164. The Homoconjugated Electron-Releasing Carbonyl Group of 1-Methylbicyclo[2.2.1]hept-5-en-2-one. Regioselective Syntheses of 5-Chloro- and 6-Chloro-1-methylbicyclo[2.2.1]hept-5-en-2-one

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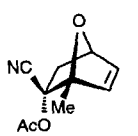
Syntheses of (±)-2-*exo*-cyano-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl acetate (**1**) and of (±)-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2**) are reported. The additon of PhSeCl to **1** afforded (±)-5-*endo*-chloro-2-*exo*-cyano-1-methyl-6-*exo*-(phenylselenenyl)-7-oxabicyclo[2.2.1]hept-2-*endo*-yl acetate (**6**), whereas **2** added to PhSeCl with the opposite regioselectivity giving (±)-6-*endo*-chloro-1-methyl-5-*exo*-(phenylselenenyl)-7-oxabicyclo[2.2.1]heptan-2-one (**7**). These adducts were converted into 5-chloro-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**9**) and 6-chloro-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**10**), respectively.

Introduction. – Recently, *Sneden* [1] has realized the potential of 1-methyl-7-oxabicyclo[2.2.1]heptan-2-one as synthetic intermediate in the total synthesis of natural products of biological interest. His report urges us to unveil our preliminary results on the synthesis of 1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives **1** and **2** and on their reactivity toward soft electrophiles. As we shall see, these olefins also undergo highly regioselective electrophilic additions as in the case of the 'naked sugars' [2] (for recent examples of synthetic applications, see [3]) which do not bear a Me group at the C(1) bridgehead centre.



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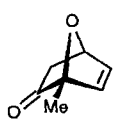

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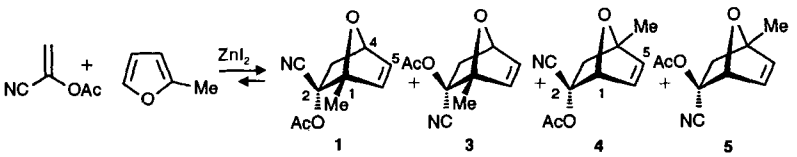
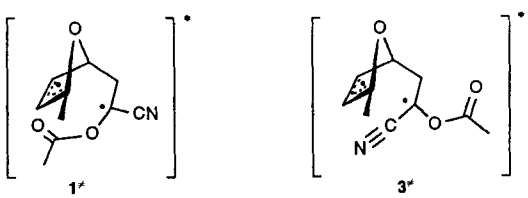
Results and Discussion. – The *Diels-Alder* addition of 1-cyanovinyl acetate to sylvane (= 2-methylfuran) was reported [4] [5] to occur only under high pressure (15 kbar, 37°, 15 h) and to yield a mixture composed mostly of the '*ortho*' adducts **1** and **3** [6]. We found that 1-cyanovinyl acetate in neat sylvane undergoes smooth cycloaddition in the presence of ZnI_2 as catalyst. Following the reaction of a 3:1:33 mixture of 1-cyanovinyl acetate, ZnI_2, and sylvane by ^{1}H-NMR, we observed that the '*ortho-exo*' adduct **1** was formed first ('kinetic adduct'). After one day at 20°, *ca.* 20% of conversion was attained, and pure **1** could be isolated in 16–17% yield, with recovery of the unreacted cycloaddents. After 7 days at 20°, a 11:13:8:1 mixture of the adducts **1**/**3**/**4**/**5** was obtained. When the reaction was run at 0° for 8 days, a 1:1 mixture of the '*ortho*' adducts **1**/**3** (52% yield) was formed. On heating to 50° (or above), rapid equilibration of the adducts **1** and **3**–**5** was reached,

the proportion of the '*ortho*' adducts (**1** + **3**) *vs.* '*meta*' adducts (**4** + **5**) remained close to 1:1, even after prolonged heating. The cycloaddition of 1-cyanovinyl acetate to sylvane was also promoted by *Lewis* acids such as $ZnBr_2$ and $BF_3 \cdot Et_2O$, but less efficiently than with anhydrous ZnI_2.

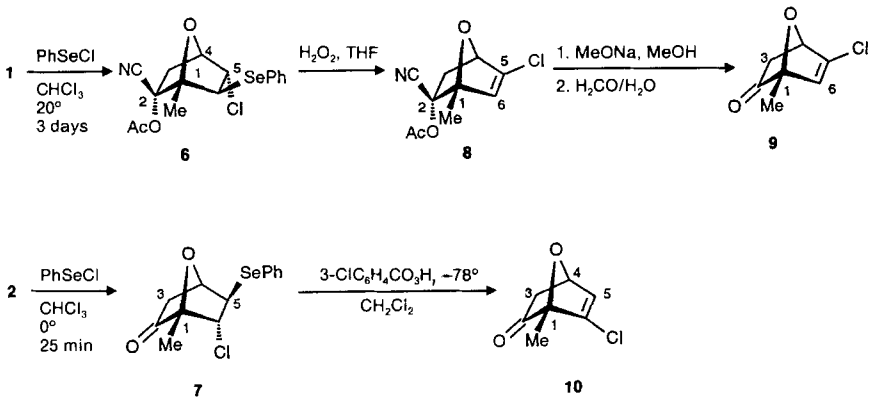


Our results demonstrate that the '*ortho*' adducts **1**/**3** have the same relative stability than the '*meta*' adducts **4**/**5**. Under conditions of kinetic control, **1** is formed faster than **3**, both being formed more rapidly than **4** and **5**. As expected for other *Diels-Alder* additions of 1-methyl-1,3-dienes, the '*ortho*' adducts are favoured for electronic reasons (electron-releasing ability of the Me group) [7]. Less obvious is the observation that adduct **1** with an *exo*-cyano substituent should be formed more rapidly than **3** with the *endo*-cyano group (*endo-Alder* rule [8]). One thus must admit that the AcO group of the dienophile allows for better secondary interactions between the diene and dienophile in the transition state of their cycloaddition, perhaps for conformational reasons, as indicated with the representations **1*** and **3*** for the transition states leading to adducts **1** and **3**, respectively.



In the presence of 1 equiv. of benzeneselenenyl chloride in $CHCl_3$, the cyano-acetate **1** gave a single adduct **6** which was isolated in 88% yield. The reaction required 3 days at 20° to be complete. The ^{1}H-NMR spectrum of the crude reaction mixture showed signals for only one regioisomeric adduct. Enone **2**, obtained in 87% yield by methanolysis of **1** (MeONa, MeOH; 20°, 1 h) followed by treatment with 40% formaldehyde/H_2O (25°, 15 min), was slightly more reactive than **1** toward PhSeCl. In the presence of 1 equiv. of the electrophile in $CHCl_3$, the reaction was complete after 15 h at 20°, and the single adduct **7** was formed quantitatively (^{1}H-NMR spectrum of the crude reaction mixture).

The structures of **1**, **2**, **6**, and **7** were given by their elemental analysis and their spectral data. ^{1}H-NMR Signal assignments were confirmed by double-irradiation experiments and NOE measurements (see *Exper. Part*). The distinction between H_{exo}- and H_{endo}-atoms was based on their coupling constants with the vicinal bridgehead protons [9]. Structures were confirmed by the following transformations. Oxidative elimination of the selenenyl group of **6** with H_2O_2 gave chloroalkene **8** which furnished the chloroenone **9** upon methanolysis. Similarly, adduct **7** underwent smooth oxidative selenenyl elimination to



the regioisomeric chloroenone **10** (79%) on treatment with 1 equiv. of 3-chloroperbenzoic acid in CH_2Cl_2 at −78°. The structures of **9** and **10** were established unambiguously from their ^{1}H-NMR spectra.

Conclusion. – Simple procedures have been developed for the synthesis of 1-methyl-7-oxabicyclo[2.2.1]hept-5-en-yl derivatives. Depending on the nature of the substituents at C(2), the electrophilic addition of their olefinic moiety can be highly regioselective. As for similar, but 1-unsubstituted homoconjugated bicyclic enones [2], the carbonyl group in 1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**2**) activates the electrophilic additions and behaves as an electron-releasing moiety, the Me substituent at the C(1)-bridgehead centre remaining a 'silent spectator'. Assuming that the methologies already developed for the 'naked sugars' [2] can be applied to compounds **1** and **2**, these systems should become useful starting materials in the total synthesis of 7-deoxyheptoses and analogues [10], 2-*C*-methyl and 5-*C*-methyl-2,5-anhydrohexonic-acid derivatives [11], and Me-substituted cyclitols and analogues [12].

We thank the *Swiss National Science Foundation*, Bern, *F. Hoffmann-La Roche AG*, Basel, and the *Fonds Herbette*, Lausanne, for generous financial support.

Experimental Part

General. See [13].

*(1RS,2SR,4RS)-2-*exo*-Cyano-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Acetate* (**1**). A mixture of anh. ZnI_2 (8.0 g, 25.1 mmol), 1-cyanovinyl acetate (8 ml, 76.3 mmol), and 2-methylfuran (75 ml, 837 mmol) was stirred at 20° in the dark. After 26 h, the unreacted reagents were distilled off *in vacuo* (0°), and AcOEt (100 ml) was added. The soln. was washed with ice-cold H_2O (100 ml, twice) and brine (50 ml), dried ($MgSO_4$), and evaporated and the residue recrystallized from Et_2O: 2.5 g (16.9%) of **1**. Colourless crystals. M.p. 86–87°. IR (KBr): 3500, 3100, 3040, 2990, 2940, 2240, 1760, 1710, 1640, 1580, 1440, 1390, 1370, 1320, 1230, 1200, 1150, 1100, 1060, 1010, 960, 930, 920, 880, 860, 710. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.64 (*dd*, ^3J = 5.7, 1.8, H–C(5)); 6.14 (*d*, ^3J = 5.7, H–C(6)); 5.02 (*dd*, ^3J = 4.8, 1.8, H–C(4)); 2.95 (*dd*, ^2J = 13.3, ^3J = 4.8, H_{exo}–C(3)); 2.00 (*s*, MeCOO); 1.85 (*s*, Me–C(1)); 1.79 (*d*, ^2J = 13.3, H_{endo}–C(3)); irradiation at 2.06 (MeCOO) led to NOE's at 1.79 (H_{endo}–C(3) and 6.14 (H–C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.0 (*s*, CO); 140.2 (*d*, ^1J(C,H) = 176, C(6)); 134.7 (*d*, ^1J(C,H) = 178, C(5)); 117.9 (*s*, CN); 88.8 (*s*, C(1)); 78.5 (*d*, ^1J(C,H) = 167, C(4)); 75.8 (*s*, C(2)); 44.4 (*t*,

^1J(C,H) = 140, C(3)); 20.5 (*q*, ^1J(C,H) = 130, *Me*COO); 15.0 (*q*, ^1J(C,H) = 128, *Me*–C(1)). CI-MS (NH_3): 212 (12), 211 (100, $[M + 18]^+$), 194 (1, $[M + 1]^+$), 146 (1), 130 (2), 129 (37), 83 (6), 82 (37), 81 (4). Anal. calc. for $C_{10}H_{11}NO_3$ (193.20): C 62.17, H 5.74, N 7.25; found: C 62.22, H 5.81, N 7.30.

*(1*RS,*2*RS,*4*RS*)-2-*endo-*Cyano-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*exo-*yl Acetate* (**3**), *(1*RS,*2*SR,*4*RS*)-2-*exo-*Cyano-4-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo-*yl Acetate* (**4**), *and (1*RS,*2*RS,*4*RS*)-2-*endo-*Cyano-4-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*exo-*yl Acetate* (**5**). When the above reaction mixture was allowed to stand for several days, its ^{1}H-NMR showed the appearance of signals attributed to **3**. On heating to 50°, **1** and **3** were equilibrated with **4** and **5**. Chromatography did not allow separation and purification of **3**–**5**. ^{1}H-NMR (250 MHz, $CDCl_3$; crude reaction mixture): **3**: 6.68 (*dd*, ^3J = 5.7, 1.8, H–C(5)); 6.26 (*d*, ^3J = 5.7, H–C(6)); 4.99 (*dd*, ^3J = 4.5, 1.8, H–C(4)); 2.45 (*d*, ^2J = 13.2, H_{endo}–C(3)); 2.15 (*s*, MeCOO); 2.01 (*dd*, ^2J = 13.2, ^3J = 4.5, H_{exo}–C(3)); 1.72 (*s*, Me–C(1)); **4** or **5**: 6.44 (*d*, ^3J = 5.5, H–C(5)); 6.20 (*dd*, ^3J = 5.5, 1.8, H–C(6)); 5.51 (*d*, ^3J = 1.8, H–C(1)); 2.47 (*d*, ^2J = 12.5, H_{endo}–C(3)); 2.07 (*s*, MeCOO); 1.86 (*d*, ^2J = 12.5, H_{exo}–C(3)); 1.68 (*s*, Me–C(4)); **5** or **4**: 6.52 (*m*, H–C(5), H–C(6)); 5.19 (*t*, ^3J = 0.8, H–C(1)); 2.39 (*d*, ^2J = 12.8, H_{endo}–C(3)); 2.20 (*s*, MeCOO); 1.97 (*d*, ^2J = 12.8, H_{exo}–C(3)); 1.69 (*s*, Me–C(4)).

*(1*RS,*4*RS*)-1-Methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**2**). A mixture of **1** (2.8 g, 14.45 mmol), MeOH (60 ml), and 30% MeONa in MeOH (52 ml, 290 mmol) was stirred at 20° for 1 h. Formaline (40% aq. CH_2O soln; 10 ml, 72.5 mmol) was added and the mixture stirred at 25° for 15 min. The mixture was poured onto a vigourously stirred mixture of ice/H_2O (120 ml) and CH_2Cl_2 (120 ml). The aq. phase was extracted with CH_2Cl_2 (120 ml, twice), the combined org. phase washed with brine (120 ml, twice) and dried ($MgSO_4$), the solvent distilled off with a *Vigreux* column (1 atm), and the residue distilled *in vacuo* (b.p. 59°/15 Torr): 1.47 g (82%) of **2**. Colourless oil. IR (film): 3490, 3080, 2980, 2930, 1850, 1750, 1625, 1570, 1440, 1410, 1380, 1320, 1300, 1280, 1205, 1130, 1075, 1040, 980, 950, 930, 880, 860, 845, 805, 760, 710. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.68 (*dd*, ^3J = 5.6, 1.7, H–C(5)); 6.17 (*d*, ^3J = 5.6, H–C(6)); 5.22 (*dd*, ^3J = 4.3, 1.7, H–C(4)); 2.26 (*ddd*, ^2J = 15.9, ^3J = 4.3, ^4J = 0.7, H_{exo}–C(3)); 1.95 (*d*, ^2J = 15.9, H_{endo}–C(3)); 1.45 (*s*, Me–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 208.6 (*s*, CO); 142.9 (*d*, ^1J(C,H) = 175), 133.9 (*d*, ^1J(C,H) = 177, C(5), C(6)); 87.6 (*s*, C(1)); 77.4 (*d*, ^1J(C,H) = 166, C(4)); 34.9 (*t*, ^1J(C,H) = 138, C(3)); 12.0 (*q*, ^1J(C,H) = 128, Me). MS (70 eV): 125 (3, $[M + 1]^+$), 96 (11), 83 (33), 69 (76), 57 (100), 55 (71), 45 (14). Anal. calc. for $C_7H_8O_2$ (124.14): C 67.73, H 6.50; found: C 67.65, H 6.41.

*(1*RS,*2*RS,*4*SR,*5*RS,*6*RS*)-5-*endo-*Chloro-2-*exo-*cyano-1-methyl-6-*exo-*(phenylselenenyl)-7-oxabicyclo-[2.2.1]hept-2-*endo-*yl Acetate* (**6**). A mixture of **1** (1.0 g, 5.18 mmol), $CHCl_3$ (15 ml), and benzeneselenenyl chloride (1.0 g, 5.2 mmol) was stirred at 20° for 3 days. After addition of CH_2Cl_2 (25 ml), the yellow soln. was washed successively with 5% aq. Na_2CO_3 soln. (15 ml, twice), H_2O (15 ml, twice), and brine (15 ml), dried ($MgSO_4$), and evaporated and the residue crystallized from Et_2O: 1.75 g (88%) of **6**. Colourless crystals. M.p. 113°. IR (KBr): 3500, 3080, 2980, 2940, 2240, 1765, 1575, 1480, 1450, 1430, 1365, 1310, 1290, 1195, 1145, 1075, 1035, 995, 960, 875, 860, 820, 750, 690. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.61–7.57 (*m*, 2 arom. H); 7.35–7.30 (*m*, 3 arom. H); 4.55 (*t*, ^3J = 5.35, H–C(4)); 4.18 (*ddd*, ^3J = 5.75, 4.9, ^4J = 1.5, H–C(5)); 3.79 (*d*, ^3J = 5.8, H–C(6)); 2.85 (*ddd*, ^2J = 15, ^3J = 5.8, ^4J = 1.5, H_{exo}–C(3)); 2.63 (*d*, ^2J = 15, H_{endo}–C(3)); 2.18 (*s*, MeCOO); 1.81 (*s*, Me–C(1)); NOE's between AcO (2.18) and H_{endo}–C(3) (2.63), AcO (2.18) and H_{endo}–C(6) (3.79), Me–C(1) (1.81) and arom. H's, H–C(4) (4.55) and H_{exo}–C(5) (4.18), and H_{exo}–C(3) (2.85) and H–C(4). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 168.5 (*s*, CO); 134.1 (*d*, ^1J(C,H) = 162), 129.4 (*d*, ^1J(C,H) = 159), 128.5 (*s*, 5 arom. C); 128.3 (*d*, ^1J(C,H) = 161, arom. C); 117.1 (*s*, CN); 90.5 (*s*, C(1)); 79.1 (*d*, ^1J(C,H) = 165, C(4)); 78.0 (*s*, C(2)); 63.3 (*d*, ^1J(C,H) = 162, C(6)); 51.0 (*d*, ^1J(C,H) = 150, C(5)); 38.1 (*t*, ^1J(C,H) = 138, C(3)); 20.4 (*q*, ^1J(C,H) = 130, *Me*COO); 17.8 (*q*, (C,H) = 129, Me). MS: (70 eV): 385 (13, $[M + 1]^+$), 342 (8), 290 (7), 209 (7), 168 (10), 157 (41), 150 (27), 95 (100), 91 (11), 82 (27), 77 (82), 65 (16), 51 (56). Anal. calc. for $C_{16}H_{16}ClNO_3Se$ (384.72): C 49.95, H 4.19, Cl 9.22, N 3.64, Se 20.52; found: C 50.07 H 4.26, Cl 9.22, N 3.68, Se 20.56.

*(1*RS,*4*SR,*5*SR,*6*SR*)-6-*endo-*Chloro-1-methyl-5-*exo-*(phenylselenenyl)-7-oxabicylo[2.2.1]heptan-2-one* (**7**). A soln. of benzeneselenenyl chloride (1.315 g, 6.84 mmol) in $CHCl_3$ (15 ml) was added slowly in 25 min to a stirred soln. of **2** (0.85 g, 6.84 mmol) in $CHCl_3$ (10 ml) at 0° and under N_2. After stirring at 0° for 30 min and at 20° overnight, $CHCl_3$ (20 ml) was added and the soln. washed with 5% aq. Na_2CO_3 soln. (15 ml, 3 times), H_2O (15 ml), and brine (20 ml). After drying ($MgSO_4$), the solvent was evaporated: 2.15 g (99%) of pure **7** (by ^{1}H-NMR). Yellow oil. Crystallization from Et_2O/light petroleum ether at 20° yielded 0.929 g (43%). M.p. 46°. IR (KBr): 3060, 2980, 2930, 1765, 1575, 1475, 1440, 1405, 1380, 1330, 1300, 1250, 1230, 1190, 1165, 1120, 1065, 1020, 1000, 980, 955, 900, 855, 810, 800, 740, 690, 670. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.65–7.62 (*m*, 2 arom. H); 7.38–7.31 (*m*, 3 arom. H); 4.76 (*dd*, ^3J = 6.1, 0.9, H–C(4)); 3.93 (*dd*, ^3J = 3.2, 0.9, H–C(5)); 3.57 (*d*, ^3J = 3.2, H–C(6)); 2.66 (*dd*, ^2J = 17.9, ^3J = 6.1, H_{exo}–C(3)); 2.32 (*d*, ^2J = 17.9, H_{endo}–C(3)); 2.48 (*s*, Me–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 205.8 (*s*, C(2)); 134.6 (*d*, ^1J(C,H) = 165), 129.5 (*d*, ^1J(C,H) = 168), 128.5 (*d*, ^1J(C,H) = 162, arom. C); 128.3 (*s*, arom. C); 88.4 (*s*, C(1)); 79.9 (*d*, ^1J(C,H) = 165, C(4)); 62.8 (*d*, ^1J(C,H) = 162, C(5)); 52.4 (*d*, ^1J(C,H) = 155, C(6)); 43.5 (*t*,

^1J(C,H) = 137, C(3)); 12.0 (*q*, ^1J(C,H) = 130, Me). MS (70 eV): 316 (23, $[M+1]^+$), 286 (4), 183 (3), 157 (45), 117 (14), 95 (100), 81 (23), 77 (42), 65 (11), 51 (52). Anal. calc. for $C_{13}H_{13}ClO_2Se$ (315.66): C 49.47, H 4.15, Cl 11.22, Se 25.01; found: C 49.48, H 4.13, Cl 11.28, Se 24.99.

*(1RS,2SR,4RS)-5-Chloro-2-*exo*-cyano-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Acetate* (**8**). A 30% aq. H_2O_2 soln. (2.06 ml, 20 mmol) was added dropwise to a stirred soln. of **6** (770 mg, 2 mmol) in THF (7 ml) at 0°. After stirring at 0° for 1 h, the mixture was stirred at 20° for 3 days. After the addition of H_2O (50 ml), the mixture was extracted with CH_2Cl_2 (10 ml, 5 times), the combined org. extract washed with 5% aq. Na_2CO_3 soln. (15 ml, 3 times), H_2O (15 ml), and brine (15 ml), dried ($MgSO_4$), and evaporated, and the residue crystallized from Et_2O/light petroleum ether: 324 mg (78.2%) of **8**. Colourless crystals. M.p. 88°. IR (KBr): 3480, 3100, 3000, 2240, 1750, 1600, 1450, 1390, 1370, 1300, 1240, 1190, 1150, 1090, 1070, 1040, 1020, 1010, 970, 940, 910, 880, 860, 810, 755, 720, 660. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.00 (*s*, H–C(6)); 4.79 (*d*, ^3J = 4.7, H–C(4)); 3.03 (*dd*, ^2J = 13.6, ^3J = 4.7, H_{exo}–C(3)); 2.10 (*s*, MeCOO); 1.97 (*d*, ^2J = 13.6, H_{endo}–C(3)); 1.84 (*s*, Me–C(1)). MS (70 eV): 228 (1, $M^{+\cdot}$), 184 (2), 129 (5), 116 (100), 87 (20), 81 (6), 53 (29), 51 (29). Anal. calc. for $C_{10}H_{10}ClNO_3$ (227.65): C 52.76, H 4.43, Cl 15.57, N 6.15; found: C 52.86, H 4.53, Cl 15.61, N 6.17.

(1RS,4RS)-5-Chloro-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**9**). A mixture of **8** (312 mg, 1.37 mmol), MeOH (15 ml), and 30% NaOMe in MeOH (14 µl, 13.7 mmol) was stirred at 20° for 2 h. Formaline (40% aq. CH_2O soln. 0.2 ml) was added and the mixture stirred at 20° for 3 h. CH_2Cl_2 (50 ml) was added and the soln. washed with H_2O (10 ml, twice) and brine (10 ml). After drying ($MgSO_4$), the solvent was distilled off at 1 atm and the residue distilled *in vacuo* (b.p. 50°/0.5 Torr): 189 mg (87%) of **9**. Colourless oil. UV (MeOH): 217 (4300), 308 (390). IR (film): 3500, 3160, 3100, 2990, 2940, 1805, 1760, 1585, 1440, 1410, 1385, 1320, 1290, 1270, 1210, 1180, 1130, 1060, 1020, 965, 920, 890, 850, 800, 750, 685. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.01 (*s*, H–C(6)); 4.96 (*d*, ^3J = 4.2, H–C(4)); 2.36 (*dd*, ^2J = 16.0, ^3J = 4.2, H_{exo}–C(3)); 2.12 (*d*, ^2J = 16.0, H_{endo}–C(3)); 1.52 (*s*, Me–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 205.8 (*s*, CO); 145.5 (*s*, C(5)); 126.9 (*d*, ^1J(C,H) = 183, C(6)); 89.2 (*s*, C(1)); 80.9 (*d*, ^1J(C,H) = 174, C(4)); 33.8 (*t*, ^1J(C,H) = 138, C(3)); 12.5 (*q*, ^1J(C,H) = 129, Me). MS (70 eV): 158 (1, $M^{+\cdot}$), 147 (64), 133 (7), 115 (2), 96 (11), 89 (2), 78 (5), 73 (100), 61 (1), 59 (4), 51 (3). Anal. calc. for $C_7H_7ClO_2$ (158.586): C 53.02, H 4.45, Cl 22.36; found: C 52.97, H 4.56, Cl 22.49.

(1RS,4SR)-6-Chloro-1-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**10**). A soln. of 3-$ClC_6H_4CO_3H$ (*Aldrich*, 85%; 528 mg, 2.4 mmol) in CH_2Cl_2 (10 ml) was added dropwise in 20 min to a stirred soln. of **7** (773 mg, 2.45 mmol) in CH_2Cl_2 (20 ml) at −70° under Ar. After stirring at −70° for 2 h, the mixture was stirred at 20° overnight. The soln. was washed successively with 5% aq. Na_2CO_3 soln. (20 ml, 3 times), H_2O (20 ml, twice), and brine (20 ml). After drying ($MgSO_4$), the solvent was distilled off at 1 atm and the residue distilled under vacuum (b.p. 100°/15 Torr): 308 mg (79%) of **10**. Colourless oil. UV (MeOH): 216 (4000), 310 (220). IR (film): 3500, 3160, 3100, 2990, 2940, 1760, 1590, 1440, 1410, 1385, 1270, 1220, 1200, 1130, 1060, 1020, 970, 935, 915, 875, 860, 810, 790. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.55 (*d*, ^3J = 2.1, H–C(5)); 5.27 (*d*, ^3J = 4.3, 2.0, H–C(4)); 2.38 (*dd*, ^2J = 16.0, ^3J = 4.3, H_{exo}–C(3)); 2.12 (*d*, ^2J = 16.0, H_{endo}–C(3)); 1.48 (*s*, Me–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 206.8 (*s*, CO); 138.8 (*s*, C(6)); 135.4 (*d*, ^1J(C,H) = 181, C(5)); 88.6 (*s*, C(1)); 77.0 (*d*, ^1J(C,H) = 170, C(4)); 34.6 (*t*, ^1J(C,H) = 138, C(3)); 10.1 (*q*, ^1J(C,H) = 129, Me). MS (70 eV): 158 (1, $M^{+\cdot}$), 129 (14), 116 (100), 95 (17), 87 (18), 81 (59), 73 (4), 61 (8), 51 (69). Anal. calc. for $C_7H_7ClO_2$ (158.586): C 53.02, H 4.45, Cl 22.36; found: C 52.94, H 4.45, Cl 22.33.

REFERENCES

[1] A. T. Sneden, *Synlett* **1993,** 313.

[2] P. Vogel, Y. Auberson, M. Bimwala, E. de Guchteneere, E. Vieira, J. Wagner, in 'Trends in Synthetic Carbohydrate Chemistry', Eds. D. Horton, L. D. Hawkins, and G. J. McGarvey, ACS Symposium Series 386, American Chemical Society, Washington, D.C., 1989, p. 197; P. Vogel, D. Fattori, F. Gasparini, C. LeDrian, *Synlett* **1990,** 173; P. Vogel, *Bull. Soc. Chim. Belg.* **1990,** *99,* 395.

[3] J.-L. Reymond, A. A. Pinkerton, P. Vogel, *J. Org. Chem.* **1991,** *56,* 2126; R. M. Bimwala, P. Vogel, *ibid.* **1992,** *57,* 2076; V. Moritz, P. Vogel, *Tetrahedron Lett.* **1992,** *33,* 5243; Y. Chen, P. Vogel, *ibid.* **1992,** *33,* 4917; P. Péchy, F. Gasparini, P. Vogel, *Synlett* **1992,** 676.

[4] H. Kotsuki, H. Nishizawa, *Heterocycles* **1981,** *16,* 1287.

[5] J. W. Scheeren, in 'High Pressure Chemical Syntheses', Eds. J. Jurczak and B. Baranowski, Elservier, Amsterdam, 1989, p. 168.

[6] For cycloadditions of sylvane, see, *e.g.*, D. T. Mowry, *J. Am. Chem. Soc.* **1947,** *69,* 573; R. Daniels, J. L. Fischer, *J. Org. Chem.* **1963,** *28,* 320; Yu. K. Yur'ev, N. S. Zefirov, R. A. Ivanova, G. Yu. Pek, *Chim. Geterosikl. Soedin., Akad. Nauk. Latv. SSR* **1965,** 5; *Chem. Abst.* **1965,** *63,* 5580; H. Prinzbach, P. Vogel,

W. Auge, *Chimia* **1967,** 472; F. Kienzle, *Helv. Chim. Acta* **1975,** *58,* 1180; R.L. Blakespoor, C.S.C. Chung, *J. Org. Chem.* **1975,** *40,* 2443; M.S. Newman, R. Kannan, *ibid.* **1976,** *41,* 3356; W.G. Dauben, H.O. Krabbenhoft, *J. Am. Chem. Soc.* **1975,** *98,* 1992; G. Jenner, M. Papadopoulos, J. Rimmelin, *J. Org. Chem.* **1983,** *48,* 748; L.L. Klein, T.M. Deeb, *Tetrahedron Lett.* **1985,** *26,* 3935; G.W. Gribble, D.J. Keavy, S.E. Branz, W.J. Kelly, M.A. Pals, *ibid.* **1988,** *29,* 6227; A. Riera, M. Marti, A. Moyano, M.A. Pericás, J. Santamaria, *ibid.* **1990,** *31,* 2173; R.G.F. Giles, M.V. Sargent, H. Siahipar, *J. Chem. Soc., Perkin Trans. 1* **1991,** 1571.

[7] R.B. Woodward, T.J. Katz, *Tetrahedron* **1959,** *5,* 70; K.N. Houk, *Acc. Chem. Res.* **1975,** *8,* 361; P.V. Alston, R.M. Ottenbrite, *J. Org. Chem.* **1975,** *40,* 1111; P.V. Alston, R.M. Ottenbrite, T. Cohen, *ibid.* **1978,** *43,* 1864; I.G. John, L. Radon, *J. Am. Chem. Soc.* **1978,** *100,* 3981; J. Sauer, R. Sustmann, *Angew. Chem. Int. Ed.* **1980,** *19,* 779; M.J.S. Dewar, S. Olivella, J.J.P. Stewart, *J. Am. Chem. Soc.* **1986,** *108,* 5771.

[8] J.G. Martin, R.K. Hill, *Chem. Rev.* **1961,** *61,* 537; J. Sauer, *Angew. Chem. Int. Ed.* **1967,** *6,* 16.

[9] D. Gagnaire, E. Payo-Subiza, *Bull. Soc. Chim. Fr.* **1963,** 2627; K.C. Ramey, D.C. Lini, *J. Magn. Reson.* **1970,** *3,* 94; W.L. Nelson, D.R. Allen, *J. Heterocycl. Chem.* **1972,** *9,* 561; F. Kienzle, *Helv. Chim. Acta* **1975,** *58,* 1180; C. Mahaim, P. Vogel, *ibid.* **1982,** *65,* 866.

[10] Y. Auberson, P. Vogel, *Helv. Chim. Acta* **1984,** *72,* 278; C. Nativi, J.-L. Reymond, P. Vogel, *ibid.* **1989,** *72,* 882; E. de Guchteneere, D. Fattori, P. Vogel, *Tetrahedron* **1992,** *48,* 10603; D. Fattori, P. Vogel, *ibid.* **1992,** *48,* 10587; J. Wagner, P. Vogel, *ibid.* **1991,** *47,* 9641.

[11] F. Gasparini, P. Vogel, *J. Org. Chem.* **1990,** *55,* 2451; V. Jeanneret, F. Gasparini, P. Péchy, P. Vogel, *Tetrahedron* **1992,** *48,* 10637.

[12] C. Le Drian, E. Vieira, P. Vogel, *Helv. Chim. Acta* **1989,** *72,* 338; C. Le Drian, J.-P. Vionnet, P. Vogel, *ibid.* **1990,** *73,* 161.

[13] J. Wagner, E. Vieira, P. Vogel, *Helv. Chim. Acta* **1988,** *71,* 624.