Photochemical Bromination of 2-Fluoroacrolein: Synthesis of Phenyl 2-Fluoroacrylate

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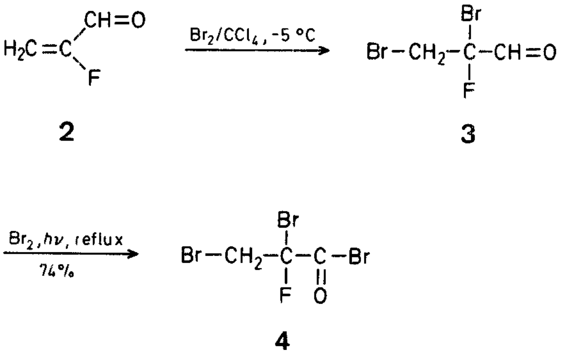
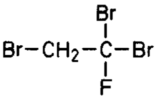
Phenyl 2-fluoroacrylate (**1**) is prepared by debromination of the dibromo compound 7, obtained in turn by the photobromination of 2-fluoroacrolein (**2**) followed by treatment with phenol.

Polymers of phenyl 2-fluoroacrylate (**1**) have a higher glass temperature than that observed for polymethacrylates and have been useful in the manufacture of windscreens and windows of high speed aircraft[1]. The reported[1] synthesis of the 2-fluoroacrylate (**1**) utilizes a poisonous fluoroacetate as starting material[2]. Moreover, the methods used for the preparation of 2-fluoroacrylic acid were generally expensive or involved use of toxic compounds[3-6].

We report here a new procedure for the synthesis of **1** based on the oxidative bromination of 2-fluoroacrolein (**2**). The preparation of **2** on a large scale has been reported[7] by us. Addition of bromine to 2-fluoroacrolein (**2**) gives 2,3-dibromo-2-fluoropropanal (**3**) which is brominated photochemically to give the acid bromide **4**.

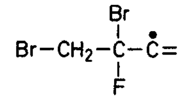


$$\underset{\mathbf{2}}{H_2C=C(F)-CH=O} \xrightarrow{Br_2/CCl_4,\ -5\ °C} \underset{\mathbf{3}}{Br-CH_2-CBr(F)-CH=O} \xrightarrow[74\%]{Br_2,\ h\nu,\ reflux} \underset{\mathbf{4}}{Br-CH_2-CBr(F)-C(=O)-Br}$$



$Br-CH_2-CBr(F)-Br$

5

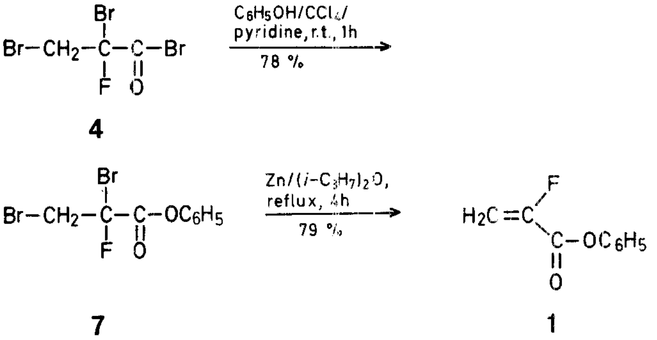


$Br-CH_2-CBr(F)-\dot{C}=O$

6

The photochemical bromination has been performed in refluxing carbon tetrachloride. Bromine concentration must be high in the reaction mixture in order to avoid formation of the side product **5**. The formation of **5** can be explained if the acyl radical **6** is an intermediate. Decarbonylation of **6** gives a trihaloradical, which is further brominated to **5**. By adding bromine before U.V. irradiation, no more side product is observed and the acid bromide **4** is obtained in 74% yield.

Numerous 2-fluoroacrylates can be obtained by reacting acid bromide **4** with appropriate alcohols and further debrominating the esters formed by zinc. With phenol as the alcohol, phenyl 2-fluoroacrylate (**1**) is obtained in 62% yield by debromination of the ester **7**. Phenyl 2-fluoroacrylate (**1**), obtained by our safe procedure, is purified easily and can be polymerised[8,9].



^{1}H-N.M.R. spectra (60 MHz, TMS) and ^{19}F-N.M.R. spectra (56.4 MHz, $CFCl_3$) were recorded on a Varian EM 360L spectrometer. ^{1}H-N.M.R. spectrum (90 MHz) was obtained on a Bruker WH 90DS spectrometer. I.R. spectra were measured on a Perkin-Elmer 167 instrument.

2,3-Dibromo-2-fluoropropanoyl Bromide (4):

Bromine (80 g, 0.5 mol) is added dropwise to a solution of 2-fluoroacrolein (**2**; 37 g, 0.5 mol) in carbon tetrachloride (37 ml) at $-5\,^\circ$C. At the end of the addition, a further amount of bromine (80 g, 0.5 mol) is quickly added to the mixture. The mixture is refluxed and irradiated with a mercury lamp (125 watt). The end of the reaction is controlled by ^{19}F-N.M.R. (no more signal for the aldehyde **3**). The solvent is evaporated under vacuum (20 torr) and the residue distilled to give 2,3-dibromo-2-fluoropropanoyl bromide (**4**); yield: 116 g (74%); b.p. 54 °C/6 torr.

I.R. ($CHCl_3$): $\nu = 1810, 1765\,cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4.0-4.7$ ppm (4 lines, AB part of ABX system).

^{19}F-N.M.R. ($CDCl_3$): $\delta = -110$ ppm (4 lines, $^3J_{FH} = 13$ Hz, 22.6 Hz).

2,3-Dibromo-2-fluoropropanal (3):

After the first addition of bromine (1 equivalent), the intermediate 2,3-dibromo-2-fluoropropanal (**3**) can be isolated, if needed. For this purpose the solvent is evaporated under vacuum (20 torr), and the residue is distilled to give 2,3-dibromo-2-fluoropropanal (**3**); yield: 60.8 g (52%); b.p. 56–57 °C/19 torr.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4.0-4.5$ (4 lines, 2H, AB part of ABX system); 9.3 ppm (d, 1 H, $^3J_{HF} = 2$ Hz).

^{19}F-N.M.R. ($CDCl_3$): $\delta = -128$ ppm (3 lines).

Phenyl 2,3-Dibromo-2-fluoropropanoate (7):

Crude 2,3-dibromo-2-fluoropropanoyl bromide [**7**; from 2-fluoroacrolein (**2**; 0.75 mol)] is slowly added to a solution of phenol (70.5 g, 0.75 mol) and pyridine (59.2 g, 0.75 mol) in carbon tetrachloride (750 ml), at 20 °C. After stirring for 1 h, water (200 ml) is added until dissolution of the salt. After decantation, the organic layer is washed with brine (2 x 100 ml), and dried with sodium sulfate. The solvent is evaporated under vacuum (20 torr) and the residue is distilled to give phenyl 2,3-dibromo-2-fluoropropanoate (**7**); yield: 191 g (78%, based on **2**); b.p. 105 °C/0.5 torr.

$C_9H_7Br_2FO_2$	calc.	C 33.16	H 2.16
(326.0)	found	32.97	2.29

I.R. ($CHCl_3$): $\nu = 1885, 1590\,cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4-4.75$ (m, 2 H, AB part of ABX system); 6.7–7.6 ppm (m, 5 H).

^{19}F-N.M.R. ($CDCl_3$): $\delta = -121$ ppm (4 lines, $^3J_{HF} = 23.5$ Hz, 12 Hz).

Phenyl 2-Fluoroacrylate (1):

A mixture of phenyl 2,3-dibromo-2-fluoropropanoate (**7**; 110 g, 0.337 mol) and zinc (65 g, 1 mol) in dry diisopropyl ether (350 ml) is refluxed under argon for at least 4 h. The end of the reaction is controlled by ^{19}F-N.M.R. (no more signal for the propanoate). After cooling the mixture is filtered, the solvent evaporated under vacuum (20 torr) and the residue quickly distilled (the receiver containing hydroquinone) to give phenyl 2-fluoroacrylate (**1**); yield: 44 g (79%); b.p. 52–54 °C/0.5 torr.

Phenyl 2-fluoroacrylate (**1**) can be stored for several months at $-30\,^\circ$C over hydroquinone without decomposition.

$C_9H_7FO_2$	calc.	C 65.06	H 4.25
(166.2)	found	65.37	4.18

I.R. ($CHCl_3$): $\nu = 1755, 1652, 1590\,cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3$, 90 MHz): $\delta = 5.55$ (dd, 1 H, $^3J_{FH} = 13$ Hz, $^2J_{HH} = 3.3$ Hz); 6.05 (dd, 1 H, $^3J_{FH} = 42$ Hz, $^2J_{HH} = 3.3$ Hz); 7.1–7.75 ppm (m, 5 H).

^{19}F-N.M.R. ($CDCl_3$): $\delta = -117$ ppm (dd, $^3J_{FH} = 13$ Hz, 42 Hz).

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