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# Mixed Anionoarylation of Tetramethylene and Diethylene Glycol Diacrylates

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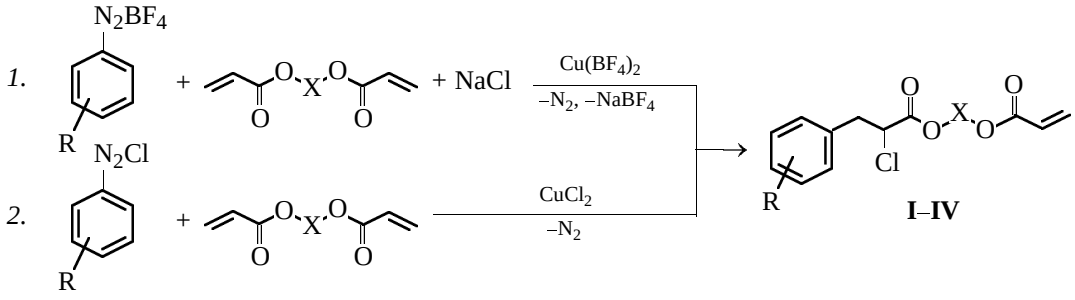
**Abstract** — The example of tetramethylene and diethylene glycol diacrylates was used to accomplish the first mixed anionoarylation. The reaction of diazonium salts with these unsaturated compounds gave chloroarylation adducts by one multiple bond: 1-acryloyloxy-4-(2-chloro-3-arylpropyonyloxy)butanes and 1-acryloyloxy-2-[2-(2-chloro-3-arylpropyonyloxy)ethoxy]ethanes. The latter were subjected to thiocyanatoarylation to obtain diadducts: 1-(2-chloro-3-arylpropyonyloxy)-4-(2-thiocyanato-3-arylpropyonyloxy)butanes and 1-(2-chloro-3-arylpropyonyloxy)-2-[2-(2-thiocyanato-3-arylpropyonyloxy)ethoxy]ethanes.

We previously showed [1–4] that under anionoarylation conditions tetramethylene and diethylene glycol and *N*,*N*-methylenecarboxamide undergo thiocyanatoarylation first by one multiple bond and then by the other to give mono- and diadducts. These data lead us to expect that anionoarylation of monoadducts in the presence of other anions would result in mixed anionoarylation.

As model compounds we chose tetramethylene and diethylene glycol diacrylates. It was found that the reactions of these unsaturated compounds react with arenediazonium tetrafluoroborates in the presence of sodium chloride and catalytic amounts of copper(II) chloride involves chloroarylation by one multiple bond to form 1-acryloyloxy-4-(2-chloro-3-arylpropyonyloxy)butanes **I** and **II** and 1-acryloyloxy-2-[2-(2-chloro-3-arylpropyonyloxy)ethoxy]ethanes **III** and **IV**. The reactions occur in aqueous acetone (1 : 2) at 10–15°C and produce much aryl chlorides, phenols, and unidentified tarry products. The yields of the monoadducts are 10–15%.

To improve the yields of the target products, we performed direct chloroarylation of the starting unsaturated compounds. In this case, the yields of the chloroarylation monoadducts were 25–45%. It should be noted that the copper-catalyzed chloroaryaltion of glycol diacrylates, like thiocyanatoarylation, stops on the stage of monoadduct **I**–**IV** formation.




X = $(CH_2)_4$ (**I, II**), $(CH_2)_2O(CH_2)_2$ (**III, IV**); R = H (**I, III**), 4-$CH_3$ (**II, IV**).

The reaction occurs in aqueous acetone (1 : 2) at –10 to –5°C in the presence of catalytic amounts of copper(II) chloride. The optimal diazonium salt : unsaturated compound : catalyst ratio is 1.6 : 1 : 0.12. With double the optimal quantities of the diazonium salt and catalyst, no adducts by two multiple bonds are formed.

Compounds **I**–**IV** are viscous orange liquids tending to polymerize on storage. Their yields,

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**Table 1.** Yields, constants, and elemental analyses of 1-acryloyloxy-4-(2-chloro-3-arylpropyonyloxy)butanes **I** and **II** and 1-acryloyloxy-2-[2-(2-chloro-3-arylpropyonyloxy)ethoxy]ethanes **III** and **IV**

| Comp. no. | Yield, % | $n_D^{20}$ | $d_4^{20}$ | *MRD* | | Found, Cl, % | Formula | Calculated Cl, % |
|---|---|---|---|---|---|---|---|---|
| | | | | found | calculated | | | |
| **I** | 41 | 1.5153 | 1.1623 | 80.67 | 80.94 | 11.35 | $C_{16}H_{19}ClO_4$ | 11.41 |
| **II** | 45 | 1.5144 | 1.1429 | 85.61 | 85.77 | 10.80 | $C_{17}H_{21}ClO_4$ | 10.92 |
| **III** | 44 | 1.5085 | 1.1815 | 82.51 | 82.69 | 10.66 | $C_{16}H_{19}ClO_5$ | 10.85 |
| **IV** | 38 | 1.5197 | 1.1840 | 87.46 | 87.51 | 10.19 | $C_{17}H_{21}ClO_5$ | 10.40 |

**Table 2.** IR and $^1$H NMR spectral data for 1-acryloyloxy-4-(2-chloro-3-arylpropyonyloxy)butanes **I** and **II** and 1-acryloyloxy-2-[2-(2-chloro-3-arylpropyonyloxy)ethoxy]ethanes **III** and **IV**

| Comp. no. | IR spectrum, $\nu$, cm$^{-1}$ | | $^1$H NMR spectrum, $\delta$, ppm ($J$, Hz) |
|---|---|---|---|
| | $CH=CH_2$ | C=O | |
| **I** | 1636 | 1716 | 7.34–7.26 m (5H, Ph), 6.33 d.d (*cis*-H, $=CH_2$, $J_{HH}$ 11), 6.16 d.d (1H, =CH, $J_{HH}$ 10), 5.93 d.d (*trans*-H, $=CH_2$, $J_{HH}$ 14), 4.88 d.d (1H, CH, $J_{HH}$ 7), 4.12 t (4H, $2OCH_2$), 3.36 d.d ($J_{HH}$ 8), 3.12 d.d (2H, $CH_2Ph$, $J_{HH}$ 8), 1.68–1.48 m (4H, $CH_2CH_2$) |
| **II** | 1636 | 1724 | 7.26–7.06 m (4H, C6H4), 6.35 d.d (*cis*-H, $=CH_2$, $J_{HH}$ 11), 6.18 d.d (1H, =CH, $J_{HH}$ 10), 5.97 d.d (*trans*-H, $=CH_2$, $J_{HH}$ 14), 4.92 d.d (1H, CH, $J_{HH}$ 7), 4.10 t (4H, $2OCH_2$), 3.33 d.d ($J_{HH}$ 8), 3.13 d.d (2H, $CH_2C_6H_4$, $J_{HH}$ 8), 2.31 s (3H, $CH_3C_6H_4$), 1.69–1.46 m (4H, $CH_2CH_2$) |
| **III** | 1644 | 1720 | 7.30–7.20 m (5H, Ph), 6.30 d.d (*cis*-H, $=CH_2$, $J_{HH}$ 10), 6.14 d.d (1H, =CH, $J_{HH}$ 10), 5.93 d.d (*trans*-H, $=CH_2$, $J_{HH}$ 15), 4.92–4.86 m (1H, CH), 4.20 t (4H, $2OCH_2$), 3.48 d.d (4H, $CH_2OCH_2$, $J_{HH}$ 2), 3.33 d.d ($J_{HH}$ 7), 3.10 d.d (2H, $CH_2Ph$, $J_{HH}$ 7) |
| **IV** | 1640 | 1720 | 7.24–7.08 m (4H, $C_6H_4$), 6.32 d.d (*cis*-H, $=CH_2$, $J_{HH}$ 10), 6.16 d.d (1H, =CH, $J_{HH}$ 10), 5.92 d.d (*trans*-H, CH2, $J_{HH}$ 15), 4.94–4.87 m (1H, CH), 4.23 t (4H, $2OCH_2$), 3.46 d.d (4H, $CH_2OCH_2$, $J_{HH}$ 2), 3.33 d.d ($J_{HH}$ 7), 3.12 d.d (2H, $CH_2C_6H_4$, $J_{HH}$ 7), 2.31 s (3H, $CH_3C_6H_4$) |

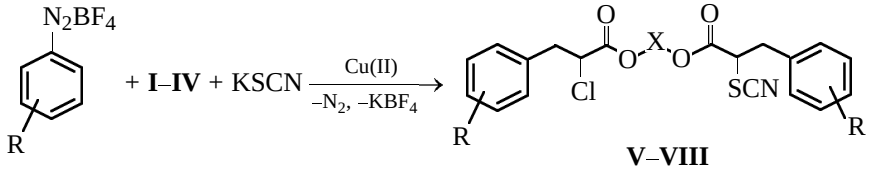
constants, elemental analyses, and $^1$H NMR and IR spectra are given in Tables 1 and 2. The samples of compounds **I**–**IV**, synthesized by schemes *1* and *2*, are identical to each other.

The structure of adducts **I**–**IV** is proved by their $^1$H and IR spectra. The IR spectra contain carbonyl absorption bands (1716–1724 cm$^{-1}$), as well as bands due to stretching (1636–1644 cm$^{-1}$) and deformation vibrations (808–812 and 980–984 cm$^{-1}$) of the multiple bond of the free acrylic fragment. The $^1$H NMR spectra contain aromatic proton signals at 7.34–7.06 ppm (multiplet). The methylene proton signals of the terminal vinyl group form a doublet of doublets at 6.35–6.30 (*cis*-H) and 5.97–5.92 ppm (*trans*-H) with coupling constants of 10 and 15 Hz, and the methane protons of the same group appear as a doublet of doublets at 6.18–6.14 ppm (coupling constant 10 Hz). The asymmetrical proton of the CH group attached to chlorine resonates at 4.94–4.86 ppm (multiplet).

Thus, the use as chloroarylating agents of arenediazonium chlorides does not alter the regioselectivity of the anionoarylation of glycol diacrylates, and the reaction does not go further monoadduct formation. The lower yields of arylalkyl chlorides compared with those of monothiocyanatoarylation products [1] are explained by a considerable difference in nucleophilicity between chloride and thiocyanate anions. In this connection we considered it important to react the monoadducts obtained with arenediazonium tetrafluoroborates in the presence of the thiocyanato group.

Monoadducts **I**–**IV** react with arenediazonium tetrafluoroborates in the presence of potassium thiocyanate to form diadducts: 1-(2-chloro-3-arylpropionyloxy)-4-(2-thiocyanato-3-arylpropionyloxy)butanes **V** and **VI** and 1-(2-chloro-3-arylpropionyloxy)-2-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]ethanes **VII** and **VIII**.

The reaction was accomplished in aqueous acetone




**V**–**VIII**

X = $(CH_2)_4$ (**V, VI**), $(CH_2)_2O(CH_2)_2$ (**VII, VIII**); R = H (**V, VII**), 4-$CH_3$ (**VI, VIII**).

(1 : 3) at 10–15°C in the presence of a catalyst, copper(II) tetrafluoroborate, with a 1,3-fold excess of the arenediazonium salt and potassium thiocyanate. The yields of diadducts **V**–**VIII** were 26–38%. The mixed chloro- and thiocyanatoarylation diadducts are white crystalline substances melting at 86–99°C (from methanol). The yields and constants of compounds **V**–**VIII** are listed in Tables 3 and 4.

The structure of diadducts **V**–**VIII** is proved by their $^1$H and IR spectra. The IR spectra contain absorption bands of the thiocyanato group at 2152–2156 $cm^{-1}$. The $^1$H NMR spectra contain aromatic proton signals at 7.35–7.01 ppm (multiplet). The asymmetric protons of the CH groups attached to the chlorine atom and the thiocyanato group form two triplets at 4.77–4.74 and 4.51–4.48 ppm, and the protons of the $CH_2$ groups attached to the aromatic fragments, multiplets at 3.38–3.27 and 3.16–3.06 ppm (Table 4).

Thus, the presence of two identical unsaturated reaction centers in the molecules of glycole diacrylates and their successive involvement into reaction allows synthesis of polyfunctional arylalkyl derivatives not only with different aromatic substituents, but also with different anions.

## EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument for thin films (adducts **I**–**IV**) or Nujol

**Table 3.** Yields, constants, and elemental analyses of 1-(2-chloro-3-arylpropionyloxy)- 4-(2-thiocyanato-3-arylpropionyloxy)butanes **V** and **VI** and 1-(2-chloro-3- arylpropionyloxy)-2-[2-(2-thiocyanato-3-arylpropionyloxy)ethoxy]ethanes **VII** and **VIII**

| Comp. no. | Yield, % | mp, °C[a] | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cl | N | S | | Cl | N | S |
| **V** | 38 | 99 | 7.71 | 3.00 | 7.05 | $C_{23}H_{24}ClNO_4S$ | 7.95 | 3.14 | 7.19 |
| **VI** | 30 | 88 | 7.39 | 2.91 | 6.59 | $C_{25}H_{28}ClNO_4S$ | 7.48 | 2.95 | 6.76 |
| **VII** | 39 | 93 | 7.51 | 2.95 | 6.82 | $C_{23}H_{24}ClNO_5S$ | 7.67 | 3.03 | 6.94 |
| **VIII** | 26 | 86 | 7.13 | 2.82 | 6.50 | $C_{25}H_{28}ClNO_5S$ | 7.24 | 2.86 | 6.54 |

[a] Recrystallized from methanol.

**Table 4.** IR and $^1$H NMR spectra of diadducts **V**–**VIII**

| Comp. no. | IR spectrum, ν(SCN), $cm^{-1}$ | $^1$H NMR spectrum, δ, ppm |
|---|---|---|
| **V** | 2156 | 7.35–7.22 m (10H, 2Ph), 4.74 t [1H, CH(Cl)], 4.50 t [1H, CH(SCN)], 4.12 t (4H, $2OCH_2$), 3.36–3.29 m, 3.15–3.06 m (4H, $2CH_2Ph$), 1.65–1.57 m (4H, $CH_2CH_2$) |
| **VI** | 2156 | 7.14–7.02 m (8H, $2C_6H_4$), 4.77 t [1H, CH(Cl)], 4.49 t [1H, CH(SCN)], 4.10 t (4H, $2OCH_2$), 3.35–3.27 m, 3.14–3.06 m (4H, $2CH_2C_6H_4$), 2.25 s (6H, $2CH_3C_6H_4$), 1.64–1.56 m (4H, $CH_2CH_2$) |
| **VII** | 2152 | 7.33–7.18 m (10H, 2Ph), 4.75 t [1H, CH(Cl)], 4.51 t [1H, CH(SCN)], 4.24 t (4H, $2OCH_2$), 3.52 d.d (4H, $CH_2OCH_2$), 3.38–3.28 m, 3.16–3.08 m (4H, $2CH_2Ph$) |
| **VIII** | 2152 | 7.16–7.01 m (8H, $2C_6H_4$), 4.76 t [1H, CH(Cl)], 4.48 t [1H, CH(SCN)], 4.23 t (4H, $2OCH_2$), 3.51 d.d (4H, $CH_2OCH_2$), 3.38–3.29 m, 3.16–3.07 m (4H, $2CH_2C_6H_4$), 2.26 s (6H, $2CH_3C_6H_4$) |

mulls (adducts **V**–**VII**). The $^1$H NMR spectra were obtained on a Varian VXR-300 instrument for DMSO-$d_6$ solutions (300 MHz), external reference HMDS. The purity of the synthesized compounds was established by TLC on Silufol UV-254 plates (eluent hexane–chloroform, 3 : 1).

**1-Acryloyloxy-4-(2-chloro-3-phenylpropionyloxy)butane (I).** *a*. To 0.05 mol of tetramethylene glycol diacrylate, 0.075 mol of sodium chloride, and 0.0076 mol of copper(II) tetrafluoroborate hexahydrate in 250 ml of aqueous acetone (1 : 2), benzenediazonium tetrafluoroborate, 0.075 mol, was added over the course of 1.5 h. Nitrogen evolution was observed at 10–15°C for 1.5 h. When nitrogen no longer evolved, the reaction mixture was treated with 200 ml of diethyl ether, and the extract was washed with water and dried with calcium chloride. The ether was removed by distillation, and the residue was subjected to column chromatography on $Al_2O_3$ (eluent hexane–chloroform, 3 : 1). The fractions collected were analyzed by IR spectroscopy and TLC. Yield 2.9 g (19%), oily orange substance.

*b*. To 0.05 mol of tetramethylene glycol diacrylate and 0.0061 mol of copper(II) chloride hexahydrate in 200 ml of aqueous acetone (1 : 2), a solution of 0.081 mol of benzenediazonium chloride was added over the course of 1 h. Nitrogen evolution was observed at –5 to –10°C for 2 h. When nitrogen no longer evolved, the reaction mixture was treated with 150 ml of diethyl ether, and the extract was washed with water and dried with calcium chloride. Compound **I** was isolated like in procedure *a*. Yield 6.4 g (41%).

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

**1-(2-Chloro-3-phenylpropionyloxy)-4-(3-phenyl-2-thiocyanatopropionyloxy)butane (V).** To 0.03 mol of 1-acryloyloxy-4-(2-chloro-3-phenylpropionyloxy)-butane (**I**), 0.003 mol if copper(II) tetrafluroborate hexahydrate, and 0.045 mol of potassium thiocyanate in 150 ml of aqueous acetone (1 : 3), 0.045 mol of benzenediazonium tetrafluroborate was added over the course of 1 h. Vigorous nitrogen evolution was observed at 10–15°C for 1 h. When nitrogen no longer evolved, the reaction mixture was treated with 100 ml of diethyl ether, and the extract was washed with water and dried with magnesium sulfate. The ether was removed by distillation, and the residue was subjected to column chromatography on $Al_2O_3$ (eluent hexane–chloroform, 3 : 1). Yield 5.7 g (38%), viscous oily substance crystallizing on standing. Recrystallization from methanol gave 3.7 g of compound **V**, mp 99°C.

Compounds **VI**–**VIII** were prepared in a similar way.

## ACKNOWLEDGMENTS

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