

Thiocyanatoarylation of Diethylene Glycol Diacrylate

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Abstract—The example of diethylene glycol diacrylate was used to demonstrate the possibility of thiocyanatoarylation both by one and by two multiple bonds of compounds with two isolated multiple bonds. The reactions of arenediazonium tetrafluoroborates with diethylene glycol diacrylate in aqueous acetone (1:2) in the presence of catalytic amounts of copper gave 1-acryloyloxy-2-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]ethanes. The latter were reacted with arenediazonium tetrafluoroborates in aqueous acetone (1:3) to obtain 1-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]-2-(2-thiocyanato-3-arylpropionyloxy)ethanes via thiocyanatoarylation by two multiple bonds.

We earlier established that thiocyanatoarylation of monounsaturated and diene compounds [1–4] can take different ways depending on the type of the unsaturated compound. Thus, arenediazonium tetrafluoroborates react with acrylic and methacrylic acid esters in the presence of potassium thiocyanate to give 1-thiocyanato-1-alkoxycarbonyl-2-arylethanes via loss of diazo group nitrogen and addition of the aryl and thiocyanato groups by the site of cleavage of the multiple bond of the monounsaturated compound [5].

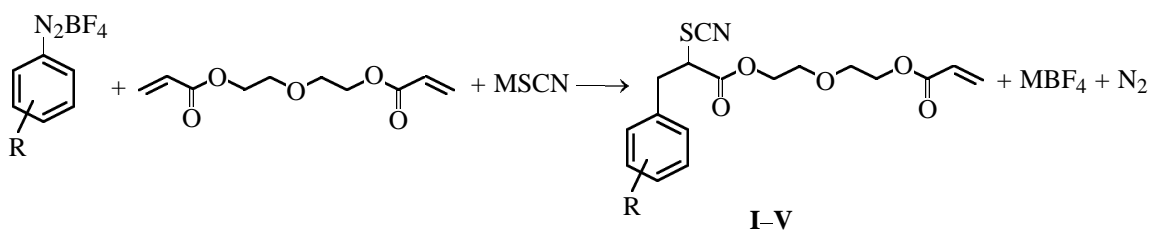
The thiocyanatoarylations with divinyl and isoprene involve 1,2 addition to form 2-isothiocyanato-1-aryl-3-butenes have been reported [6]. Thus, for mally, dienes behave in this reaction as unsaturated compounds with two isolated multiple bonds.

As shown in [7], diazonium salts react with diallyl ether in the presence of the thiocyanate nucleophile, yielding 3-allyloxy-1-aryl-2-thiocyanatopropanes.

Independent of reactant ratio, the second allyl fragment of diallyl ether takes no part in the reaction.

Preceding with these studies, in the present work we reacted diazonium salts with unsaturated compounds containing two isolated multiple bonds, in the presence of foreign nucleophiles. For the model unsaturated compound we chose an ester, diethylene glycol diacrylate, which has never been brought into anionarylation reactions [3].

It was found that arenediazonium tetrafluoroborates react with diethylene glycol diacrylate in aqueous acetone (1:2) in the presence of alkali metal or ammonium thiocyanates and catalytic amounts of copper tetrafluoroborate and at $-5-0^{\circ}\text{C}$ to give 1-acryloyloxy-2-[2-(2-thiocyanato-3-arylpropionyl-oxy)ethoxy]ethanes **I–V** via loss of diazo group nitrogen and addition by one of the two multiple bonds.



R = H (**I**), *o*-CH₃ (**II**), *m*-CH₃ (**III**), *p*-CH₃ (**IV**), *p*-CH₃O (**V**); M = Na, K, NH₄.

The yields of monoadducts **I–V** are 35–59%. *Ortho*-, *meta*-, or *para*-methyl substituents in the aromatic ring decrease the yields of the target products by 10–25%. Therewith, the lowest yield is observed in the reaction of diethylene glycol diacrylate with *o*-toluenediazonium tetrafluoroborate.

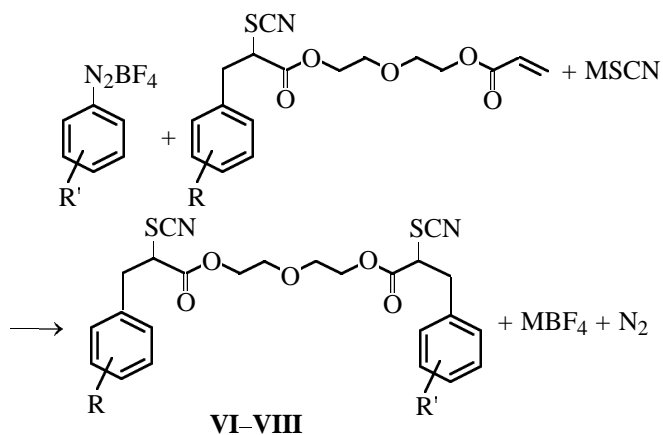
The optimal arenediazonium salt:ester:sodium (potassium, ammonium) thiocyanate:copper tetrafluoroborate ratio was found to be 1.2:1:1.4:0.1. The by-products are aryl isothiocyanates (9–15%) and aryl thiocyanates (2–3%).

The reaction temperature is reduced to –25 to –20°C if alkali metal or ammonium thiocyanates are introduced in the reaction medium last.

The same result was obtained if diazonium salt and diethylene glycol diacrylate were first reacted at a 1:1 ratio and then, when nitrogen no longer evolved, additional amounts of benzenediazonium tetrafluoroborate, ammonium thiocyanate, and catalyst were introduced in a ratio optimal counting upon the second multiple bond.

With doubled quantities of diazonium salt, catalyst, and thiocyanate compared with optimal, the yields of aryl isothiocyanates and thiocyanates are sharply increased (58–65 and 8–10%, respectively).

Thus, using diethylene glycol diacrylate as example, we showed that a compound containing two isolated multiple bonds undergoes anionarylation by only one multiple bond under the given conditions. Apparently, this anomalous behavior is explained by a much lower solubility in aqueous acetone (1:2) of monoadducts **I–V** compared with the starting ester. For this reason, the products leave the reaction medium, thereby giving way to prevailing formation of Sandmeyer adducts, aryl isothiocyanates and thiocyanates.

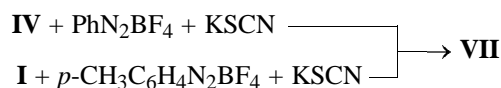


R = R' = H (**VI**); R = R' = *p*-CH₃ (**VII**); R = H, R' = *p*-CH₃ (**VIII**); M = Na, K, NH₄.

It was found that the free multiple bond of monoadducts **I** and **IV** can be involved in thiocyanatoarylation via reaction with arenediazonium tetrafluoroborates in aqueous acetone (1:3).

The reaction occurs at 10–15°C in the presence copper(II) tetrafluoroborate and 1.5-fold excesses of diazonium salt and thiocyanate. Adducts **VI–VIII** were obtained in 39–47% yields. They are white crystalline substances melting at 69–80°C.

Compound **VII** was obtained from benzenediazonium tetrafluoroborate and monoadduct **I**, as well as from *p*-toluenediazonium tetrafluoroborate and monoadduct **IV**. The two samples had identical physicochemical characteristics.



Heating of monoadducts **I–V** adducts **VI–VIII** in alcohol produced both no isomerization of thiocyanates into isothiocyanates and no heterocyclization.

The yields, constants, elemental analyses, and ¹H NMR and IR spectra of compounds **I–VIII** are given in Tables 1 and 2.

The IR spectra of compounds **I–V**, in agreement with the proposed structures, contain carbonyl and thiocyanate absorption bands at 1724 and 2156–2160 cm⁻¹, respectively. Moreover, in the spectra of compounds **I–V**, bands at 1636–1640 cm⁻¹ appeared due to vinyl absorption. The narrow bands at 812 and 988 cm⁻¹ are assignable to out-of-plane CH vibrations of the vinyl group.

The ¹H NMR spectra of compounds **I–VIII** show aromatic proton signals at 7.39–7.08 ppm (multiplet). The proton signals of the vinyl CH₂ group of monoadducts **I–V** appear as a doublet of doublets at 6.30–6.34 (*cis*-H) and 5.92–5.94 ppm (*trans*-H) with coupling constants of 10 and 15 Hz, and the methine proton signals of the vinyl group appear as a doublet of doublets at 6.14–6.16 ppm and a coupling constant of 10 Hz.

In the ¹H NMR spectra of compounds **VI–VIII**, the protons of the CH groups bound with the thiocyanato group (a triplet at 4.47–4.48 ppm) and protons of the methylene groups (two doublets of doublets at 3.33–3.34 and 3.10–3.11 ppm) bound with the aromatic nuclei form an ABX system (*J*_{AX} 8, *J*_{BX} 7, and *J*_{AB} 14 Hz).

EXPERIMENTAL

The IR spectra of compounds **I–V** were recorded

Table 1. Yields, constants, and elemental analyses of 1-acryloyloxy-2-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]ethanes **I–V** and 1-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]-2-(2-thiocyanato-3-arylpropionyloxy)ethanes **VI–VIII**

Comp. no.	Yield, %	n_D^{20} (mp, °C) ^a	d_4^{20}	MR_D		Found, %		Formula	Calculated, %	
				found	calculated	N	S		N	S
I	59	1.5052	1.1580	89.53	89.85	3.87	9.06	C ₁₇ H ₁₉ NO ₅ S	4.01	9.18
II	35	1.5136	1.1598	94.28	94.50	3.61	8.70	C ₁₈ H ₂₁ NO ₅ S	3.85	8.82
III	42	1.5124	1.1608	94.01	94.50	3.58	8.63	C ₁₈ H ₂₁ NO ₅ S	3.85	8.82
IV	47	1.5128	1.1588	94.23	94.50	3.76	8.67	C ₁₈ H ₂₁ NO ₅ S	3.85	8.82
V	44	1.4956	1.1513	96.21	96.28	3.72	8.21	C ₁₈ H ₂₁ NO ₆ S	3.69	8.45
VI	47	(80)	–	–	–	5.59	13.10	C ₂₄ H ₂₄ N ₂ O ₅ S ₂	5.78	13.23
VII	39	(69)	–	–	–	5.51	12.71	C ₂₅ H ₂₆ N ₂ O ₅ S ₂	5.62	12.86
VIII	45	(74)	–	–	–	5.40	12.42	C ₂₆ H ₂₈ N ₂ O ₅ S ₂	5.46	12.51

^a Recrystallized from ethanol.**Table 2.** IR and ¹H NMR spectra of 1-acryloyloxy-2-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]ethanes **I–V** and 1-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]-2-(2-thiocyanato-3-arylpropionyloxy)ethanes **VI–VIII**

Comp. no.	IR spectrum, ν , cm ⁻¹			¹ H NMR spectrum, δ , ppm (<i>J</i> , Hz)
	SCN	CH=CH ₂	C=O	
I	2156	1636	1724	7.30–7.20 m (5H, Ph), 6.30 d.d (<i>cis</i> -H, =CH ₂ , J_{HH} 10), 6.14 d.d (1H, =CH–, J_{HH} 10), 5.93 d.d (<i>trans</i> -H, =CH ₂ , J_{HH} 15), 4.50–4.44 m (1H, CH), 4.20 t (4H, 2OCH ₂), 3.48 d.d (4H, CH ₂ –O–CH ₂ , J_{HH} 2), 3.33 d.d (J_{HH} 7), 3.10 d.d (2H, CH ₂ Ph, J_{HH} 7)
II	2156	1640	1720	7.22–7.10 m (4H, C ₆ H ₄), 6.32 d.d (<i>cis</i> -H, =CH ₂ , J_{HH} 10), 6.15 d.d (1H, =CH, J_{HH} 10), 5.94 d.d (<i>trans</i> -H, =CH ₂ , J_{HH} 15), 4.51–4.45 m (1H, CH), 4.22 t (4H, 2OCH ₂), 3.46 d.d (4H, CH ₂ –O–CH ₂ , J_{HH} 2), 3.32 d.d (J_{HH} 7), 3.09 d.d (2H, CH ₂ –C ₆ H ₄ , J_{HH} 7), 2.25 s (3H, <i>o</i> -CH ₃ –C ₆ H ₄)
III	2160	1636	1724	7.34–7.16 m (4H, C ₆ H ₄), 6.34 d.d (<i>cis</i> -H, =CH ₂ , J_{HH} 10), 6.15 d.d (1H, =CH, J_{HH} 10), 5.94 d.d (<i>trans</i> -H, =CH ₂ , J_{HH} 15), 4.50–4.44 m (1H, CH), 4.24 t (4H, 2OCH ₂), 3.45 d.d (4H, CH ₂ –O–CH ₂ , J_{HH} 2), 3.31 d.d (J_{HH} 7), 3.10 d.d (2H, CH ₂ –C ₆ H ₄ , J_{HH} 7), 2.31 s (3H, <i>m</i> -CH ₃ –C ₆ H ₄)
IV	2156	1636	1724	7.24–7.08 m (4H, C ₆ H ₄), 6.32 d.d (<i>cis</i> -H, =CH ₂ , J_{HH} 10), 6.16 d.d (1H, =CH, J_{HH} 10), 5.92 d.d (<i>trans</i> -H, =CH ₂ , J_{HH} 15), 4.50–4.44 m (1H, CH), 4.23 t (4H, 2OCH ₂), 3.46 d.d (CH ₂ –O–CH ₂ , J_{HH} 2), 3.33 d.d (J_{HH} 7), 3.12 d.d (2H, CH ₂ –C ₆ H ₄ , J_{HH} 7), 2.37 s (3H, <i>p</i> -CH ₃ –C ₆ H ₄)
V	2156	1636	1724	7.24–7.14 m (4H, C ₆ H ₄), 6.32 d.d (<i>cis</i> -H, =CH ₂ , J_{HH} 10), 6.16 d.d (1H, =CH, J_{HH} 10), 5.91 d.d (<i>trans</i> -H, =CH ₂ , J_{HH} 15), 4.51–4.45 m (1H, CH), 4.22 t (4H, 2OCH ₂), 3.70 s (3H, <i>p</i> -CH ₃ O–C ₆ H ₄), 3.46 d.d (4H, CH ₂ –O–CH ₂ , J_{HH} 2), 3.33 d.d (J_{HH} 7), 3.13 d.d (2H, CH ₂ –C ₆ H ₄ , J_{HH} 7)
VI	2152	–	1716	7.34–7.24 m (10H, 2Ph), 4.47 t (2H, 2CH, J_{AB} 14), 4.22 t (4H, 2OCH ₂), 3.49 d.d (4H, (CH ₂ –O–CH ₂), 3.34 d.d (J_{AX} 8), 3.10 d.d (4H, 2CH ₂ Ph, J_{BX} 7)
VII	2152	–	1716	7.39–7.30 m (5H, Ph), 7.22–7.14 m (4H, C ₆ H ₄), 4.52 t, 4.47 t (2H, 2CH), 4.22 t (4H, 2OCH ₂), 3.48 d.d (4H, CH ₂ –O–CH ₂), 3.39–3.27 m, 3.17–3.07 m (4H, CH ₂ –C ₆ H ₄ , CH ₂ Ph), 2.26 s (3H, <i>p</i> -CH ₃ –C ₆ H ₄)
VIII	2156	–	1720	7.21–7.13 m (8H, 2C ₆ H ₄), 4.48 t (1H, CH, J_{AB} 14), 4.21 t (4H, 2OCH ₂), 3.48 d.d (4H, CH ₂ –O–CH ₂), 3.33 d.d (J_{AX} 8), 3.11 d.d (4H, 2CH ₂ –C ₆ H ₄ , J_{BX} 7), 2.27 s (6H, 2 <i>p</i> -CH–C ₆ H ₄)

in thin films and of compounds **VI–VIII**, as suspensions in mineral oil, on a Specord M-80 instrument. The ^1H NMR spectra were obtained in DMSO on a Varian Gemini instrument, working frequency 300 MHz, internal reference HMDS. The individuality of the synthesized compounds was proved by TLC on Silufol UV-254 plates (eluent hexane–chloroform–diethyl ether, 7:5:2). Chromatographic separation of the reaction products was performed on a column of Al_2O_3 [eluent hexane–chloroform–diethyl ether, 7:5:2 (compounds **VI–VIII**), and hexane–chloroform, 3:1].

1-Acryloyloxy-2-[2-(2-thiocyanato-3-phenylpropionyloxy)ethoxy]ethane (I). Benzenediazonium tetrafluoroborate, 0.12 mol, was added over the course of 60–75 min to 0.10 mol of diethylene glycol diacrylate, 0.01 mol of copper(II) tetrafluoroborate, and 0.14 mol of ammonium thiocyanate in 200 ml of aqueous acetone (1:2). Nitrogen evolution was observed at $-5-0^\circ\text{C}$ for 2 h. When nitrogen evolution had ceased, the reaction mixture was treated with 250 ml of diethyl ether and the extract was washed with water and dried with magnesium sulfate. The solvent was then removed, and the residue was subjected to chromatography to obtain 20.7 g (59%) of compound **I**.

Compounds **II–V** were obtained in a similar way.

Reaction of diethylene glycol diacrylate with a double excess of benzenediazonium tetrafluoroborate. *a.* Benzenediazonium tetrafluoroborate, 0.13 mol, was added over the course of 120 min to 0.05 mol of diethylene glycol diacrylate, 0.01 mol of copper(II) tetrafluoroborate, and 0.14 mol of ammonium thiocyanate in 200 ml of aqueous acetone (1:2). Nitrogen evolution was observed at $-5-0^\circ\text{C}$ for 2.5 h. The mixture was then 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 chromatography to obtain 8.2 g of compound **I**, 10.8 g of phenyl isothiocyanate, and 1.4 g of phenyl thiocyanate.

b. By analogy with procedure *a*, when nitrogen evolution had ceased, additional 0.01 mol of copper(II) tetrafluoroborate and 0.14 mol of ammonium thiocyanate were added and then, over the course of 2 h, 0.13 mol of benzenediazonium tetrafluoroborate. The reaction mixture was kept for 3 h at 0°C until

nitrogen no longer evolved. We obtained 8.3 g of compound **I**, 20.5 g of phenyl isothiocyanate, and 3.3 g of benzenethiocyanate.

1-[2-(2-Thiocyanato-3-phenylpropionyloxy)ethoxy]-2-(2-thiocyanato-3-phenylpropionyloxy)ethane (VI). Benzenediazonium tetrafluoroborate, 0.045 mol, was added over the course of 60 min to 0.03 mol of 1-acryloyloxy-2-[2-(2-thiocyanato-3-phenylpropionyloxy)ethoxy]ethane, 0.003 mol of copper(II) tetrafluoroborate, and 0.045 mol of potassium thiocyanate in 150 ml of aqueous acetone (1:3). Nitrogen vigorously evolved at $10-15^\circ\text{C}$ for 60 min. When the reaction had been complete, the mixture was treated with 100 ml of diethyl ether, the extract was washed with water, dried with sodium sulfate, the ether was evaporated, and the residue was subjected to column chromatography on Al_2O_3 (eluent hexane–chloroform, 3:1) to obtain 6.1 g (44%) of a viscous oily substance that crystallized on standing. Double recrystallization from ethanol gave 4.3 g of compound **VI**.

Compounds **VII** and **VIII** were obtained in a similar way.

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