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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis of Some α-Fluoroacryl Esters

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Abstract—A possibility of producing α-fluoroacrylic esters by dehydrochlorination of the products of reaction of α-fluoro-β-chloropropanoic acid or respective acyl chloride with ethylene glycol, ethylene oxide, glycidol, epichlorohydrin and glycidyl methacrylate is examined.

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In the large class of α-substituted acrylates the α-fluoroacrylic acid derivatives are the less accessible and insufficiently studied compounds. The data concerning methods of synthesis and properties of the α-fluoroacrylates as well as of polymer materials based on these compounds can mostly be found in the patent sources [1]. It is known from these data that the fluoroacrylates are highly reactive compounds in polymerization [2], and the characteristics of the respective polymers makes the latter very valuable for practical application: high thermal stability, transparency, and stability against light with the resistance to aggressive media as well [3–11]. Therefore the synthesis and study of properties of α-fluoroacrylates is important both in theoretical and practical aspects.

In this communication we present the results of investigation of a series of α-fluoroacrylates based on α-fluoro-β-chloropropanoic acid [12, 13] and some of its derivatives. Formulas, physico-chemical constants, analytical data and yields of the obtained compounds are listed in Tables 1 and 2. Structures of the synthesized substances are confirmed by the data of elemental analysis, IR and ^{19}F NMR spectra.

The ethylene glycol mono- and di-α-fluoroacrylates (**IX**) and (**X**) are prepared [3] by esterification of glycol with α-fluoro-β-chloropropanoic acid followed by separate dehydrochlorination of the ethylene glycol mono- and di-α-fluoro-β-chloropropanoates (I) and (**II**) by the reaction with triethylamine along the Scheme 1.

The first step (eq. 1) proceeds readily in boiling benzene in the presence of *p*-toluenesulfonic acid as a catalyst. With 1.5-fold excess of glycol in the reaction mixture the yield of compound **I** equals 50%, at the 3-fold excess 65%, therewith the yield of **II** is 25% and 15%, respectively. At the 2-fold excess of α-fluoro-β-chloropropanoic acid is formed predominantly compound II in the yield up to 75% of the theoretical one.

The second and the third steps (equations 2 and 3) were carried out separately, also in benzene medium, in the presence of the polymerization inhibitirs, copper(I) chloride and hydroquinone. In the IR spectra of the

Scheme 1.

$$HO(CH_2)_2OH + HO{-}R_1 \quad (\text{FCPA})$$
$$\xrightarrow[C_6H_6,\,-H_2O]{80^\circ C} HO(CH_2)_2{-}O{-}R_1 \quad (\mathbf{I})$$
$$+ R_1{-}O{-}(CH_2)_2{-}O{-}R_1, \quad (\mathbf{II}) \qquad (1)$$

$$HO(CH_2)_2{-}O{-}R_1 \xrightarrow[-HCl]{Et_3N} HO(CH_2)_2{-}O{-}R_2, \quad (\mathbf{IX}) \qquad (2)$$

$$R_1{-}O{-}(CH_2)_2{-}O{-}R_1$$
$$\xrightarrow[-2HCl]{2Et_3N} R_2{-}O{-}(CH_2)_2{-}O{-}R_2, \quad (\mathbf{X}) \qquad (3)$$

R_1 = –C(O)CHF–CH_2Cl, R_2 –C(O)CF=CH_2.

Table 1. Physico-chemical characteristics of esters of α-fluoro-β-chloropropanoic acid R–O–C(O)–CHF–CH_2Cl

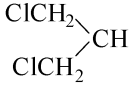
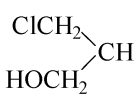
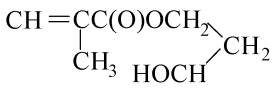
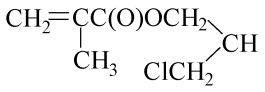
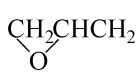
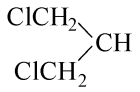
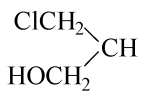
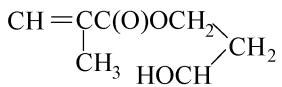
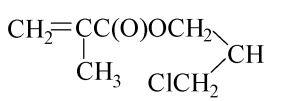
Compd.	R	bp, °C / *P*, mm Hg	n_D^{20}	d_4^{20}, g cm^{-3}	Formula	Elemental analysis, %						Yield, %
						C		H		Cl		
						Found	Calcd.	Found	Calcd.	Found	Calcd.	
I	$HOCH_2CH_2$	90–92 / 0.005	1.4579	1.4170	C_5H_8ClFO	35.83; 35.38	35.23	4.84; 4.82	4.73	20.91; 20.74	20.79	65
II	$ClCH_2CHFC(O)OCH_2CH_2$	mp / 64–66	–	–	$C_8H_{10}Cl_2F_2O_4$	34.28; 34.44	34.34	3.61; 3.43	3.62	25.55; 25.42	25.42	75
III		65–67 / 0.002	1.4512	1.3553	$C_6H_8ClFO_3$	39.36; 39.23	39.41	4.18; 4.31	4.42	19.50; 19.40	19.41	74
IV	$ClCH_2CH_2$	123–125 / 10	1.4519	1.3935	$C_5H_7Cl_2FO_2$	32.26; 32.53	31.76	4.20; 3.92	3.73	38.24; 38.28	37.51	75
V		mp / 34–36	–	–	$C_6H_8Cl_3FO_2$	30.95; 30.65	30.34	3.42; 3.72	3.40	45.20; 45.30	44.79	70
VI		101–102 / 0.005	1.4708	1.43139	$C_6H_9Cl_2FO_3$	32.32; 32.62	32.80	4.25; 4.30	4.15	32.55; 32.49	32.38	45
VII		103–105 / 0.02	1.4680	1.2887	$C_{10}H_{14}ClFO_5$	45.43; 45.11	44.69	5.43; 5.69	5.27	12.85; 12.91	13.19	52
VIII		108–110 / 0.002	1.4698	1.3045	$C_{10}H_{13}Cl_2FO_4$	42.68; 42.97	41.82	4.29; 4.43	4.57	25.10; 25.15	24.69	71

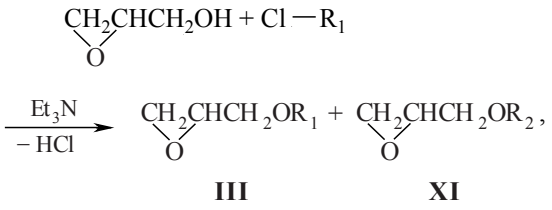
Table 2. Physico-chemical characteristics of esters of α-fluoroacrylic acid R–O–C(O)–CF=CH_2

Compd.	R	bp, °C / *P*, mm Hg	n_D^{20}	d_4^{20}, g cm^{-3}	Formula	Elemental analysis, %						Yield, %
						C		H		Cl		
						Found	Calcd.	Found	Calcd.	Found	Calcd.	
IX	$HOCH_2CH_2$	90–91 / 10	1.43419	1.2312	C_5H_7FO3	44.38; 44.46	44.78	5.31; 5.30	5.72	–	–	55
X	$CH_2=CFC(O)OCH_2CH_2$	50–52 / 0.01	1.4345	1.2784	$C_8H_8F_2O_4$	46.41; 46.16	46.62	4.26; 4.24	3.92	–	–	80
XI		74–76 / 10	1.4348	1.2122	$C_6H_7FO_3$	50.29; 50.05	49.31	5.20; 5.45	4.84	–	–	65
XII	$ClCH_2CH_2$	58–59 / 10	1.4350	1.2573	$C_5H_6ClFO_2$	39.77; 40.06	39.35	4.45; 4.66	3.97	24.01; 23.79	23.24	80
XIII		90–92 / 10	1.4626	1.3426	$C_6H_7Cl_2FO_2$	35.92; 35.65	35.85	3.45; 3.57	3.51	34.90; 35.10	35.28	87
XIV		59–60 / 0.015	1.4640	1.3222	$C_6H_8ClFO_3$	41.06; 50.77	39.48	5.19; 5.21	4.41	20.05; 20.07	19.93	79
XV		59–60 / 0.015	1.4610	1.2035	$C_{10}H_{13}FO_5$	51.46; 12.91	51.69	5.66; 6.09	5.65	–	–	80
XVI		68–70 / 0.002	1.4608	1.2352	$C_{10}H_{12}ClFO_4$	47.08; 46.79	47.90	5.08; 5.04	4.83	15.46; 15.75	14.95	85

products of dehydrochlorination **IX** and **X** appear the absorption bands in the region of 1657 and 3140 cm^{-1} that are asegned to the vibrations $\nu_{C=C}$, and of α-fluoroacryloyl fragment of the molecules.

From the ^{19}F NMR spectra follows that chemical shifts of fluorine nuclei in the parent α-fluoro-β-chloropropanoic acid (121.93 ppm) and in the products of its esterification **I** and **II** (121.94 and 121.79 ppm respectively) are practically the same, that is, the structural changes distant from the F atoms do not affect their chemical shifts. Therefore the fluorine chemical shifts of compounds **IX** and **X** are practically the same. In contrast, in going from fluorochloropropanoates **I** and **II** to α-fluoroacrylates **IX** and **X** chemical shifts of the fluorine nuclei differ: they suffer a downfield shift (to 40.59 and 41.29 ppm respectively) that reflect difference in shielding of fluorine nuclei in the compared compounds. Compounds **I**, **IX** and **X** are colorless liquids, **II** is crystalline substance. They all are well soluble in ether, benzene, acetone and other organic solvents.

The rest esters (Tables 1, 2) are prepared by the reaction of α-fluoro-β-chloropropanoic acid and (or) respective acyl chloride with some epoxy compounds followed by dehydrochlorination of the formed derivatives. Therewith the reactions with glycidol were occurred at the hydroxy group in the presence of HCl acceptor, and at the three-membered ring in the presence of catalyst $TiCl_4$. Thus in the reaction of α-fluoro-β-chloropropanoyl chloride with glycidol in equimolar amounts at the hydroxy group in ether solution in the presence of triethylamine two products are obtained:

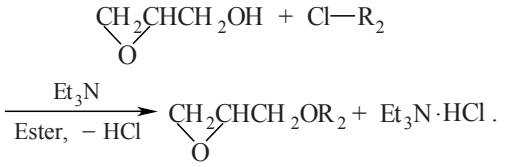


III **XI**

where R_1 is $-C(O)CHFCH_2Cl$, R_2 is $-C(O)CF=CH_2$.

Alongside the main product glycidyl α-fluoro-β-chloropropanoate (**III**) whose yield after triple distillation achieves 70% is formed also glycidyl α-fluoroacrylate (**XI**) whose formation can be explained by partial dehydrochlorination of **III** at the action of the triethylamine in the reaction medium. The possibility of this reaction we showed by the independent synthesis where by reaction of **III** with triethylamine was prepared glycidyl α-fluoroacrylate (**XI**) in high yield. Also The formation of compound **XI** may proceed by a thermal dehydrochlorination of **III** in the course of distillation as has been observed for the case of the phospholeneglycol α-fluoro-β-chloropropanoate [14].

The glycidyl α-fluoroacrylate (**XI**) was also prepared by another scheme [15], in the reaction of glycidol with α-fluoroacryloyl chloride [16] in ether in the presence of triethylamine:



XI

The reacton with glycidol at the three-membered ring and related reactions with other epoxy compounds are shown in Scheme 2.

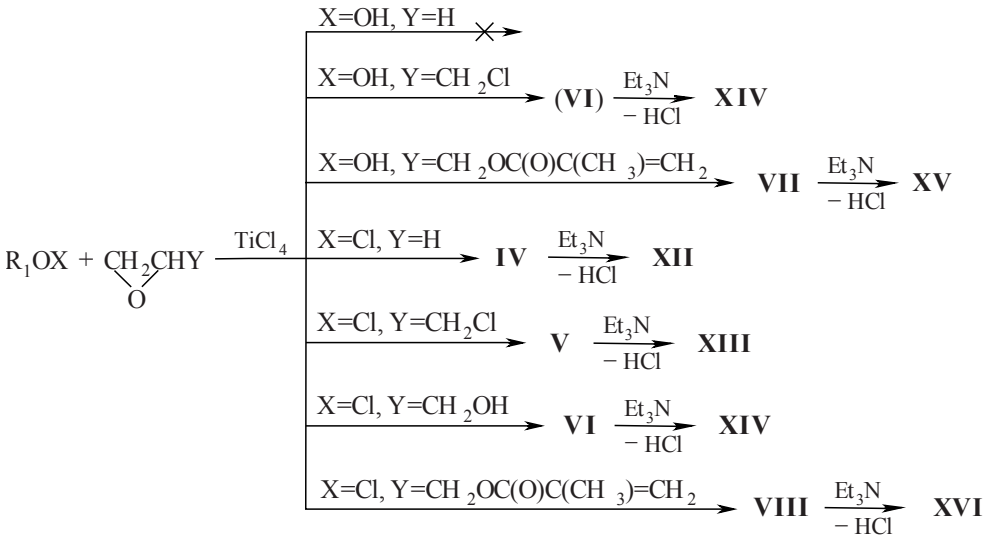
As shown in the scheme, ethylene oxide does not react with α-fluoro-β-chloropropanoic acid in the presence of the catalyst $TiCl_4$, but readily reacts with the respective acyl chloride even at 5–10°C affording ester **IV**, that after dehydrochlorination under the action of triethylamine in boiling benzene is converted into ester **XII**.

Epychlorohydrin, glycidol [17] and glycidyl methacrylate [18] react without a solvent in the presence of $TiCl_4$ at 50–80°C with α-fluoro-β-chloropropanoic acid and at 5–10°C with the respective acyl chloride affording esters of α-fluoro-β-chloropropanoic acid. In the reaction of α-fluoro-β-chloropropanoic acid with epichlorohydrine the same ester **VI** is formed that is produced by the pair glycidol – acyl chloride. In all the cases after dehydrochlorination respective α-fluoroacrylates were formed.

For the reactions with epichlorohydrin, glycidol and glycidyl methacrylate it is important to consider the order of the oxide ring cleavage by α-fluoro-β-chloropropanoic acid and the respective acyl chloride. By analogy with the reactions of epichlorohydrine with some phosphorus halides [19] one can expect the addition of the acid group at the β-carbon atom, that is, formation of compound with iso structure of the propyl fragment.

The α-fluoroacrylates obtained can be polymerized in bulk or in a solution at heating under inert atmosphere in the presence of the initiators of radical polymerization [20]. The polymerization leads, depending on the structure of the initial monomers, to the transparent

Scheme 2.



soft resinous or solid glassy polymer materials with glass transition temperature from –10 to 95°C and decomposition temperature from 230 to 400°C (according to thermomechanical curves). The polymers obtained are insoluble in organic solvents but swell in a different degree in dimethylformamide, dioxane, tetrahydrofuran and benzene. They are flammable in the flame of gas jet but self-extinguish upon removal of the flame. An exclusion is glycidyl α-fluoroacrylate polymer which is not self-extinguishing.

EXPERIMENTAL

α-Fluoro-β-chloropropanoic acid of "technical" grade was purified along the procedure described in [12], α-fluoro-β-chloropropanoyl and α-fluoroacryloyl chlorides were prepared and purified according to [16], commercial ethylene oxide, epichlorohydrin, glycidol, glycidyl methacrylate, triethylamine and benzene were used freshly disttilled.

The ^{19}F NMR spectra were recorded on a Teesla BS-487 instrument at the operating frequency 80 MHz, at room temperature, with external reference trifluoroacetic acid and internal reference fluorobenzene.

The IR spectra were taken on a UR-10 spectrometer in the region from 400 to 3800 cm^{-1} from liquid films, the crystalline products from suspensions in mineral oil.

Ethlene glycol mono-α-fluoroacrylate (IX). a. A mixture of 100 g (0.8 mol) of α-fluoro-β-chloropropanoic acid, 150 g (2.2 mol) of ethylene glycol and 500 ml of anhydrous benzene was refluxed for 12 h in the presence of 2 g of *p*-toluensulfonic acid in a flask equipped with a Dean–Stark trap and reflux condenser. After completing the reaction (collecting the maximal amount of warer) the solvent was distilled off, and the residue was fractionated in a vacuum. 86 g (65%) of ethylene glycol mono-α-fluoro-β-chloropropanoate (**I**) was isolated as a viscous colorless liquid; its physico-chemical characteristics are listed in Table 1.

b. To a solution of 47.5 g (0.28 mol) ethylene glycol mono-α-fluoro-β-chloropropanoate in 250 ml of anhydrous benzene at room temperature while stirring was added dropwise 28 g (0.28 mol) of triethylamine and the mixture was refluxed for 5 h in the presence of 0.1 g of copper(I) chloride as the polymerization inhibitor. The triethylamine hydrochloride perecipitate formed was filtered off and from the filtrate the solvent was distilled off and the residue was twice distilled in a vacuum in the presence of 0.1 g of copper(I) chloride as the polymerization inhibitor. 20.2 g (55%) of compound **IX** was obtained, colorless labile liquid, its physio-chemical characteristics are listed in Table 2.

Ethylene glycol di-α-fluoroacrylate (X). a. Ethylene glycol di-α-fluoro-β-chloropropanoate (**II**) was prepared like above from 25.3 g (0.2 mol) of α-fluoro-β-chloropropanoic acid and 6.2 g (0.1 mol) of ethylene glycol in 200 ml of anhydrous benzene in the presence of 1 g of *p*-toluensulfonic acid. After fractionation in a vacuum (bp128–130°C at 0.005 mm Hg) and double crystallization from chloroform we isolated 21 g (75%) of

compound II, of white color, mp 64–66°C. Chracteristics are listed in Table 1.

b. 12 g (0.043 mol) of the prepared ethylene glycol di-α-fluoro-β-chloropropanoate (**II**) and 8.7 g (0.086 mol) of triethylamine in 150 ml of anhydrous benzene were refluxed for 4 h in the presence of 0.05 g of copper(I) chloride. After fractionation in a vacuum we obtained 7 g (80%) of compound **X** as a labile colorless liquid (Table 2).

β,β′-Dichloroisopropyl α-fluoroacrylate (XIII). a. To a four-neck flask equiooed with mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer was loaded 14.5 g (0.1 mol) of α-fluoro-β-chloropropanoyl chloride and 0.01 g of caralyst $TiCl_4$. At the temperature 45–55°C while stirring was added dropwise 9.25 g (0.1 mol) of epichlorohydrin and the reaction mixture was heated for 1.5–2 h at 95–100°C. After cooling the reaction mixture and crystallization from ether – cyclohexane mixture we obtained 16.5 g (70%) of a powder-like substance **V**, mp 34–36°C.

b. In a flask as described above to a solution of 4.75 g (0.02 mol) of compound **V** in 50 ml of anhydrous benzene was added initially 0.01 g of copper(I) chloride and then a solution of 2.1 g (0.02 mol) of triethylamine in 10 ml of anhydrous benzene. The reaction mixture was heated for 1.5–2 h at slow boiling. The triethylamine hydrochloride precipitate dropped was filtered off and the solvent was removed in a vacuum. From the residue by fractionation in a vacuum was isolated 3.5 g (87%) of compound **XIII** as a colorless labile liquid.

β-Chloro-β′-hydroxyisopropyl α-fluoroacrylate (XIV) was obtained from epichlorohydrine by analogy with the above procedure. a. From 37.8 g (0.3 mol) of α-fluoro-β-chloropropanoic acid heated to melting (55–60°C), and 27.75 g (0.3 mol) of epichlorohydrine was obtained after fractionation in a vacuum 42 g (64%) of β-chloro-β′-hydroxyisopropyl α-fluoro-β-chloropropanoate (**VI**).

b. From 6.87 g (0.03 mol) of compound VI dissolved in 80 ml of anhydrous benzene, and 3.5 g (0.35 mol) of triethylamine dissolved in 20 ml of anhydrous benzene was obtained 4.3 g (79%) of β-chloro-β'-hydroxyisopropyl α-fluoroacrylate (**XIV**) as a colorless labile liquid.

β-Chloro-β′-hydroxyisopropyl α-fluoroacrylate (XIV) from glycidol. a. From 14.5 g (0.1 mol) of α-fluoro-β-chloropropanoyl chloride and 7.5 g (0.1 mol) of glycidol after fractionation in a vacuum we obtained 15.5 g (70%) of β-chloro-β′-hydroxyisopropyl α-fluoro-β-chloropropanoate (**VI**) as a viscous colorless liquid.

b. From compound (**VI**) by the reaction with triethylamine like above was obtained β-chloro-β′-hydroxyisopropyl α-fluoroacrylate (**XIV**).

β-Chloroethyl α-fluoroacrylate (XII). a. To a four-neck flask equipped with mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer was loaded a solution of 16.5 g (0.14 mol) of α-fluoro-β-chloropropanoyl chloride in 50 ml of anhydrous ether. While stirring at the temperature 6–8°C to the solution was added dropwise a solution of 5.5 g (0.14 mol) of ethylene oxide in 40 ml of anhydrous ether and 3–4 drops of concentrated H_2SO_4. Stirring was continued for 3 h with stepwise temperature elevating to 10–12°C. Then the mixture was kept for 20 days in a thick-walled glass bottle at room temperature and then it was evaporated in a vacuum. From the residue by fractionation we obtained 15 g (75%) of β-chloroethyl α-fluoro-β-chloropropanoate (**IV**) as a colorless viscous liquid.

b. Likewise preceding, from 14.5 g (0.077 mol) of β-chloroethyl α-fluoro-β-chloropropanate and 7.8 g (0.077 mol) of triethylamine in 100 ml of anhydrous benzene after double distillation in a vacuum we obtained 7.6 g (65%) of β-chloroethyl α-fluoroacrylate (**XII**) as a colorless labile liquid.

Glycidyl α-fluoro-β-chloropropanoate (**III**) was synthesized by mixing of a solution of 7.4 g (0.1 mol) of glycidol and 10.1 g (0.1 mol) of triethylamine in 75 ml of anhydrous ether with a solution of 14.5 g (0.1 mol) of α-fluoro-β-chloropropanoyl chloride in 40 ml of anhydrous ether at the temperature about –10°C. After stirring and filtering off the precipitate, evaporation of the filtrate and double fractionation of the residue in a vacuum we obtained two fractions: 1 g (ca. 5%) of compound as a labile colorless liquid, bp 36–38°C (0.002 mm Hg) and 13.46 g (74%) of compound XI as a viscous colorless liquid, bp 65–67°C (0.002 mm Hg).

Glycidyl α-fluoroacrylate (XI). To a solution of 7.4 g (0.1 mol) of glycidol in 75 ml of anhydrous ether cooled between –5 and –10°C was added dropwise at stirring initially 10.2 g (ca. 0.1 mol) of anhydrous triethylamine and then a solution of 10.8 g (0.1 mol) of α-fluoroacryloyl chloride in 25 ml of anhydrous ether. The reaction mixture was stirred for 2 h at room temperature. The precipitate formed was filtered off, and the filtrate was evaporated in a vacuum. From the residue by double fractionation in a vacuum in the presence of copper(I) chloride we obtained 9.5 g (65%) of compound **XI** as a colorless labile liquid.

β-Hydroxy-β′-methacryloyloxyisopropyl α-fluoroacrylate (XV). a. From 23.5 g (0.185 mol) of α-fluoro-β-chloropropanoic acid and 26.5 g (0.185 mol) of glycidyl methacrylate by stirring at 60–80°C for 3 h in the presence of 0.01 of $TiCl_4$ and 0.1 g of copper(I) chloride followed by heating for 3 h at 100°C, after fractionation in a vacuum we obtained 22 g (52%) of β-hydroxy-β′-methacrylyloxyisopropyl α-fluoro-β-chloropropanoate (**VII**) as a viscous colorless liquid, soluble in benzene, acetone, dichloroethane, and other organic solvents.

b. From 21.5 g (0.08 mol) of compound **VIII** and 8.01 g (0.08 mol) of triethylamine in 150 ml of anhydrous benzene we obtained after double vacuum distillation 14.65 g (80%) of β-hydroxy-β′-methacryloyloxyisopropyl α-fluoroacrylate **XV** as a colorless labile liquid.

β-Chloro-β′-methacryloyloxyisopropyl α-fluoroacrylate (XVI). a. From 10.5 g (0.0725 mol) of α-fluoro-β-chloropropanoyl chloride and 10.3 g (0.0725 mol) of glycidyl methacrylate in the presence of 0.005 g of $TiCl_4$ and 0.1 g of copper(I) chloride by stirring at 30–50°C followed by heating for 2 h at 100°C, after fractionation we obtained 10.8 g (71%) of β-chloro-β′-methacryloyloxyisopropyl α-fluoro-β-chloropropanoate (**VIII**) as a viscous colorless liquid, soluble in benzene, tetrahydrofuran and other organic solvents.

b. From 10.7 g (0.037 mol) of β-chloro-β′-methacryloyloxyisopropyl α-fluoro-β-chloropropanoate (**VIII**) and 3.8 g (0.35 mol) of triethylamine in 75 ml of anhydrous benzene we obtained after double vacuum distillation 6.7 g (71%) of colorless labile liquid, β-chloro-β′-methacyloyloxyisopropyl α-fluoroacrylate (**XVI**).

CONCLUSIONS

1. At the esterification of ethylene glycol with α-fluoro-β-chloropropanoic acid are formed both mono- and di-α-fluoro-β-chloropropanoates that by the reaction with triethylamine are readily transformed to the respective α-fluoroacrylates.

2. α-Fluoro-β-chloropropanoic acid and related acyl chloride in the presence of Lewis acid react readily with epoxy compounds to form the products of epoxide ring cleavage that after dehydrochlorination with triethylamine are converted into corresponding α-fluoroacrylates.

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