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HYDROSILYLATION OF BICYCLO[2.2.1]HEPTENE DERIVATIVES BY TRICHLOROSILANE WITH THE USE OF Ni CATALYTIC SYSTEMS

A STUDY OF THE STEREOCHEMISTRY OF THE PROCESS

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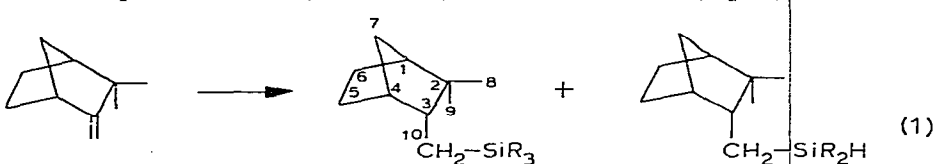
Summary

Hydrosilylation of *endo*- and *exo*-cyanonorbornenes, *endo*-methylnorbornene and camphene by trichlorosilane on a Ni catalytic system was investigated. Based on the spectral data obtained from ^{13}C and ^{1}H NMR studies, using $Eu(fod)_3$ as the shift reagent and by employing the double resonance technique, the stereochemistry of the process has been studied. Stereoselective *exo*-addition of hydrosilane to bicyclo[2.2.1]heptene derivatives has been noted.

There is a large number of publications on the synthesis of organosilicon monomers with bicyclic groups by adding hydrosilanes to unsaturated compounds in the presence of various catalysts [1—3]. The stereochemistry of this process, however, is practically unexplored. There is a report [4] on the orientation of the addition of some hydrosilanes to norbornadiene, where it is concluded that the *exo*-addition product predominated using Pt/C or azobis(isobutyronitrile) as catalyst and the *endo*-adduct on H_2PtCl_6.

In our investigations on the use of Ni catalytic systems for hydrosilylation [5] we studied the stereochemistry of trichlorosilane (TCS) addition to camphene, *endo*- and *exo*-cyanonorbornenes and *endo*-methylnorbornene. 1.5 mole TCS, 5×10^{-3} mole $Ni(acac)_2$ and 1×10^{-2} mole triphenylphosphene (TPP) were used per mole of initial olefin. The process was conducted at 100—120°C for 4—10 hours.

The reaction with camphene proceeds with a quantitative yield. Conversion with respect to olefin, however, amounts to 20% (eq. 1).



(1)

(I) R = Cl (II) R = Cl
(III) R = Me (IV) R = Me

Apart from the main product, 2,2-dimethyl-3-*endo*(trichlorosilylmethyl)bicyclo[2.2.1]heptane (I), up to 20% of dichlorohydrosilic derivative II was obtained. Its formation should be regarded as resulting from the disproportionation of the initial TCS, which is confirmed by the presence of silicon tetrachloride in the reaction products (eq. 2).

$$2\ HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4 \qquad (2)$$

After the methylation of mixture I and II, the products were individually identified with the help of preparative GLC, and characterized. The addition of TCS to camphene proved to take place exclusively at the end carbon atom of the methylene group. This is indicated by the PMR spectrum of product III, where two protons at C(10) resonate with a characteristic signal at 0.44 ppm (AB portion of ABX system).

The configuration of the product is inferred from the ^{13}C NMR spectrum. Due to the steric interaction of C(5) and C(9) carbon atoms with the *endo*-trimethylsilylmethyl group, these carbons resonate at 20.8 and 23.0 ppm, i.e., they undergo a strong-pole shift by 4—8 ppm, as compared with similar signals of 2,2-dimethylbicyclo[2.2.1]heptane taken as the model compound [6]. In the latter case, the C(5) and C(9) signals are located at 28.7 and 27.2 ppm, respectively. The signals due to C(7) and C(8) carbon atoms, located practically at the same field value as that for the model compound (37.9 and 33.0 ppm), confirm the absence of an *exo*-addition product.

The methylated product of disproportionation was characterized as 2,2-dimethyl-3-*endo*(dimethylhydrosilylmethyl)bicyclo[2.2.1]heptane (IV). In contrast to III, in the IR spectrum of product IV there is a characteristic absorption band due to the Si—H bond in the region of 2220 cm^{-1}, the signal of silyl proton in the ^1H NMR spectrum is located at 3.93 ppm, with the protons of the methyl group at the silicon atom resonating, in this case, as a doublet (0.02 ppm).

The *endo*-position of the substituent in the hydrosilane IV is inferred from analysis of the ^{13}C NMR spectrum (Fig. 1) which is in every way similar to the spectrum of product III.

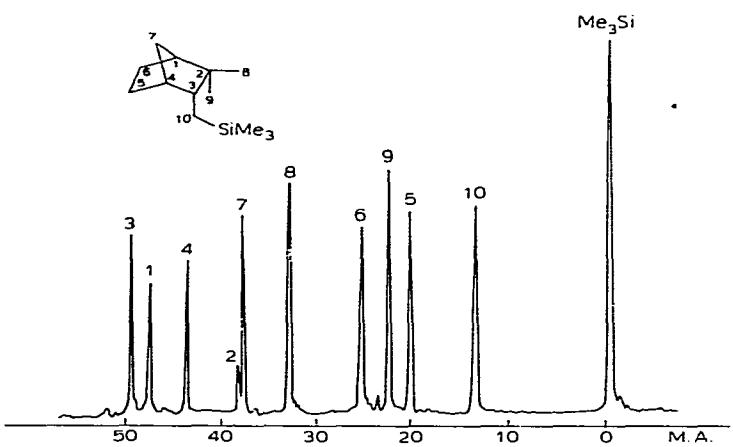
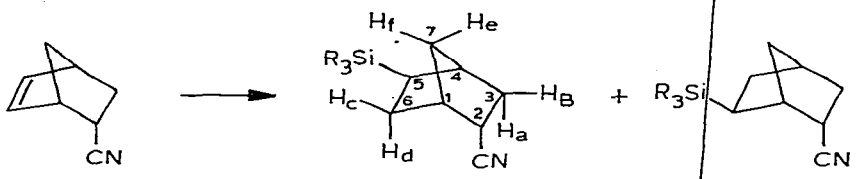


Fig. 1. ^{13}C NMR spectrum of the adduct.

The hydrosilylation of *endo*-cyanonorbornene proceeds with a quantitative yield and a high degree of conversion (82%). Two isomers are formed, V and VI, in the ratio of 11/10 (eq. 3).



(3)

(V) R = Cl
(VII) R = Me

(VI) R = Cl
(VIII) R = Me

After methylation, the individual products were separated. The ^{13}C NMR spectra of 2-*endo*-cyano-5-(trimethylsilyl) (VII) and 2-*endo*-cyano-6-(trimethylsilyl)bicyclo[2.2.1]heptanes (VIII) (Fig. 2) confirmed the structures of these compounds. It is, however, rather difficult to form an opinion on the site of the trimethylsilyl group addition solely on the basis of these spectra. At the same time, proceeding from the strong-pole shift of C(5) in product VII (29.7 ppm) and

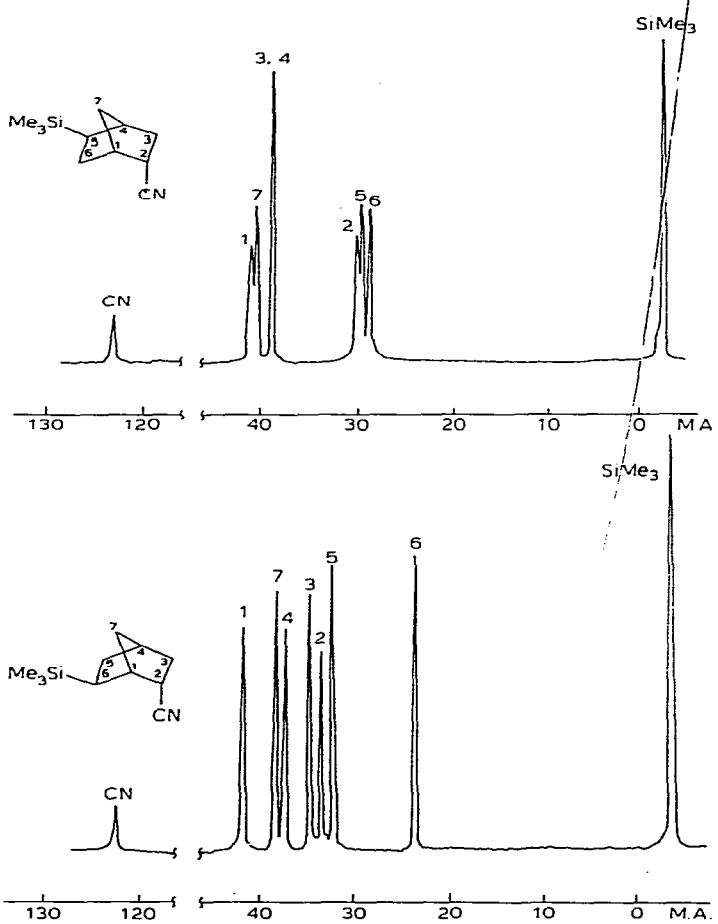


Fig. 2. ^{13}C NMR spectra of adducts VII and VIII.

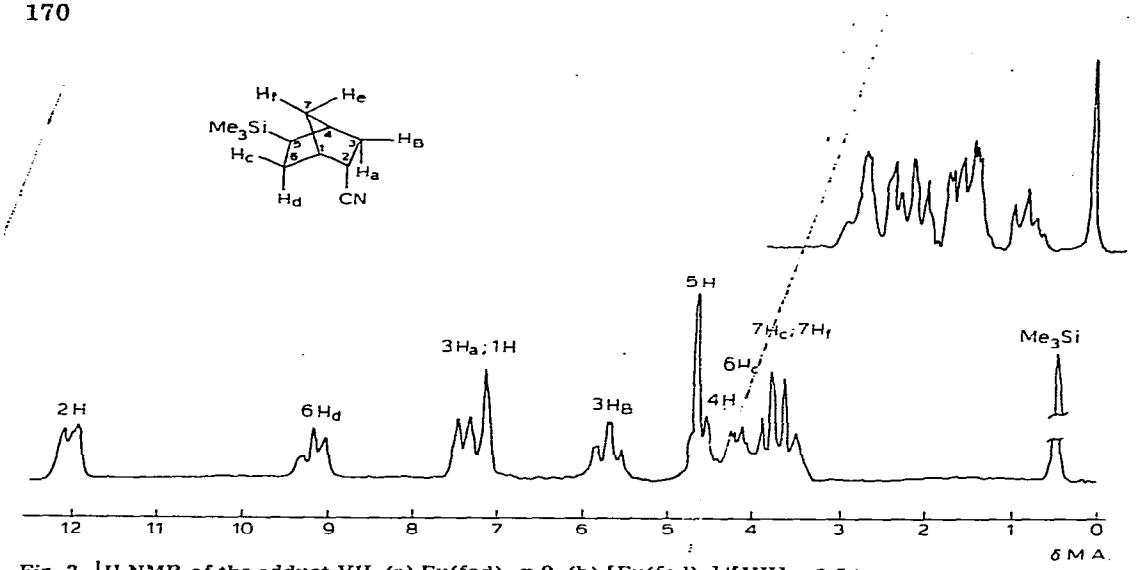


Fig. 3. ^{1}H NMR of the adduct VII. (a) Eu(fod)$_3$ = 0, (b) [Eu(fod)$_3$]/[VII] = 0.54.

C(6) in product VIII (24.6 ppm), one can say that the silyl group is, correspondingly, located at the fifth and the sixth carbon atoms.

To determine the silyl group orientation in products VII and VIII, ^{1}H NMR spectra were taken using Eu(fod)$_3$ as the shift agent (Figs. 3 and 4). This resulted in the separation of signals, with clearly defined spin—spin interaction constants (SSIC) being observed practically for all protons. Using the double resonance method, the values of these constants were determined. The spectral data indicate, first of all, that the *endo*-form of the nitrile group is preserved in substances VII and VIII, in which the SSIC of the *exo*-proton at C(2) with the *endo*- and *exo*-protons at C(3) are equal to 4—5 and 11—12 Hz, respectively. Constants of 8 Hz, associated with the *endo*—*endo* and *endo*—*exo* interaction of

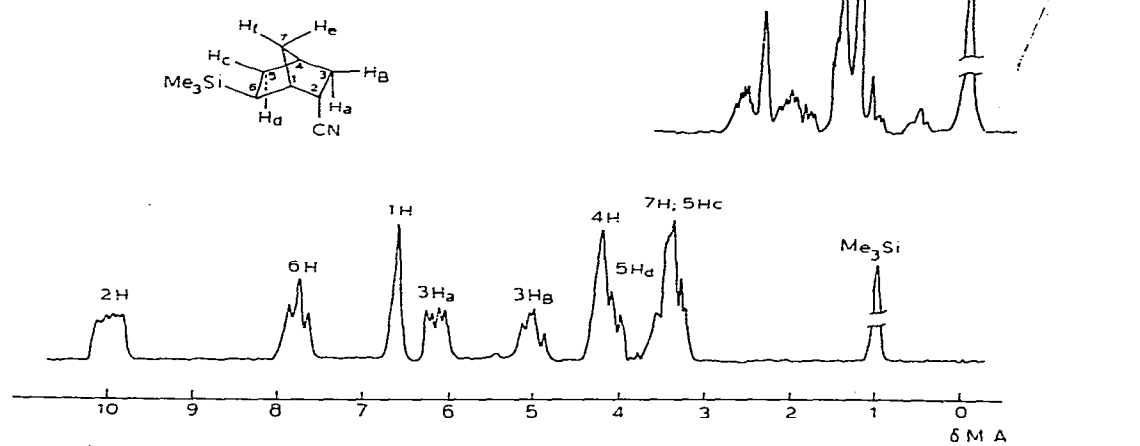
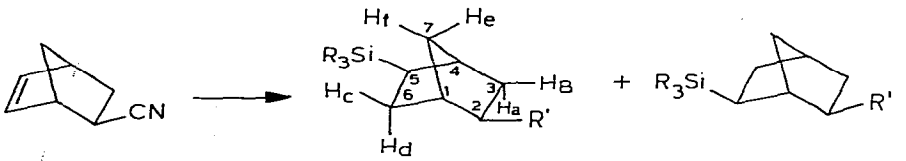


Fig. 4. ^{1}H NMR spectrum of the adduct VIII. (a) Eu(fod)$_3$ = 0, (b) [Eu(fod)$_3$]/[VIII] = 0.46.

protons at C(5) of VII and C(6) of VIII, confirm the *exo*-position of the trimethylsilyl group in both isomers.

The hydrosilylation of *exo*-cyanonorbornene by $HSiCl_3$, also proceeds stereoselectively. A mixture of isomers IX and X in the ratio of 4/5 was obtained (eq. 4).



(4)

(IX) R = Cl, R' = CN (X) R = Cl, R' = CN

(XI) R = Me, R' = CN (XII) R = Me, R' = CN

(XIII) R = Me, R' = $-\overset{\overset{O}{\|}}{C}-Me$ (XIV) R = Me, R' = $-\overset{\overset{O}{\|}}{C}-Me$

After methylation and preparative separation, compounds XI and XII were characterized individually. As in the case of the *endo*-isomers, PMR spectra of the products were taken using the shift agent and the double resonance method. The presence of *endo*—*endo* and *endo*—*exo* constants at C(2), equal to 6 and 8 Hz respectively, confirms that the CN group in products XI and XII is retained in the *exo*-position. Another indication of this is the appearance of a geminal constant of protons at C(7), equal to 11 Hz. As to the constants of the interaction of protons at C(5) and C(6) in products XI and XII, they are the same as the constants of similar protons in compounds VII and VIII and prove the *exo*-addition of the silyl group.

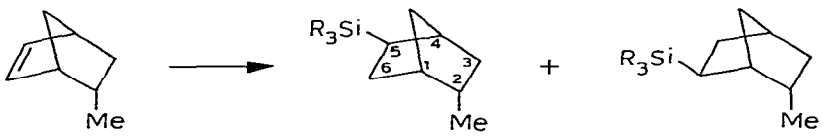
During the methylation of the mixture of haloid derivatives IX and X by MeMgI, up to 25% of the mixture of acyl derivatives XIII and XIV, in the ratio of 1 : 1, is formed in addition to XI and XII. These products are formed as a result of the partial interaction of the CN group with the organomagnesium compound [7]. Products XIII and XIV were identified individually and characterized. Instead of a CN group absorption band, a band characteristic of an acyl group was recorded in the IR spectra of these products in the region of 1720 cm^{-1}. The ^1H NMR spectra taken with the shift reagent and the SSIC found with the help of the double resonance method, confirm the *exo*-position of the acyl group in 2-*exo*-acetyl-5-*exo*- (XIII) and 2-*exo*-acetyl-6-*exo*-(trimethylsilyl)bicyclo[2.2.1]-heptanes (XIV).

It should be noted that during the methylation of a mixture of haloid derivatives with the CN group in the *endo*-position (V,VI) the amount of acyl derivatives formed does not exceed 5%. After their preparative separation, however, they fully co-chromatograph with products XIII and XIV. This enabled us to assume that stability of the *endo*-cyano group towards the Grignard reagent is higher than that of the *exo*-cyano group. The *exo*-position of the substituent at C(2) is explained by the reversal of the configuration, i.e., *endo*-acetyl group into the more stable *exo*-form. The fact that the *endo*-acetyl group acquires the *exo*-form when an attempt is made at preparative GLC separation of a mixture of the two forms at 150°C adds support to the existence of such isomerization.

endo-Methylnorbornene hydrosilylation proceeds practically in a similar way (eq. 5). As a result, a mixture of XV and XVI was obtained, and a Ni catalytic

system makes it possible to conduct this process at 100°C for 7 hours with a quantitative yield. Conversion with respect to olefin amounts to 71%, whereas when H_2PtCl_6 is used the total yield does not exceed 20% [1].

As a result of methylating a mixture of chlorides XV and XVI, followed by preparative GLC separation trimethylsilyl derivatives XVII and XVIII were individually identified (eq. 5).



(XV) R = Cl (XVI) R = Cl
(XVII) R = Me (XVIII) R = Me
(XIX) R = OMe (XX) R = OMe

Based on the spectral data, product XVII was assigned the structure of 2-*endo*-methyl-5-*exo*(trimethylsilyl)bicyclo[2.2.1]heptane, and in product XVIII the silyl group is in the *exo*-position at C(6). The strong-pole shift (18.84 ppm in XVII and 17.48 ppm in XVIII) of the C(8) signal in ^{13}C NMR spectra, as compared with the model methylnorbornane [8], confirms the retention of *endo*-orientation by the CH_3 group. The shift into a weak field of the C(4) (XVII) and the C(1) (XVIII) signal, as compared with *endo*-methylnorbornane, indicates that the trimethylsilyl group is, correspondingly, located at C(5) and C(6), and the unchanged chemical shift values of C(3) and C(8) in both products are indicative of the *exo*-addition of the silyl group. The ^1H NMR spectral characteristics of the individual methoxy derivatives XIX and XX are similar to those of XVII and XVIII and differ from these only by the presence of signals due to the methoxylic protons at silicon (3.44 ppm).

The above experimental data make it possible to draw the conclusion that hydrosilylation of norbornene derivatives with TCS, catalyzed by Ni, should be regarded exclusively as stereoselective *exo*-addition along the double bond.

A comprehensive study of the results published in ref. 4, where it is said that an *endo*-adduct is formed with the hydrosilylation of norbornadiene on H_2PtCl_6, shows that the authors commited some errors when interpreting the PMR spectral data.

The effect of magnetic anisotropy of *endo*-substituents in norbornenes results in the appearance of a signal from double bond protons in the form of a widened multiplet. The nature of the shift of the signal from the olefin proton closest to the substituent depends on the type of the latter. In *endo*-methyl norbornene, a strong-pole shift of the signal by 0.10 ppm has been noted, whereas in *endo*-cyano-norbornene the signal due to the same proton undergoes a weak-pole shift by 0.18 ppm.

The PMR spectrum pattern for *endo*-2-trimethylsilylbicyclo[2.2.1]hept-5-ene, presented by the authors in ref. 4, where the olefin protons resonate in the form of a narrow "triplet", is more typical of the *exo*-orientation of trimethylsilyl group. In all likelihood, the rule of *exo*-addition is actualized in the hydrosilylation of bicyclo[2.2.1]heptene with the use of both the Ni and the Pt catalysts.

Experimental

The IR spectra of the substance in a thin layer were recorded on a UR-20 spectrophotometer. The mass spectra were recorded on an MKh-13-03 spectrometer with electron ionization energy 50 eV, ionization temperature 200°C. The GLC analysis was conducted on an LKhM-8 MD instrument (detection by heat conduction), length 2 m, diameter 3 mm, solid carrier, tsvetokhrom, liquid phase, carbowax 20 m (20%), velocity of carrier gas (helium 40 ml/min ^{1}. The preparative separation was conducted on (a) "PAVKh-7", length 1 m, diameter 26 mm, solid carrier, tsvetokhrom, liquid phase, carbowax 20 m (20%), velocity of carrier gas 500—1500 ml min^{-1}; (b) "Tsvet-3-66", length 1.5 m, diameter 14 mm, solid carier, tsvetokhrom, liquid phase, PFMS (14%), velocity of carrier gas 120—200 ml s^{-1}. The ^{13}C NMR spectra were recorded on a "Bruker WH-90" spectrometer at 22.63 MHz operating in the "monoresonance" mode with a broad-band proton suppression. Internal standard-signal of solvent, CCl_4. The PMR spectra were recorded on a "Tesla BS-487B" instrument, operating frequency 80 MHz. Solvent, CCl_4, internal standards, HMDS and $CHCl_3$. $Eu(fod)_3$, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate)europium was used as the shift reagent.

Procedure of hydrosilylation with trichlorosilane

A steel autoclave thoroughly purged with argon was charged with 0.1 mol olefin, 0.15 mol trichlorosilane, 5×10^{-4} mol $Ni(acac)_2$ and 1×10^{-3} mol TPP. The mixture was kept at 100°C for 7 h. Vacuum distillation was conducted in the flow of argon.

Camphene hydrosilylation produced a mixture of *2,2-dimethyl-3-(trichlorosilylmethyl)- (I) and 2,2-dimethyl-3-(dichlorohydrosilylmethyl)bicyclo[2.2.1]-heptanes (II)*, I/II 4/1, total yield 98% (conversion with respect to olefin 20%), b.p. of mixture 86—92°C/4 mmHg. IR spectrum (ν, cm^{-1}): 520, 570, 590, 720, 800, 1080, 1470, 2220, 2890—2970; PMR spectrum (δ, ppm): 0.75 s (CH_3), 0.90 s (CH_3), 1.04—2.25 m (CH, CH_2), 5.38 m (SiH).

After methylation following the procedure in ref. 9 and preparative separation we obtained: *2,2-dimethyl-3-endo(trimethylsilylmethyl)bicyclo[2.2.1]heptane (III)*, b.p. 72°C/5 mmHg, n_D^{20} 1.4695. IR spectrum (ν, cm^{-1}): 700, 860, 1080, 1250, 1470, 2890—2970. PMR spectrum (δ, ppm): —0.04 s (9H, CH_3Si), 0.44 m (2 H, CH_2Si), 0.72 s (3 H, CH_3), 0.87 s (3 H, CH_3), 1.00—2.00 m (9 H, CH, CH_2). ^{13}C NMR spectrum (δ, ppm): —1.94 q (CH_3Si), 14.05 t C(10), 20.78 t C(5), 22.98 q C(9), 25.64 t C(6), 32.96 q C(8), 37.94 t C(7), 38.40 s C(2), 43.77 43.77 d C(4), 47.59 d C(1), 49.47 d C(3); *m/e* 210. *2,2-dimethyl-3-endo(dimethylhydrosilylmethyl)bicyclo[2.2.1]heptane (IV)*, b.p. 65°C/5 mmHg, n_D^{20} 1.4730. IR spectrum (ν, cm^{-1}): 710, 720, 780, 840, 900, 1080, 1255, 1470, 2130, 2890—2980. PMR spectrum (δ, ppm): —0.02 d (6 H, CH_3Si), 0.45 m (2 H, CH_2Si), 0.71 s (3 H, CH_3), 0.85 s (3 H, CH_3), 1.04—2.02 m (9 H, CH, CH_2), 3.93 m (H, SiH). ^{13}C NMR spectrum (δ, ppm): —3.03 q (CH_3Si), 12.10 t (C(10)), 20.65 t (C(5)), 22.73 q (C(9)), 25.57 t (C(6)), 32.83 q C(8), 36.32 s C(2), 37.81 t C(7), 43.77 d C(4), 47.72 d C(1), 49.66 d C(3); *m/e* 196.

Hydrosilylation of *endo*-cyanonorbornene yields a mixture of *2-endo-cyano-5-(V) and 2-endo-cyano-6-(trichlorosilylbicyclo[2.2.1]heptanes (VI)*, V : VI 11 : 10,

yield 98% (conversion 82%), b.p. of mixture 105—107°C/2 mmHg, n_D^{20} 1.5071. IR spectrum (ν, cm^{-1}): 490, 590, 710, 800, 915, 1080, 1150, 1460, 2255, 2890—2980. PMR spectrum (δ, ppm): 1.21—2.58 m; *m/e* 253.

After methylation and preparative separation we obtained: *2-endo-cyano-5-exo(trimethylsilyl)bicyclo[2.2.1]heptane (VII)*, b.p. 98°C/3 mmHg, n_D^{20} 1.4787. IR spectrum (ν, cm^{-1}): 695, 760, 860, 910, 1250, 1460, 2255, 2880—2960. ^{13}C NMR spectrum (δ, ppm): —1.75 q (CH_3Si), 28.75 t C(6), 29.75 d C(5), 30.04 d C(2), 38.91 t C(3), 38.91 d C(4), 40.73 t C(7), 41.05 d C(1), 122.35 s (CN). ^1H NMR spectrum, with shift reagent {[Eu(fod)$_3$]/[VII] = 0.54} (δ, ppm): 0.50 s (9 H, CH_3Si), 3.56 d (H(7f), J_{7f}^{7e} 10 Hz), 3.84 d (H(7e)), J_{7e}^{7f} 10 Hz), 4.19 (H(6c) J_{6c}^{6d} 11 Hz), 4.56 s H(4), 4.63 t (H(5), J_5^{6d} 8 Hz, J_5^{6c} 8 Hz), 5.79 (H(3b), J_{3b}^{2} 11 Hz, J_{3b}^{3a} 12 Hz), 7.12 s H(1), 7.41 (H(3a), J_{3a}^{2} 4 Hz, J_{3a}^{3b} 12 Hz), 9.15 (H(6d), J_{6d}^{5} 8 Hz, J_{6d}^{6c} 11 Hz), 11.94 (H(2), J_2^{3a} 4 Hz, J_2^{3b} 11 Hz); *m/e* 193. *2-endo-cyano-6-exo(trimethylsilyl)bicyclo[2.2.1]heptane (VIII)*, b.p. 97°C/3 mmHg, n_D^{20} 1.4761. IR spectrum (ν, cm^{-1}): 695, 860, 910, 1250, 1460, 2255, 2880—2960. ^{13}C NMR spectrum (δ, ppm): —1.88 q (CH_3Si), 24.60 d C(6), 32.81 t C(5), 34.19 d C(2), 35.22 t C(3), 37.81 d C(4), 38.85 t C(7), 42.28 d C(1), 122.30 s (CN). ^1H NMR spectrum, {[Eu(fod)$_3$]/[VIII] = 0.46} (δ, ppm): 1.00 s (9H, CH_3Si), 3.37 m H(7), 3.37 m H(5c), 4.00 (H(5d), J_{5d}^{6} 8 Hz, J_{5d}^{5c} 10 Hz), 4.25 s H(4), 5.00 dd (H(3b), J_{3b}^{2} 12 Hz, J_{3b}^{3a} 13 Hz), 6.12 dd (H(3a), J_{3a}^{2} 5 Hz, J_{3a}^{3b} 13 Hz), 6.58 s H(1), 7.75 t (H(6), J_6^{5d} 8 Hz, J_6^{5c} 8 Hz), 9.95 (H(2), J_2^{3a} 5 Hz, J_2^{3b} 12 Hz); *m/e* 193.

Hydrosilylation of *exo*-cyanonorbornene yields a mixture of *2-exo-cyano-5-(IX) and 2-exo-cyano-6-(trichlorosilyl)bicyclo[2.2.1]heptanes (X)*, IX/X 3/4, yield 98% (conversion 73%), b.p. of mixture 102—103°C (2 mmHg), m.p. 52—58°C. IR spectrum (ν, cm^{-1}): 500, 590, 720, 790, 920, 1050, 1460, 2250, 2870—2980. PMR spectrum (δ, ppm): 1.20—2.60 m; *m/e* 253.

After methylation and preparative separation we obtained: *2-exo-cyano-5-exo(trimethylsilyl)bicyclo[2.2.1]heptane (XI)*, b.p. 104°C/4 mmHg, n_D^{20} 1.4778. IR spectrum (ν, cm^{-1}): 695, 755, 840—860, 1255, 1460, 2880—2960. ^1H NMR spectrum, {[Eu(fod)$_3$]/[XI] = 0.67} (δ, ppm): 0.73 s (9H, CH_3Si), 2.62 t (H(5), J_5^{6d} 8 Hz, J_5^{6c} h Hz), 3.45 (H(6c), J_{6c}^{5} 8 Hz, J_{6c}^{6d} 11 Hz), 3.07 (H(7f), J_{7f}^{7c} 11 Hz), 4.10 (H(6d), J_{6d}^{5} 8 Hz, J_{6d}^{6c} 11 Hz), 4.50 s H(4), 5.52 (H(3d), J_{3a}^{2} 8 Hz, J_{3a}^{3c} 13 Hz), 6.62 (H(7e), J_{7e}^{7f} 11 Hz), 7.93 (H(3b), J_{3b}^{2} 6 Hz, J_{3b}^{3a} 13 Hz), 8.20 s H(1), 11.58 (H(2), J_2^{3b} 6 Hz, J_2^{3a} 8 Hz); *m/e* 193. *2-exo-cyano-6-exo-(trimethylsilyl)bicyclo-[2.2.1]heptane (XII)*, b.p. 103—104°C/4 mmHg, n_D^{20} 1.4792. IR spectrum (ν, cm^{-1}): 695, 755, 840—860, 1255, 1460, 2880—2960. ^1H NMR spectrum, {[Eu(fod)$_3$]/[XII] = 0.64} (δ, ppm): 0.75 s (9 H, CH_3Si), 2.95 d (H(7f), J_{7f}^{7e} 11 Hz), 3.25 m H(5c), 3.25 m H(5d), 3.71 t (H(6), J_6^{5d} 8 Hz, J_6^{5c} 8 Hz), 4.75 s H(4), 5.5 5.59 t (H(3a), J_{3a}^{2} 8 Hz, J_{3a}^{3b} 13 Hz), 7.25 d (H(7e), J_{7e}^{7f} 11 Hz), 7.88 s H(1), 8.19 (H(3b), J_{3b}^{2} 4 Hz, J_{3b}^{3a} 13 Hz), 11.71 (H(2), J_2^{3b} 4 Hz, J_2^{3a} 8 Hz); *m/e* 193. *2-exo-Acetyl-5-exo(trimethylsilyl)bicyclo[2.2.1]heptane (XIII)*, b.p. 113—114°C/8 mmHg, n_D^{20} 1.4739. IR spectrum (ν, cm^{-1}): 695, 755, 840—860, 1180, 1255, 1360, 1460, 1710, 2870—2960. ^1H NMR spectrum, {[Eu(fod)$_3$]/[XIII] = 0.44} (δ, ppm): 0.70 s (9H , CH_3Si), 3.10 t (H(5), J_5^{6d} 8 Hz, J_5^{6c} 8 Hz), 3.72 H(6c), 3.78 d (H(7f), J_{7f}^{7e} 12 Hz), 4.40 H(6d), 4.75 s H(4), 6.12 (H(3a), J_{3a}^{2} 8 Hz, J_{3a}^{3b} 12 Hz), 8.77 d (H(7e), J_{7e}^{7f} 12 Hz), 9.88 s H(1), 10.40 (H(2), J_2^{3b} 6 Hz, J_2^{3a} 8 Hz), 11.25 (H(3b), J_{3b}^{2}, J_{3b}^{2} 6 Hz, J_{3b}^{3a} 12 Hz), 12.50 s (3 H, $OCCH_3$); *m/e* 210. *2-exo-Acetyl-6-exo(trimethylsilyl)bicyclo[2.2.1]heptane (XIV)*, b.p. 113°C/8 mmHg,

n_D^{20} 1.4751. IR spectrum (ν, cm^{-1}): 695, 755, 840—860, 1180, 1255, 1360, 1460, 1710, 2870—2960. ^1H NMR spectrum, {[Eu(fod)$_3$]/[XIX] = 0.34} (δ, ppm): 0.85 s (CH, CH_3Si), 3.15 m H(5d), 3.60 d (H(7f), J_{7f}^{7e} 10 Hz), 3.60 m H(5c), 3.70 t (H(6), J_6^{5d} 8 Hz, J_6^{5c} 8 Hz), 4.75 s H(4), 5.85 (H(3a), J_{3a}^{2} 8 Hz, J_{3a}^{3b} 12 Hz), 9.08 s H(1), 9.17 d (H(7e), J_{7e}^{7f} 10 Hz), 10.25 (H(2), J_2^{3b} 4 Hz, J_2^{3a} 8 Hz), 11.38 (H(3b), J_{3b}^{2} 4 Hz, J_{3b}^{3a} 12 Hz), 13.05 s (3 H, $OCCH_3$); *m/e* 210.

endo-Methylnorbornene hydrosilylation produced a mixture of *2-endo-methyl-5- (XV) and 2-endo-methyl-6-(trichlorosilyl)bicyclo[2.2.1]heptanes (XVI)*, XV/XVI 5/4, yield 98% (conversion 71%), b.p. of mixture 92—96°C/8 mmHg, n_D^{20} 1.4910. IR spectrum (ν, cm^{-1}): 495, 580, 660, 690, 790, 905, 930, 990, 1100, 1160, 1380, 1460, 2890—2990. PMR spectrum (ν, ppm): 0.94 d (CH_3, J 6 Hz), 1.19—2.44 m; *m/e* 242.

After methylation and preparative separation we obtained: *2-endo-methyl-5-exo(trimethylsilyl)bicyclo[2.2.1]heptane (XVII)*, b.p. 46°C/3 mmHg, n_D^{20} 1.4620. IR spectrum (ν, cm^{-1}): 695, 760, 870, 910, 1260, 1460, 2880—2970. PMR spectrum (δ, ppm): —0.13 s (9 H, CH_3Si), 0.42 m (H, =CH—Si), 0.89 d (3 H, CH_3, J 6 Hz), 1.16—2.00 m (9 H, CH, CH_2). ^{13}C NMR spectrum (δ, ppm): —1.55 q (CH_3Si), 18.84 q C(8), 26.09 t C(6), 31.01 d C(5), 34.45 d C(2), 39.95 t C(7), 40.66 t C(3), 42.93 d C(1), 43.64 d C(4); *m/e* 182. *2-endo-Methyl-6-exo-(trimethylsilyl)bicyclo[2.2.1]heptane (XVIII)*, b.p. 45°C/3 mmHg, n_D^{20} 1.4621. IR spectrum (ν, cm^{-1}): 695, 760, 870, 910, 1260, 1460, 2880—2970. PMR spectrum (δ, ppm): —0.13 s (9 H, CH_3Si), 0.38 t (H, =CHSi, J 6 Hz), 0.85 d (3 H, CH_3, J 6 Hz), 1.15—2.02 m (9 H, CH, CH_2). ^{13}C NMR spectrum (δ, ppm): —1.55 q (CH_3Si), 17.48 q C(8), 20.13 d C(6), 33.99 t C(5), 37.68 d C(2), 38.27 t C(7), 38.78 d C(4), 40.47 d C(3), 44.10 d C(1); *m/e* 182.

After methoxylation following the procedure in [10] and preparative separation we obtained: *2-endo-methyl-5-exo(trimethoxysilyl)bicyclo[2.2.1]heptane (XIX)*, b.p. 78°C/2 mmHg, n_D^{20} 1.4440. IR spectrum (ν, cm^{-1}): 900, 1020—1150, 1210, 1260, 1380, 1460, 2880—2970. PMR spectrum (δ, ppm): 0.60 m (H, =CH—Si), 0.89 d (3 H, CH_3 J 6 Hz), 1.20—2.38 m (9 H, CH, CH_2), 3.44 s (9 H, CH_3O); *m/e* 230. *2-endo-Methyl-6-exo(trimethoxysilyl)bicyclo[2.2.1]heptane (XX)*, b.p. 77°C/2 mmHg, n_D^{20} 1.4462. IR spectrum (ν, cm^{-1}): 900, 1020—1130, 1200, 1260, 1380, 1460, 2870—2970. PMR spectrum (δ, ppm): 0.50 t (H, =CHSi, J 6 Hz), 0.88 d (3 H, CH_3, J 6 Hz), 1.13—2.02 m (9 H, CH, CH_2), 3.44 s (9 H, CH_3O); *m/e* 230.

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