Supporting Information

A Novel Bornane Synthesis by an Old Idea

Baldur Föhlisch*, Derar Abu Bakr, and Peter Fischer

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Solvents. Methanol was dried by refluxing with magnesium turnings and distillation. Dry acetoneitrile was made by refluxing with phosphorus pentoxide and distillation. For the other solvents, see printed Experimental Section.

1. Methanolysis of 3',3'-dichlorospiro(cyclopropane-1,7'-[2]thiabicyclo[2.2.1]hept[5]ene) (2): methyl cis-7-mercaptospiro[2.4]hept-5-ene-4-carboxylate (7a) and O-methyl spiro[2.4]-hepta-4,6-diene-4-thiocarboxylate (8a): Cycloadduct 2 (3.10 g, 15.0 mmol) was added portion-wise and with magnetic stirring to dry methanol (60 mL), chilled in an ice bath. The ice bath was removed and stirring was continued for 1 h. The yellow solution became red-brown. The solvent was evaporated at reduced pressure at ca. 30°C (bath temperature), finally using the vacuum of an oil pump. The remaining red-brown oil (2.54 g) was purified by gravity chromatography at silica (250 g) with PE/EA (30:1). The first fraction gave a red-brown liquid of analytically pure 8a (975 mg, 41%); a second fraction was eluted with PE/EA (20:1), affording 7a (907 mg, 34%) as an orange-colored oil. The latter (7a) was purified by MPLC at Lichroprep sorbent (15–25 μm) with PE/EA (30:1) giving a colorless liquid.


8a: IR (film): 3090, 3015, 2990, 2940, 2840 (CH), 1550 (C=C), 1460, 1435, 1390, 1370, 1290, 1215 cm⁻¹; Anal. Calcd. for C₉H₁₀OS (166.2): C 65.03, H 6.06, S 19.29. Found: C 65.03, H 6.05, S: 19.09.

2. Methyl spiro[2.4]hepta-4,6-diene-4-carboxylate (10a): A solution of silver nitrate (1.54 g, 9.1 mmol) in water (5 mL) was added dropwise at room temperature to a solution of 8a (657 mg, 4.0 mmol) in diethyl ether (20 mL) with magnetic stirring. A black precipitate was formed that was filtrated and washed with diethyl ether (2 × 15 mL). The aqueous layer was separated and extracted with diethyl ether (3 × 20 mL). The combined ether solutions were washed neutral with saturated aqueous NaHCO₃ solution (2 × 20 mL), and with water (2 × 20 mL), and dried over MgSO₄. After filtration and rotary evaporation of the ether, the remaining yellowish-orange liquid (252 mg) was distilled in a Kugelrohr apparatus at 60–70°C/0.01 Torr to yield 142 mg (24%) of 10a as a colorless liquid.


3. Ethyl spiro[2.4]hepta-4,6-diene-4-carboxylate (10b) from 9b: A solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (785 μL, 5.5 mmol) in dry THF (20 mL) and a 1.6 molar solution of n-butyllithium in hexane (3.13 mL, 5.0 mmol) was cooled to -60°C. With magnetic stirring, a solution of 9b (cis+trans-isomers, 1.35 g, 6.0 mmol) in THF (10 mL) was added dropwise and stirred at -60°C for 3 hours. The cooling bath was removed; when the reaction mixture had warmed to 0°C, an ice bath was used. 2M aqueous hydrochloric acid (7 mL) was added
slowly. The mixture was transferred to a separatory funnel, diluted with THF (50 mL), and washed with saturated NaHCO₃ solution (2 x 30 mL) and water (2 x 30 mL). The organic layer was separated, dried with MgSO₄, and concentrated in a rotary evaporator. Kugelrohr distillation at 80-90°C/11 Torr gave a colorless liquid (0.66 g); the NMR spectra were identical with those of 10b (vide infra and printed Experimental Section). Yield 67%.

4. Reaction of O-ethyl spiro[2.4]hepta-4,6-diene-4-thiocarboxylate (8b) with ethene-1,1,2,2-tetracarbonitrile (TCNE): O-Ethyl 2,2,3,3-tetracyanospiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane)-1-thiocarboxylate (12a): To a solution of TCNE (1.28 g, 10.0 mmol) in dry acetonitrile (10 mL), 8b (2.30 g, 12.8 mmol) in dry acetonitrile (10 mL) was added dropwise and with magnetic stirring at room temperature. After 24 h at room temperature the solvent was removed in a rotary evaporator and the residue, a wine-red solid, triturated with PE/EA (20:1) and washed with the same solvent (2 x 10 mL). The wine-red solid (2.70 g, 88% 12a) decomposed on heating for the determination of the melting point at ca. 100°C.

IR (KBr): 3065, 2980, 2220 (CN), 1455, 1435, 1410, 1380, 1360, 1285, 1265, 1240 cm⁻¹; UV/Vis (acetonitrile): λ_max (lg ε) = 257 (shoulder, 4.29), 262 (4.28), 273 (4.20), 343 nm (4.06); Anal. Calcd. for C₁₆H₁₂N₄OS (308.4): C 62.32, H 3.92, N 18.17, S 10.40. Found C 61.84, H 3.86, N 17.83, S 10.40, 10.29, 10.49, 10.59. MS (EI, 20 eV) m/z (%): 180 (100, [M⁺ from (8b)]), 179 (47), 152 (4), 11 (20), 136 (5), 135 (5), 121 (5), 105 (2), 91 (3); MS (EI, 70 eV) m/z (%): 180 (62, [M⁺ from (8b)]), 151 (54), 135 (35), 128 (100) [M⁺ from TCNE], 119 (24), 91 (67), 76 (69), 27 (26).

Interpretation of the mass spectra (Figure S7 and S8)

In the EIMS of 12a the molecular ion could not be detected, even at 20 eV ionization energy. It is well known that many Diels-Alder adducts suffer [4+2] cycloelimination of the molecular ion, in other words by retro-DAR. Specially, the parent unsaturated hydrocarbon, i.e. spiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane) (13a) is cleaved on electron impact ionization (70 eV) with formation of ethene and the cation of the spirodiene 1 (98%, M⁺ – C₂H₄) followed by loss of a hydrogen atom (100%, M⁺ – C₂H₄ – H); the peak of the molecular ion (M⁺ from 1) is weak.
(2%).¹ [4 + 2] Cycloadducts of 1 with acrylonitrile and similar dienophiles behave in an analogous manner.² In the case of 12a, obviously tetracyanoethylene and the cation of spiroester 8 (m/z = 180) are formed. At 20 eV this gives the base peak (100%). The peak for the expected³ McLafferty rearrangement of 12⁺ (m/z = 152) was not found, but instead a peak at m/z = 151 (20% at 20 eV), possibly the radical cation of the corresponding thio dicarboxylic acid. A weak peak at m/z = 135/136 (ca. 5%) is consistent with the expected loss of C₂H₄O (acetaldehyde) and subsequent loss of a hydrogen atom.³ At 70 eV ionization energy the base peak in the MS at m/z = 128 (100%) indicates the radical ion from tetracyanoethylene, the second product of the retro-DAR.

5. Ethyl 2,2,3,3-tetracyanoisopropyl[bicyclo[2.2.1]hept-5-ene-7,1’-cyclopropane]-1-carboxylate (12b): To a stirred ice-cooled solution of 10b (2.46 g, 15.0 mmol) in dry acetonitrile (15 mL), TCNE (1.28 g, 10.0 mmol), dissolved in dry acetonitrile (15 mL), was added dropwise; a red color developed which gradually faded (CT-complex?). The ice-bath was removed and stirring continued for 24 h. The solvent was distilled off in a rotary evaporator, and the remaining solid washed out with tert-butylmethyl ether (50 mL), filtered off and washed with tert-butylmethyl ether (2 × 10 mL). After drying in vacuo a white solid was obtained with mp 148–150°C. Yield 2.27 g (78%) of analytically pure 12b.

IR (KBr): 3145, 3095, 2970, 2885, 2225 (CN), 1725 cm⁻¹ (COOR); Anal. Calcd. for C₁₆H₁₂N₂O₂ (292.3): C 65.75, H 4.14, N 19.16. Found: C 65.64, H 4.06, N 19.10.

6. 1-Hydroxymethylspiro[bicyclo[2.2.1]hept-5-ene-7,1’-cyclopropane]-2,2,3,3-tetracarbonitrile (12c): TCNE (0.64 g, 5.0 mmol) in dry acetonitrile (7 mL) was allowed to react with 11 (0.85 g, 7.0 mmol) in dry acetonitrile (5 mL) at room temperature for 14 h, as described for 12a (from 8a). The white solid cycloadduct (12c, 1.10 g, 88%) turned brown at ca. 175°C and decomposed at a mp determination.

IR (KBr): 3585, 3505 (OH), 3065, 3010, 2930, 2875 (CH), 2235 cm⁻¹ (CN); Anal. Calcd. for C₁₄H₁₀N₂O (250.3): C 67.19, H 4.03, N 22.39. Found C 67.27, H 4.14, N 22.28.

7. Diels-Alder reaction between 2-chloroacrylonitrile and spiro[2.4]hepta-4,6-diene-4-methanol (11): 2-Chloro-1-hydroxymethylspiro[bicyclo[2.2.1]hept-5-ene-7,1’-cyclopropane]-2-carbonitrile (14a) and 3-Chloro-1-hydroxymethylspiro[bicyclo[2.2.1]hept-5-ene-7,1’-cyclopropane]-3-carbonitrile (14b): Alcohol 11 (1.83 g, 15.0 mmol) and 2-chloroacrylonitrile (1.75 g, 20.0 mmol) were dissolved in dry benzene (10 mL) and heated to 80°C with magnetic stirring for

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¹ Hätel, M.; Klärner F.-G. unpublished results; Härtel, M. Vertiefungsarbeit, Universität GH Essen, 1994. — We thank Prof. Klärner for communicating the spectroscopic data to us (11.08.1998).


22 h. The solvent was removed under reduced pressure and the brown suspension (2.8 g) taken up in dichloromethane (5 mL). Chromatographic separation on silica (250 g) with PE/EA (3:2) gave a white solid (14a) (1.79 g, 57%) with mp 177–178°C. Evaporation of the second fraction gave a slighty yellow liquid (80 mg) that was not pure; according to the \(^1\)H NMR spectrum (vide infra), the liquid contained mostly 14b (80 mg, ca. 2.5% yield). No crystals and no satisfying combustion analysis could be obtained.

8. Data from \(^1\)H NMR and \(^{13}\)C NMR spectra with peak assignments

**Methyl cis-7-mercaptopspiro[2.4]hept-5-ene-4-carboxylate (7a)**

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.82–1.12\) (m, 4H, 1-CH\(_2\) and 2-CH\(_2\)); 1.95 (d, \(^3\)J\(_{SH, 7H}\) = 10.7 Hz, 1H, -SH); 3.13 (m, dd?, appearing as a t, line distance 2.2 Hz, 1H, 4-H); 3.34 (m, appearing as a dq, \(^3\)J\(_{7H, SH}\) = 10.7 Hz, \(J = 1.1–1.3\) Hz, 1H, 7-H); 3.69 (s, 3H, OCH\(_3\)); 5.80 (m, 1H, 6-H); 6.20 (m, 1H, 5-H).

\(^{13}\)C NMR/DEPT (62.9 MHz, CDCl\(_3\)): \(\delta = 10.3\) (CH\(_2\)), 20.7 (CH\(_2\)) [C-1 and C-2], 30.5 (C\(_q\)) [C-3], 51.95 (CH), 53.15 (CH) [C-4 and C-7], 57.5 (CH\(_3\)) [OCH\(_3\)], 128.0 (CH), 138.8 (CH) [C-5 and C-6], 173.8 (C\(_q\)) [C=O].

**O-Methyl spiro[2.4]hepta-4,6-diene-4-thiocarboxylate (8a)**

\(^1\)H NMR (250 MHz, CDCl\(_3\)): AA’BB’ sub-spectrum with mirror-symmetric lines, centered at \(\delta = 2.11\) with gravity centers at \(\delta = 1.83\) and \(\delta = 2.40\) (1-CH\(_2\) and 2-CH\(_2\)); \(\delta = 4.07\) (s, 3H, OCH\(_3\)); ABX sub-spectrum with 8+4 = 12 lines and the calculated parameters \(\delta_A = 6.52\) (7-H), \(\delta_B = 6.57\) (6-H), \(\delta_X = 7.67\) (5-H), \(J_{AB} = 3J_{6,7} = 5.0\) Hz, \(J_{AX} = 4J_{5,7} = 1.8\) Hz, \(J_{BX} = 3J_{5,6} = 2.8\) Hz.

\(^{13}\)C NMR/DEPT (62.9 MHz, CDCl\(_3\)): \(\delta = 18.7\) (CH\(_2\)) [C-1 and C-2], 38.85 (C\(_q\)) [C-3], 56.9 (CH\(_3\)) [OCH\(_3\)], 127.0 (CH) [C-6], 139.7 (CH) [C-7], 144.6 (C\(_q\)) [C-4], 151.6 (CH) [C-5], 203.95 (C\(_q\)) [C=S].

**Ethyl cis-7-mercaptopspiro[2.4]hept-5-ene-4-carboxylate (7b)**

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.82–1.12\) (m, 4H, 1-CH\(_2\) and 2-CH\(_2\)); 1.27 (t, \(J = 7.1\) Hz, 3H, OCH\(_2\)CH\(_3\)); 1.97 (d, \(^3\)J\(_{SH, 7H}\) = 10.8 Hz, 1H, -SH); 3.11 (m, dd?, appearing as a t, line distance 2.2 Hz, 1H, 4-H); 3.32 (m, appearing as a dq, \(^3\)J\(_{7H, SH}\) = 10.8 Hz, \(J = 1.3\) Hz, 1H, 7-H); 4.15 (m, 2H, diastereotopic OCH\(_2\)CH\(_3\)); 5.80 (m, 1H, 6-H); 6.19 (m, 1H, 5-H).

\(^{13}\)C NMR/DEPT (62.9 MHz, CDCl\(_3\)): \(\delta = 10.2\) (CH\(_2\)), 20.8 (CH\(_2\)) [C-1 and C-2], 14.3 (CH\(_3\)) [OCH\(_2\)-CH\(_3\)], 30.5 (C\(_q\)) [C-3], 53.2 (CH), 57.8 (CH) [C-4 and C-7], 60.8 (CH\(_2\)) [OCH\(_2\)-CH\(_3\)], 128.1 (CH), 138.8 (CH) [C-5 and C-6], 173.3 (C\(_q\)) [C=O].

**O-Ethyl spiro[2.4]hepta-4,6-diene-4-thiocarboxylate (8b)**

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 1.41\) (t, 3H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\)); AA’BB’ sub-spectrum with mirror-symmetric lines, centered at \(\delta = 2.11\) with gravity centers at \(\delta = 1.82\) and \(\delta = 2.39\) (1-CH\(_2\)).
and 2-CH₂); δ = 4.53 (q, J = 7.1 Hz, 2H, OCH₂CH₃); ABX sub-spectrum with 8+4 = 12 lines and the calculated parameters δₐ = 6.50 (7-H), δₐ = 6.57 (6-H), δₓ = 7.70 (5-H), Jₓₓ = 3Jₐ,b = 5.0 Hz, Jₐₙₚ = 4Jₐₕ,ₗ = 1.8 Hz, Jₐₚₚ = 3Jₐₕ,ₗ = 2.8 Hz.

¹³C NMR/DEPT (62.9 MHz, CDCl₃): δ = 13.8 (CH₃) [OCH₂CH₃], 18.45 (CH₂) [C-1 and C-2], 38.6 (Cₐ) [C-3], 66.0 (CH₂) [OCH₂CH₃], 127.1 (CH) [C-6], 140.4 (CH) [C-7], 144.95 (Cₐ) [C-4], 151.3 (CH) [C-5], 203.6 (Cₐ) [C=S].

**Ethyl cis/trans-7-acetoxyspiro[2.4]hepta-5-ene-4-carboxylate (9b)**

*First eluted diastereomer: trans-(9b):* ¹H NMR (250 MHz, CDCl₃): δ = 1.00–0.67 (m, 4H, cyclopropane-H), 1.25 (t, J = 7.1 Hz, 3H, CH₂CH₃), 2.04 (s, 3H, CH₃), 3.66 (d, J = 2.0 Hz, 1H, 4-H), 4.13 (q, J = 7.1 Hz, 2H, CH₂CH₃), 5.49 (m, dd?, appearing as a t, line distance 1.9 Hz, 1H, 7-H), 6.08–6.04 (m, 1H, 6-H or 5-H), 6.18–6.15 (m, 1H, 5-H or 6-H).

¹³C NMR/DEPT (62.9 MHz, CDCl₃): δ = 9.15 (CH₂), 11.8 (CH₂) [C-1 and C-2], 14.3 (CH₃) [CH₂CH₃], 21.1 (CH₃) [CH₃CO], 27.1 (Cₐ) [C-3], 55.7 (CH) [C-4], 60.7 (CH₂) [CH₂CH₃], 83.8 (CH) [C-7], 132.6 (CH), 135.7 (CH) [C-5 and C-6], 170.9 (Cₐ), 172.05 (Cₐ) [C=O].

*Second eluted diastereomer: cis-(9b):* ¹H NMR (250 MHz, CDCl₃): δ = 0.75–1.01 (m, 4H, cyclopropane-H), 1.26 (t, J = 7.1 Hz, 3H, CH₂CH₃), 2.04 (s, 3H, CH₃), 3.15 (t, J = 2.1 Hz, 1H, 4-H), 4.18–4.12 (partially covered quartet, J = 7.1 Hz, 2H, CH₂CH₃), 5.30 (d, J = 2.3 Hz, 1H, 7-H), 6.13–6.09 (m, 1H, 6-H or 5-H), 6.21–6.15 (m, 1H, 5-H or 6-H).

¹³C NMR/DEPT (62.9 MHz, CDCl₃): δ = 7.1 (CH₂), 16.8 (CH₂) [C-1 and C-2], 14.3 (CH₃) [CH₂CH₃], 21.2 (CH₃) [CH₃CO], 27.5 (Cₐ) [C-3], 56.8 (CH) [C-4], 60.7 (CH₂) [CH₂CH₃], 84.1 (CH) [C-7], 132.6 (CH), 135.8 (CH) [C-5 and C-6], 171.2 (Cₐ), 172.1 (Cₐ) [C=O].

**Assignment of the diastereomers**

The diastereomers (cis/trans isomers) differ by the carbon resonances of the cyclopropane methylene carbon atoms (δ (¹³C) = 7.1 and 16.8 vs 9.15 and 11.8 ppm, respectively), whereas the other carbon resonances are close to one another. We tentatively assign the epimer with the high-field chemical shift (δ (¹³C) = 7.1) to the cis-diastereomer (cis-9b). In agreement with this assignment, the 4-H resonance of the cis mercapto ester 7b in the proton NMR spectrum (δ = 3.11) is close to
the resonance of \textit{cis-9b} (δ = 3.15). The second diastereomer (\textit{trans-9b}) shows a downfield shift of the 4-H (δ = 3.66), consistent with a deshielding effect by the acetoxy group at C-7, which is \textit{trans}, but \textit{cis to the hydrogen atom} at C-4. The same trend, but with a weaker effect, is observed for the 7-H of the epimers (δ = 5.30 vs 5.49).

**Methyl spiro[2.4]hepta-4,6-diene-4-carboxylate (10a)**

$^1$H NMR (250 MHz, CDCl$_3$): AA′BB′ sub-spectrum with mirror-symmetric lines, centered at δ = 2.00 with gravity centers at δ = 1.78 and 2.21 (4H, 1-CH$_2$ and 2-CH$_2$); δ = 3.73 (s, 3H, OCH$_3$); ABX sub-spectrum with 8 + 3 = 11 lines and the calculated parameters δ$_A$ = 6.44 (7-H), δ$_B$ = 6.55 (6-H), δ$_X$ = 7.45 (5-H), $J_{AB} = 3J_{6,7} = 5.0$ Hz, $J_{AX} = 4J_{5,7} = 1.7$ Hz, $J_{BX} = 3J_{5,6} = 2.6$ Hz.

$^{13}$C NMR/DEPT (62.9 MHz, CDCl$_3$): δ = 16.5 (CH$_2$) [C-1 and C-2], 38.4 (C$_q$) [C-3], 50.6 (CH$_3$) [OCH$_3$], 127.1 (CH) [C-6], 136.6 (C$_q$) [C-4], 140.4 (CH) [C-7], 148.6 (CH) [C-5], 163.3 (C$_q$) [C=O].

**Ethyl spiro[2.4]hepta-4,6-diene-4-carboxylate (10b)**

$^1$H NMR (250 MHz, CDCl$_3$): δ = 1.30 (t, $J = 7.1$ Hz, 3H, OCH$_2$CH$_3$); AA′BB′ sub-spectrum with mirror-symmetric lines, centered at δ = 2.00 with gravity centers at δ = 1.78 and 2.22 (1-CH$_2$ and 2-CH$_2$); δ = 4.19 (q, $J = 7.1$ Hz, 2H, OCH$_2$CH$_3$); ABX sub-spectrum with 8+3 = 11 lines and the calculated parameters δ$_A$ = 6.43 (7-H), δ$_B$ = 6.56 (6-H), δ$_X$ = 7.46 (5-H), $J_{AB} = 3J_{6,7} = 5.0$ Hz, $J_{AX} = 4J_{5,7} = 1.7$ Hz, $J_{BX} = 3J_{5,6} = 2.6$ Hz.

$^{13}$C NMR/DEPT (62.9 MHz, CDCl$_3$): δ = 14.4 (CH$_3$) [OCH$_2$-CH$_3$], 16.6 (CH$_2$) [C-1 and C-2], 38.5 (C$_q$) [C-3], 59.5 (CH$_2$) [OCH$_2$-CH$_3$], 127.2 (CH) [C-6], 137.1 (C$_q$) [C-4], 140.4 (CH) [C-7], 148.6 (CH) [C-5], 163.1 (C$_q$) [C=O].

**Spiro[2.4]hepta-4,6-diene-4-methanol (11)**

$^1$H NMR (250 MHz, CDCl$_3$): δ = 1.66 (m, with mirror-symmetry, 4H, evidently an AA′BB′ sub-spectrum of the cyclopropane -CH$_2$CH$_2$- protons, 1-CH$_2$ and 2-CH$_2$); 1.91 (s, 1H, OH); 4.17 (s, 2H, CH$_2$OH); 6.10 (m, 1H, 7-H?); 6.46 (2H, 5-H and 6-H). The signal at δ = 1.91 disappeared after shaking the sample with D$_2$O.

$^1$H NMR (250 MHz, C$_6$D$_6$): AA′BB′ sub-spectrum with mirror-symmetric lines, centered at δ = 1.64 with centers of gravity at δ = 1.53 and δ = 1.74 (1-CH$_2$ and 2-CH$_2$); δ = 2.51 (br s, 1H, OH); 4.23 (d, $J = 2.6$ Hz, 2H, CH$_2$OH); 6.16 (m, 1H), 6.61 (m, 1H) and 6.70 (m, 1H), evidently an AMX spectrum with 9 lines resulting from the protons 5-H, 6-H and 7-H. The approximately calculated parameters are δ$_A$ = 6.16 (7-H?), δ$_B$ = 6.61 (5-H?), δ$_X$ = 6.71 (6-H?), $J_{AX} = 3J_{6,7} = 5.15$ Hz, $J_{AM} = 4J_{5,7} = 1.6$ Hz, $J_{MX} = 3J_{5,6} = 2.25$ Hz.

$^{13}$C NMR/DEPT (62.9 MHz, CDCl$_3$): δ = 13.7 (CH$_3$) [C-1 and C-2], 37.15 (C$_q$) [C-3], 58.4 (CH$_2$) [CH$_2$-OH], 127.8 (CH), 128.05 (CH) [C-5 and C-6], 140.4 (CH) [C-7], 148.0 (C$_q$) [C-4].
O-Ethyl 2,2,3,3-tetracyanospiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane)-1-thiocarboxylate (12a)

$^1$H NMR (250 MHz, CD$_3$CN): $\delta = 0.85$ (m, 1H, 2'-H on the cyclopropane ring); 1.20 (m, 2H, 3'-H on the cyclopropane ring); 1.31–1.48 (m, 4 H, 2'-H and -OCH$_2$CH$_3$, the latter at $\delta = 1.45$ (t, $J = 7$ Hz); 3.74 (m, line distance 2.2 Hz, 1H, presumably the X-part of an ABX sub-system, 4-H); 4.64 (q, $J = 7.0$ Hz, 2H, OCH$_2$CH$_3$); 6.81–6.90 (m, presumably the AB part of an ABX sub-spectrum with 4 stronger lines, 2H, 5-H and 6-H).

$^{13}$C NMR/DEPT (62.9 MHz, CD$_3$CN): $\delta = 4.55$ (CH$_2$) [C-2'], 10.8 (CH$_2$) [C-3'], 12.5 (CH$_3$) [CH$_2$-CH$_3$], 45.8 (C$_q$) [C-7], 48.6 (C$_q$), 51.8 (C$_q$) [C-2 and C-3], 59.9 (CH) [C-4], 70.6 (CH$_2$) [CH$_2$-CH$_3$], 74.5 (C$_q$) [C-1], 110.9 (C$_q$), 111.6 (C$_q$), 111.8 (C$_q$), 112.0 (C$_q$) [CN], 141.05 (CH), 141.2 (CH) [C-5 and C-6], 207.55 (C$_q$) [C=S].

Ethyl 2,2,3,3-tetracyanospiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane)-1-carboxylate (12b)

$^1$H NMR (250 MHz, CD$_3$CN): $\delta = 0.83$ (m, 1H, 2'-H, anti?), 1.05–1.30 (m, 3H, 2’-H- syn? and 3'-H); 1.32 (t, $J = 7.1$ Hz, 3H, OCH$_2$CH$_3$); 3.765 (4 lines from the X part of an ABX sub-spectrum, 1H, 4-H); 4.35 (m, 2H, diastereotopic OCH$_2$CH$_3$); AB part (8 lines from an ABX sub-spectrum with the parameters $\delta_A = 6.81$ (6-H), $\delta_B = 6.92$ (5-H), $J_{AB} = 3J_{5,6} = 5.8$ Hz, $J_{AX} = 4J_{4,6} = 1.0$ Hz, $J_{BX} = 3J_{4,5} = 3.2$ Hz).

$^{13}$C NMR/DEPT (62.9 MHz, CD$_3$CN): $\delta = 5.0$ (CH$_2$) [C-2'], 11.6 (CH$_2$) [C-3'], 14.1 (CH$_3$) [CH$_2$CH$_3$], 45.9 (C$_q$) [C-7], 48.9 (C$_q$), 51.0 (C$_q$) [C-2 and C-3], 60.4 (CH) [C-4], 64.3 (CH$_2$) [CH$_2$CH$_3$], 69.5 (C$_q$) [C-1], 111.8 (C$_q$), 111.4 (C$_q$), 112.6 (C$_q$), 112.7 (C$_q$) [CN], 139.65 (CH), 140.7 (CH) [C-5 and C-6], 165.7 (C$_q$) [COOR].

1-Hydroxymethylspiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane)-2,2,3,3-tetracarbonitrile (12c)

$^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.70$ (m, 2H, 2'-H), 1.10 (m, 2H, 3'-H); 3.66 (m, 2H, 4-H and OH), 3.82 (m, 2H, CH$_2$OH); AB part (8 lines) from an ABX sub-spectrum with the parameters $\delta_A = 6.79$ (5-H), $\delta_B = 6.84$ (6-H), $\delta_X = ca. 3.66$ (vide supra), $J_{AB} = 3J_{5,6} = 5.8$ Hz, $J_{AX} = 4J_{4,6} = 0.8$ Hz, $J_{BX} = 3J_{4,5} = 3.2$ Hz. — After shaking the sample with D$_2$O the integral of the signal at $\delta = 3.66$ was reduced by half, approximately. A signal with 4 lines appeared ($\delta = 3.68$), apparently the X part (4-H) of an ABX sub-spectrum of the protons 4-H, 5-H and 6-H. From the outer lines of the X part $|J_{AX} + J_{BX}| = 4.0$ Hz was derived, consistent with the sum of the coupling constants $^4J_{4,6} = 0.8$ Hz and $^3J_{4,5} = 3.2$ Hz.

$^{13}$C NMR/DEPT (62.9 MHz, CDCl$_3$): $\delta = 3.75$ (CH$_2$) [C-2'], 10.7 (CH$_2$) [C-3'], 44.7 (C$_q$) [C-7], 49.1 (C$_q$), 51.0 (C$_q$) [C-2 and C-3], 57.7 (CH$_2$) [CH$_2$OH], 60.5 (CH) [C-4], 67.35 (C$_q$) [C-1], 111.9 (C$_q$), 113.05 (C$_q$), 113.1 (C$_q$), 113.2 (C$_q$) [CN], 139.0 (CH), 141.1 (CH) [C-5 and C-6].
2-Chloro-1-hydroxymethylspiro[bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane]-2-carbonitrile (14a)

$^1$H NMR (250 MHz, CDCl$_3$): δ = 0.59 (m, 2H, 2'-H), 0.89 (m, 2H, 3'-H), 2.03 (br s, 1H, OH), 1.97 (d, $J = (-)$ 13.0 Hz, 1H, 3n-H), A part of an AMX sub-spectrum with the parameters δ$_A$ = 1.97 (3n-H), δ$_M$ = 2.44 (4-H), δ$_X$ = 2.98 (3x-H), $J_{AX} = 2J_{3n,3x} = (-)$ 13.0 Hz, $J_{AM} = 3J_{3n,4} = 0$, $J_{MX} = 3J_{3x,4} = 3.9$ Hz; AB sub-spectrum with δ$_A$ = 3.87 and δ$_B$ = 4.12, centered at δ = 4.00, $J_{AB} = (-)$ 12.0 Hz (diastereotopic CH$_2$OH); AB part of an ABX sub-spectrum with the parameters δ$_A$ = 6.21 (6-H), δ$_B$ = 6.56 (5-H), 6x = ca. 2.44 (4-H) (see above), $J_{AB} = 3J_{5,6} = 5.8$ Hz, $J_{AX} = 4J_{4,5} = 0$ Hz, $J_{BX} = 3J_{4,5} = 3.1$ Hz. — The br s at δ = 2.03 disappeared after shaking the sample with D$_2$O.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 0.59 (m, 2H, 2'-H), 0.82 (m, 1H, 3'-H), 0.95 (m, 1H, 3'-H) 2.06 (br s, 1H, OH), 1.97 (d, $J_{3n,3x} = 13.0$ Hz, 1H, 3n-H), 2.45 (dd, appearing as a t, line distance 3.5 Hz, corresponds to $3J_{3x,4} = 3J_{4,5}$, 1H, 4-H), 2.98 (dd, $J_{3n,3x} = 13.0$ Hz, $J_{3x,4} = 3.9$ Hz, 3x-H), 3.87 (d, $J = 11.9$ Hz, 1H) and 4.12 (d, $J = 11.9$ Hz, 1H), diastereotopic CH$_2$OH (AB sub-spectrum with δ$_A$ = 3.87 and δ$_B$ = 4.12, centered at δ = 4.00, $J_{AB} = 11.9$ Hz); 6.225 (d, $J = 5.8$ Hz $J_{5,6} = 5.8$ Hz, 1H, 6-H), 6.56 (dd, $J_{5,6} = 5.8$, $J_{4,5} = 3.1$ Hz, 1H, 5-H).

$^{13}$C NMR/DEPT (62.9 MHz, CDCl$_3$): δ = 5.2 (CH$_2$) [C-2'], 8.0 (CH$_2$) [C-3'], 44.9 (C$_q$) [C-7], 48.4 (CH$_2$) [C-3], 48.8 (CH) [C-4], 58.0 (CH$_2$) [CH$_2$-OH], 58.8 (C$_q$), 62.9 (C$_q$) [C-1 and C-2], 119.7 (C$_q$) [CN], 133.7 (CH), 139.3 (CH) [C-5 and C-6].

3-Chloro-1-hydroxymethylspiro[bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane]-3-carbonitrile (14b, impure substance)

$^1$H NMR (250 MHz, CDCl$_3$): δ = 0.24–0.99 (m, 2'-H and 3'-H), due to overlap with signals of by-products, the integral could not be evaluated; 1.77 (br s, 1H, OH), 1.92 (d, 1H, $J = 13.0$ Hz = $J_{2,2} = (-)$ 13.0 Hz, A part of an AB sub-spectrum, 2n-H (?); 2.79 (d, $J = 13.0$ Hz, B part of an AB sub-spectrum, $J_{2,2} = (-)$ 13.0 Hz, 1H, 2x-H(?)), 2.92 (m, 1H, 4-H), 3.64 (m, 2H, diastereotopic CH$_2$-OH), 6.31 (double A part of an ABX sub-spectrum, $J_{AB} = 3J_{5,6} = 5.8$ Hz, $J_{4,5} = 3.1$ Hz, 1H, 5-H); 6.48 (double B part of an ABX sub-spectrum, $J_{AB} = 3J_{5,6} = 5.8$ Hz, $J_{4,6} = 0.6$ Hz, 1H, 6-H).

$^{13}$C NMR/DEPT (62.9 MHz, CDCl$_3$): δ = 4.1 (CH$_2$) [C-2'?], 8.5 (CH$_2$) [C-3'?], 45.5 (C$_q$) [C-7], 48.55 (CH$_2$) [CH$_2$-OH], 55.9 (C$_q$), 56.45 (C$_q$) [C-1 and C-3], 60.0 (CH$_2$) [C-2], 60.7 (CH) [C-4], 121.0 (C$_q$) [CN], 132.8 (CH), 140.4 (CH) [C-5 and C-6].

2-Chloro-1-hydroxymethylspiro[bicyclo[2.2.1]heptane-7,1'-cyclopropane]-2-carbonitrile (15)

$^1$H NMR (250 MHz, CDCl$_3$): δ = 0.50 (m, 1H, 2'-H$_b$?), 0.74 (m, 2H, 2'-H$_b$ + 3'-H$_a$?), 0.95 (m, 1H, 3'-H$_b$?), 1.50 (m, appearing as a t, $J = 7$-9 Hz, 1H, 5x-H?), 1.66 (m, 1H, 4-H?), 1.82–2.13 (m, 4 H, 5n-H, 6n-H, 6x-H + OH) surmounted by a d at δ = 2.00, $J = 13.8$ Hz, 3n-H), 2.23 (m, appearing as a t, $J = ca. 9$ Hz, 1H), 2.90 (m, appearing as a ddd, $J = 13.8$ Hz, $J = 4.8$ Hz, $J = 2.3$ Hz, 1H, 3x-H), AB sub-spectrum with δ$_A$ = 3.64 and δ$_B$ = 3.83, centered at δ = 3.74 ($J_{AB} = 11.9$ Hz, 2H, diastereotopic HOCH$_2$-). — After shaking the sample with D$_2$O the multiplet at δ = 1.82–2.13 be-
came better resolved and its integral was reduced to approximately 75% (3H, replacement of OH by OD).

$^{13}$C NMR/DEPT (62.9 Hz, CDCl$_3$): $\delta = 4.6$ (CH$_2$), 5.7 (CH$_2$) [C-2' and C-3'], 26.1 (CH$_2$), 27.8 (CH$_2$) [C-5 and C-6], 35.4 (C$_q$) [C-7], 43.1 (CH) [C-4], 49.25 (CH$_2$) [C-3], 55.4 (C$_q$) [C-2], 60.6 (CH$_2$) [CH$_2$-OH], 61.9 (C$_q$) [C-1], 120.0 (C$_q$) [CN].

1-Hydroxymethylspiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane)-2-one (16)

$^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.41$–0.64 (m, 3H, 2'-H and 3'-H), 0.81 (m, 1H, 3'-H?), 1.48–2.12 (m, 6H), 2.36–2.46 (m, 1H, 3-H?), 2.50 (t, $J = 6.6$ Hz, 1H, OH), 3.57 (m, 2H, diastereotopic HOCH$_2$-). After shaking the sample with D$_2$O the intensity of the triplet at $\delta = 2.50$ was reduced, and the low-field part of the multiplet at 2.36–2.46 (relative intensity 1H) became exposed.

$^{13}$C NMR/DEPT (62.9 Hz, CDCl$_3$): $\delta = 4.4$ (CH$_2$), 4.55 (CH$_2$) [C-2' and C-3'], 26.9 (CH$_2$), 27.3 (CH$_2$) [C-5 and C-6], 35.2 (C$_q$) [C-7], 41.7 (CH) [C-4], 45.4 (CH$_2$) [C-3], 57.7 (C$_q$) [C-1], 59.75 (CH$_2$) [CH$_2$-OH], 219.1 (C$_q$) [C-2].

1-Hydroxymethyl-7,7-dimethylbicyclo[2.2.1]heptan-2-one (rac-10-hydroxycamphor, 17)

$^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.99$ (s, 3H, 8-CH$_3$), 1.02 (s, 3H, 9-CH$_3$) [these assignments may be reversed], 1.39 (m, 1H, 6n-H), 1.58 (m, 1H, 6x-H), 1.80–2.17 (m, 4H, 4-H, 5n-H, 5x-H, surmounted by a d at 1.87, $J = 18.4$ Hz, 3n-H), 2.42 (m, 1H, 3x-H), 2.79 (br s, 1H, OH); AB sub-spectrum with $\delta_A = 3.65$ and $\delta_B = 3.87$, centered at $\delta = 3.76$ ($J_{AB} = 11.9$ Hz, 2H, diastereotopic HOCH$_2$). After shaking the NMR sample with D$_2$O the broad signal at $\delta = 2.79$ vanished.

$^{13}$C NMR/DEPT (62.9 Hz, CDCl$_3$): $\delta = 19.4$ (CH$_3$), 20.8 (CH$_3$) [C-8 and C-9], 25.9 (CH$_2$), 26.7 (CH$_2$) [C-5 and C-6], 43.5 (CH$_2$) [C-3], 44.0 (CH) [C-4], 46.8 (C$_q$) [C-7], 60.4 (CH$_2$) [CH$_2$-OH], 61.7 (C$_q$) [C-1], 220.9 (C$_q$) [C-2].

9. Discussion of the NMR spectra of the cycloadducts 12-14

$^{13}$C NMR spectra

In the $^{13}$C NMR of 12a–c all carbon resonances were evident and could be assigned for the most part by means of the DEPT technique, thus proving the four non-equivalent cyano groups and the functional groups at the bridgehead carbon atom (C-1). Comparison of the $^{13}$C chemical shifts with those of the parent unsaturated hydrocarbon 13a, 12d and other [4+2] cycloadducts of spiro[2.4]hepta-4,6-diene, 10 and 11 shows that the cyano groups exert a pronounced effect on both the resonances of the methylene carbon atoms and of the vinylene group C=C (Table S1). The latter are shifted down-field, though, considering the $\gamma$-effect of the substituents, a high-field shift would we expected.
The chemical shifts of the methylene carbon atoms at the cyclopropane ring differ widely. In bornene, the geminal methyl carbon atoms at C-7 have almost the same chemical shift (δ = 19.6, 19.7) which is almost the same as in the saturated hydrocarbon bornane (δ = 19.2), i.e. the C=C double bond has no influence on the resonance of the methyl groups. In contrast with these bornanes, for the methylene carbon atoms at C-7 in spiro(bicyclo[2.2.1]hept-5-ene-7,1′'-cyclopropane) (13a, C-2′ and C-3′) different chemical shifts were observed (Δδ = 1.4 ppm), presumably reflecting the special electronic structure (cyclopropyl homoconjugation) of the spiro hydrocarbon. The carbon syn to the C=C double bond absorbs at lower field strength (δ = 7.7 ppm) than the anti (δ = 6.3 ppm).

In the TCNE cycloadducts 12a-c this trend is increased: Compared with the parent unsaturated hydrocarbon 13a, one of the methylene carbon atoms of the cyclopropane ring resonates at low field strength, i.e. is strongly deshielded, whereas the other is shifted to high field. The same phenomenon is seen with the simple tetracarbonitrile 12d (Δδ = 6.2–7.8 ppm). Obviously the cyano groups exert a strong effect on the electronic structure of the unsaturated spiro system which is reflected in the NMR spectra.

![Diagram of chemical structures](image)

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Table S1. Selected Chemical Shifts ($\delta^{(13}C)$) from the $^{13}$C NMR spectra of Spiro(bicyclo[2.2.1]hept-5-ene-7,1′-cyclopropanes) (12, 13 and 14).

<table>
<thead>
<tr>
<th></th>
<th>C-2'</th>
<th>C-3'</th>
<th>C-7</th>
<th>C-5, C-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>7.64</td>
<td>5.95</td>
<td>43.81</td>
<td>135.42, 135.42 $^b$</td>
</tr>
<tr>
<td>12d</td>
<td>4.68</td>
<td>12.67</td>
<td>44.85</td>
<td>139.84, 139.84</td>
</tr>
<tr>
<td>12a</td>
<td>4.55</td>
<td>10.79</td>
<td>45.76</td>
<td>141.05, 141.24</td>
</tr>
<tr>
<td>12b</td>
<td>5.00</td>
<td>11.58</td>
<td>45.94</td>
<td>139.65, 140.72</td>
</tr>
<tr>
<td>12c</td>
<td>3.75</td>
<td>10.70</td>
<td>44.66</td>
<td>139.02, 141.08</td>
</tr>
<tr>
<td>14a</td>
<td>5.21</td>
<td>8.02</td>
<td>44.91</td>
<td>133.66, 139.28</td>
</tr>
<tr>
<td>14b</td>
<td>4.08</td>
<td>8.49</td>
<td>45.54</td>
<td>132.82, 140.41</td>
</tr>
</tbody>
</table>

$^a$ Ref. 1 (Härtel and Klärner), solvent CDCl$_3$; cf. also ref. 6 (Kazimirchik and Lukin): $\delta = 7.7, 6.3, 43.8, 135.1, 135.1$, solvent not specified (CDCl$_3$ or CCL$_4$). $^b$ corresponds to C-2 and C-3 of the hydrocarbon 13a. $^c$ solvent CDCl$_3$. $^d$ solvent CD$_3$CN.

**$^1$H NMR spectra**

The hydrogen atoms 4-H, 5-H and 6-H of the unsaturated spirotricycles generate an ABX proton sub-spectrum; in the case of 12b and 12c all 12 lines were detected in the 250 MHz $^1$H NMR. The values of the coupling constants (see above and/or Table S2) agree with those reported for another spirobicyclo[2.2.1]hept-5-ene-7,1′-cyclopropane compound (13b)$^2$ and are close to the typical values derived from many norbornenes (with no spirocyclopropane ring).$^8$ The protons 4-H, 5-H and 6-H of 12a generate a deceptively simple sub-spectrum and therefore the coupling constants could not be calculated in this case. Due to the neighbor chiral bridgehead centers the ethoxycarbonyl- and the hydroxymethyl-substituents in 12b and 12c, respectively, show diastereotopic CH$_2$-protons, giving rise to multiplets (in 12a the usual quartet is observed).

Compared with spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) 13a ($\delta$(CH$_2$) = 0.27 (syn protons, i.e. H$_2$C-2′) and 0.42 (anti protons, i.e. H$_2$C-3′))$^1$ (for the spiro-diene, i.e. spiro(bicyclo[2.2.1]hepta-2,5-diene-7,1′-cyclopropane), $\delta$(CH$_2$) = 0.50,$^1$ see also ref.$^9$) the cyclopropane protons are distinctly deshielded, giving rise to multiplets with different chemical shift centers (Table S2). Deshielding is observed also with the olefinic protons 5-H and 6-H.

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Table S2. Selected Chemical Shifts ($\delta(^1\text{H)}, \text{ppm})$ and Coupling Constants ($J \text{ [Hz]}$) from the $^1\text{H}$ NMR spectra of Spiro(bicyclo[2.2.1]hept-5-ene-7,1'-cyclopropanes) (12-14).

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ ($^1\text{H})$</th>
<th>$\delta$ (=C-H)</th>
<th>$^3J_{4,5}$</th>
<th>$^4J_{4,6}$</th>
<th>$^3J_{5,6}$</th>
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</thead>
<tbody>
<tr>
<td>13a</td>
<td>0.27 (mc, syn); 0.46 (mc, anti)</td>
<td>6.10</td>
<td>— b</td>
<td>— b</td>
<td>— b</td>
</tr>
<tr>
<td>12d</td>
<td>0.72–0.79; 1.12–1.18</td>
<td>6.76</td>
<td>ca. 2.0</td>
<td>— b</td>
<td>— b</td>
</tr>
<tr>
<td>12a</td>
<td>0.78–0.91; 1.14–1.25</td>
<td>6.81–6.90</td>
<td>2.2</td>
<td>2.2</td>
<td>— b</td>
</tr>
<tr>
<td>12b</td>
<td>0.78–0.87; 1.05–1.30</td>
<td>6.81, 6.92</td>
<td>3.2</td>
<td>1.0</td>
<td>5.8</td>
</tr>
<tr>
<td>12c</td>
<td>0.61–0.77; 1.03–1.16</td>
<td>6.79, 6.84</td>
<td>3.2</td>
<td>0.8</td>
<td>5.8</td>
</tr>
<tr>
<td>14a</td>
<td>0.58 (2'-H$<em>\beta$), 0.61 (3'-H$</em>\beta$)</td>
<td>6.22 (6-H)</td>
<td>3.1</td>
<td>1.1</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>0.82 (2'-H$<em>\alpha$), 0.96 (3'-H$</em>\alpha$)</td>
<td>6.56 (5-H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14b</td>
<td>0.65 (mc) – 0.99 (covered)</td>
<td>6.31, 6.48</td>
<td>3.1</td>
<td>0.6</td>
<td>5.8</td>
</tr>
</tbody>
</table>

$^a$ Ref. 1 (Härtel and Klärner), solvent CDCl$_3$. — b not determined. — c solvent CD$_3$CN. — d solvent CDCl$_3$. — mc: center of the multiplet.

On the following pages spectra are reproduced:

10. Figures S1 – S14

Figures of the $^1\text{H}$ NMR spectra of compounds 8a, 8b, 10a, 10b, 11, 12a, 14a, 14b, 15, 16, 17, a $^{13}\text{C}$ NMR spectrum of the impure compound 14b, and mass spectra of the cycloadduct 12a at 20 eV and 70 eV.
Figure S9