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EXPERIMENTAL

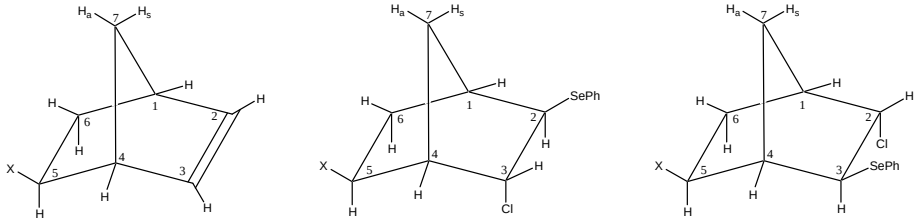
General

All of the 5-substituted-2-norbornenes prepared were known compounds. Unfortunately almost all are liquids at room temperature, making comparison of the products obtained with those obtained by others a problem, since melting points could not be used. Their identity and purity were established by analysis of their ^{1}H and ^{13}C nuclear magnetic resonance spectra, using standard techniques. It was considered that identifying the product and establishing its purity by this means was superior to comparison of its properties with ones listed in the literature, especially since most of the previous preparations pre-dated the widespread use of high field NMR.

^{13}C NMR spectra were recorded on a Varian Unity 300 MHz instrument, operating at 75 MHz. All other NMR measurements (^{1}H, 1-D NOESY, COSY, GHSQC, and GHMBC) were recorded on a Varian Unity 500 MHz instrument fitted with a 3 mm probe, using standard pulse sequences and parameters. All measurements were made on dilute solutions in $CDCl_3$ at 23 ºC.

A note on nomenclature

The strict application of systematic nomenclature to compounds based on the bicyclo[2.2.1]heptane skeleton can lead to carbons C1-C6 requiring different numbers depending on the priorities of other substituents present. To avoid any confusion we have where possible used the prefix forms for X-, PhSe-, and Cl-. For the bicyclo[2.2.1]hept-2-enes the C=C bond is between C2 and C3, and X always at C5. For clarity the phenylselenyl chloride adducts have also been numbered so as to place X always on C5.



Preparation of the 5-X-2-Norbornenes

2-Norbornene is commercially available, but very few of the 5-X-norbornenes are, and then only as *endo* rich mixture of the two isomers. Separation of such mixtures is usually possible by chromatography but only on a small scale. The most accessible pure *endo* and *exo* pair are the two 5-CO_2H compounds which can be conveniently separated on a relatively large scale by treating a mixture of the two with iodine. The *endo* isomer reacts to form an iodolactone which can be readily separated from unreacted *exo* acid and reduced back to the *endo* acid by treatment with zinc dust. A number of the norbornenes were prepared from these pure acids by functional group interconversions.The remainder were synthesised either by methods previously used in the literature or adaptations of known reactions. The products obtained were purified by chromatography on silica, using petroleum ether-ethyl acetate as eluent. Their structures were confirmed by analysis of their ^{1}H and ^{13}C NMR spectra.

Brief summaries of the methods used for the individual alkenes are given below.

5-exo-carboxy-2-norbornene and 5-endo-carboxy-2-norbornene

An *endo*/*exo* mixture of the acids was prepared by the addition of cyclopentadiene to acrylic acid and the two isomers separated by the method of Berson.[1,2]

5-exo-cyano-2-norbornene* and *5-endo-cyano-2-norbornene

These were prepared by the reaction of the appropriate 5-carboxy-2-norbornene with ethyl polyphosphate and ammonia.[3]

The 2-Norbornene-5- -carboxylic acid (350 mg, 2.5 mmol) was mixed with 2 mL of dry chloroform and 2 g of ethyl polyphosphate[4]in a two necked 100 mL flask. It was then stirred under anhydrous ammonia gas in an ice bath at -5°C for 30 minutes. A further 3 g of PPE was then added, the ice bath removed, and stirring under ammonia was continued for a further 90 minutes at room temperature. At this point the treatment with NH_3 gas was discontinued, a further 3 g of PPE added, and the mixture heated on a water bath for 6 hours. After cooling, the mixture was washed with 50 mL of 25% Na_2CO_3 solution and extracted with ether. Evaporation of the ether gave ca. 350 mg of a coloured product. Passing this through a short silica column using ether as eluent gave the pure 5-cyano-2-norbornene. The overall yield was 70-80%.

5-exo- methoxycarbonyl-2-norbornene and 5-endo- methoxycarbonyl-2-norbornene

These were obtained by the esterification of the appropriate 5-acid. In order to avoid possible epimerisation of the carboxyl group or protonation of the double bond that could lead to skeletal rearrangement, conversion to the esters was carried out by alkylation of their lithium salts with dimethyl sulfate.[5]

The 5-norbornene-2-carboxylic acid (345 mg, 2.5 mmol), was dissolved in 2.5 mL of dry tetrahydrofuran, and stirred with $LiOH.H_2O$ (110 mg, 2.5 mmol), at room temperature for 30 minutes. To this 0.250 μL of dimethyl sulphate was added and the solution refluxed on a water bath for 5 hours. The condenser was then removed and the heating continued until all of the tetrahydrofuran had evaporated. The residue was washed with saturated $NaHCO_3$ solution and extracted with ether. Evaporation of the dried extract gave 250- 300 mg of the ester**.**

5-exo-acetyl-2-norbornene and 5-endo-acetyl-2-norbornene

Both could be prepared repared from the appropriate 5-acid by reaction with methyllithium.[6,7] in yields of the order of 80%. However the *endo* isomer could also be obtained free of the *exo* isomer more conveniently by the reaction of cyclopentadiene and butenone in acetonitile using cobaltous chloride as a catalyst.[8]

5-exo-acetyl-2-norbornene. 2-Norbornene -5-*exo*-carboxylic acid (300 mg, 2.2 mmol) was dissolved in 18 mL of anhydrous tetrahydrofuran This solution was cooled in an ice-salt bath and 6.6 mmol, (14.4 mL of 0.6 molar) methyllithium in ether) was added with vigorous stirring. Stirring was continued at this temperature for three hours. After this time, 7 mL of chlorotrimethylsilane was added, and after stirring for 2 minutes, 15 mL of 1M HCl. Stirring was continued for a further 30 minutes at room temperature. The ether layer was separated and the aqueous layer extracted twice with 25 mL of ether. The ether extracts were mixed, washed with water, dried and evaporated. This was further purified by chromatography on silica using 1:1 ether:petroleum ether as eluent. The second fraction to come off the column was pure *exo*-5-acetyl-2-norbornene. The yield obtained was ca 250 mg,

5-endo-acetyl-2-norbornene In a two necked 100 mL R.B. flask 1.5 g (0.23 mol) of freshly cracked cyclopentadiene and 500 mg cobaltous chloride were dissolved in 15 mL of dry acetonitrile. To this solution 1.44 g (0.02 mol) of freshly distilled butenone was added. The solution was stirred under nitrogen for 14 hours. The acetonitrile was then removed by means of a rotary evaporator and the residue extracted with ether. Evaporation of the dried extract gave 1.46 g of product. This was further purified by passing through a silica column, eluting with 3:7 ether : petroleum ether. The first fraction to elute was hydrocarbon and the second, pure 5-*endo*-acetyl-2-norbornene. The yield (850 mg) was only 30%, but no attempt had been made to optimise the reaction conditions.

5-exo-hydroxy-2-norbornene

Oxymercuration/demercuration of norbornadiene had been used previously as a route to the *exo* alcohol. The method of Tam[9] gave the best yields.

5-endo-hydroxy-2-norbornene

This was prepared by the sodium borohydride reduction of 5-norbornen-2-one, obtained by the oxidation of commercially available 2-norbornenol.

(a) 5-norbornen-2-one. 1 g of the 5-Norbornen-2-ol mixture was dissolved in dichloromethane (20 mL) and this was added in one batch to a stirred suspension of 25 g of pyridinium chlorochromate/alumina[10] in 20 mL of the same solvent. The mixture was stirred at room temperature for 6 hours. The solid residue was then filtered off and the residue washed with ether. Evaporation of the filtrate under reduced pressure gave the ketone as a light yellow oil. It was further purified by chromatography using 75:25 petroleum ether:ethyl acetate as eluent. The yield of norbornenone was obtained was 0.69 g (77% of theory).

(b) 5-endo-hydroxy-2-norbornene. The norbornenone (690 mg, 6.3 mmol) was dissolved in 20 mL of anhydrous methanol and the solution cooled to –15 ºC. To this 400 mg of sodium borohydride was added in two equal portions over 30 minutes and the solution was stirred for 1 hour. Sodium bicarbonate solution (20 mL of 5%) was added and the *endo* alcohol product was extracted from this with ethyl acetate (3 x 100 mL). The residue after the ethyl acetate was evaporated was columned on silica column using 1:1 petroleum ether:ethyl acetate as eluent. The yield of the ketone was 620 mg (84%).

5-exo- acetoxy-2-norbornene and 5-exo- acetoxy-2-norbornene

These esters were prepared is ca. 70% yield by acetylation of the corresponding 5-hydroxy-2-norbornene using acetic anhydride in pyridine containing a small amount of DMAP as a catalyst. The method in both cases was that used previously by Tam for the *exo* isomer.[9]

5- exo-methoxy-2-norbornene and 5- endo-methoxy-2-norbornene

These compounds were synthesised from 5-*exo* or 5-*endo*-hydroxy-2-norbornene by converting it to its sodium salt and reacting this with methyl iodide. The method was based on that used by Tam[9] for the preparation of the *endo* –OBn derivative.

5-exo-methoxy-2-norbornene. Sodium hydride (0.135 g, 5.58 mmol) was washed with pentane, dried under nitrogen and suspended in 5 mL of anhydrous THF cooled in ice. To this suspension 410 mg (3.72 mmol) of 5-

exo-hydroxy-2-norbornene was added and the mixture was then refluxed on a water bath at 50-55 °C for three hours. After it had cooled to room temperature; 1.58 g (11.1 mmol) of iodomethane was added, and the contents of the flask stirred for twelve hours. At this point it was quenched with aqueous NH_4Cl (1 g in 5 mL water) and the product extracted with diethyl ether (10 mL × 3). The ether extract was washed with brine (10 ml), dried with anhydrous $MgSO_4$, and the ether evaporated. The crude product was obtained as a colourless liquid (0.315 g, 68%). It was purified by passing through a silica column (1:30) using petroleum ether:ether, 90:10 as eluent.

5-endo-methoxy-2-norbornene was prepared by the same method in 64% yield.

5-*exo*-phenyl-2-norbornene

This was prepared in 95% yield by coupling norbornadiene and iodobenzene using a palladium acetate-triphenylphosphine complex catalyst.[11]

Norbornadiene (1.095 g, 11.9 mmol) and iodobenzene (0.816 g, 4 mmol) were added to 5 mL of dry dimethyl sulfoxide under argon. To this mixture 166 mg (0.22 mmol) of the catalyst was introduced, followed by triethylamine (1.9 mL, 11.6 mmol) and formic acid (0.4 mL, 13.6 mmol). The mixture was heated on water bath at 60 °C under argon for 18 hours. It was then extracted with pentane. Evaporation of the pentane gave 5-*exo*-phenyl-2-norbornene (740 mg, 95%). Further purification by dry column chromatography on silica using petroleum ether as eluent gave pure 5- *exo*- phenyl-2-norbornene (740 mg, 84%).

5-exo-amino-2-norbornene

The above compound was prepared by hydrolysis of the *exo* isothiocyanate, which was in turn obtained by addition of isothiocyanic acid to one of the double bonds of norbornadiene.[12]

5-endo-amino-2-norbornene

This was prepared by the Curtius rearrangement of 2-norbornene-5-*endo*-carboxylic acid.

2-Norbornene-5-*endo*-carboxylic acid (1 g, 7.2 mmol) was dissolved in 20 mL of dry dichloromethane. To this solution, oxalyl chloride (4 mL, 0.044 mol) was added and the whole refluxed for 3 hours. The solvent was then removed under reduced pressure. The residual oil was mixed with 40 mL of acetone (previously dried over 4A molecular sieves for 24 hours) and sodium azide (4 g, 0.061 moles) and the mixture refluxed on a water bath at 70 °C for 2 hours. The residue was then removed by filtration and washed with acetone. The solvent was evaporated from the filtrate under reduced pressure and the residue was refluxed in 50 mL of dry toluene for six hours. Dilute hydrochloric acid (1:1, 50 mL) was added and the mixture refluxed to extract the amine into the aqueous phase. The aqueous layer was then separated, made alkaline with 20% sodium hydroxide solution, and the precipitated amine extracted with ether. Evaporation of the ether layer after drying gave 0.41 g of the *endo* amine (53% theory).

The 5-exo-halogeno- 2-norbornenes

The standard method for preparing these compounds is by the addition of hydrogen halide to norbornadiene. For the chloro and bromo compounds the addition is normally carried out by passing the gaseous hydrogen halide into a solution of the diene in dichloromethane at -78º. This method cannot be used for the iodo compound. The latter was instead prepared by treating the alkene with a mixture of potassium iodide and phosphoric acid. It was

discovered that this method could be adapted to make both the bromide and chloride and that it proved not only more convenient, but gave better yields. Preparations of all three compounds were contaminated with about 25-30% of the isomeric 3-halogenonortricyclene. Attempts were made to rid the samples of these by HPLC. They were successful for the 5-*exo*-iodo and 5-*exo*-bromo compounds, but not for the 5-*exo*-chloro compound.

5-exo-iodo-2-norbornene

Norbornadiene 2.0 g, (0.02 mol) was dissolved in 20 mL of dichloro-methane and to this solution 10.0 g (0.06 mol) of potassium iodide and 15.0 g (0.15 mol) of orthophosphoric acid were added. The mixture was vigorously stirred for 4 hours at room temperature. Excess dichloromethane was then added and the organic layer separated. This was washed with water (30 mL), and then with sodium bicarbonate solution until the water was no longer acidic. Finally it was washed with 10% sodium thiosulphate solution to remove iodine, dried over $MgSO_4$ and the solvent evaporated to give 3.55 g (75%) of a colourless liquid. This was shown by ^{1}H NMR to consist of separated by HPLC and examination of its NMR spectra showed it to be the desired compound together together with about 25% of the isomeric 3-iodotricyclene.

5-exo-chloro-2-norbornene

When the potassium iodide was replaced by potassium chloride a colourless liquid was obtained in 75% yield. Analyis of a sample by NMR showed that it consisted of 5-*exo*-chloro-2-norbornene and 3-*exo*-chloronortricyclene in a ratio of 73:27.

5-exo-bromo-2-norbornene

Under the above conditions but using potassium bromide instead of the other halides, a mixture of 5-*exo*-bromo-2-norbornene and 3-*exo*-bromonortricyclene in a ratio of 77:23.

The alkenes prepared were all known compounds but in most cases their NMR spectra had either not been reported or had not been fully unassigned. The structures and purity of our samples were confirmed by examination of their ^{1}H and ^{13}C NMR spectra. In no case was there evidence for the presence of significant amounts of *endo* isomer in an *exo* product or *vice versa*.

The assignment of ^{1}H and ^{13}C NMR chemical shifts in norbornyl systems has proved a problem in the past. The availability of high field instruments and the development of new processing techniques in recent years has made the task easier, but has not eliminated problems entirely. In 5-substituted 2-norbornenes, the presence of the C=C bond, and a substituent at C5 simplifies the situation considerably. In our case the availability of spectra of a number of closely related structures was also useful. Once the ^{1}H chemical shifts had been assigned, those for the ^{13}C shifts for the various carbons could be made from HSQC-DEPT data. The assigned ^{1}H chemical shifts are given in Tables 1 and 2.

The ^{1}H data in the Tables show that in the *exo* series the substituent on C5 has relatively little effect on the shifts of all protons other than the C5 *endo* one, and even less on their coupling constants. There are useful generalisations that can be made that aid in the assignments. For example, in both the *endo* and *exo* series geminal coupling of the C7 protons is normally around 8-9 Hz, whereas that for C6 is greater (11-13 Hz). The 7s proton is coupled to the 6n and 5n ones ($J \approx 2$ Hz) but there is no coupling between the 7a one and those on C2 and C3. Not all couplings can be observed in the ^{1}H spectra. For example, the H1 protons in both series and H4 in the *exo* one appear as broad singlets, although COSY spectra show that couplings were present.

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Table 1. ^{1}H NMR Chemical shifts of 5-X-*exo*-2--norbornenes

X	H1	H2	H3	H4	H5n	H6x	H6n	H7a	H7s	OTHER
H	2.85(**t**)	6.00(**t**)	6.00(**t**)	2.85(**t**)	0.96(**dd**)	1.61(**d**)	0.96(**dd**)	1.08(**bd**)	1.32(**dt**)	
	1.5 Hz	1.7 Hz	1.7 Hz	1.5 Hz	2.4,9.3 Hz	2.4,6.8 Hz	2.4,9.3 Hz	7.8 Hz	2.0,8.3 Hz	
NH_2	2.79(**bs**)	6.08(**dd**)	6.02(**dd**)	2.50(**bs**)	2.89(d**d**)	1.07 (**dt**)	1.58(**ddd**)	1.58(**bd**)	1.49(**dt**)	
		2.8, 5.5 Hz	3.2, 5.9Hz		2.4,7.5 Hz	3.4,11.9 Hz	2.8,7.3,12.1 Hz	7.90	2.0,8.3	
OH	2.71(**s**)	6.17(**dd**)	5.95(**dd**)	2.81(**s**)	3.87(**d**)	1.30(**dt**)	1.65(**ddd**)	1.73(**bd**)	1.55-1.58(**m**)	
		2.9,5.9 Hz	3.2,5.6		6.8 Hz	2..4,13.2 Hz	2.4,6.8,13.2	8.8 Hz		
OMe	2.77(**s**)	6.16(**dd**)	5.90(**dd**)	2.88(**s**)	3.36(**d**)	1.30(**dt**)	1.50-1.55(**m**)	1.62(**d**)	1.50(**bd**)	3.31(**s**)
		2.9,5.9 Hz	3.4,5.4 Hz		6.3 Hz	2.9,12.2 Hz	(2.4,6.4 Hz)	7.8 Hz	7.3 Hz	
OAc	2.85(**s**)	6.23(**dd**)	5.98(**dd**)	2.88(**s**)	4.65(**d**)	1.41(**dt**)	1.70(**ddd**)	1.65(**bd**)	1.57(**bd**)	2.04(**s**)
		2.7,5.6 Hz	3.3,5.6 Hz		7.0 Hz	2.7,12.7 Hz	2.4,6.8.12.7 Hz	8.8 Hz	8.8 Hz	
Cl	2.90(**s**)	6.21(**dd**)	5.98(**dd**)	2.99(**s**)	3.78(**dt**)	1.78(**dt**)	1.83(**dt**)	1.84 (**d**)	1.61(**dt**)	
		2.7,5.6 Hz	3.2,5.6 Hz		2.0,6.8	3.2,12.7 Hz	2.4,7.8.12.7 Hz	8.3 Hz	1.9,8.8 Hz	
Br	2.90(**s**)	6.19(**dd**)	5.98(**dd**)	3.10(**d**)	3.77(**dt**)	2.00(**dt**)	1.87(**ddd**)	1.90(**bd**)	1.64(**dt**)	
		2.9,5.4 Hz	3.2,5.6 Hz	1.5 Hz	2.0,7.3 Hz	3.4,12.7 Hz	2.4,7.3,13.2 Hz	8.8 Hz	2.2,8.8 Hz	
I	2.85(**s**)	6.15(**dd**)	5.97(**dd**)	3.18(**d**)	3.59(**dt**)	2.16(**dt**)	1.83(**ddd**)	1.92(**d**)	1.64(**dt**)	
		2.9,5.4 Hz	3.2,5.6 Hz	1.5 Hz	2.7,7.8 Hz	3.4,12.7 Hz	2.4,7.8,13.2 Hz	8.8 Hz	2.0,8.8 Hz	
Ph	2.96(**s**)	6.16(**dd**)	6.25(**dd**)	2.91(**s**)	2.72(**dd**)	1.74(**dt**)	1.63(**ddd**)	1.58(**d**)	1.43(**dt**)	7.15-7.31(**m,** 5H)
		3.2, 5.6 Hz	2.9,5.9 Hz		4.9,8.3 Hz	3.4,11.7 Hz	2.4,8.8 11.7 Hz	8.3 Hz	2.0,8.8 Hz	
CO_2Me	2.92(**s**)	6.14(**dd**)	6.10(**dd**)	3.04(**d**)	2.23(**dd**)	1.92(**dt**)	1.34-1.39(**m**)	1.53(**d**)	1.36-1.39(**m**)	3.69(**s**)
		3.0, 5.7 Hz	3.2,5.6 Hz	1 Hz	4.7,9.9 Hz	4.2,11.9 Hz	not resolved	8.3 Hz	not resolved	
CO_2H	2.94(**s**)	6.16(**dd**)	6.12(**dd**)	3.11(**d**)	2.27(**ddd**)	1.96(**dt**)	1.40(**ddd**)	1.54(**d**)	1.40(**dd**)	
		2.9,5.9 Hz	3.2,5.6 Hz	1.5 Hz	2.0,4.4,8.8 Hz	3.9,11.7 Hz	2.4,9.3, 14.2 Hz	8.3 Hz	2.4,8.8 Hz	
Ac	2.89(**s**)	6.15(**dd**)	6.13(**dd**)	2.99(**bs**)	2.38(**dd**)	1.88(**dt**)	1.27(**t**)	1.33(**s**)	1.33(**s**)	2.22(**s**)
		2.9.5.9 Hz	2.9, 5.9 Hz		4.4,8.8 Hz	4.1,11.7 Hz	10.3 Hz			
CN	3.05(**s**)	6.16(**dd**)	6.04(**dd**)	3.23(**d**)	2.18(**m**)	1.97(**dt**)	1.54-1.58(**m**)	1.56(**s**)	1.56(**s**)	
		2.9, 5.6 Hz	2.9,5.9 Hz	1.5 Hz	2.0,4.9,9.8 Hz	3.9,12.2 Hz				

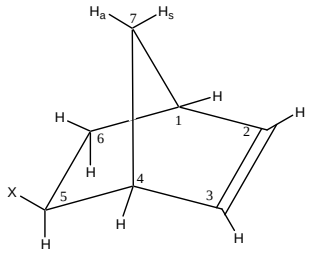

Table 2. ^{1}H NMR Chemical shifts of 5-X-*endo*-2--norbornenes

X	H1	H2	H3	H4	H5x	H6x	H6n	H7a	H7s	OTHER
H	2.85(**t**)	6.00(**t**)	6.00(**t**)	2.85(**t**)	0.96(**dd**)	1.61(**d**)	0.96(**dd**)	1.08(**bd**)	1.32(**dt**)	
	1.5 Hz	1.70 Hz	1.70 Hz	1.50 Hz	2.4,9.3 Hz	2.4,6.8 Hz	2.4,9.3 Hz	7.80 Hz	2.0,8.30 Hz	
NH_2	2.78(**s**)	(**dd**)	(**dd**)	2.80(**s**)	3.47(d**t**)	2.08(**ddd**)	0.55 (**dt**)	1.30(**d**)	1.43-1.47(**m**)	
		2.8, 5.5 Hz	3.2, 5.9Hz		3.9,8.3 Hz	4.0,8.7,12.3 Hz	3.4,11.9 Hz	8.7 Hz		
OH	2.80(**s**)	6.44(**dd**)	6.05(**dd**)	2.98(**s**)	4.46(**dt**)	2.09(**ddd**)	0.75(**dt**)	1.27(**bd**)	1.45-1.48(**m**)	
		3.2,5.6 Hz	2.9,5.9 Hz		3.3,8.0 Hz	3.9,8.3,12.2 Hz	3.2,12.7 Hz	8.8 Hz		
OMe	2.80(**s**)	6.33(**dd**)	5.97(**dd**)	3.11(**s**)	4.06(**dt**)	1.96(**ddd**)	0.88(**dt**)	1.24(**d**)	1.45(**m**)	3.29(**s**)
		2.9,5.9 Hz	2.9,5.4 Hz		3.2,7.8 Hz	3.9,7.8,12.0 Hz	3.3,12.2 Hz	8.8 Hz		
OAc	2.84(**s**)	6.34(**dd**)	5.97(**dd**)	3.14(**s**)	5.27(**dt**)	2.14(**ddd**)	0.93(**dt**)	1.32(**d**)	1.45-1.48(**m**)	1.98(**s**)
		2.9,5.9 Hz	2.9,5.4 Hz		3.3,8.3 Hz	3.7,8.3,12.2 Hz	3.2,12.7 Hz	9.3 Hz		
CO_2Me	2.90(**s**)	6.18(**dd**)	5.92(**dd**)	3.19(**s**)	2.95(**dt**)	1.90(**ddd**)	1.40-1.44(**m**)	1.27(**d**)	1.40-1.44(**m**)	3.62(**s**)
		3.2,5.5 Hz	2.8,5.5 Hz		4.0,9.1 Hz	3.6,9.1,12.5 Hz		8.3 Hz		
CO_2H	2.91(**bs**)	6.20(**dd**)	5.99(**dd**)	3.23(**s**)	2.99(**dt**)	1.91(**ddd**)	1.40(**dt**)	1.28(**d**)	1.43-1.46(**m**)	
		3.2,5.5 Hz	2.8,5.5 Hz		3.9,9.1 Hz	3.6,9.1,11.7 Hz	2.8,11.7 Hz	7.9 Hz		
Ac	2.89(**s**)	6.14(**dd**)	5.85(**dd**)	3.24(**bs**)	3.01(**dt**)	1.75(**ddd**)	1.49(**dt**)	1.33(**d**)	1.45(**m**)	2.12(**s**)
		3.2,5.6 Hz	2.9,5.7 Hz		4.0,8.7 Hz	4.0,9.1,11.9 Hz	3.4,11.5 Hz	7.9 Hz		
CN	3.02(**bs**)	6.33(**dd**)	6.19(**dd**)	3.23(**s**)	2.86(**dt**)	2.14(**ddd**)	1.32(**dt**)	1.20(**d**)	1.51(**m**)	
		2.9, 5.9 Hz	2.9,5.9 Hz		3.9,9.3 Hz	3.4,9.312.0 Hz	2.9,11.7 Hz	8.8 Hz		

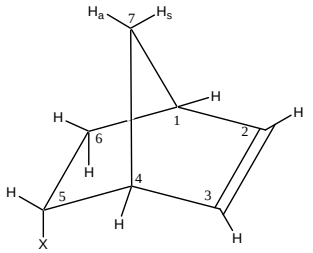

Table 3. ^{13}C NMR Chemical shifts of 5-X-*exo*- and 5-X-*endo*-2-norbornenes

X	C1	C2	C3	C4	C5	C6	C7	Other
H	41.73	135.33	135.33	41.73	24.58	24.58	48.50	
***x*-NH_2**	41.15	138.00	134.97	50.73	51.83	36.87	44.78	
***x*-OH**	40.63	140.18	133.29	45.45	72.44	37.02	50.08	
***x*-OMe**	40.30	140.58	133.10	45.86*	82.00	34.16	45.82*	56.72
***x*-OAc**	40.56	141.02	132.57	47.21	75.20	34.54	46.17	21.39,171.18
***x*-Cl**	41.62	140.31	133.25	51.36	58.36	45.94	38.15	
***x*-Br**	42.14	139.81	133.28	51.73	49.28	46.19	38.26	
***x*-I**	42.93	138.02	133.42	52.80	24.25	39.13	46.24	
***x*-Ph**	48.18	137.32*	137.27*	42.28	43.70	33.62	45.74	127.57,128.23,127.52,146.12
***x*-CO_2Me**	42.96	138.04	135.72	46.55	41.61	30.32	46.34	51.70,176.74
***x*-CO_2H**	43.13	138.12	135.69	46.68	41.64	30.30	46.37	182.81
***x*-Ac**	41.66	138.23	135.78	45.34	51.68	29.02	45.93	29.84,210.73
***x*-CN**	41.59	137.88	133.81	47.23	26.97	31.98	46.94	123.36
***n*-NH2**	43.39	139.76	131.41	48.93	52.02	37.66	49.39	
***n*-OH**	42.86	140.41	130.79	48.07	72.46	37.76	48.26	
***n*-OMe**	42.16	138.05	131.21	44.99	81.67	34.04	47.28	56.70
***n*-OAc**	42.15	138.47	131.49	45.69	75.06	34.21	47.60	21.12, 171.31
***n*-CO_2Me**	42.45	137.66	132.29	45.58	43.09	29.18	49.54	51.39, 175.15
***n*-CO_2H**	42.49	137.86	132.40	45.63	43.24	29.04	49.66	181.36
***n*-Ac**	42.85	138.01	131.41	46.02	52.50	27.57	50.12	29.36, 209.07
***n*-CN**	42.25	138.74	132.61	48.39	27.07	32.35	45.62	123.00

Reactions of 5-X-2-norbornenes with phenylselenyl chloride

General

The reactions of phenylselenyl chloride with 2-norbornene and 5-substituted-2-norbornenes were carried out in dichloromethane. Essentially the same general method was used in each case. However there were considerable differences in the rates of reaction of the alkenes, and reaction times tended to differ as these were mostly based on the time required for the colour of the phenylselenyl chloride to disappear from the reaction mixture.

Determination of the relative yields of the products formed was simplified when it was found that in most cases the reaction led to the formation of one or two products only. Previous reports that the PhSe- group always added *exo* and the Cl- *endo* were confirmed, and no adduct with a rearranged structure was identified with certainty. The relative yields of the products could be readily obtained by integration of suitable peaks in the ^{1}H NMR spectrum of the initial product mixture. No attempt was made to characterise the phenylselenyl chloride adducts, as in the majority of cases these were only prepared on a small scale and were obtained as inseparable mixtures of the two regioisomers. However analyses of the ^{1}H and ^{13}C NMR spectra of the mixtures were consistent with their having the assigned structures.

Preliminary experiments were carried out on 2-norbornene to establish the optimum conditions. It was found that adducts could react further if excess phenylselenyl chloride was present to give the corresponding 2-*endo*-chloro-3-*exo*-phenyldichloroselanyl[2.2.1]bicycloheptanes. In practice such problems were only encountered with norbornenes that reacted very slowly with the halide, and this complication could be minimised by using an excess of alkene. It was subsequently found that when the initial product was heated to 60º C under reduced pressure, the second reaction reversed, and the phenyldichloroselanyl adduct disappeared from the system. Experiments on 5-X-substituted -2-norbornenes showed that the regiochemistry of the adduct formation did not change as a result of raising the temperature to this level. This applied even to reactions carried out at low temperatures, suggesting that adduct formation was under kinetic rather than thermodynamic control.

The following procedure is typical of that adopted for the additions to the 5-X-2-norbornenes:

A solution of ca. 0.1-0.5 mmol of the appropriate alkene in 2 mLof dichloromethane was placed in a reacti-vial. To this a solution containing an equimolar amount of phenylselenyl chloride in the same solvent was added dropwise with stirring at room temperature. In most cases the subsequent reaction was very fast. Addition was continued until the solution acquired a faint permanent colour due to the presence of excess phenylselenyl chloride. The solvent was evaporated and the residue heated under reduced pressure (5 mm) at 60 ºC for a short time in order to remove any unreacted starting materials and break down any phenyldichloroselanyl adduct that may have been present. A ^{1}H NMR spectrum of this crude product was then obtained. Chromatography of the crude material on silica gave a mixture of the pure adducts. NMR analysis of this mixture was used to establish their structures.

Inspection of ^{1}H NMR spectra of the crude products and the weights of isolated products showed that the reactions took place in close to quantitative yield. Details of individual reactions that differed in some respects from the norm follow.

Reactions of the 5-exo-halogeno-2-norbornenes

The additions were carried out on halogenoalkenes that contained about 25% of the corresponding 3-halogenonortricyclene. However these latter compounds did not react with phenylselenyl chloride. Since the halogenonortricyclenes were considerably more volatile than the adducts, these were mostly lost to the system at the stage where the product was heated under reduced pressure.

Reaction of 5-exo-and 5-endo-hydroxynorborn-2-enes

Addition of an equimolar amount of phenylselenyl chloride left some alkene unreacted. Addition of excess, reagent followed by workup in the usual way gave the two adducts together with unreacted phenylselenyl chloride. There was no sign of any product containing a phenylselanyl group bonded to the oxygen of the hydroxyl group in the final products, but it is possible that at least some of this could have been present at some stage of the reaction.

Reaction of 5-exo-and 5-endo-amino-2-norbornenes

In both cases there was evidence that the phenylselenyl chloride attacked the nitrogen at a rate comparable with the rate of addition. Treament with an equimolar quantity of phenylselenyl chloride appeared to give a product that consisted of a mixture of a single adduct and 5-*exo*-phenylselanylamino-2-norbornene in a ratio of 33:67. However the NMR spectra consisted of broad singlets and coupling constants could not be determined. Attempts to purify the products by column chromatography proved unsuccessful.

Identification of the Adduct Structures.

As noted, the adduct mixtures obtained could not be separated from one another for characterisation. However this was not considered necessary for the purposes of the study as their identities could be confirmed and their relative yields established by standard NMR techniques. Assignments were assisted by comparison of the shifts and coupling constants with those of the parent alkenes. For example, in the antimarkovnikov isomer the proton on C5 has a similar chemical shift and coupling constants to that for the alkene, while for the markovnikov isomer the coupling constants are also similar, but the chemical shift lay about 0.6-1.0 ppm further downfield. The various couplings of this to the protons at C6 and C7 allow its assignment via a COSY spectrum. The protons on carbons bearing a chlorine could be readily identified from their shifts (ca 4 ppm), but there were occasional problems in assigning the bridgehead protons at C1 and C4, and the ones on the carbon bearing the phenylselenyl group in cases where the two isomers were present in comparable amounts, because peak areas could not be used to assist this. The biggest problems were encountered with assigning the protons on C6 and C7 because these all tended to lie in the 1.5-2.0 ppm region of the spectrum and overlapped extensively. The result was that if one adduct dominated, the shifts for the other were difficult to identify, while if both were present in comparable amounts the individual components were difficult to assign. However analysis of the COSY and GHSQ spectra permitted confirmation of the structure of the compounds, although determination of the precise positions of the ^{1}H chemical shifts and coupling constants was not always feasible. For this reason we have elected to report the ^{1}H chemical shifts and coupling constants only for protons on C1-C5.

An important consideration was confirming that the two expected adducts were the only isomers present in the system, as the formation of an adduct having a rearranged carbon skeleton was a definite possibility. However such a rearrangement product would have the phenylselenyl substituent at C7 and the Cl at C2 and unlike that between C2 and C3, any coupling that existed would be very weak. Since the observed coupling between the protons on the selenium and chlorine bearing carbons two was invariably of the order of 3-4 Hz, it was concluded that rearrangement had not taken place.

A summary of the ^{1}H and ^{13}C chemical shift data for the adducts is presented in Tables 4 and 5. Cases in which the chemical shifts for the C1-C5 protons of the isomeric adducts overlapped are indicated in the Tables by means of an asterisk. Their multiplicities were not determined.

Table 4. ^{1}H NMR Chemical shifts of 5-X-*endo*-PhSeCl Adducts

X	H1	H2	H3	H4	H5n	Other
H	2.34(d) 3.9 Hz	3.12(t) 6.8 Hz	4.18(dt) 1.5,3.9 Hz	2.46(bs)	1.99(m)	
n-OH(m)	2.34-2.39*(m)	3.46(t) 3.7 Hz	4.34-4.37*(m)	2.64(bs)	4.35-4.39*(m)	
***n*-OH(a)**	2.40*(bs)	4.27(t) 3.7 Hz	3.91(dd) 2.4,3.9 Hz	2.40*(bs)	4.30-4.33(m)	
***n*-OMe(m)**	2.41(bs)	3.60(bt) 3.6 Hz	4.28(t) 2.6 Hz	2.88(bs)	3.78-3.84*(m)	3.38(OMe)
***n*-OMe(a)**	2.45(bs)	4.20(dt) 1.2,4.4 Hz	3.68(dd) 2.8,4.8 Hz	2.51(d) 4.0 Hz	3.75(dt) 3.6,9.5 Hz	3.09(OMe)
***n*-OAc(m)**						
***n*-OAc(a)**	2.45(bt) 4,4 Hz	4.23(dt) 2.0,4.4 Hz	3.68(dd) 2.9,4.4 Hz	2.60(dd) 1.0,2.9 Hz	5.03(dt) 3.9,10.7 Hz	2.03(OAc)
***n*-CO_2Me(m)†**						
***n*-CO_2Me(a)**	2.50(dt) 1.6,4.6 Hz	4.10(dt) 2.0,4.5 Hz	3.22(dd) 3.2,4.4 Hz	2.67(dd) 1.4,2.8 Hz	2.90(ddd) 3.2,4.4,11.9 Hz	3.57(OMe)
***n*-CO_2H(m)**	2.51(s)	3.31(d) 2.40Hz	4.72(d) 4.9 Hz	3.25(ddd) 1.2,3.6,6.3 Hz	2.58(dd) 4.8,11.1 Hz	
***n*-CO_2H(a)**						
***n*-Ac(m)**						2.18(Ac)
***n*-Ac(a)**						2.12(Ac)
***n*-CN(a)**	2.55*(s)	4.17(dd) 2.4,3.9 Hz	3.66(t) 3.7 Hz	2.55*(s)	2.85(dt) 4.6,11.7 Hz	

Table 5. ^{1}H NMR Chemical shifts for H1-H5 of 5-X-*exo*-PhSeCl Adducts

X	H1	H2	H3	H4	H5n	X
H	2.34(d) 3.9 Hz	3.12(t) 6.8 Hz	4.18(dt) 1.5,3.9 Hz	2.46(bs)	1.99(m)	
x-OH(m)	2.37(d) 4.4 Hz	3.05(t) 2.9 Hz	4.14(t) 4.2 Hz	2.47(d) 3.9 Hz	4.50(d) 6.8 Hz	
***x*-OH(a)**	2.43(d) ~8 Hz	4.08(t) 3.9 Hz	2.87(t) 2.9 Hz	2.36(s)	3.87(d) 6.3 Hz	
***x*-OMe(m)**	2.34(d) 4.9 Hz	3.06(dd) 2.4,6.6 Hz	4.16(t) 4.4 Hz	2.62(d) 4.4 Hz	3.95(dd) 2.4,6.8 Hz	3.29(OMe)
***x*-OMe(a)**	2.45*(bs)	4.12(dt) 1.5,3.9 Hz	2.87(dd) 2.4,3.9 Hz	2.45*(bs)	3.35(d) 6.7 Hz	3.25(OMe)
***x*-OAc(m)**	2.39(d) 4.4 Hz	3.10(t) 3.2 Hz	4.16(t) 4.2 Hz	2.62(d) 3.9 Hz	5.29(d) 6.8 Hz	3.02(OAc)
***x*-OAc(a)**	2.50(bs)	4.09(bs)	2.99(t) 3.2 Hz	2.42(s)	4.70(d) 6.3 Hz	2.00(OAc)
***x*-Cl(m)**	2.42(d) 3.9 Hz	3.05(t) 3.4 Hz	4.20(t) 4.4 Hz	2.68(d) 2.9 Hz	4.57(dt) 2.8,7.3 Hz	
***x*-Cl(a)**	2.54(s)	4.10(dt) 2.0,4.4 Hz	2.94(t) 3.7 Hz	2.51(s)	3.93(dt) 2.0,7.3 Hz	
***x*-Br(m)e**	2.40(bs)	3.03(t) 3.4 Hz	4.19(t) 4.2 Hz	2.78(d) 4.9 Hz	4.63(ddd) 2.0,3.9,6.3 Hz	
***x*-Br(a)**	2.82(bs)	4.11(dt) 2.0,4.4 Hz	2.07(t) 3.7 Hz	2.60(s)	3.99(dt) 2.4,7.3 Hz	
***x*-I(m)**	2.31(d) 2.0 Hz	3.02(t) 3.9 Hz	4.13(t) 4.2 Hz	2.83(bs)	4.64-4.67(m)	
***x*-I(a)**	2.44(bs)	4.14(dt) 2.0,4.4 Hz	3.02(t) 3.9 Hz	2.67(s)	3.99(ddd) 2.4,3.9,7.8 Hz	
***x*-Ph(m)**	2.47(bs)	3.20(t) 3.4 Hz	4.23-4.25*(m)	2.57(bs)	3.61(t) 7.5 Hz	
***x*-Ph(a)**	2.59(bs)	4.23-4.25*(m)	3.32(t) 3.0 Hz	2.50(s)	2.94(dd) 5.6,8.7 Hz	
***x*-CO_2Me(m)**	2.40(d) 4.0 Hz	3.08(t) 3.6 Hz	4.19(t) 4.4 Hz	2.76(d) 3.6 Hz	3.16(dd) 5.4,9.8 Hz	3.69(OMe)
***x*-CO_2Me(a)**	2.53(bs)	4.17(dd) 1.6,4.0 Hz	3.12(t) 3.2 Hz	2.62(s)	2.50*(dd) 5.0,8.7 Hz	3.66(OMe)
***x*-CO_2H(m)**	2.41(d) 3.9 Hz	3.08(t) 3.2 Hz	4.19(t) 4.4 Hz	2.81(d) 3.9 Hz	3.20(dd) 5.4,9.3 Hz	
***x*-CO_2H(a)**	2.54(s)	4.16(t) 3.9 Hz	3.13(t) 2.7 Hz	2.66(s)	2.53*(dd) 5.4,9.3 Hz	
***x*-Ac(m)**	2.39(d) 3.4 Hz	3.09(t) 3.4 Hz	4.21(t) 4.2 Hz	2.69(d) 3.4 Hz	3.24(dd) 5.4,8.3 Hz	2.18(Ac)
***X*-Ac(a)**	2.51(bs)	4.17(dt) 1.5,3.9 Hz	3.16(t) 3.2 Hz	2.55(s)	2.58(dd) 5.4,8.8 Hz	2.12(Ac)
***x*-CN(m)**	2.47(d) 3.4 Hz	3.04(t) 3.4 Hz	4.19(t) 4.2 Hz	2.80(d) 3.9 Hz	3.24(ddd) 1.4,4.9.8.8 Hz	
***x*-CN(a)**	2.60(bs)	4.12(dt) 1.7,4.2 Hz	2.99(t) 3.40 Hz	2.64(s)	2.48-2.52(m)	

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