–1.70 m (4H, –CH <sub>2</sub> –CH <sub>2</sub> –)
<b>III</b>	2152	1640	7.36–7.26 m (4H, C <sub>6</sub> H <sub>4</sub> ), 6.35 d.d ( $\text{H}_{\text{cis}}$ , =CH <sub>2</sub> , $J_{\text{HH}}$ 11 Hz), 6.18 d.d (1H, =CH–, $J_{\text{HH}}$ 10 Hz), 5.97 d.d ( $\text{H}_{\text{trans}}$ , =CH <sub>2</sub> , $J_{\text{HH}}$ 14 Hz), 4.51 d.d (1H, CH, $J_{\text{HH}}$ 7 Hz), 4.12 t [4H, 2(–OCH <sub>2</sub> )], 3.35 d.d. ( $J_{\text{HH}}$ 8 Hz), 3.12 d.d (2H, CH <sub>2</sub> –C <sub>6</sub> H <sub>4</sub> , $J_{\text{HH}}$ 8 Hz), 2.35 s (3H, <i>p</i> -CH <sub>3</sub> –C <sub>6</sub> H <sub>4</sub> ), 1.46–1.72 m (4H, –CH <sub>2</sub> –CH <sub>2</sub> –)
<b>IV</b>	2152	1640	7.44–7.36 m (4H, C <sub>6</sub> H <sub>4</sub> ), 6.36 d.d ( $\text{H}_{\text{cis}}$ , =CH <sub>2</sub> , $J_{\text{HH}}$ 11 Hz), 6.18 d.d (1H, =CH–, $J_{\text{HH}}$ 10 Hz), 5.98 d.d ( $\text{H}_{\text{trans}}$ , =CH <sub>2</sub> , $J_{\text{HH}}$ 14 Hz), 4.53 d.d (1H, CH, $J_{\text{HH}}$ 7 Hz), 4.14 t [4H, 2(–OCH <sub>2</sub> )], 3.37 d.d ( $J_{\text{HH}}$ 8 Hz), 3.14 d.d (2H, –CH <sub>2</sub> –C <sub>6</sub> H <sub>4</sub> , $J_{\text{HH}}$ 8 Hz), 1.47–1.69 m (4H, –CH <sub>2</sub> –CH <sub>2</sub> –)

## EXPERIMENTAL

The IR spectra of compounds **II–IV** were obtained on a Specord M-80 instrument for thin films. The  $^1\text{H}$  NMR spectra were measured on a Varian Gemini instrument in DMSO, working frequency 300 MHz, internal reference HMDS.

The purity of the synthesized compounds was established by TLC on Silufol UV-254 plates (eluent hexane–chloroform–methanol–diethyl ether, 5:3:3:1). The mixtures were analyzed on a Milikhrom-4 liquid chromatograph with a UV detector on a 80×2-mm column packed with Separon SC-RP-S-Super C<sub>18</sub> (average grain size 5  $\mu\text{m}$ ). The detection was performed at 220, 230, 254, 274, 284 nm. Eluent isopropanol–water–acetonitrile, 6:11:33. Measurement time 0.02 s, recording scale 10. Regeneration volume 150  $\mu\text{l}$ , buffer volume 20  $\mu\text{l}$ , sample volume 5  $\mu\text{l}$ , eluent rate 30  $\mu\text{l}/\text{min}$ .

**1-Acryloyloxy-4-(2-thiocyanato-3-arylpropionyl-oxy)butane (II).** Benzenediazonium tetrafluoroborate, 0.1 mol, was added over the course of 45–60 min to 0.12 mol of 1,4-bis(acryloyloxy)butane, 0.01 mol of copper(II) tetrafluoroborate, and 0.13 mol of ammonium thiocyanate in 200 ml of aqueous acetone (1:2). Nitrogen evolution was observed at –5 to –10°C for 2 h. When nitrogen no longer evolved, the reaction mixture was treated with 250 ml of diethyl ether, and the extract was washed with water and dried with magnesium sulfate. The ether was removed, and the residue was subjected to column chromatography on Al<sub>2</sub>O<sub>3</sub> (eluent hexane–chloroform–methanol–diethyl ether, 5:3:3:1). The fractions whose IR spectra contained isothiocyanate, isothiocyanate and thiocyanate, or thiocyanate absorption bands were

analyzed by HPLC to find that the latter fractions contain exclusively the target product. The eluent was removed by distillation and traces of solvents were purged off with argon to obtain 24.2 g of compound **II**.

Compound **III** and **IV** were obtained in a similar way.

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