Russian Journal of Organic Chemistry, Vol. 38, No. 8, 2002, pp. 1228–1229. From Zhurnal Organicheskoi Khimii, Vol. 38, No. 8, 2002, pp. 1279–1280.

SHORT COMMUNICATIONS

Fluorine-containing Monomers for Polycondensation

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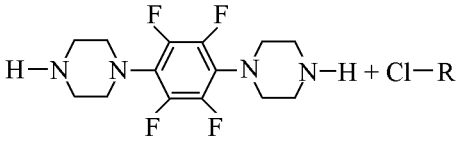
Received November 23, 2001

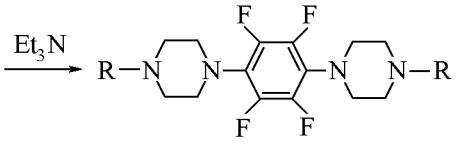
Fluorine-containing polymers command the attention thanks to a number of unique physicochemical and biologomedicinal properties. Monomers based on 1,4-diaryl-substituted tetrafluorobenzene are known [1–6].

Here we report on preparation of previously unknown derivatives of 1,4-bis(piperazin-1-yl)-2,3,5,6-tetrafluorobenzene.*

The synthesis of monomers was performed by reaction of base **I** with ethylene chlorohydrin or with esters of halocarboxylic acids at heating in organic solvents or without solvent.



I



II–VIII

R = CH_2CH_2OH (**II**), $CH_2C_6H_4COOH$-*p* (**III**), $CHd2C_6H_4COOCH_3$-*p* (**IV**), CH_2COOH (**V**), $CH_2COOC_2H_5$ (**VI**), $(CH_2)_3COOH$ (**VII**), $(CH_2)_3COOC_2H_5$ (**VIII**).

By alkaline hydrolysis of compounds **IV, VI, VIII** followed by acidification we isolated acids **III, V, VII.**

1,4-Bis[4-(2-hydroxyethyl)piperazin-1-yl]-2,3,5,6-tetrafluorobenzene (II). A mixture of 1.06 g of base **I**, 0.6 g of ethylene chlorohydrin, and 0.8 g of triethylamine was heated under reflux, then the heating was stopped for 10 min, 0.6 g of ethylene chlorohydrin was again added, and the mixture was heated to 120°C for 10 min. On cooling the reaction mixture it was diluted with water, the separated precipitate was filtered off, dried, and crystallized.

Similarly, but in ethanol (compounds **IV** and **VI**) or DMSO (compound **VIII**) solution were prepared the other compounds (see the table on p. 1229).

^{1}H NMR spectra were registered on spectrometer Varian VXR-300. TLC was performed on Silufol plates.

* Authors are grateful to P.N. Logvinenko (Joint-Stock Co. "NARKOR") for the sample of compound **I**.

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Yields, constants, ^{1}H NMR spectra, and elemental analysis data of compounds **II**–**VIII**

Compd. no.	Yield, %	mp, °C solvent for crystallization	TLC, R_f eluent	Found, %			Formula	Calcd.			^{1}H NMR spectra, δ, ppm in DMSO-d_6		
				C	H	N		C	H	N	CH_2 in piperasine	$(CH_2)_n$	others
II[a]	60	208–210 (ethanol)	0.3 (methanol)	52.93, 53.34	6.30, 6.70	13.50, 13.87	$C_{18}H_{26}F_4N_4O_2$	53.20	6.40	13.79	2.52, 3.11 (4)	2.44 t (2), 3.52 t (2)	4.29 s (1) (OH)
III	85	>300, decomp.	0.55 (methanol)	61.25, 61.56	5.23, 5.37	9.26, 9.60	$C_{30}H_{30}F_4N_4O_4$	61.43	5.12	9.53	2.5 s, 3.13 (4)	3.60 s (2)	7.44 e (2), 7.91 e (2), (C_6H_4)
IV	98	206–3208 (hexane)	0.65 (EtAc)	62.35, 62.48	5.32, 5.78	9.17, 9.42	$C_{32}H_{34}F_4N_4O_4$	62.54	5.54	9.12			
V	52	260–270, decomp.	0.2 (methanol)	49.83, 50.21	5.13, 5.49	12.62, 12.95	$C_{18}H_{22}F_4N_4O_4$	49.77	5.07	12.90	2.67 s (4), 3.15 s (4)	3.15 s (2)	6.4 br (COOH)
VI	78	110–112 (aqueous hexane)	0.9 (toluene)	53.80, 53.96	6.23, 6.40	11.28, 11.48	$C_{22}H_{30}F_4N_4O_4$	53.88	6.12	11.43			
VII	70	220 (hexane)	0.25 (methanol)	54.25, 54.74	6.19, 6.47	11.02, 11.38	$C_{22}H_{30}F_4N_4O_4$	53.88	6.12	11.43	2.64 s (4), 3.19 s (4)	1.74 t (2), 2.27 t (2), 2.51	4.2 br (COOH)
VIII	90	92–94 (heptane)	0.6 (toluene, EtAc, 2 : 1)	56.91, 57.20	7.07, 7.13	10.46, 10.53	$C_{20}H_{38}F_4N_4O_4$	57.14	6.96	10.26			

[a] ^{19}F NMR spectrum (CCl_3F), δ, ppm: –151.0 s.