

Supporting Information

for

Acid catalyzed cyclodimerization of 2,2-bis(trifluoromethyl)-4-alkoxy-oxetanes and -thietanes. Synthesis of 2,2,6,6-tetrakis(trifluoromethyl)-4,8-dialkoxy-1,5-dioxocanes and 3,3,7,7-tetrakis(trifluoromethyl)-9-oxa-2,6-dithiabicyclo[3.3.1]nonane

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Experimental details and analytical data for compounds 2a–2e, 3a–3e and 5.

Experimental Part.

^1H and ^{19}F NMR spectra were recorded on a Varian 500 (499.87 MHz) instrument, respectively, using CFCl_3 or TMS as an internal standards and CDCl_3 or acetone- d_6 as a lock solvent. The purity of isolated materials was established using NMR and GC and was 97–99%. GC and GC/MS analysis were carried out on a HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) or mass selective (GS/MS) detectors, respectively. Hexafluoropropene, hexafluoroacetone (DuPont), $\text{CF}_3\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$, CH_3OH , $(\text{CH}_3)_2\text{CHOH}$, $\text{BF}_3\cdot\text{Et}_2\text{O}$, H_2SO_4 (96%) (Aldrich) and were used without further purification.

Oxetanes **1a–d** were prepared using a slightly modified literature procedure [1] by bubbling hexafluoroacetone into a solution of the vinyl ether in CH_2Cl_2 at 10–25 °C, followed by the removal of solvent under reduced pressure. The crude products (purity >97%, NMR) were stored refrigerated, over a small amount of solid K_2CO_3 to prevent polymerization and used for further reactions without further purification. Thietanes **4a–c** were prepared according to literature procedures [2].

Crystallography:

X-ray data for **2a**, **2b**, **2d** and **5** were collected at –100 °C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator. The structures were solved and refined using the SHELXTL [3] software package, refinement by full-matrix least squares on F^2 , scattering factors from Int. Tab. Vol C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #761670 to #761573. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Reaction of oxetanes **1a–c** with **BF₃·Et₂O**.

To a stirred solution of 0.5–3 g of oxetane **1a**, **1b** or **1c** in 10–15 ml of CH₂Cl₂ was added 1–3 drops of BF₃·Et₂O at ambient temperature. After the addition of the catalyst, the appearance of an intense dark blue color was observed and the reaction temperature rose to 30–35 °C. Over the next 15–30 min the color of the reaction mixture went from blue to dark red and finally brown. At this point the formation of a brown precipitate was observed. The reaction mixture was cooled to –70 °C, filtered cold and the filter cake washed several times with water and then with a small amount of cold hexane to give 0.2–1.5 g of white or slightly yellow solids, compounds **2a–c**. Analytically pure samples of **2a–c** were prepared by crystallization from hexane. Melting points and NMR and elemental analysis data for **2a–c** are given in Table 1.

Reaction of oxetane **1d** with **BF₃·Et₂O**.

To a stirred solution of 26.6 g (0.1 mol) of oxetane **1d** in 50 ml of CH₂Cl₂ was added 3 drops of BF₃·Et₂O at ambient temperature. Addition of the catalyst was not exothermic. The reaction mixture was stirred for 7 days at ambient temperature. At this point the conversion of **1d** was ~85% (NMR, ratio of **1d**:**2d**:**2e** – 15:15:70). The reaction mixture was washed with water (2 x 100 ml), organic layer separated, dried over MgSO₄ and the solvent was removed under vacuum (~100 mm Hg, <20 °C). The residue was distilled at 20 mmHg to give two fractions:

- 5 g of material bp 30–40 °C/5mmHg (olefin **2d**, *trans*-isomer, purity >98%, isolated yield 19%), crystallized on standing, mp 69–70 °C;
- 12 g of material bp 50–55 °C/5mmHg – mixture of liquid and solid materials, based on NMR mixture of **1d**, **2e** and **2d** in ratio 16:16:68. Calculated yield of **2d** - 31%.
- In the cold trap 4 g of **1d** (purity 90%, contaminated by an equal amount of **2d** and **2e**) was collected. Spectroscopic data for **2e** and **2d** are given in Table 1.

Reaction of oxetanes **1b, c** with alcohols.

Oxetane **1** (0.02 mol) was added slowly to 20 ml of the corresponding alcohol at such a rate that the internal temperature was kept at <30 °C. The reaction mixture was stirred for

2–16 h at ambient temperature and then diluted with 200 ml of water. The organic layer was separated, washed with water, dried over MgSO₄ and analyzed. NMR data for compounds **3a–e** are given in Table 1.

Reaction of thietanes **4a, b with H₂SO₄.**

Thietane **4a** (5.4 g, 0.02 mol) or **4b** (5.6 g, 0.02 mol) was added to 25 ml of 96% H₂SO₄ at such a rate that the reaction temperature was kept between 25–35 °C. The reaction mixture was stirred at ambient temperature for 2–16 h, poured onto crushed ice and extracted with 50 ml of CH₂Cl₂. The organic layer was washed with 10% solution of NaHCO₃, dried over MgSO₄, the solvent was removed under vacuum and the solid residue recrystallized from hexane to give 1.65 g (35%) and 2.4 g (50%) of **5**, mp 90–91 °C (from **4a**) and 91–92 °C (from **4b**), respectively. Data of ¹H, ¹³C and ¹⁹F NMR spectroscopy are given in Table 1. GC/MS (*m/z*, in CH₂Cl₂, relative intensity %): 434 (M⁺, C₁₀H₆F₁₂OS₂⁺, 35%), 270 (C₆H₄F₆OS₂⁺, 30%), 241 (40%), 209 (C₅H₃F₆S⁺, 100%), 189, 171, 145 (C₄H₂F₅⁺), 113, 69(CF₃⁺).

Reaction of thietane **4c with H₂SO₄**

6.3 g (0.025 mol) of **4c** was added in small portions to 25 ml of 96% H₂SO₄ at such a rate that the temperature of the reaction mixture was kept at <20 °C. The reaction mixture was stirred at ambient temperature for 1 h, poured onto crushed ice and extracted with 50 ml of CH₂Cl₂. The organic layer was washed with 10% solution of NaHCO₃, dried over MgSO₄, the solvent was removed under vacuum and the solid residue recrystallized from hexane to give 2.8 g (45%) of **5** mp 91–92 °C. ¹H, ¹³C and ¹⁹F NMR spectra of the material obtained were identical to the spectra of samples prepared from **4a** and **4b**.

Table 1: Yields, boiling (melting) points and NMR data for compounds **2a–e**, **3a–e** and

5.

Entry No	Comp.	Yield (%)	bp (°C/mmHg) (mp °C)	¹⁹ F NMR ^a (δ, ppm, J, Hz)	¹ H NMR ^a (δ, ppm, J, Hz)
1	2a ^{b,c}	31	(127–128)	–76.06 (3F, q, 10.5) –77.15 (3F, q, 10.5)	1.2 (3H, t, 7.2) 2.61 (1H, d, 17.1) 3.04 (1H, dd, 17.1, 5.9) 3.63 (1H, m) 3.83 (1H, m) 5.65 (1H, d, 5.8)
2	2b ^{b,d}	34	(68–69)	–75.63 (3F, q, 10.2) –76.60 (3F, q, 10.2)	0.95 (3H, t, 7.6) 1.60 (2H, m) 2.58 (1H, d, 16.8) 2.84 (1H, dd, 16.8, 5.5) 3.40 (1H, m) 3.72 (1H, m) 5.53 (1H, d, 5.5)
3	2c ^{b,e}	42	(54–55)	–75.63 (3F, q, 10.2) –76.60 (3F, q, 10.2)	0.95 (3H, t, 7.2) 1.41 (2H, m) 1.59 (2H, m) 2.57 (1H, d, 17.3) 2.84 (1H, dd, 17.3, 6.2) 3.45 (1H, m) 3.77 (1H, m) 5.53 (1H, d, 5.6)

4	2d	30	(69–70)	–78.98 (s)	1.35 (9H, s) 2.90 (1H, s) 5.06 (1H, d, 12.1) 7.00 (1H, d, 12.1)
5	2e	—	43–55/10	–73.14 (3F, q, 11.2) –73.83 (3F, q, 11.2) –75.82 (3F, q, 10.0) –79.79 (3F, q, 10.0)	1.37 (9H, s) 2.24 (1H, dm, 15.7) 2.46 (1H, dd, 15.7, 2.8) 5.03 (1H, d, 12.6) 6.61 (1H, d, 9.1) 5.71 (1H, s) 7.03 (1H, d, 12.6)
6	3a	—	—	–77.82 (3F, q, 10.2) –78.16 (3F, q, 10.2)	0.95 (3H, t, 7.5) 1.66 (2H, m) 2.24 (2H, d) 3.50 (3H, s) 3.53 (1H, m) 3.70 (1H, m) 4.85 (1H, t, 5.3) 5.70 (1H, s)

7	3b	—	—	-77.31 (3F, q, 10.2) -77.72 (3F, q, 10.2)	0.94 (3H, t, 7.5) 1.40 (2H, m) 1.60 (2H, m) 2.23 (2H, d, 6) 3.43 (3H,s) 3.53 (1H, m) 3.73 (1H, m) 4.83 (1H, t, 5.3) 5.68 (1H, s)
8	3c	—	—	-74.82 (3F,t, 7.9) -76.89 (3F, q, 10.2) -78.87 (3F, q, 10.2)	0.97 (3H, t, 7.4) 1.41 (2H, m) 1.65 (2H, m) 2.31 (2H, m) 2.84 (1H, dd, 17.3, 6.2) 3.58 (1H, m) 3.84 (1H, m) 5.08 (1H, dd, 5.4, 7.2) 5.26 (1H, s)
9	3d	—	—	-73.28 (3F,dq, 9.5, 5.7) -77.57 (3F,dq, 9.5, 5.7) -76.20 (3F, q, 9.5) -78.72 (3F, q, 9.5)	0.95 (3H, t, 7.5) 1.39 (2H, m) 1.64 (2H, m) 2.35 (2H, m) 3.58 (1H, m) 3.92 (1H, m) 4.39 (1H, sept, 5.5)

					5.00 (1H, s) 5.13(1H, dd, 8.0, 4.5)
10	3e	—	—	-77.40 (3F, q, 10.0) -77.54 (3F, q, 10.0)	0.92 (3H, t, 7.0) 1.18 (3, d, 6.0) 1.22 (3, d, 6.0) 1.38 (2H, m) 1.57 (2H, m) 2.20 (2H, d, 6.0) 3.47 (1H, m) 3.67 (1H, m) 3.93 (1H, sept, 6.0) 4.93 (1H, t, 6.0) 5.89 (1H, s)
11	5	35–50	(91–92) ^f	-71.25 (3F,q, 11.0) -72.31 (3F,q, 11.0) ^{g,h}	2.83 (1H, ddq, 16.6, 8.4, 1.6) 3.42 (1H, dd, 16.6, 8.9) 5.96 (1H, t, 8.5) ^{g,i}

^a in CDCl₃

^b Elemental analysis: Found (calcd) % for:

2a: C = 35.08 (35.31), H = 3.10 (3.39), F = 47.64 (47.87)

2b: C = 38.02 (38.11), H = 3.80 (4.00), F = 44.99 (45.21)

2c: C = 40.59 (40.61), H = 4.62 (4.54), F = 42.60 (42.82)

^c ¹³C NMR (CDCl₃): 14.74, 36.94, 63.69, 79.06 (sept, *J* = 28.8 Hz), 96.90, 122.34 (q, *J* = 290 Hz), 122.72 (q, *J* = 290 Hz) ppm.

^d ¹³C {H} NMR (CDCl₃): 13.54, 19.00, 31.10, 67.94, 79.15 (sept, *J* = 28.3 Hz), 96.90, 122.34(q, *J* = 290 Hz), 122.68 (q, *J*=290 Hz) ppm.

^e ¹³C{H} NMR (CDCl₃): 10.21, 22.44, 37.00, 69.19, 69.86, 79.13 (sept, *J* = 28.3 Hz), 97.10, 122.34 (q, *J* = 290 Hz), 122.71 (q, *J* = 290 Hz) ppm.

^f reported for compound **5a** : mp 91–92 °C [2].

^g in acetone-*d*₆

^h NMR data reported for compound **5a**: ¹H NMR (CDCl₃) : 2.72 (1H, dd, *J* = 15.0 Hz), 3.05 (1H, dd, *J* = 15.0, 5.0 Hz), 5.45(1H, t, *J* = 9.0 Hz) ppm; ¹⁹F (CCl₄): –70.0 (m) ppm [2].

ⁱ ¹³C{H} NMR: (acetone-*d*₆): 29.47, 55.18 (sept, *J* = 28.3 Hz), 69.77, 123.50 (qq, *J* = 282, 1.5 Hz), 123.85 (q, *J* = 282 Hz) ppm.

References

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