Acid-Catalyzed Reactions of 1-Oxadispiro[2.1.2.2]nonane: In Search of Transannular Ring Expansion in Monocyclic Substrates

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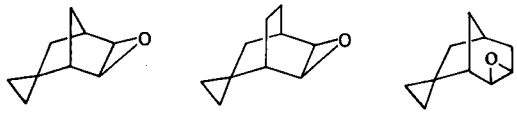
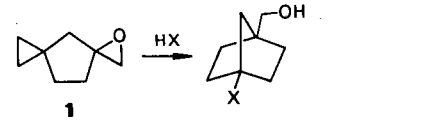
1-Oxadispiro[2.1.2.2]nonane (**1**), prepared in 62% yield by epoxidation of 5-methylenespiro[2.4]heptane with *m*-chloroperbenzoic acid, gave on treatment with trifluoroacetic acid in CCl_4 the isomeric hydroxy esters 5-(hydroxymethyl)-5-(trifluoroacetoxy)- (**2a**) and 5-hydroxy-5-[(trifluoroacetoxy)methyl]spiro[2.4]heptane (**2b**) as major products. Hydrolysis of **2a,b** with KOH in ethanol led to 5-hydroxy-5-(hydroxymethyl)spiro[2.4]heptane (**3**) in 61% yield. As minor products were isolated the isomeric unsaturated alcohols 5-(hydroxymethyl)spiro[2.4]hept-5-ene and -4-ene (**4a,b**), spiro[2.4]heptane-5-carboxaldehyde (**5**) (which was readily autoxidized to carboxylic acid **6**), and the isomeric acetals 7-(spiro[2.4]hept-5-yl)-6,8-dioxadispiro[2.1.4.2]undecane (**7a,b**). These products were all rationalized in terms of standard carbenium ion chemistry of the protonated oxirane. No evidence could be provided for transannular ring expansion of the spirocyclopropane moiety to yield bridgehead-substituted norbornanes.

Säurekatalysierte Reaktionen des 1-Oxadispiro[2.1.2.2]nonans: Auf der Suche nach transannularen Ringerweiterungen in monocyclischen Substraten

Die Epoxidierung von 5-Methylenspiro[2.4]heptan mit *m*-Chlorperbenzoesäure lieferte mit 62% Ausbeute 1-Oxadispiro-[2.1.2.2]nonan (**1**). Als Hauptprodukt entstanden bei der Reaktion von **1** mit Trifluoressigsäure in CCl_4 die isomeren Hydroxyester 5-(Hydroxymethyl)-5-(trifluoracetoxy)- (**2a**) bzw. 5-Hydroxy-5-[(trifluoracetoxy)methyl]spiro[2.4]heptan (**2b**). Mit KOH in Ethanol wurden diese zu 5-Hydroxy-5-(hydroxymethyl)-spiro[2.4]heptan (**3**) in 61proz. Ausbeute hydrolysiert. Als Nebenprodukte wurden die ungesättigten Alkohole 5-(Hydroxymethyl)spiro[2.4]hept-5-en bzw. -4-en (**4a,b**) gebildet sowie Spiro-[2.4]heptan-5-carboxaldehyd (**5**) (das leicht zur Carbonsäure **6** autoxidiert wurde) und die isomeren Acetale 7-(Spiro[2.4]hept-5-yl)-6,8-dioxadispiro[2.1.4.2]undecan (**7a,b**). Diese Produkte entsprechen der bekannten Carbenium-Ionen-Chemie von protonierten Oxiranen. Es gab keinen Hinweis für die Bildung von brückenkopfsubstituierten Norbornanen, wie sie durch transannulare Ringerweiterungen des Spirocyclopropansubstituenten hätten entstehen können.

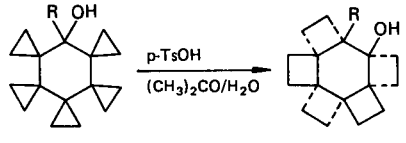
In the preceding papers of this series we reported on the transannular ring expansions of spirocyclopropane-substituted oxiranes derived from bicyclo[2.2.1]heptane[1], bicyclo-[2.2.2]octene[2], and bicyclo[3.2.1]octene[3]. These transformations permitted preparing complex tricyclic carbon skeletons such as brendanes, homobrendanes, and isotwistanes.





(1)

1



(2)

R = H, CH_3

We were encouraged, therefore, to extend such transannular ring expansions to spirocyclopropane-substituted monocyclic substrates, for example the oxirane **1** derived from 5-methylenespiro[2.4]heptane (eq. 1). On treatment with a protic acid, the bridgehead-functionalized norbornanes would become conveniently available. The literature is devoid of such synthetic methodology involving formally 1,3-carbon migrations, although rather complex examples of 1,2-carbon shifts with spirocyclopropane-substituted substrates are well documented (eq. 2)[4].

Presently we report our results on the acid-catalyzed transformations of 1-oxadispiro[2.1.2.2]nonane (**1**) with trifluoroacetic acid. Instead of the desired transannular ring expansion leading to disubstituted norbornanes (eq. 1), standard carbenium-type chemistry was observed (eq. 3).

Results

1-Oxadispiro[2.1.2.2]nonane (**1**) was prepared in 62% yield by epoxidation of the known[5] 5-methylenespiro-[2.4]heptane with *m*-chloroperbenzoic acid (*m*-CPBA) in chloroform (eq. 3). The characterization of **1** rests on spectral and analytical data (cf. Experimental).

Treatment of **1** with stoichiometric amounts of trifluoroacetic acid in CCl_4 gave the complex mixture of products

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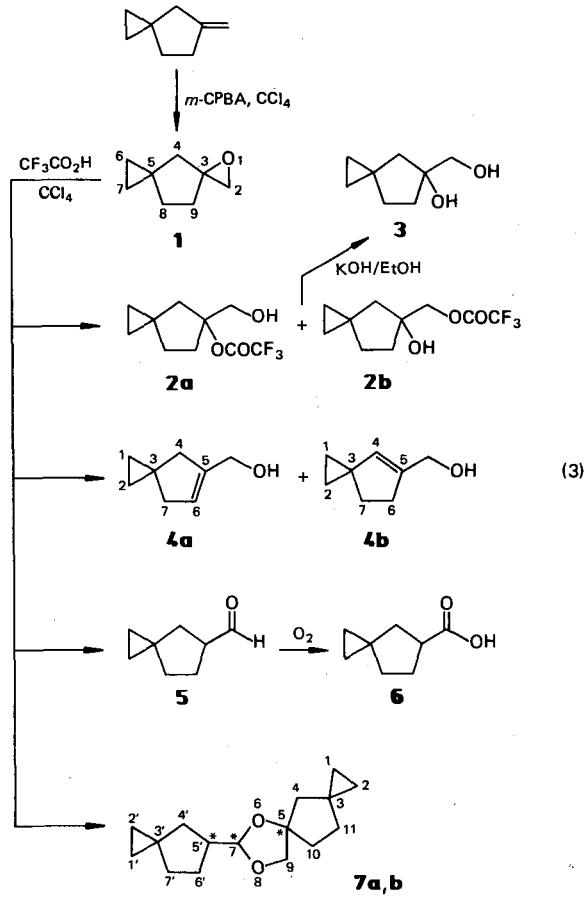
shown in eq. (3) to the extent of ca. 46%, the remainder being higher molecular weight material. Flash chromatography proved successful in separating these compounds. The main product was a mixture of isomeric hydroxy trifluoroacetates **2a,b**, formed in a 66:34 ratio (determined by ^{13}C NMR; two C-5 and two C-6 signals, cf. Table 1). It was not possible to separate these isomers by flash chromatography; however, hydrolysis with KOH in ethanol gave the diol **3** (eq. 3) in 61% yield, whose characteristic ^{13}C-NMR data are collected in Table 1.



The unsaturated alcohols **4a,b** (eq. 3) were formed in a ca. 50:50 ratio (determined by means of ^{13}C NMR, Table 1). Also these could not be separated by chromatography. The spectral data (cf. Experimental) are consistent with these structures. Decoupling experiments directly on the isomeric mixture were partly helpful in the structure elucidation. Irradiation of the broad ddd pattern at $\delta = 1.96$ eliminated the smaller vicinal coupling in the $\delta = 2.51$ signal, leaving the large geminal coupling ($J = 18$ Hz) and vice versa. Thus, these two ddd signals at $\delta = 1.96$ and 2.51 belong to the 7- and 6-methylenic protons of the **4b** isomer, respectively. Consequently, the multiplet at $\delta = 2.33-2.39$ corresponds to the 4- and 7-methylene protons of the **4a** isomer. On irradiation of the olefinic protons at $\delta = 5.13$ and 5.64, respectively, the proton 6-H in isomer **4a** and 4-H in isomer **4b** caused only insignificant changes in the ^1H-NMR spectrum. Other decoupling experiments were not feasible.

Table 1. Characteristic ^{13}C-NMR data[a] of the monomeric products **2**–**6** derived from the trifluoroacetic acid-catalyzed reaction of 1-oxadispiro[2.1.2.2]nonane (**1**)

	C-3	C-4	C-5	C-6
1	21.68(s)	41.34(t)	64.90(s)	52.25(t)
2a	20.67(s)	46.21(t)[b]	83.40(s)	69.24(t)
2b	20.67(s)	46.43(t)[b]	81.00(s)	73.30(t)
3	20.79(s)	46.28(t)	82.92(s)	69.39(t)
4a	20.00(s)	42.70(t)	142.49(s)[b]	62.14(t)[b]
4b	28.74(s)	132.33(d)	144.40(s)[b]	62.29(t)[b]
5	22.31(s)	39.01(t)	44.15(d)	203.78(d)
6	22.31(s)	39.05(t)	44.12(d)	182.25(s)

[a] 100 MHz in $CDCl_3$ as solvent and as internal standard; the numbering of these carbons pertains to that of oxirane **1**. — [b] The assignment of these resonances to the individual isomers is uncertain.

The aldehyde **5** was obtained in pure form after flash chromatography and was readily recognized by its characteristic aldehyde proton at $\delta = 9.63$ in the ^1H NMR and the aldehyde carbon at $\delta = 203.78$ as doublet in the ^{13}C NMR. The IR exhibited the aldehyde C–H absorption at 2870 cm^{-1} and the carbonyl frequencies at 1710 and 1740 cm^{-1}. On standing in solution **5** was readily autoxidized within 48 h to the corresponding carboxylic acid **6** (eq. 3). Its characteristic carboxylic acid proton appeared at $\delta = 10.9-11.4$ in the ^1H NMR and the carboxylic acid carbon at $\delta = 182.25$ in the ^{13}C NMR. The broad OH absorption at 3500–3200 cm^{-1} in the IR clearly speaks for the carboxylic acid functional group. In addition to these monomeric products, the two isomeric acetals **7a,b** were obtained in 3% yield as a ca. 50:50 mixture (^{13}C NMR shows clearly two sets of related signals; cf. Experimental).

Neither flash chromatography nor capillary GC enabled separation of the isomeric acetals **7a,b**. Thus, the stereochemistry at three chirality centers could not be defined. Although the acetal carbon atoms C-7 appeared as a single doublet at $\delta = 106.77$, the quarternary C-5 carbons were visible as two distinct singlets at $\delta = 88.49$ and 88.57 and the methylene C-9 carbons as two distinct triplets at $\delta = 75.12$ and 75.30. Decoupling experiments revealed that the dd signals of the protons 7-H at $\delta = 4.79$ and 4.83 of the two isomeric acetals **7a,b** are coupled to the 5′-H protons with $J_{7,5'} = 5.8$ Hz. The other coupling constant with $J' = 4.2$ Hz could not be assigned (cf. Experimental). The protons

9-H are observed as two AB patterns, of which the A parts fall together at δ = 3.70 and the B parts occur as distinct resonances at δ = 3.83 and 3.86 with J_{AB} = 7.8 Hz. At higher dilution, the bimolecular products **7a, b** could be diminished.

Discussion

The monomeric products **2a, b, 4a, b,** and **5** are all readily explained by standard carbenium-type chemistry of the protonated oxirane **1**. Capture by trifluoroacetic acid at the two oxirane carbons leads to the isomeric hydroxy esters **2a, b**, while deprotonation affords the two isomeric unsaturated alcohols **4a, b**. Pinacol-type rearrangement (1,2-hydrogen shift) gives the aldehyde **5**. The dimeric products **7a, b** are presumably derived from attack on the protonated oxirane **1** by another oxirane molecule, followed by cyclization to the 1,3-dioxolane ring.

There is no evidence for the formation of bicyclic products such as the bridgehead disubstituted norbornanes (eq. 1) by transannular ring expansion of the spirocyclopropane moiety. Thus, this latter process appears to be restricted to rigid skeletons with proximate disposal of the spirocyclopropane group relative to the incipient carbenium ion center. This condition is presumably optimally realized in the norbornane skeleton[1].

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Experimental

General Aspects: Consult Experimental in ref.[3].

1-Oxadispiro[2.1.2.2]nonane (**1**): 2.00 g (18.5 mmol) of 5-methylenespiro[2.4]heptane[5] was dissolved in 50 ml of absol. CCl_4 and while stirring at 0°C 5.59 g (25.9 mmol) of 80% *m*-chloroperbenzoic acid (*m*-CPBA) was added in portions. After stirring at room temp. for an additional 4 h, ^{1}H-NMR monitoring revealed that all spiroheptane was consumed. The mixture was filtered to remove solids, the filtrate was washed with aqu. Na_2SO_3 (2 × 50 ml), with aqu. $NaHCO_3$ (2 × 50 ml), and with water (2 × 50 ml), dried with Na_2SO_4 and the solvent roto-evaporated. Kugelrohr distillation at 40–50°C/13–15 Torr of the crude product afforded 1.42 g (62%) of colorless oil. – IR (CCl_4): 3065 cm^{-1}, 3030, 3000, 2950, 2860, 1485, 1460, 1435, 1395, 1280, 1155, 1105, 1010, 990, 960, 920. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 0.39–0.56 (m; 4H, 6-, 7-H), 1.56 (m; 1H), 1.67 (d, $J_{4x,4n}$ = 14.0 Hz; 1H, 4-H_x), 1.79–1.84 (m; 2H), 1.87 (d; $J_{4n,4x}$ = 14.0 Hz; 1H, 4-H_n), 2.07 (mc; 1H), AB signal (δ_A = 2.78, δ_B = 2.80, J_{AB} = 5.0 Hz; 2H, 2-H_x, 2-H_n). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 11.79 and 12.22 (two t; C-6, -7), 21.68 (s; C-5), 33.02, 34.62, and 41.34 (three t; C-4, -8, -9), 52.25 (t; C-2), 64.90 (s; C-3). – MS (70 eV): *m/z* (%) = 125 (2; $M^+ + 1$), 124 (22; M^+), 109 (48), 93 (61), 79 ($C_6H_7^+$; 100), 67 (76), 66 (35), 55 (36), 41 (50), 39 (61), 28 (CO^+; 38).

$C_8H_{12}O$ (124.2) Calcd. C 77.38 H 9.74
Found C 77.46 H 9.74

Reaction of Oxirane **1** *with Trifluoroacetic Acid:* 1.00 g (8.10 mmol) of **1** was dissolved in 300 ml of absol. CCl_4 and under stirring at 0°C was added 918 mg (8.10 mmol) of trifluoroacetic acid. After stirring at 0°C for an additional 15 min, the yellow-colored reaction mixture was washed with aqu. $NaHCO_3$ (2 × 50 ml), the organic phase separated and dried with Na_2SO_4. After roto-evaporation of the solvent, 894 mg of an yellow oil was obtained consisting of at least four products as exhibited by TLC on silica gel, eluting with petroleum ether (30–50°C)/ethyl acetate (6:1). Repeated flash chromatography on silica gel (substrate-adsorbant ratio 1:100) with petroleum ether (30–50°C)/ethyl acetate (6:1) as eluant afforded four pure products:

5-(Hydroxymethyl)-5-(trifluoroacetoxy)- and 5-Hydroxy-5-[(trifluoroacetoxy)methyl]spiro[2.4]heptane (**2a, b**): Isolated as third fraction (119 mg, 0.50 mmol) in the repeated flash chromatography of the reaction mixture of **1** with trifluoroacetic acid; colorless liquid, b.p. 80–100°C/0.1 Torr. – IR (CCl_4): 3620 cm^{-1} (s), 3500–3200, 3080, 3000, 2960, 2870, 1790, 1395, 1350, 1225, 1010, 940. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 0.4–0.6 (m; 8H, cyclopropane), 1.50–1.98 (m; 12H), AB signal (δ_A = 3.63, δ_B = 3.67, J_{AB} = 11.6 Hz; 2H, CH_2O), 3.68–3.75 (br. s; 2H, OH), AB signal (δ_A = 4.37, δ_B = 4.41, J_{AB} = 11.1 Hz; 2H, CH_2O). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 12.34 (t), 12.46 (t), 12.58 (t), 20.67 (s; C-3), 33.41 (t), 33.59 (t), 36.93 (t), 37.20 (t), 46.21 (t), 46.43 (t), 69.24 (t; CH_2O), 73.30 (t; CH_2O), 81.00 (s; C-5), 83.40 (s; C-5), 114.62 (q; CF_3), 157.34 and 157.77 (two q; C=O). – MS (70 eV): *m/z* (%) = 221 (M^+ – OH; 0.1), 220 ($M^+ - H_2O$; 0.7), 111 (57), 106 (93), 93 (100), 91 (47), 83 (51), 77 (32), 69 (82), 67 (69), 55 (95), 41 (60), 39 (36).

$C_{10}H_{13}F_3O_3$ (238.2) Calcd. C 50.42 H 5.50
Found C 50.18 H 5.50

5-(Hydroxymethyl)spiro[2.4]heptan-5-ol (**3**): 490 mg (2.06 mmol) of the isomeric hydroxy esters **2a, b** in 10 ml of ethanol and 230 mg (4.11 mmol) of KOH were stirred at room temp. for 3 d. The reaction mixture was diluted to double volume with water and extracted with ethyl acetate (5 × 30 ml). The combined extracts were dried with Na_2SO_4 and after roto-evaporation of the solvent, followed by kugelrohr distillation at 100–110°C/0.5 Torr, was obtained 180 mg (61%) of the diol **3** as colorless oil. – IR (CCl_4): 3580 cm^{-1}, 3500–3200, 3060, 2980, 2930, 2845, 1060, 1040, 1000, 950, 900. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 0.34–0.55 (m; 4H, cyclopropane), 1.4–1.5 (m; 1H), AB signal (δ_A = 1.64, δ_B = 1.69, J_{AB} = 13.4 Hz; 2H, 4-H), 1.75–1.91 (m; 3H), 2.93 (s; 1H, OH), 3.05 (s; 1H, CH_2OH), AB signal (δ_A = 3.56, δ_B = 3.59, J_{AB} = 11.2 Hz; 2H, CH_2OH). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 12.24 and 12.67 (two t; C-1, -2), 20.79 (s; C-3), 33.72 (t), 37.02 (t), 46.28 (t; C-4), 69.39 (t; CH_2OH), 82.92 (s; C-5). – MS (70 eV): *m/z* (%) = 125 ($M^+ + 1 - H_2O$; 0.7), 124 ($M^+ - H_2O$; 3), 111 ($M^+ - CH_2OH$; 90), 106 ($M^+ - 2H_2O$; 0.3), 93 ($M^+ - CH_2OH, - H_2O$; 100), 83 (22), 77 (23), 69 (24), 67 (42), 55 (74), 41 (45), 39 (25), 31 (CH_2OH^+; 18), 28 (23), 18 (H_2O^+; 6).

$C_8H_{14}O_2$ (142.2) Calcd. C 67.57 H 9.92
Found C 67.32 H 10.18

5-(Hydroxymethyl)spiro[2.4]hept-5-ene and -4-ene (**4a, b**): Isolated as fourth fraction (30.3 mg, 0.24 mmol) in the flash chromatography of the reaction mixture of **1** with trifluoroacetic acid; colorless liquid, b.p. 80–100°C/0.1 Torr. – IR (CCl_4): 3620 cm^{-1}, 3500–3300, 3080, 3000, 2920, 2840, 1650, 1450, 1375, 1220, 1120, 1015, 955, 855. – ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 0.52–0.67 (m; 8H, cyclopropane), 1.66 (br. s; 2H, OH), 1.96 (ddd, $J_{7,7}$ = 18.0; $J_{7,6x}$ = $J_{7,6n}$ = 7.5 Hz; 2H, 7-H), 2.33–2.39 (m; 4H), 2.51 (ddd, $J_{6,6}$ = 18.0; $J_{6,7x}$ = $J_{6,7n}$ = 7.5 Hz; 2H, 6-H), 4.16–4.20 (m; 4H, CH_2OH), 5.13 (mc; 1H, 4-H), 5.64 (mc; 1H, 6-H). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 12.97 (t), 14.55 (t), 20.00 (s; C-3), 28.74 (s; C-3), 32.12 (t), 33.06 (t), 42.70 (t), 62.14 (t; CH_2O), 62.29 (t; CH_2O), 125.29 (d; C-6), 132.33 (d; C-4), 142.49 (s; C-5), 144.40 (s; C-5). –

MS (70 eV): *m/z* (%) = 124 (M^+; 47), 109 (41), 96 (100), 91 (93), 77 (80), 67 (86), 39 (58).

$C_8H_{12}O$ (124.1) Calcd. C 77.38 H 9.74
Found C 77.33 H 9.80

Spiro[2.4]heptane-5-carboxaldehyde (**5**): Isolated as second fraction (36.7 mg, 0.30 mmol) in the flash chromatography of the reaction mixture of **1** with trifluoroacetic acid; colorless liquid, b.p. 90–100°C/0.1 Torr. – IR (CCl_4): 3080 cm^{-1}, 2960, 2870, 1740, 1710, 1450, 1425, 1290, 1230, 1135, 1015. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 0.3–0.6 (m; 4H, cyclopropane), 1.50–2.10 (m; 6H, 4-, 6-, 7-H), 2.98 (quint.; 1H, 5-H), 9.63 (d, $J_{CH=O,5}$ = 2.4 Hz; 1H, aldehydic H). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 11.96 (t), 12.86 (t), 22.31 (s; C-3), 29.90, 35.04, 39.01 (three t; C-4, -6, -7), 44.15 (d; C-5) 203.78 (d; aldehydic C). – MS (70 eV): *m/z* (%) = 125 ($M^+ + 1$; 4), 95 (M^+ – CHO; 100), 79 (41), 67 (51), 39 (28).

$C_8H_{12}O$ (124.1) Calcd. C 77.38 H 9.74
Found C 77.33 H 9.83

Spiro[2.4]heptane-5-carboxylic Acid (**6**): A solution of 50.0 mg (0.40 mmol) of aldehyde **5** in 5 ml of $CDCl_3$ gave on standing for 48 h in the presence of air the carboxylic acid **6** quantitatively. Roto-evaporation of the solvent and kugelrohr distillation at 100–110°C/0.1 Torr afforded the pure product. – IR (CCl_4): 3500–3200 cm^{-1}, 3080, 2960, 2870, 1740, 1710, 1450, 1425, 1290, 1230, 1135, 1015. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 0.3–0.6 (m; 4H, cyclopropane), 1.5–2.1 (m; 6H, 4-, 6-, 7-H), 2.98 (quint.; 1H, 5-H), 10.9–11.4 (br. s; 1H, CO_2H). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 11.98 (t), 12.85 (t), 22.31 (s; C-3), 29.91 and 35.06 (two t; C-6, -7), 39.05 (t; C-4), 44.12 (d; C-5), 182.25 (s; CO_2H). – MS (70 eV): *m/z* (%) = 140 (M^+; 0.6), 139 ($M^+ - 1$; 3), 122 (3), 107 (15), 95 ($M^+ - CO_2H$; 100), 94 (25), 79 (49), 73 (17), 68 (22), 67 (53), 41 (32), 39 (33).

7-(Spiro[2.4]hept-5-yl)-6,8-dioxadispiro[2.1.4.2]undecane (**7a,b**): Isolated as first fraction (70 mg, 0.28 mmol) in the flash chromatography of the reaction mixture of **1** with trifluoroacetic acid; colorless oil, b.p. 135°C/0.1 Torr. – IR (CCl_4): 3070 cm^{-1}, 3000, 2950, 1445, 1425, 1400, 1135, 1110, 1045, 1010, 955. – ^1H NMR ($CDCl_3$; 400 MHz): δ = 0.29–0.62 (m; 16H; cyclopropane), 1.26–2.22 (m; 24H), 2.57–2.69 (m; 2H, 5′-H), two AB signals showing further splittings (δ_A = 3.70, $\delta_{A'}$ = 3.70, δ_B = 3.83, $\delta_{B'}$ = 3.86, J_{AB} = $J_{A'B'}$ = 7.8 Hz; 4H, 9-H), 4.79 (dd, $J_{7,5'}$ = 5.8; 4.2 Hz; 1H, 7-H), 4.83 (dd, $J_{7,5'}$ = 5.8; 3.5 Hz; 1H, 7-H). – ^{13}C NMR ($CDCl_3$; 100 MHz): δ = 11.53 (t), 12.01 (t), 12.17 (t), 12.31 (t), 13.15 (t), 13.30 (t), 13.52 (t; cyclopropane), 20.46 (s), 20.58 (s), 22.19 (s), 27.74 (t), 27.97 (t), 33.87 (t), 33.92 (t), 35.29 (t), 36.50 (t), 36.94 (t), 37.24 (t), 37.30 (t), 37.37 (t), 44.23 (d), 45.72 (t), 46.57 (t), 75.12 (t), 75.30 (t; C-9), 88.49 (s) and 88.57 (s; C-5), 106.77 (d; C-7). – MS (70 eV): *m/z* (%) = 248 (M^+; 0.1), 153 (26), 107 (100), 79 (40), 67 (15), 41 (13).

$C_{16}H_{24}O_2$ (248.4) Calcd. C 77.37 H 9.74
Found C 77.29 H 9.87

CAS Registry Numbers

1: 109532-56-1 / **2a**: 109532-57-2 / **2b**: 109532-63-0 / **3**: 109532-58-3 / **4a**: 109532-59-4 / **4b**: 109532-64-1 / **5**: 109532-60-7 / **6**: 109532-61-8 / 7: 109532-62-9 / 5-methylenespiro[2.4]heptane: 37745-02-6

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