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LETTERS TO THE EDITOR

REACTIONS OF VINYL EPOXYETHERS WITH POLYFLUOROALKANOLS: A SIMPLE ROUTE TO FLUORINE-CONTAINING CYCLIC POLYETHERS

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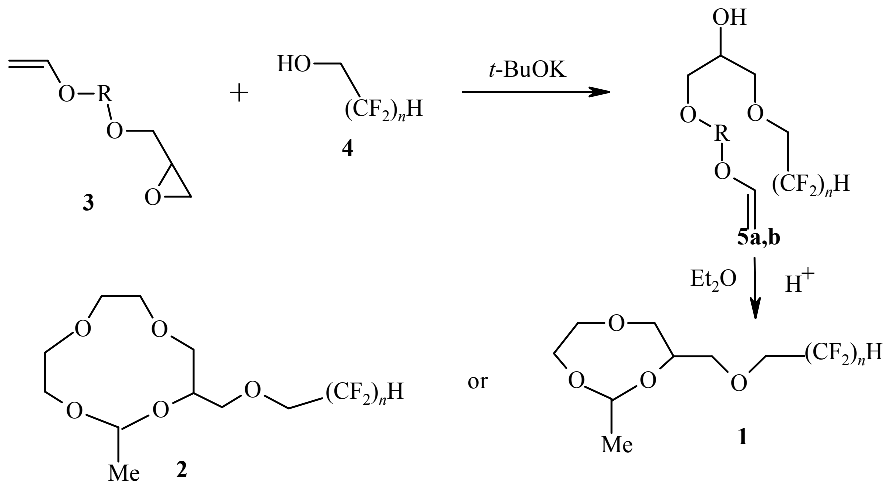
Macroheterocyclic compounds, including macrocyclic polyethers, are widely used in organic synthesis and in practice and have aroused considerable interest [1-6]. Cyclic polyethers, covalently bonded to a fluorocarbon side chain, have claimed the attention of investigators as components of membranes, guaranteeing "complete" thermal control of phase transitions in the composite membranes [5, 6]. The condensation reaction is the basis of most methods for obtaining macroheterocycles [1-4]:



5 a R = $(CH_2)_2$, **b** R = $(CH_2)_2O(CH_2)_2$; $n = 4$

We have proposed a simple and original route for the synthesis of oxygen-containing macrocycles, including some with polyfluoroalkyl substituents, for example, the previously unknown 2-methyl-4-[(polyfluoroalkoxy)methyl]-1,3,6-trioxocanes **1** and 2-methyl-4-[(polyfluoroalkoxy)methyl]-1,3,6,9-

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tetraoxacycloundecanes **2**, starting from the available (ω-vinyloxy)alkoxymethyloxiranes **3** [R = $(CH_2)_n$, $n \geq 2$; $(CH_2)_2O(CH_2)_2$ etc.] [7] and polyfluoroalkanols **4** [8], with subsequent nucleophilic reactions (with opening of the oxirane ring under the influence of the alkoxide anion) and electrophilic addition (trifluoroacetic acid catalysed intramolecular cyclization to give 3-[ω(vinyloxy)alkoxy]-1-(polyfluoroalkoxy)-2-propanol **5** with participation of the vinyloxy group).

The possibility of the proposed route for the synthesis of macrocyclic polyethers with fluorocarbon substituents is not limited to the examples given here. Evidently introduction of other combination of compounds **3** and **4** permits variation in the length of the fluorocarbon chain and the size of the heterocycle, leading by a simple route to new range of 1,3,6-trioxocanes, 1,3,6-trioxonanes, 1,3,6-trioxasecanes, 1,3,6,9-tetraoxacycloundecanes, etc..

3-[2-(Vinyloxy)ethoxy]-1-[(2,2,3,3,4,4,5,5-octafluoropentyl)oxy]-2-propanol (5a). *t*-BuOK (1.13 g, 3 mass %) was added with stirring to an equimolar mixture of 2-[2-(vinyloxy)ethoxy]methyloxirane (14.4 g) and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (23.2 g). The mixture heated spontaneously from 21 to 35°C – the mixture was heated at 75-80°C for 7 h and was then distilled without preliminary treatment to give compound **5a**. Yield 27.64 g (from 36.3 g), 76%; bp 125-126°C (1.5 mm Hg), n_D^{20} 1.3922. IR spectrum, ν, cm^{-1}: 1050-1200 (C–F, C–O), 1630 (C=C), 3450 (O–H). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 6.47 (1H, q, $^3J_{trans}$ = 14.3, $^3J_{cis}$ = 6.8, OCH=); 6.20, 6.07, and 5.94 (1H, tt, *J* = 52.0, 5.5, HCF_2); 4.21 and 4.17 (1H, dd, $^3J_{trans}$ = 14.3, ^2J = 2.2, CH_2=); 4.02 and 4.01(1H, dd, $^3J_{cis}$ = 6.8, ^2J = 2.2, CH_2=); 3.96, 3.72, 3.67, and 3.55 (9H, all m, 4 OCH_2, CHO); 3.83 (2H, m, OCH_2CF_2); 2.96 (1H, d, *J* = 4.8, OH). ^{13}C NMR spectrum, δ, ppm: 151.84 (OCH=), 118.22 t, 115.67 t, 112.50 t (2-CF_2), 110.43 t, 107.91 t, 105.39 t (5-CF_2), 87.10 (CH_2=), 74.06, 72.24, 70.07, 69.62, 67.44 (4 OCH_2, OCH), 68.39 t ($O\underline{C}H_2CF_2$). Found, %: C 37.96; H 4.38; F 39.86. $C_{12}H_{16}F_8O_4$. Calculated, % C 38.31; H 4.29; F 40.40.

2-Methyl-4-[(2,2,3,3,4,4,5,5-octafluoropentyl)oxy]methyl-1,3,6-trioxsocane (1). CF_3CO_2H (0.0218 g, 1 mass%) was added with stirring to a solution of compound **5a** in diethyl ether (50 ml). The mixture was heated at 33-34°C for 9 h, and the solvent was removed on a rotary evaporator. The product (a colorless, transparent, slightly viscous liquid, n_D^{20} 1.3960) was shown to be compound **1** by IR ans ^{1}H NMR spectroscopy. IR spectrum, ν, cm^{-1}: 1050-1200 (C–F, C–O), 2980 (Me), absorptions for the OH and vinyloxy groups were absent. ^{1}H NMR spectrum, δ, ppm: 6.19, 6.06, 5.93 (1H, tm, HCF_2); 4.86 (1H, m, OCHO); 3.96, 3.71-3.52 (11H, m, 5 OCH_2, OCH); 1.30 (3H, m, Me). Signals of the protons of the OH and vinyloxy groups were absent. Found, %: C 37.94; H 4.60; F 39.96. $C_{12}H_{16}F_8O_4$. Calculated, %: C 38.31; H 4.29; F 40.40.

15,15,16,1,17,17,18,18,-Octafluoro-3,6,9,13-tetraoxa-1-octadecen-11-ol (5b). To a stirred mixture of 2-{2-[2-(vinyloxy)ethoxy]ethoxymethyl}oxirane (3.76 g) and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (5.57 g) was added *t*-BuOK (0.28 g, 3 mass %) (the temperature of the mixture increased spontaneously from 23 to 32°C). The mixture was heated at 75-80°C for 5 h. Compound **5b** was isolated by distillation; bp 165-166°C (1.5 mm Hg), n_D^{20} 1.4024, yield 5.33 g (from 7.8 g) (68%). IR spectrum, ν, cm^{-1}: 1100-1200 (C–F, C–O), 1630, 1640sh (C=C), 3450 (OH). ^{1}H NMR spectrum, δ, ppm: 6.41 (1H, q, OCH=); 6.16, 6.03, and 5.90 (1H, tt, HCF_2); 4.14 and 4.10 (1H, dd, CH_2=); 3.95 and 3.93 (1H, dd, CH_2=); 3.94 (1H, m, CHO); 4.00-3.45 (14H, all m, 7 OCH_2); 3.11 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 151.54 (OCH=); 115.35 (tt, $OCH_2\underline{C}F_2$); 110.82, 110.11 (tm, 2 CF_2); 107.59 (tt, CF_2H); 86.59 (CH_2=); 73.79, 71.96, 70.58, 70.44, 69.42, 69.33, 68.05 (t), 67.10 (OCH_2, OCH). Found, %: C 40.35; H 5.26; F 35.07. $C_{14}H_{20}F_8O_5$. Calculated, %: C 40.01; H 4.80; F 36.16.

2-Mehyl-4-[(2,2,3,34,4,5,5-octafluoropentyl)oxy]methyl-1,3,6,9-tetraoxacycloundecane (2). To a solution of compound **5b** (2.05 g) in diethyl ether (50 ml) CF_3CO_2H (0.0205 g, 1 mass %) was added, the solution was stirred at 33-34°C for 7 h, and the solvent was removed on a rotary evaporator. The reaction product (a colorless, transparent, slightly viscous liquid, n_D^{20} 1.4068) was shown by IR and ^{1}H NMR spectroscopy to be compound **2** as an approximately 1:1 mixture of the *d,l* and *meso* diastereomers). IR spectrum: ν, cm^{-1}: 1050-1200 (C–F, C–O), 2980 (Me); absorptions for the OH and vinyloxy groups were absent. ^{1}H NMR spectrum, δ, ppm: 6.21, 6.08, and 5.95 (1H, tm, HCF_2); 4.88 (1H, q, OCHO); 3.97 (3H, m, OCH_2CF_2, OCH); 3.72, 3.60, 3.52 (12H, all m, 6 OCH_2); 1.30 (3H, d, Me). Signals of the protons of the OH and vinyloxy groups were absent. ^{13}C NMR spectrum, δ, ppm, *J* (Hz): 115.65 (tt, $^{1}J_{C–F}$ = 257.7, ^{2}J = 30.6, $OCH_2\underline{C}F_2$); 111.13, 110.74 (2 tq, 2 CF_2); 107.90 (tt, $^{1}J_{C–F}$ = 253, ^{2}J = 29.3, CF_2H); 100.54, 100.24 (s, OCHO); 74.35, 73.91 (s, C^4); 73.58, 73.47 (s, C^{11}); 71.08, 70.99, 70.89, 70.79, 70.64, 73.39, 72.28 ($C^{7,8,10}$); 64.37, 64.09 (s, C^5); 64.22, 63.96 (s, OCH_2); 68.38 (t, $^{2}J_{C–F}$ = 25.9, $O\underline{C}H_2CF_2$); 20.37, 20.26 (s, Me). Found, %: C 40.73; H 5.24; F 35.50. $C_{14}H_{20}F_8O_5$. Calculated, %: C 40.01; H 4.80; F 36.16.

REFERENCES

1. K. D. Pedersen and H. K. Frensdorf, *Usp. Khim.,* **42**, 492 (1973).
2. M. G. Voronkov and V. I. Knutov, *Usp. Khim.,* **51,** 1484 (1982).
3. M. Chiraoka, *Crown Compounds* [Russian translation], Mir, Moscow (1986).
4. M. G. Voronkov and V. I. Knutov, *Macroheterocycles: Advances in Viability, Science, and Technology* [in Russian], Khimiya, Znanie, Moscow (1988).
5. S. Shinkai, S. Nakamura, S. Tachiki, O. Manabe, and T. Kajiyama, *J. Am. Chem. Soc.,* **107**, 3363 (1985).
6. S. Shinkai, K. Torigoe, O. Manabe, and T. Kajiyama, *J. Chem. Soc. Chem. Commun.,* 933 (1986).
7. B. A. Trofimov and N. A. Nedolya, *Reviews on Heteroatom. Chem. (Japan),* **9**, 205 (1993).
8. A. A. Krolevets, *Chemistry of Aliphatic Alcohols Containing Fluorine* [in Russian]. *Itogi nauki i tekhniki. Organicheskaya khimiya.* VINITI, Moscow, **6**, 150 (1985).