# The Chemistry of Substituted Norbornenes. Reactions of 5-Vinyl-2-norbornene and 5-Ethylidene-2-norbornene with Formic Acid

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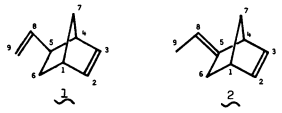
Addition of formic acid to 5-vinyl-2-norbornene(**1**) and subsequent hydrolysis afford 6-vinyl-*exo*-2-norbornanol(**5**) and 5-vinyl-*exo*-2-norbornanol(**6**). Similarly, from 5-ethylidene-2-norbornene(**2**) are formed 6-ethylidene-*exo*-2-norbornanol(**14**), 5-ethylidene-*exo*-2-norbornanol(**15**), and 6-ethyltricyclo[2.2.1.$0^{2,6}$]heptan-3-ol(**16**). The hydroboration of **2** also leads to the formation of **14** and **15**. Thus, the vinyl- and ethylidene-*exo*-norbornanols, **5**, **6**, **14**, and **15**, and the corresponding *endo*-norbornanols, **9**, **10**, **21**, and **22**, have been synthesized. A structural analysis of these products by $^{13}C$ NMR revealed that under certain conditions, the ethylidene group of **2** exerts a great influence upon the reactivity of the norbornenyl ring double bond. Moreover, the fact that **16** derived from the addition of formic acid to **2** consists of both *exo*- and *endo*-hydroxy epimers is inconsistent with the previous observations that the *exo*-isomer is generally the sole product in related systems.

Much less work has been done on the chemical properties of both **1** and **2** which are commercially available norbornenes having an olefinic side chain. Especially, detailed investigations concerning the reactivity difference of the two different types of double bonds in **1** and **2** have not been made so far.

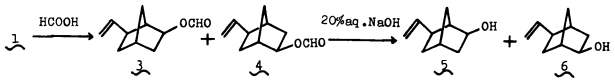


Recent studies of comparing the reactivity of the two double bonds in either **1** or **2** have clarified that the Diels-Alder reaction takes place more readily on the norbornenyl ring double bond in both **1** and **2**;[1] similarly, **2** undergoes addition of sulfur on the ring double bond,[2] whereas singlet oxygen,[3] peroxy acids,[4] and chlorosulfonyl isocyanate[5] add to **2** on the ethylidene group. On the other hand, the Prins reaction takes place on both double bonds in **2**,[6] and in addition, both **1** and **2** undergo hydroformylation on their both double bonds.[7] In any event, earlier studies as stated above have not clearly revealed the chemical behavior of both **1** and **2** from the standpoint of regio- and stereochemistry. In addition, the anticipation that the norbornanols having such an olefinic side chain could provide the intriguing reactive intermediate[4,8] has also encouraged us to initiate the current study.

The purpose of this work is to obtain a better understanding of what stereoelectronic influence is exerted on the reactivity of the norbornenyl ring double bond by participation of the unsaturated substituents, and to determine which one of the two double bonds in either **1** or **2** undergoes certain addition reactions preferentially.

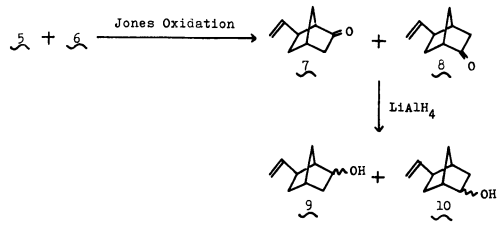
## Results and Discussion

In order to prepare vinylnorbornanols from **1** and to gain further information on reactivity difference between the two double bonds in **1**, we first studied addition of formic acid to **1**, leading to the formation of a mixture of 6-vinyl-*exo*-2-norbornyl formate(**3**) and 5-vinyl-*exo*-2-norbornyl formate(**4**) in a good yield.




Here, products from the addition to the vinyl group and Wagner-Meerwein-type rearrangements *via* the bridged carbonium ion were not observed. A stereochemical assignment of the mixture of **3** and **4** was carried out by hydrolysis to a mixture of **5** and **6**, whose analysis by $^{13}C$ NMR showed that the hydroxyl group in both **5** and **6** exclusively occupied the *exo* position. It was also revealed that the ratio of **5** and **6** is *ca.* 1:1 by GC analysis. The result thus obtained is in accord with the earlier observation that the addition of formic acid to norbornene gives solely an *exo*-product[9], and also indicates that the vinyl group has no influence on the direction of the addition of formic acid to **1**.

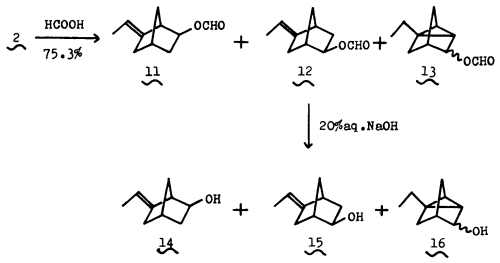
Alternatively, application of the Jones oxidation to the mixture of **5** and **6** afforded a mixture of 6-vinyl-2-norbornanone(**7**) and 5-vinyl-2-norbornanone(**8**), which was subsequently reduced by $LiAlH_4$ to form a mixture of 6-vinyl-2-norbornanol(**9**) and 5-vinyl-2-norbornanol(**10**); the $^{13}C$ NMR spectrum of these products was in striking contrast to that of the mixture of **5** and **6** and revealed that the mixture of **9** and **10** had 78% *endo*- and 22% *exo*-hydroxyl group.




The direct preparation of the mixture of **7** and **8** by the oxidation of the mixture of **3** and **4** was successfully conducted according to the procedure described in the case of norbornyl formate.[9]

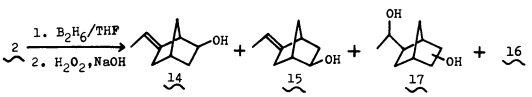
In order to achieve the synthesis of ethylidenenorbornanols from **2** and to examine the reactivity difference in the two double bonds in **2**, the addition of formic acid to **2** was carried out to give three prominent products, 6-ethylidene-*exo*-2-norbornyl formate(**11**), 5-ethylidene-*exo*-2-norbornyl formate(**12**), and 6-ethyltricyclo[2.2.1.

$0^{2,6}$]heptan-3-yl formate(**13**), in product ratio of 11+12/13=61:39.



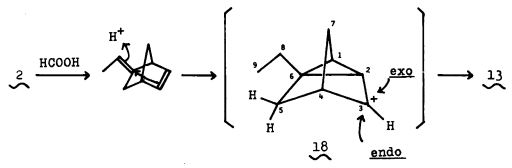
Although the three structural isomers, **11**, **12**, and **13**, can be distinguished readily by gas chromatography, isolation of pure compounds from the mixture by distillation was extremely difficult. In order to ascertain whether this reaction is stereospecific, the product mixture of **11**, **12**, and **13**, was hydrolyzed under alkaline conditions to yield a mixture of the corresponding alcohols, **14**, **15**, and **16**. The $^{13}$C NMR spectrum of the alcohol mixture showed clearly that both **14** and **15** consist of 97% of the *exo* hydroxy epimer and that the ratio of **14** and **15** is 85:15. This particular positional orientation can be explained by preferential attack of $H^+$ upon C-2 of **2**, since C-2 (and, of course, C-8) has the richest electron density in the highest occupied frontier orbital of the homoconjugated diene system consisted of C-2, C-3, C-5, and C-8, and therefore, C-2 will be the site of attack by electrophile with its LUMO.[10]

For further study of stereochemical aspect of this reaction, an attempt was also made to prepare these compounds, **14** and **15**, by an alternative route. Thus, hydroboration-oxidation sequence was applied to **2** to provide a mixture of isomeric products, **14**, **15**, and 5-or 6-(1-hydroxyethyl)-2-norbornanol(**17**), together with *ca.* 1% of **16** unexpectedly formed.[11] Interestingly, $^{13}$C NMR analysis of the mixture of **14** and **15** revealed that it consists of more than 91% of *exo*-isomer with the ratio of **14** and **15** being *ca.* 10:1. In the light of the fact that the hydroboration of norbornene gives 99.5% *exo*- and 0.5% *endo*-norbornanol,[12] we suggest that the lack of the *endo*-hydrogen at C-5 in **2** exerts a smaller steric effect on the addition of diborane to its norbornenyl ring double bond from the *endo* direction compared to norbornene, facilitating *endo* attack to increase the total amount of *endo*-products: this results in the diminished preference (~8.5%) for *exo* attack.



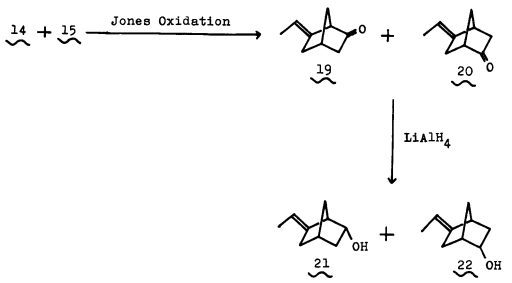
In the context of the structural investigation of the ethylidene-2-norbornanols, **14** and **15**, obtained from the two different types of methods illustrated above, preference of *exo* addition can be best explained by both the perturbation effect on the planarity of the $\pi$ system[13] and the smaller steric hindrance.[11a]

Hydroboration of the mixture of **11**, **12**, and **13**, followed by distillation afforded **16**. The $^{13}$C NMR spectrum of **16** revealed that it consists of 43% *exo*- and 57% *endo*-hydroxy epimers. This stereochemical outcome is surprising since most of addition reactions to norbornenyl ring double bonds proceed almost exclusively from the *exo* direction.[10,11b,11c,14] At this juncture, we propose the following mechanistic explanation; in the addition of formic acid to **2**, it is conceivable that protonation of **2** which occurs on C-8 having the richest electron density as stated above would give the carbonium ion intermediate(**18**),[15] whose molecular model suggests that the bond formation between C-2 and C-6 in **18** evidently renders the distance between C-2 and C-6 in **18** shorter than that between C-3 and C-5 in **2**.[13,16] Concurrently, the torsional strain in **18** thus generated puts C-3 and C-5 in **18** far away from each other, resulting in diminishing the steric interference induced by *endo*-hydrogen attached to C-5 toward a nucleophilic attack by formate anion at C-3 from the *endo* direction.



Alternative rationalization is that once the carbonium ion like **18** is formed, there is no need for considerations of electronic distribution governed by the molecular orbital theory, thereby giving no special preference for the direction of the addition.

Meanwhile, the mixture of **14** and **15** was oxidized by the Jones procedure to 6-ethylidene-2-norbornanone (**19**) and 5-ethylidene-2-norbornanone(**20**). Subsequent reduction with $LiAlH_4$ gave the corresponding norbornanols, **21** and **22**, whose $^{13}$C NMR spectrum showed that the hydroxyl group occupied mainly the *endo* position.



## Experimental

Boiling points are uncorrected. GC analyses were carried out with a Hitachi Model 163 gas chromatograph, using either (A) a 90-m, 0.25-mm i.d. stainless-steel column coated with Silicone SE-30 at a flow rate of 1.2 ml/min., or (B) a 1-m, 5-mm i.d. stainless-steel column packed with 10% Silicone SE-30 on Chromosorb W at a flow rate of 30 ml/min. Percentages indicated for each component refer to computer-calculated peak areas without correction for response, and the retention time is given as ($t_R$) min. for each peak. $^1$H NMR spectra were recorded with a Hitachi Model R-24B, using tetramethylsilane as internal reference. Proton decoupled $^{13}$C NMR spectra were obtained on a JEOL FX 90Q with $CDCl_3$ as an internal lock; absorptions are reported relative to tetramethylsilane. The ratio of each component was determined by computer-calculated line intensities without correction for response. IR spectra were obtained with a Hitachi Model 160-10 infrared spectrophotometer. Elemental ana-

lyses were performed by the Laboratory for Organic Elemental Microanalysis, Faculty of Pharmaceutical Sciences, Kyoto University.

*Materials.* 5-Vinyl-2-norbornene, obtained from Aldrich Chemicals Corp., and 5-ethylidene-2-norbornene, obtained from Tokyo Chemicals Corp., were vacuum distilled before use. The 5-vinyl-2-norbornene employed consists of two stereoisomers,[17] *exo*-5-vinyl-2-norbornene and *endo*-5-vinyl-2-norbornene, and was determined on the basis of $^1$H NMR spectra and GC (column A, 80 °C) analysis to be in the ratio *exo*/*endo* of 2/3. The 5-ethylidene-2-norbornene consists of *E*- and *Z*-isomers, and it was determined on the basis of $^{13}$C NMR spectrum and GC (column A, 80 °C) analysis to be in the ratio *E*/*Z* of 77/23.[18]

*6-Vinyl*-exo-*2-norbornyl Formate(3) and 5-Vinyl*-exo-*2-norbornyl Formate(4).* Approximately 92.0 g (2.0 mol) of 98—100% formic acid was added to 60.0 g (0.5 mol) of 5-vinyl-2-norbornene(**1**), and the mixture was stirred at about 70 °C for 4 h. After removal of excess formic acid, the residue was distilled under reduced pressure to give 52.8 g (63.6% yield) of a mixture of **3** and **4**, bp 104—105 °C (22 mmHg, 1 mmHg≈133.322 Pa), $n_D^{14}$ 1.4821. GC(column A, 140 °C) analysis of this compound indicated that the ratio of four components ($t_R$ 19.3, 19.9, 20.4, and 21.0 min) was 3:27:35:35. IR (neat) $\nu_{max}$ 3090, 2920, 1720, 1640, 1170 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$=7.90(s,1H), 6.00—5.40(m,1H), 5.15—4.90(m, 2H), 4.80(s, 1H), 2.40—1.35(m, 9H). Found: C, 72.20; H, 8.36; O, 19.44%. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43; O, 19.28%.

*6-Vinyl*-exo-*2-norbornanol(5) and 5-Vinyl*-exo-*2-norbornanol (6).* To 30.0 g (0.18 mol) of the mixture of **3** and **4** was added 36.0 g (0.18 mol) of 20% NaOH solution and 25 ml of methanol, and then the mixture was refluxed for 2 h. After removal of methanol, the residual solution was saturated with NaCl and extracted with a mixture of ether and benzene. After the extract was dried over $MgSO_4$, the solvent was evaporated. The residue was vacuum distilled to afford 24.0 g (96.6% yield) of the mixture of **5** and **6**, bp 72—73 °C (1.5 mmHg), $n_D^{18.5}$ 1.5004, whose GC (column A, 140 °C) showed to consist of three components in the yields of 5 ($t_R$ 14.9 min.), 45 ($t_R$ 15.4 min.), and 51 ($t_R$ 15.7 min)%, respectively. IR (neat) $\nu_{max}$ 3350, 3090, 2920, 1640, 1100 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=6.10—5.40 (m, 1H), 5.10—4.65 (m, 2H), 3.80—3.60 (s, 1H), 2.95—2.80 (s, 1H), 2.30—1.10 (m, 9H); $^{13}$C NMR ($CDCl_3$, 4 lines as C-2 for the predominant isomers) (relative intensity) 74.2 (40.7), 74.0 (22.4), 73.9 (33.1), 69.2 (3.8) ppm. Found: C, 78.14; H, 10.20; O, 11.66%. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14; O, 11.59%.

*6-Vinyl-2-norbornanone(7) and 5-Vinyl-2-norbornanone(8).*
*Method A*: A sulfuric acid solution of chromium trioxide was prepared by dissolving 5.6 g (0.056 mol) of chromium trioxide in 8 ml of water, adding 8.6 g (0.088 mol) of concentrated sulfuric acid to the solution and then diluting the mixture with 16 ml of water. This solution was then added dropwise over a period of 30 min to a solution of 11.0 g (0.080 mol) of the mixture of **5** and **6** in 50 ml of acetone with stirring below 5 °C. The mixture was stirred at a temperature below 20 °C for 3 h and then mixed with $NaHSO_3$ solution to form two layers. The lower layer was extracted with petroleum ether, and the petroleum ether layer was then combined with the upper layer previously obtained. The combined layers were washed with saturated $NaHCO_3$ solution until they turned slightly basic and then with water and dried over $MgSO_4$. After the drying agent was removed by filtration, the solvent was distilled off. The residue was distilled under reduced pressure to afford 7.3 g (67.1% yield) of the mixture of **7** and **8**, bp 68—70 °C (7.0 mmHg), $n_D^{18.5}$ 1.4883, which gave a GC (column A, 150 °C) analysis consisting of two components in the yields of 54 ($t_R$ 15.5 min) and 46 ($t_R$ 16.0 min)%, respectively. IR (neat) $\nu_{max}$ 3090, 2950, 2870, 1740, 1630 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$=6.20—5.50 (m, 1H), 5.20—4.80 (m, 2H), 2.75—1.60 (m, 9H). Found: C, 79.30; H, 8.87; O, 11.83%. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82; O, 11.76%.

*Method B*: To a solution of 10.0 g (0.060 mol) of the mixture of **3** and **4** in 25 ml of acetone was added dropwise, with stirring, 31.0 ml of 8M (1M=1 mol dm$^{-3}$) chromic acid solution [this solution was prepared by dissolving 10.7 g (0.107 mol) of chromium trioxide in 20 ml of water, adding 8.9 ml (0.167 mol) of concentrated sulfuric acid to the solution and then diluting this solution with 40 ml of water] while the reaction mixture was maintained at temperatures in the range of 20 to 30 °C. After being stirred at room temperature overnight, the mixture was treated with $NaHSO_3$ until the dark-brown solution turned dark-green. Thus, the solution separated into two layers and the lower layer was extracted with petroleum ether. The extract was then treated as described in Method A; as the product was obtained 6.2 g (75.7% yield) of the mixture of **7** and **8**, bp 54—55 °C (1.2 mmHg), whose physical properties and spectroscopic data proved identical to those of the compound prepared by Method A.

*6-Vinyl*-endo-*2-norbornanol(9) and 5-Vinyl*-endo-*2-norbornanol(10).* To the ice-cooled suspension of 0.70 g (0.018 mol) of $LiAlH_4$ in 50 ml of dry tetrahydrofuran was added dropwise, with stirring, 5.0g (0.037 mol) of the mixture of **7** and **8**. After being stirred at room temperature for 3 h, the mixture was treated with ethyl acetate to destroy excess reducing agent and then with dilute sulfuric acid solution until the solution became slightly acidic. This solution was extracted with ether and then the extract was washed with saturated $NaHCO_3$ solution, with water, and dried over $MgSO_4$. After removal of the drying agent, the solvent was distilled off. The residue was distilled under reduced pressure to yield 4.7 g (92.0% yield) of the mixture of **9** and **10**, bp 80—81 °C (2.8 mmHg), $n_D^{18.5}$ 1.5004; the GC (column A, 140 °C) showed that the ratio of three peaks ($t_R$ 15.5, 15.7, and 15.9 min) was 26:35:39; the IR and $^1$H NMR data are identical to those of the mixture of **5** and **6**: $^{13}$C NMR ($CDCl_3$, 7 lines as C-2 for the predominant isomers) (relative intensity) 74.3 (8.1), 74.2 (9.4), 74.0 (6.1), 72.6 (31.2), 72.1 (29.3), 71.8 (22.9), 65.6 (1.1) ppm. Found: C, 78.12; H, 10.30; O, 11.58%. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14; O, 11.59%.

*6-Ethylidene*-exo-*2-norbornyl Formate(11), 5-Ethylidene*-exo-*2-norbornyl Formate(12), and 6-Ethyltricyclo[2.2.1.0$^{2,6}$]heptan-3-yl Formate(13).* To 120.0 g (1.0 mol) of **2** was added 184.0 g (8.0 mol) of 98—100% formic acid, and the mixture was stirred at 80—90 °C for 5 h. After removal of excess formic acid, the residual liquid was distilled under reduced pressure to give 125.0 g (75.3% yield) of the mixture of **11**, **12**, and **13**, bp 58—62 °C (1.8—3.0 mmHg) [lit,[4] 69—71 °C (6 mmHg)], $n_D^{18.5}$ 1.4685, whose GC (column B, 80—130 °C) showed that the ratio of two peaks ($t_R$ 5.6 and 6.6 min) was 39:61. IR (neat) $\nu_{max}$ 3090, 2930, 2870, 1720, 1660, 1170 cm$^{-1}$; $^1$H NMR ($CCl_4$) $\delta$=7.90 (s, 1H), 5.50—5.25 (m, 1H), 4.80 (s, 1H), 2.80—0.75 (m, 12H). Found: C, 72.35; H, 8.40; O, 19.25%. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43; O, 19.28%.

*6-Ethylidene*-exo-*2-norbornanol(14), 5-Ethylidene*-exo-*2-norbornanol(15), and 6-Ethyltricyclo[2.2.1.0$^{2,6}$]heptan-3-ol(16).*
A mixture of 20.0 g (0.120 mol) of the ester, **11**, **12**, and **13**, and 29.0 g of 20% NaOH solution was refluxed for 2 h and then extracted with a mixture of ether and benzene. The extract was rinsed with water and then dried over $MgSO_4$. After removal of the solvent, the residue was disitilled under reduced pressure to yield 15.3 g (92.4% yield) of a mixture of **14**, **15**, and **16**, bp 65—66 °C (1.0 mmHg) [lit,[4] 82—85 °C (6 mmHg)], $n_D^{18.5}$ 1.4911, which was proved by GC (column B, 80 °C) to consist of two components in the yields of 39 ($t_R$

4.6 min.) and 61($t_R$ 6.0 min)%, respectively: IR (neat) $\nu_{max}$ 3630, 3090, 2930, 2870, 1660, 1110 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$=5.50—5.05 (m, 1H), 3.85 (s, 1H), 2.95 (s, 1H), 2.45—0.70 (m, 11H); $^{13}C$ NMR ($CDCl_3$, 4 lines as C-2 for the predominant isomers) (relative intensity) 78.2 (14.5), 77.1 (24.5), 73.9 (50.0), 72.8 (11.0) ppm. Found: C, 78.31; H, 10.19; O, 11.50%. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14; O, 11.59%.

*6-Ethylidene-oxo-2-norbornanol(14), 5-Ethylidene-*exo*-2-norbornanol(15), and 5-or 6-(1-Hydroxyethyl)-2-norbornanol(17).* To a solution of 72.0 g (0.600 mol) of **2** in 250 ml of dry tetrahydrofuran was added 5.0 g (0.129 mol) of solid $NaBH_4$. To the ice-cooled solution was dropwise added 14.0 ml (0.111 mol) of boron trifluoride etherate over about 30 minutes, and then the mixture was stirred at 10—20 °C for about 2 h. To the reaction mixture was added 25.2 ml of water and 34.1 ml of 3M NaOH solution, and then 34.1 ml of 30% $H_2O_2$ solution was dropwise added. The resultant mixture was stirred at about 50 °C for 2 h and poured into 100 ml of a mixture of ether and benzene. The mixture was washed several times with small amounts of saturated NaCl solution. The separated organic layer was dried over $MgSO_4$, and the solvent was distilled off to afford residual materials which in turn were distilled under reduced pressure to give a colorless liquid, 23.7 g of a mixture of **14**, **15**, and **16** [yield based on boron trifluoride etherate: 52%; bp 60—61 °C (0.45 mmHg)]; $n_D^{18.5}$ 1.5060, as the first fraction, and the second fraction obtained a colorless, viscous liquid, 6.4 g of **17** [yield based on boron trifluoride etherae: 37%; bp 110—113 °C (0.5 mmHg)]; $n_D^{18.5}$ 1.5022. The GC (column A, 140 °C) analysis of the mixture of **14** and **15** indicated that the ratio of three peaks ($t_R$ 13.7, 16.2, and 16.3 min) was 1:46:53; the data for the mixture of **14** and **15** are as follows: IR (neat) $\nu_{max}$ 3630, 3090, 2930, 2870, 1660, 1115 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$=5.65—5.15 (m, 1H), 3.85 (s, 1H), 3.00 (s, 1H), 2.55—0.70 (m, 11H); $^{13}C$ NMR ($CDCl_3$, 4 lines as C-2 for the predominant isomers)(relative intensity) 78.4(6.7), 77.1(5.7), 74.2(79.4), 73.1(8.20) ppm. Found: C, 78.05; H, 10.08; O, 11.87%. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14; O, 11.59%.

In turn, the GC (column B, 140 °C) analysis of **17** showed a single peak ($t_R$ 3.0 min): IR (neat) $\nu_{max}$ 3625, 2920, 2870, 1110 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=4.80—4.50 (s, 1H), 4.35—3.80 (m, 1H) 3.75—3.25 (m, 1H), 2.50—0.75 (m, 13H). Found: C, 69.29; H, 10.18; O, 20.53%. Calcd for $C_9H_{16}O_2$: C, 69.23; H, 10.26; O, 20.51%.

*6-Ethyltricyclo [2.2.1.$0^{2,6}$] heptan-3-ol(16).* The mixture of **11**, **12**, and **13**, 25.0 g (0.151 mol), was dissolved in 100 ml of tetrahydrofuran and to the solution was added 3.23 g (0.042 mol) of solid $NaBH_4$. To the ice-cooled solution was dropwise added, with stirring, 14.2 ml (0.056 mol) of boron trifluoride etherate. After the mixture was stirred at room temperature for 1 h and at about 50 °C for 1 h, it was treated with 8.0 ml of water, 11.0 ml of 3M NaOH solution, and then slowly with 11.0 ml of 30% $H_2O_2$ solution, and the mixture was stirred at about 40 °C for 2 h. The mixture was extracted with ether and the ether extract was rinsed with water, and dried over $MgSO_4$. After removal of the ether, the residue (27.5 g) was dissolved in 50 ml of methanol and treated with 20 g of 10% NaOH solution. After the mixture was stirred under reflux for 2 h, methanol was removed by distillation and the residual oil was extracted with ether. After the ether layer was washed with water and dried over $Na_2SO_4$, the solvent was evaporated. The residue was distilled under reduced pressure to yield 6.5 g (31.2% yield) of **16**, bp 46 °C (0.06 mmHg); $n_D^{18.5}$ 1.4855. The GC (column A, 130 °C) analysis of **16** showed to consist of two components in the yields of 43($t_R$ 15.6 min.) and 57($t_R$ 16.1 min)%, respectively. IR (neat) $\nu_{max}$ 3630, 2925, 2870, 1115 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$=4.05 (s, 1H), 3.80 (s, 1H), 2.00—0.75 (m, 12H); $^{13}C$ NMR ($CDCl_3$, 2 lines as C-2 for the predominant isomers) (relative intensity) 78.2(45.5), 77.1(54.5) ppm. Found: C, 78.41; H, 10.23; O, 11.36%. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14; O, 11.59%.

*6-Ethylidene-2-norbornanone(19) and 5-Ethylidene-2-norbornanone(20).* To an ice-cooled solution of 5.0 g (0.036 mol) of a mixture of **14** and **15**, obtained *via* hydroboration, in 30 ml of acetone was added dropwise, with stirring 20.0 ml of 8M chromium trioxide solution prepared according to Method B previously described in this section. The chromium trioxide solution was added at such a rate that the temperature did not rise above 30 °C. After being stirred at room temperature overnight, the mixture was worked up in the identical manner to that described in Method B. The product, a mixture of **19** and **20**, was obtained by vacuum distillation as a colorless liquid [yield, 68.0%; bp 49—50 °C (0.40 mmHg)]; $n_D^{18.5}$ 1.4930, whose GC (column A, 140 °C) indicated that the ratio of three components ($t_R$ 16.0, 16.5, and 16.8 min) was 53:2:45; IR (neat) $\nu_{max}$ 3090, 2925, 2870, 1740, 1660 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$=5.50—5.20 (m, 1H), 2.85—0.75 (m, 11H). Found: C, 79.37; H, 8.88; O, 11.75%. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82; O, 11.76%.

*6-Ethylidene-*endo*-2-norbornanol(21) and 5-Ethylidene-*endo*-2-norbornanol(22).* To a stirred ice-cooled solution of 0.5 g (0.013 mol) of $LiAlH_4$ in 30 ml of tetrahydrofuran was added dropwise 3.6 g (0.026 mol) of a mixture of **19** and **20**. After the mixture was stirred at room temperature for 2 h, the reaction was quenched by slow addition of water, acidified with 10% sulfuric acid solution, and extracted with ether. The ether layer was washed with saturated $NaHCO_3$ solution, with water, and then dried over $MgSO_4$. After removal of the drying agent, the residual liquid was subjected to vacuum distillation.

The product, a mixture of **21** and **22**, was obtained as a colorless liquid [yield, 91.0%; bp 57—58 °C (0.20 mmHg)]; $n_D^{18.5}$ 1.5050, whose GC (column A, 140 °C) showed that it consists of three components in the yields of 11($t_R$ 15.0 min), 70($t_R$ 16.5 min.), and 19($t_R$ 16.8 min)%, respectively. IR (neat) $\nu_{max}$ 3630, 3090, 2920, 2875, 1660, 1110 $cm^{-1}$; $^1H$ NMR ($CCl_4$) $\delta$=5.50—4.95(m, 1H), 3.80(s, 1H), 2.95(s, 1H), 2.50—0.75(m, 11H); $^{13}C$ NMR ($CDCl_3$, 4 lines as C-2 for the predominant isomers) (relative intensity) 78.5(6.5), 77.2(6.8), 74.0(12.5), 73.1(1.8), 71.9(60.6), 70.9(11.9) ppm. Found: C, 78.34; H, 10.09; O, 11.57%. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14; O, 11.59%.

## Assignment of $^{13}C$ Chemical Shifts in Substituted Norbornanols

The previous studies[19] suggest that the $^{13}C$ proton-decoupled NMR spectrum for the substituted norbornanols described above mainly shows resonances at 75.0—65.0 ppm characteristic of C-2, $\alpha$-carbon of a hydroxyl group and lead to the conclusion that the C-2 resonances of substituted 2-norbornanols are different in an *exo-endo* pair of isomers and $\gamma$-effect generates marked chemical-shift changes. On the basis of this empirical definition, the assignment of C-2 resonances was performed on vinylnorbornanols, **5**, **6**, **9**, and **10**, ethylidene norbornanols, **14**, **15**, **21**, and **22**, and ethyltricyclanol, **16**.

Firstly, as for 6-vinyl-2-norbornanol and 5-vinyl-2-norbornanol, the characteristic shift changes of the C-2 are best interpreted on the basis of the $\gamma$-effect. Thus, the *endo*-6-vinyl group is considered to cause a relatively marked upfield shift at C-2 due to steric interac-

tion between *endo*-6-vinyl group and either *endo*-hydrogen or *endo*-hydroxyl oxygen at C-2. In the case of *exo*-6-vinyl-2-norbornanol, C-2 should show a small upfield shift. By contrast, introduction of *endo*- and *exo*-vinyl group at C-5 is not expected to cause a significant shift change at C-2. Thus, the peaks at 74.2, 74.0, and 73.9 ppm for the mixture of **5** and **6** are reasonably identified as C-2 for *exo*-6-vinyl-*exo*-2-norbornanol, *endo*-5-vinyl-*exo*-2-norbornanol, and *exo*-5-vinyl-*exo*-2-norbornanol (but not differentiated respectively) and the absorption at 69.2 ppm can be assigned to C-2 for *endo*-6-vinyl-*exo*-2-norbornanol. Since there is no absorption between 73.0 and 72.0 ppm where the *endo*-hydroxy isomers should show C-2 resonances, we can conclude that no *endo*-hydroxy isomers can be detected in the mixture of **5** and **6**.

Turning to the $^{13}C$ NMR spectrum of the mixture of **9** and **10**, the peaks at 74.3, 74.2, and 74.0 ppm were identified as C-2 of *exo*-6-vinyl-*exo*-2-norbornanol, *endo*-5-vinyl-*exo*-2-norbornanol, and *exo*-5-vinyl-*exo*-2-norbornanol, although they are not differentiated respectively. Three lines at 72.6, 72.1, and 71.8 ppm should belong to C-2 of *endo*-5-vinyl-*endo*-2-norbornanol, *exo*-5-vinyl-*endo*-2-norbornanol, and *exo*-6-vinyl-*endo*-2-norbornanol (but not differentiated respectively) and the remaining peak at 65.6 ppm is identified as C-2 of *endo*-6-vinyl-*endo*-2-norbornanol, whereas the characteristic absorption for C-2 of *endo*-6-vinyl-*exo*-2-norbornanol is not observed in the chemical shift range predicted on the basis of the $\gamma$-effect.

By contrast with the influence of vinyl group, especially *endo*-vinyl group, upon the $^{13}C$ chemical shift at C-2 of the compounds above mentioned, the ethylidene group is considered to have very little influence on chemical shift from the well-known concept that the influence of the double bond upon the chemical shift is very weak when several bonds away.[20] Thus, the $^{13}C$ NMR spectra of both the mixture of **14** and **15**, obtained *via* hydroboration, and of **21** and **22** are demonstrated as follows: first in the case of the mixture of **14** and **15**, the peak at 74.2 ppm was assigned to C-2 of 6-ethylidene-*exo*-2-norbornanol and the line at 73.1 ppm could be assigned to C-2 of 5-ethylidene-*exo*-2-norbornanol. Interestingly, in this case, two absorptions at 78.4 and 77.1 ppm are observed, which apparently indicates the formation of **16** whose $^{13}C$ NMR spectrum will be discussed later in this section. Similarly, in the case of the mixture of **21** and **22**, two absorptions at 74.0 and 73.1 ppm are identified as C-2 of 6-ethylidene-*exo*-2-norbornanol and 5-ethylidene-*exo*-2-norbornanol, respectively. The remaining two main peaks at 71.9 and 70.9 ppm are assigned to C-2 of 6-ethylidene-*endo*-2-norbornanol and 5-ethylidene-*endo*-2-norbornanol, respectively.

Analogous effort to assign the C-2 resonances of the mixture of **14** and **15**, derived from the addition of formic acid to **2**, has been made. The two peaks at 78.2 and 77.1 ppm are identified as C-2 of the two epimers of **16**. Two lines at 73.9 and 72.8 ppm are assigned to C-2 of 6-ethylidene-*exo*-2-norbornanol and 5-ethylidene-*exo*-2-norbornanol, respectively.

The simplicity in the structure of **16**, including only two epimers, allows an unambiguous assignment of C-2. Thus, the peak at 78.2 ppm is identified as C-2 of *exo*-hydroxy epimer of **16**, and hence the remaining absorption at 77.1 ppm is assigned to C-2 of *endo*-hydroxy epimer of **16**.

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