*Russian Journal of General Chemistry, Vol. 72, No. 5, 2002, pp. 760–766. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 5, 2002, pp. 814–820.*

# Fluorine-containing Vinyl Ethers: I. Reactions with Carboxylic Acids

**N. A. Nedolya, N. I. Shlyakhtina, V. P. Zinov'eva, L. L. Dmitrieva, and G. I. Sarapulova**

*Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia*

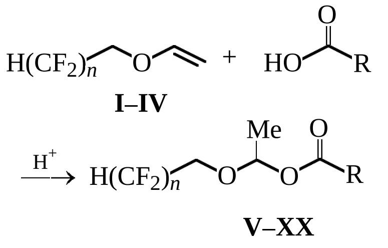
Received August 9, 2000

**Abstract**—Polyfluoroalkyl vinyl ethers take up aliphatic and aromatic carboxylic acids in the presence of 0.2–5 wt% of trifluoroacetic acid at 55–105°C to give fluorine-containing hemiacetals in 60–100% yields.

Organic fluorine compounds attract both scientific and practical interest [1–3]. Development of methods of synthesis of fluorine-containing organic compounds for use in production of drugs, agricultural chemicals, and materials for high technologies (electronics, aviation, energetics, power engineering, etc.) has become one of the priority branches of synthetic organic chemistry [3, 4].

Polyfluoroalkyl vinyl ethers which are easily obtained by direct vinylation of fluoroalkanols with acetylene [5, 6] are suitable building blocks for design of fluorine-containing structures. However, the properties and synthetic potential of such ethers have scarcely been studied [5–11]. The only exception is 2,2,2-trifluoroethyl vinyl ether (Fluroxene, Fluoromar, Fluorene) [1, 2] which has provoked interest as the first accepted fluorine-containing preparation for inhalation narcosis.

Proceeding with studies on unsaturated polyatomic, including fluorine-containing, compounds [5, 6, 12–15], we turned to reaction of 2,2,3,3-tetrafluoropropyl, 2,2,3,3,4,4,5,5-octafluoropentyl, 2,2,3,3,4,4,5,5,6,6,7,7-decafluoroheptyl, and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononyl vinyl ethers (**I**–**IV**) with carboxylic acids (acetic, butyric, isobutyric, valeric, isovaleric, trimethylacetic, and benzoic), with the aim to estimate the reactivity of the ethers and to synthesize previously unknown polyfluoroalkyl-substituted hemiacetals (mixed acetal–acylals) **V**–**XX** which are prospective candidates for biological studies, intermediate products for organic synthesis, plasticizers, surfactants, impregnating agents, etc. [1–3, 16–18].



$n$ = 2 (**I**), 4 (**II**), 6 (**III**), 8 (**IV**).

For R and reaction conditions, see Table 1.

Reaction progress was followed by the $^1$H and IR spectra of the reaction mixtures, i.e. by the decreasing intensity of absorption at 820–840, 960, 1200, 1320, 1630, and 1650 cm$^{-1}$ or the proton signals (δ, ppm) 6.43–6.46 q (CH=), 4.29–4.32 d.d ($CH_2$=, *trans*), 4.17–4.20 d.d ($CH_2$=, *cis*) of the vinyloxy group until its complete disappearance, as well as by the appearance and intensity of proton signals of the acetal–acylal fragment OCH(Me)OC(O) at (δ, ppm) 5.90–6.18 q (OCHO) and 1.40–1.55 d (Me).

The reaction of carboxylic acids with alkyl vinyl ethers is thoroughly studied [16–24]. It is most commonly accomplished without catalysts either by heating equimolar reactant amounts or by slowly adding (dropwise) an acid to a boiling vinyl ether. Hemiacylals are formed in an yield of 60–94% per consumed vinyl ether [19, 20]; therewith, the reactions of ethyl and butyl vinyl ethers with acetic acid at room temperature are accompanied by a weak exothermic effect (temperature rise 18 and 6°C, respectively), but for complete reactions the reaction mixtures should first be kept at ~60°C for 2–6 h and then at room temperature for 16–18 h.

We found that, in the absence of catalysts, ether **I**, unlike nonfluorinated analogs, fails to react even with acetic acid, the strongest of the aliphatic acids studied, both at room temperature and under heating (70–80°C, 3 h) (Table 1, run no. 1). In the $^1$H NMR spectra of the reaction mixtures we could identify no signals of acylal **V**. Under similar conditions, ether **II** and acetic acid give as little as < 1% of acylal **VI** (Table 1, run no. 6).

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**Table 1.** Conditions of addition of monocarboxylic acids RCOOH to polyfluoroalkyl vinyl ethers **I–IV**

| Run no. | Ether | R | Catalyst $CF_3CO_2H$, wt% | Reaction temperature, °C | Reaction time, h | Acylal no. | Yield of acylal, %[a] |
|---|---|---|---|---|---|---|---|
| 1 | **I** | Me | – | 70–80 | 3 | **V** | ~0 |
| 2 | **I** | Me | – | 88–92[b] | 3 | **V** | 2.1 |
| 3 | **I** | Me | – | 88–92[c] | 3 | **V** | 19.7 |
| 4 | **I** | Me | 0.27 | 70–80 | 5 | **V** | 42 |
| 5 | **I** | Me | 2.3 | 70–80 | 2 | **V** | 75 (~100)[d] |
| 6 | **II** | Me | – | 70–80 | 3 | **VI** | <1 |
| 7 | **II** | Me | – | 88–92[b] | 3 | **VI** | 6.2 |
| 8 | **II** | Me | – | 88–92[c] | 3 | **VI** | 10.3 |
| 9 | **II** | Me | 0.16 | 70–80 | 16 | **VI** | 83 |
| 10 | **II** | Me | 2.3 | 70–80 | 5 | **VI** | 72 (~100)[d] |
| 11 | **III** | Me | – | 88–92[b] | 3 | **VII** | 2.8 |
| 12 | **III** | Me | 2.3 | 70–80 | 5 | **VII** | (~90)[d] |
| 13 | **III** | Me | 2.1 | 70–80 | 7 | **VII** | 81 (~100)[d] |
| 14 | **IV** | Me | – | 88–92[b] | 3 | **VIII** | 3.5 |
| 15 | **IV** | Me | 2.3 | 70–80 | 7 | **VIII** | (~90)[d] |
| 16 | **IV** | Me | 2 | 70–80 | 10.5 | **VIII** | 82 (~100)[d] |
| 17 | **I** | Pr | 0.20 | 80–90 | 5 | **IX** | 83 |
| 18 | **II** | Pr | 0.20 | 80–90 | 10 | **X** | 85 |
| 19 | **I** | *i*-Pr | 0.20 | 85–95 | 5 | **XI** | 80 |
| 20 | **II** | *i*-Pr | 0.20 | 85–95 | 9 | **XII** | 86 |
| 21 | **I** | Bu | 0.17 | 95–105 | 5 | **XIII** | 88 |
| 22 | **II** | Bu | 0.15 | 95–105 | 9.5 | **XIV** | 85 |
| 23 | **I** | *i*-Bu | 0.16 | 95–105 | 4.5 | **XV** | 87 |
| 24 | **II** | *i*-Bu | 0.17 | 95–105 | 6 | **XVI** | 88 |
| 25 | **I** | *t*-Bu | 0.20 | 85–95 | 5 | **XVII** | 68 |
| 26 | **II** | *t*-Bu | 0.18 | 90–100 | 13 | **XVIII** | 81 |
| 27[e] | **I** | Ph | 5.00 | 55–65 | 3.5 | **XIX** | 60 |
| 28[e] | **II** | Ph | 5.00 | 55–65 | 3.5 | **XX** | 79 |

[a] Preparative yields per taken vinyl ether. [b] Without stirring (Glycerin bath). [c] With stirring. [d] Estimated from the $^1H$ NMR spectrum. [e] In benzene solution.

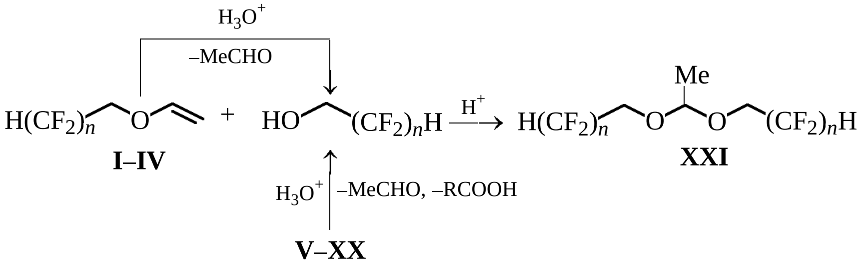
Thus, polyfluoroalkyl vinyl ethers are much less reactive. This result is consistent with the notion of substituent effects on the reactivity the $\pi$ bond in alkoxyethenes with respect to electrophiles [23–25]: electron-donor (alkyl) substituents increase the reactivity of vinyloxy group, while electron-acceptors, vice versa, decrease it.

Preparatively reasonable yields of fluorine-containing acylals could be achieved when equimolar mixtures of carboxylic acids and ethers **I** and **II** were heated for a long time (70–105°C, 5–16 h) in the presence of a catalyst ($CF_3CO_2H$, 0.15–0.3 wt%).

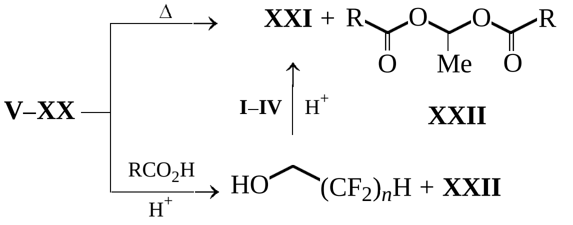
As seen from Table 1, the reaction time with ether **II** is almost always 2 times longer than with ether **I** (under the same experimental conditions and comparable conversions of starting reagents), i.e. the relative reaction rate with ether **II** is ~2 times lower than with ether **I**. The relative reactivity of ethers **I** and **II** qualitatively agrees with the relative acceptor powers of substituents $H(CF_2)_nCH_2$: In going from $n = 2$ to $n = 4$, the Taft $\sigma^*$ constants of the substituents change from 0.57 to 0.85, respectively [9].

As the catalyst concentration is increased to 2.3 wt%, the reaction times of, for instance, ethers **I** and **II** with acetic acid decrease from 5 and 16 h to 2 and 5 h, respectively (Table 1, run nos. 4, 5 and 9, 10). In the presence of 2–2.1 wt % of $CF_3CO_2H$, ethers **III** and **IV** quantitatively take up acetic acid at 70–80°C for 7 and 10.5 h, respectively (Table 1, run nos. 13 and 16). The reaction with benzene was performed in benzene in the presence of 5 wt% of $CF_3CO_2H$ (Table 1, run nos. 27 and 28).

In certain cases, in the $^1H$ NMR spectra of undistilled reaction products and distillation products we detected traces of symmetrical acetals **XXI** [δ, ppm: 4.98–4.90 q (OCHO) and 1.44–1.36 d (Me), $^3J$ 5.5 Hz], identified by the $^1$H NMR spectra of specially prepared samples. Acetals **XXI** are most likely formed by trifluoroacetic acid–catalyzed addition to ethers **I**–**IV** of polyfluoroalkanols which may result from acid hydrolysis in the presence of traces of moisture (for instance, from air) both of vinyl ethers **I**–**IV** and of acylals **V**–**XX**.



Acetals **XXI** may also be formed by disproportionation or acidolysis reactions, which are generally incharacteristic of hemiacylals [17] but sometimes observed [19]. However, these processes are quite minor here, as judged from the incommensurably low, compared with the signal of symmetrical acetal **XXI**, integral intensity of the doublet proton signal at 1.60 ppm, which might be assigned to the methyl group of symmetrical acylal **XXII**.



The effect of the structure of an acid on its reactivity, we revealed in kinetic studies on uncatalytic addition of carboxylic acids to butyl vinyl ether (kinetic measurements were performed at initial acid concentrations of 1.425–2.95 M, i.e. when the acids are predominantly dimeric, and their reaction rates are concentration-independent) [21–23], showed up in a considerable deceleration of the reaction with increasing length and branching of the hydrocarbon chain.

| R | Me | Pr | *i*-Pr | *t*-Bu |
|---|---|---|---|---|
| $k \times 10^4$, $M^{-1}\,s^{-1}$ | 1.66 | 0.96 | 0.64 | 0.24 |

In this case, the effect of substituents is qualitatively no so evident and compensated for as the reaction temperature rises in going from lower to higher carboxylic acids (Table 1).

Undistilled acylals **V**–**XX** proved fairly stable at usual conditions but underwent partial decomposition on distillation (especially without preliminary removal or binding of the catalyst, which reduced the preparative yield by ~15–30%). Most commonly, the $^1$H NMR and IR spectra of the first fractions, unlike those of undistilled products, contained respectively signals and bands of polyfluoroalkanols and carboxylic acids, formed by hydrolysis. Small amounts (2–3 wt%) of an amine, such as $Et_3N$, added to the acylals before distillation appreciably inhibited their decomposition.

Hydrolytic stability of fluorine-containing acylals was qualitatively checked on an example of compound **V**. The IR spectrum of compound **V** shortly (~5 min) contacted with aqueous dioxane at room temperature showed traces of acetic acid and fluoroalkanol, while principal signals of **V** were preserved. At the same time, upon heating for 30 min at 70–80°C in aqueous dioxane compound **V** undewent hydrolytic decomposition by ~50% ($^1$H NMR data).

Compounds **V**–**XX** are colorless or slightly colored liquids with a specific acylal odor. They are readily soluble in most organic solvents. The composition and structure of acylals **V**–**XX** are consistent with their elemental analyses and NMR and IR spectra (Tables 2–4).

The IR spectra of acylals **V**–**XX** (Table 3) contain strong C–F stretching absorption bands ($\nu_{CF_2}$ 1050–1250 cm$^{-1}$) which essentially overlap with the C–O–C absorption bands at 1040–1290 cm$^{-1}$. Therefore, assignment of these broad bands with several maxima to each of the two types of vibrations was difficult to perform unambiguously. The carbonyl group gives a strong absorption band at 1730–1780 cm$^{-1}$. In addi-

**Table 2.** Constants and elemental analyses of acylals **V**–**XX**

| Comp. no. | bp, °C ($p$, mm) | $n_D^{20}$ | Found, % |  |  | Formula | Calculated, % |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H | F |  | C | H | F |
| **V** | 63–65 (15) | 1.3580 | 37.98 | 4.52 | 35.15 | $C_7H_{10}F_4O_3$ | 38.54 | 4.62 | 34.84 |
| **VI** | 85–88 (9) | 1.3475 | 33.73 | 3.42 | 48.57 | $C_9H_{10}F_8O_3$ | 33.98 | 3.17 | 47.77 |
| **VII** | 78–80 (3.5–4) | 1.3370 | 31.40 | 2.45 | 54.17 | $C_{11}H_{10}F_{12}O_3$ | 31.59 | 2.41 | 54.52 |
| **VIII** | 98–102 (3) | 1.3360 | 30.41 | 2.10 | 58.01 | $C_{13}H_{10}F_{16}O_3$ | 30.13 | 1.95 | 58.66 |
| **IX** | 54–58 (1–1.5) | 1.3700 | 43.85 | 5.95 | 30.71 | $C_9H_{14}F_4O_3$ | 43.91 | 5.73 | 30.87 |
| **X** | 85–86 (1–1.5) | 1.3580 | 37.71 | 3.64 | 43.42 | $C_{11}H_{14}F_8O_3$ | 38.16 | 4.08 | 43.90 |
| **XI** | 42–52 (2.5–3) | 1.3715 | 43.69 | 5.82 | 30.27 | $C_9H_{14}F_4O_3$ | 43.91 | 5.73 | 30.87 |
| **XII** | 77–79 (2.5–3) | 1.3570 | 38.20 | 4.08 | 44.14 | $C_{11}H_{14}F_8O_3$ | 38.16 | 4.08 | 43.90 |
| **XIII** | 67–75 (2.5–3) | 1.3800 | 46.22 | 6.01 | 28.84 | $C_{10}H_{16}F_4O_3$ | 46.15 | 6.20 | 29.20 |
| **XIV** | 88–90 (1.5–2) | 1.3650 | 39.63 | 4.28 | 42.51 | $C_{12}H_{16}F_8O_3$ | 40.01 | 4.48 | 42.19 |
| **XV** | 41–44 (1–1.5) | 1.3800 | 46.65 | 6.15 | 29.39 | $C_{10}H_{16}F_4O_3$ | 46.15 | 6.20 | 29.20 |
| **XVI** | 70–72 (1–1.5) | 1.3620 | 39.50 | 4.12 | 41.71 | $C_{12}H_{16}F_8O_3$ | 40.01 | 4.48 | 42.19 |
| **XVII** | 58–60 (2.5–3) | 1.3780 | 45.81 | 6.65 | 29.60 | $C_{10}H_{16}F_4O_3$ | 46.15 | 6.20 | 29.20 |
| **XVIII** | 73–76 (2.5–3) | 1.3600 | 39.71 | 4.63 | 41.88 | $C_{12}H_{16}F_8O_3$ | 40.01 | 4.48 | 42.19 |
| **XIX** | 105–107 (2) | 1.4440 | 51.90 | 4.43 | 27.20 | $C_{12}H_{12}F_4O_3$ | 51.43 | 4.32 | 27.12 |
| **XX** | 129–132 (2) | 1.4080 | 43.90 | 3.02 | 40.40 | $C_{14}H_{12}F_8O_3$ | 44.22 | 3.18 | 39.97 |

tion, fairly strong bands at 2870–3000 cm$^{-1}$ ($\nu_{CH}$, $\nu_{CH_2}$, $\nu_{CH_3}$) are observed.

Analysis of the $^1$H NMR spectra showed that the structure of R (in aliphatic acids) and the number of difluoromethylene groups in the polyfluoroalkyl substituent only slightly affect the chemical shifts of acylal protons, whereas the chemical shifts of protons of the $HCF_2$ and $CF_2CH_2O$ groups of the acylals obtained from ethers **I** and **II** notably differ from each other ($\Delta\delta$ ~0.15 ppm) (Table 4). The same difference is observed in the $^1$H NMR spectra of the starting vinyl ethers: These proton signals of ether **II** are shifted downfield from the respective signals of ether **I** by ~0.15 [5].

## EXPERIMENTAL

The IR spectra were measured on Specord IR-75 and IFS-25 spectrophotometers in thin films. The $^1$H and $^{13}$C NMR spectra were obtained on Bruker DPX-400 (400 and 100 MHz, respectively) and Jeol FX-90Q (90 MHz) for $CDCl_3$ solutions at room temperature (internal reference HMDS).

Polyfluoroalkyl vinyl ethers **I**–**IV** were synthesized according to [5]. All the acids used were commercial products purified by distillation or recrystallization.

**1-Buthoxyethyl acetate.** A mixture of 5 g of butyl vinyl ether and 3 g of acetic acid was heated for 3 h at 88–92°C and distilled at reduced pressure Yield 7.3 g (91%), bp 65–67°C (16 mm), $n_D^{20}$ 1.4024. IR spectrum, ν, cm$^{-1}$: 830, 930, 970, 1000, 1020, 1050, 1070, 1140, 1165, 1240, 1370, 1410, 1450, 1730, 2870, 2940, 2960, 2990. $^1$H NMR spectrum, δ, ppm: 5.90 q (1H, OCHO), 3.64 m and 3.46 m (2H, $OCH_2$), 2.04 s (3H, Me), 1.54 m (2H, $CH_2$), 1.38 d (3H, Me), 1.38 m (2H, $CH_2$), 0.90 t (3H, Me). $^{13}$C NMR spectrum, $\delta_C$, ppm: 169.64 (C=O), 95.57 (OCHO), 68.06 ($OCH_2$), 31.12 (β-$CH_2$), 18.64 (γ-$CH_2$), 20.26 (Me), 20.06 (Me), 13.11 (Me). Found, %: C 59.78; H 9.99. $C_8H_{16}O_3$. Calculated, %: C 59.97; H 10.07.

**Acylals V–XVIII.** To a stirred mixture of 0.01–0.02 mol of vinyl ether **I**–**IV** and a carboxylic acid, 0.15–2.3 wt% of $CF_3CO_2H$, and the reaction was performed in conditions given in Table 1. The reaction product was distilled at reduced pressure in the presence of 2–3 wt% of triethylamine.

**1-(2,2,3,3-Tetrafluoropropoxy)ethyl benzoate (XIX) and 1-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-ethyl benzoate (XX).** To a solution of 0.03 mol of ether **I** or **II** in 8 ml of benzene, 0.03 mol of benzoic acid and 5 wt% of $CF_3CO_2H$ were added. The reaction was performed at 55–65°C for 3.5 h. Unreacted benzoic acid was filtered off, the solvent and vinyl ethers were removed from the filtrate by distillation, and the residue was distilled at reduced pressure. The yields and characteristics of compounds **V**–**XX** are given in Tables 1–4.

**Table 3.** IR spectra of acylals **V**–**XX**

| Comp. no. | ν, $\text{cm}^{-1}$ |
|---|---|
| **V** | 540, 555 sh, 590, 610, 690, 740, 790, 830, 840 sh, 900 sh, 930, 1000, 1040, 1100, 1200 sh, 1240, 1280 sh, 1370, 1420, 1450, 1740, 2890, 2950 3000 |
| **VI** | 540, 600, 630, 710, 740 sh, 760, 800, 845, 900, 930, 960, 970, 990, 1000, 1040, 1090 sh, 1120, 1170, 1250, 1290, 1370, 1390, 1420 sh, 1450, 1740 br, 2890, 2940, 3000 |
| **VII** | 540, 605, 630, 660, 700, 715, 740, 770, 800, 835, 850, 860 sh, 930, 960 sh, 1005, 1040, 1090 sh, 1140, 1190, 1240, 1310 sh, 1380, 1390, 1420 sh, 1450, 1740, 2900, 2950, 3000 |
| **VIII** | 530, 600, 620, 650, 700, 710, 730, 760, 800, 840, 860, 930, 950 sh, 1000, 1040, 1090 sh, 1140, 1200, 1240 sh, 1370, 1380 sh, 1390 sh, 1450, 1740, 2950, 3000 |
| **IX** | 540, 680, 820, 900, 940, 1040, 1100 br, 1180, 1200, 1230, 1270, 1410, 1460, 1730, 2870, 2940, 2970, 3000 sh |
| **X** | 530, 760, 800, 830, 890, 920, 980, 1040–1160–1290 br, 1320, 1350 sh, 1370, 1410, 1450, 1730, 2870, 2940 sh, 2960, 3000 sh |
| **XI** | 560, 700, 760, 840, 860, 910, 940, 950 sh, 1050–1100–1300 br, 1350, 1360, 1400, 1430, 1470, 1480, 1740, 2890, 2950, 2990 |
| **XII** | 540, 700, 750, 800, 840, 860 sh, 900, 920, 960, 990, 1040–1160–1290 br, 1340, 1360, 1390, 1470, 1730, 2880, 2940, 2980 |
| **XIII** | 520, 690, 720, 900, 920, 1030, 1100 br, 1200, 1220–1270 br, 1380, 1420, 1480, 1730, 2870, 2940, 2960, 3000 sh |
| **XIV** | 540, 700, 750, 800, 840, 890, 920, 950, 990, 1050–1160–1280, 1320, 1390, 1410, 1460, 1740, 2870, 2940, 2960, 3000 sh |
| **XV** | 530, 690, 830, 920, 1030, 1100 br, 1200 br, 1290, 1380, 1420, 1460, 1730, 2870, 2920, 2970, 3000 sh |
| **XVI** | 520, 740, 800, 900, 960, 1040, 1120, 1180–1200 br, 1290, 1390, 1420, 1460, 1730, 2870, 2940, 2960, 3000 sh |
| **XVII** | 520, 680, 760, 820, 900, 930, 1020, 1100 br, 1200 br, 1300 br, 1350, 1400, 1460, 1480, 1730, 2870, 2920, 2980 |
| **XVIII** | 520, 730, 800, 900, 1030, 1120 br, 1170 br, 1280, 1380, 1450, 1470, 1730, 2870, 2900, 2940, 2960 |
| **XIX** | 540, 690, 700, 820, 900, 1120 d, 1100 br, 1140, 1270, 1320, 1380, 1460, 1580, 1600, 1720, 2870, 2940, 3000, 3060 |
| **XX** | 540, 680, 700, 800, 900, 1020–1040, 1120 br, 1180 br, 1280, 1310, 1380, 1450, 1580, 1600, 1720, 2870, 2940, 3000, 3060 |

**Table 4.** $^1$H NMR spectra of acylals **V**–**XX**, δ, ppm ($CDCl_3$)

| Comp. no. | R | $HCF_2$, t.t | $CH_2CF_2$, m | OCHO, q | Me, d | R |
|---|---|---|---|---|---|---|
| **V** | Me | 5.78, 5.92, 6.05 | 4.01 | 5.94 | 1.44 | 2.10 s (Me) |
| **VI**[a] | Me | 5.90, 6.03, 6.16 | 4.12 | 5.92 | 1.43 | 2.07 s (Me) |
| **VII** | Me | 5.90, 6.02, 6.16 | 4.13 | 5.92 | 1.42 | 2.08 s (Me) |
| **VIII** | Me | 5.90, 6.04, 6.17 | 4.14 | 5.92 | 1.44 | 2.08 s (Me) |
| **IX** | Pr | 5.74, 5.88, 6.01 | 3.96 | 5.93 | 1.41 | 0.97 t (Me), 1.65 m (β-$CH_2$), 2.31 t (α-$CH_2$) |
| **X** | Pr | 5.90, 6.02, 6.16 | 4.12 | 5.94 | 1.43 | 0.96 t (Me), 1.66 m (β-$CH_2$), 2.31 t (α-$CH_2$) |
| **XI**[b] | *i*-Pr | 5.75, 5.89, 6.01 | 3.96 | 5.92 | 1.41 | 2.56 m (CH), 1.18 d.d (2Me) |
| **XII** | *i*-Pr | 5.91, 6.04, 6.17 | 4.13 | 5.94 | 1.44 | 2.58 m (CH), 1.19 d.d (2Me) |
| **XIII**[c] | Bu | 5.75, 5.94, 6.01 | 3.96 | 5.93 | 1.41 | 0.95 t (Me), 1.32 m (γ-$CH_2$), 1.59 m (β-$CH_2$), 2.33 t (α-$CH_2$) |
| **XIV** | Bu | 5.88, 6.01, 6.14 | 4.10 | 5.90 | 1.40 | 0.94 t (Me), 1.31 m (γ-$CH_2$), 1.59 m (β-$CH_2$), 2.31 t (α-$CH_2$) |
| **XV** | *i*-Bu | 5.75, 5.94, 6.02 | 3.97 | 5.93 | 1.41 | 0.97 t (Me), 2.10 m (CH), 2.22 m ($CH_2$) |
| **XVI** | *i*-Bu | 5.90, 6.03, 6.15 | 4.12 | 5.94 | 1.43 | 0.97 t (Me), 2.10 m (CH), 2.21 d.d ($CH_2$) |
| **XVII** | *t*-Bu | 5.75, 5.88, 6.02 | 3.96 | 5.90 | 1.41 | 1.22 s (*t*-Bu) |
| **XVIII** | *t*-Bu | 5.94, 6.06, 6.15 | 4.12 | 5.94 | 1.45 | 1.19 s (*t*-Bu) |
| **XIX** | Ph | 5.77, 5.90, 6.04 | 4.08 | 6.17 | 1.55 | 7.43 t ($H_m$), 7.56 d.t ($H_p$), 8.03 d.d ($H_o$) |
| **XX** | Ph | 5.90, 6.01, 6.17 | 4.20 | 6.18 | 1.55 | 7.45 t ($H_m$), 7.57 d.t ($H_p$), 8.04 d.d ($H_o$) |

[a] *J*, Hz: $^2J_{HCF}$ 52.2, $^3J_{HCCF}$ 5.4, $^3J_{OCHMe}$ 5.2, $^3J_{OCHCF}$ 13.9, $^4J_{OCHCCF}$ 1.6. $^{13}$C NMR spectrum, $\delta_C$, ppm: 170.56 (C=O), 109.30 t ($CF_2$), 96.12 (OCHO), 65.82 t ($CH_2O$), 20.77 (Me), 20.08 (Me). [b] *J*, Hz: $^2J_{HCF}$ 53.4, $^3J_{HCCF}$ 5.1, $^3J_{OCHMe}$ 5.4, $^3J_{OCHCF}$ 9.5. [c] $^{13}$C NMR spectrum, $\delta_C$, ppm: 173.47 (C=O), 109.17 t ($CF_2$), 96.02 (OCHO), 65.92 t ($CH_2O$), 34.10 (α-$CH_2$), 26.87 ($CH_2$), 22.27 ($CH_2$), 20.32 (Me), 13.69 (Me). [d] *J*, Hz: $^2J_{HCF}$ ~52.0, $^3J_{HCCF}$ ~5.5, $^3J_{OCHMe}$ 5.3, $^3J_{OCHCF}$ 13.9.

**Hydrolysis of acylal V.** *a*. A solution of 0.2 g of acylal **V** in a mixture of 3 ml of dioxane and 3 ml of water was shaken at room temperature for ~5 min, the reaction products were extracted with diethyl ether, dried with $K_2CO_3$, and the solvents were distilled at reduced pressure (8 mm). The $^1$H NMR spectrum of the residue was identical to that of the parent acylal; signals of acetic acid and fluoroalkanol were very weak. In the IR spectrum, a weak asymmetric $\nu_{OH}$ band of acetic acid appeared, with a maximum at 3400 cm$^{-1}$; this band is likely to overlap with the $\nu_{OH}$ band of 2,2,3,3-tetrafluoropropan-1-ol which, too, is formed by hydrolysis of acylal **V**.

*b*. A solution of 0.2 g of acylal **V** in a mixture of 3 ml of dioxane and 3 ml of water was stirred for 30 min at 70–80°C and then treated as described above. The conversion of acylal **V**, estimated from the $^1$H NMR spectrum [by the integral intensity ratio of the singlet signals of the methyl group of acetic acid (2.03 ppm) and acylal (2.10 ppm)], was ~50%. The IR spectrum of the hydrolysis products showed a medium $\nu_{OH}$ band at 3400 cm$^{-1}$.

**1-(2,2,3,3-Tetrafluoropropoxy)ethyl 2,2,3,3-tetrafluoropropyl ether (XXI, *n* = 2).** $^1$H NMR spectrum, δ, ppm: 6.15 t, 6.02 t, 5.89 t (1H, $HCF_2$), 4.97 q (1H, OCHO), 4.00 m (2H, $CH_2CF_2$), 1.39 d (3H, Me).

**2,2,3,3,4,4,5,5-Octafluoropentyl 1-(2,2,3,3,4,4,5,5-octafluoropentyloxy)ethyl ether (XXI, *n* = 4).** $^1$H NMR spectrum, δ, ppm: 6.14 m, 6.01 m, 5.90 m (1H, $HCF_2$), 4.97 m (1H, OCHO), 4.01 m (2H, $CH_2CF_2$), 1.38 m (3H, Me).

The $^1$H NMR spectra of acetals **XXI** (*n* = 6, 8) are almost identical to the above-described (for *n* = 2, 4).

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