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Reaction of Arenediazonium Tetrafluoroborates with Allyl Methacrylate in the Presence of the Thiocyanate Anion

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Abstract—Allyl 2-thiocyanato-2-methyl-3-arylpropionates were obtained by the reaction of arenediazonium tetrafluoroborates with allyl methacrylate in a water–acetone (1 : 5) medium, involving thiocyanatoarylation by the C=C bond of the methacrylic fragment. Under the examined conditions, the allylic fragment of the biunsaturated compound does not react.

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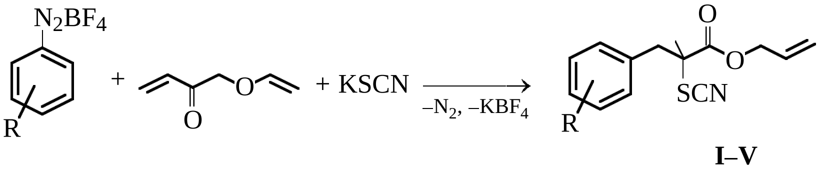
By now a variety of biunsaturated compounds with two equivalent multiple bonds have been studied in the thiocyanatoarylation reaction [1]. Thus, glycol diacrylates [2, 3] and *N*,*N*-methylenebisacrylamide [4] form monoanionarylated derivatives whose reaction with arenediazonium tetrafluoroborates and thiocyanates provides thiocyanatoarylated diadducts [5]. Thiocyanatoarylation of diallylic derivatives (diallyl ether [6], diallyl sulfide [7], diallyl phthalate and isophthalate [8], and 2,2-bis(allyloxymethyl)butan-1-ol [9]) involves exclusive formation of monoadducts even with a great excess of both the arylating and anionoid reagents. Thiocyanatoarylation of biunsaturated compounds containing isolated multiple bonds in different fragments was first studied with *N*-allylacrylamide as an example [10]. The reaction was found to involve the C=C bond of the acrylamide fragment only. To reveal the effect of the unsaturated fragment on the regioselectivity of anionarylation, we studied the behavior of allyl methacrylate in the thiocyanatoarylation reaction. Arenediazonium tetrafluoroborates were found to react with allyl methacrylate in the presence of thiocyanate anions and catalytic amounts of Cu(II) salts in a water–acetone (1 : 5) medium to form allyl 2-thiocyanato-2-methyl-3-arylpropionates **I**–**V** in 32–56% yields.



I–**V**

R = H (**I**), 4-CH_3 (**II**), 4-CH3O (**III**), 4-Br (**IV**), 2,5-Cl_2 (**V**).

This reaction proceeds at –15 to –50°C. The optimal diazonium salt : unsaturated compound : potassium thiocyanate : catalyst ratio is 1.4 : 1 : 1.4 : 0.14. The reaction gives a mixture of thio- and isothiocyanatoarenes as by-products. The use of a double excess of the diazonium salt or anionoid reagent or elevation of the temperature have no regioselectivity effect and do not involve the allylic fragment in thiocyanatoarylation.

Thus, the example of allyl methacrylate was used to show that the presence of two different C=C bonds in the biunsaturated compound does not influence the regioselectivity of the thiocyanatoarylation reaction:

Table 1. Yields, constants, and elemental analyses of allyl 2-thiocyanato-2-methyl-3-arylpropionates **I**–**V**

Comp. no.	Yield, %	n_D^{20}	d_4^{20}	MR_D		Found, %		Formula	Calculated, %	
				found	calculated	N	S		N	S
I	56	1.5472	1.1368	72.92	72.97	5.30	12.33	$C_{14}H_{15}NO_2S$	5.36	12.27
II	49	1.5448	1.1196	77.74	77.80	5.03	11.58	$C_{15}H_{17}NO_2S$	5.09	11.64
III	43	1.5498	1.1660	79.58	79.65	4.79	10.95	$C_{15}H_{17}NO_3S$	4.81	11.01
IV	32	1.5694	1.3857	80.49	80.66	4.04	9.33	$C_{14}H_{14}BrNO_2S$	4.12	9.42
V	47	1.5684	1.3067	82.69	82.76	4.15	9.62	$C_{14}H_{13}Cl_2NO_2S$	4.24	9.71

Table 2. ^{1}H NMR spectra of allyl 2-thiocyanato-2-methyl-3-arylpropionates **I**–**V**, δ, ppm (*J*, Hz)

Comp. no.	Ar	CH=	CH_2	OCH_2	CH_2Ar	CH_3	R
I	7.33–7.18 m	5.96–5.83 m	5.38 d (17 Hz), 5.29 d (11 Hz)	4.67 d (6 Hz)	3.33 d	1.79 s	–
II	7.14–7.08 m	5.97–5.84 m	5.39 d (17 Hz), 5.30 d (11 Hz)	4.67 d (6 Hz)	3.32 d	1.80 s	2.31 s
III	7.12–6.83 m	5.98–5.86 m	5.40 d (17 Hz), 5.30 d (11 Hz)	4.66 d (6 Hz)	3.32 d	1.80 s	3.73 s
IV	7.49–7.15 m	5.96–5.84 m	5.39 d (17 Hz), 5.30 d (11 Hz)	4.68 d (6 Hz)	3.34 d	1.81 s	–
V	7.27–7.09 m	5.96–5.84 m	5.38 d (17 Hz), 5.28 d (11 Hz)	4.66 d (6 Hz)	3.32 d	1.79 s	–

It proceeds by the more reactive methacrylic fragment. The synthesized 2-thiocyanato-2-methyl-3-arylpropionates **I**–**V** are viscous orange or light brown liquids. The yields, constants, and elemental analyses of compounds **I**–**V** are shown in Table 1.

The structure of compounds **I**–**V** is confirmed by IR and ^{1}H NMR spectroscopy. The IR spectra of compounds **I**–**V** show absorption bands of the thiocyanato (2152–2160 cm^{-1}) and carbonyl groups (1716–1730 cm^{-1}), as well as the allylic double bond (1624–1644 cm^{-1}). The ^{1}H NMR spectra of adducts **I**–**V** contain aromatic proton signals at 7.49–6.83 ppm (multiplets), the methylene and methine protons of the allylic fragment form two doublets at 5.40–5.38 and 5.30–5.28 ppm and a multiplet at 5.98–5.83 ppm, respectively. Protons of the CH_2 groups attached to the aromatic rings form a doublet at 3.34–3.32 ppm (Table 2).

EXPERIMENTAL

The IR spectra were registered on an IKS-29 instrument from thin films. The ^{1}H NMR spectra were obtained on Varian VXR-300 (300 MHz) and Varian Mercury (400 MHz) spectrometers, external reference HMDS. The purity of the synthesized compounds was established by TLC on Silufol UV-254 (eluent hexane–chloroform–methanol, 5 : 3 : 1).

Allyl 2-methyl-3-phenyl-2-thiocyanatopropionate (I). To a mixture of 0.12 mol of allyl methacrylate, 0.017 mol of copper(II) tetrafluoroborate hexahydrate, and 0.17 mol of potassium thiocyanate in 250 ml of a water–acetone mixture (1 : 5), 0.17 mol of phenyldiazonium tetrafluoroborate was added over the course of 2 h. Nitrogen evolution was observed at –15 to –10°C for 2 h. The reaction mixture was then treated with 200 ml of diethyl ether, washed with water, and dried over calcium chloride. The ether was removed, and the residue was subjected to column chromatography on alumina (eluent hexane–chloroform, 5 : 3). Yield 17.4 g (56%), dark orange viscous oil.

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

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