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Novel Epoxynorbornane Monomers. 1. Synthesis and Characterization

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ABSTRACT: The synthesis of a series of mono-, di-, and multifunctional monomers bearing the epoxynorbornane group has been carried out. Key to their preparation is the chemoselective epoxidation of 5-vinyl-2-norbornene, which affords the 5-vinyl-*exo*-2,3-norbornane epoxide in high yields. Monomers were prepared using this substrate and carrying out hydrosilations to make mono-, di-, tri-, and tetrafunctional epoxides. The esterification and etherification of 5-norbornene-2-methanol with succinic acid and 1,4-butanediol gives the corresponding bisnorbornene compounds, which were epoxidized to give diepoxynorbornane monomers containing ester and ether linkages. All monomers were fully characterized by means of IR and ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis.

Introduction

In recent years a great deal of emphasis has been placed on the discovery of chemically based products and processes that are low-energy consumptive and nonpolluting.[1] Specifically, the technology of the photoinduced curing of monomers has experienced considerable growth in the past decade in the area of inks, coatings, and adhesives.[2−4] While photoinduced free-radical polymerization has enjoyed the bulk of the commercial success, the corresponding cationic systems are also finding increasing use in many specialized applications. To serve this growing market, a wide variety of novel epoxide,[5] vinyl ether,[6] and more recently 1-propenyl ether monomers[7] are currently under intensive development and some have already become commercially available. Of special interest are polymers obtained from multifunctional epoxide monomers, which typically possess excellent adhesion, low shrinkage, and superior chemical resistance as compared to their acrylate counterparts. For this reason, they are presently finding manifold uses in high-performance protective and decorative coatings for metals, plastics, and wood and in pressure-sensitive adhesives.[8] Such applications require rapid polymerization rates. The literature contains little information regarding the relative reactivities of various types of epoxy monomers. Preliminary studies in this laboratory showed that the photoinduced cationic ring-opening polymerization of epoxy monomers is highly dependent on the structure of the monomer.[9] Glycidyl esters were less reactive than glycidyl ethers, which were, in turn, less reactive than epoxidized α-olefins. The most reactive monomers were cycloaliphatic epoxy monomers bearing the epoxycyclohexane moiety. The reasons for the observed differences in reactivity are not known with certainty. However, it may be speculated that one contributor to the differences is the substantial difference in ring strain in the cycloaliphatic epoxides as compared to their linear aliphatic or glycidyl ether counterparts. Published data from the calculations of the ring strain for various epoxides lend some support for the credence of this hypothesis.[10] Based on this rationalé, it should be possible to design new types of epoxy monomers with enhanced ring strain which undergo rapid cationic ring-opening polymerization.

The ring strain in the norbornene ring system is considerably higher than that in the corresponding cyclohexene ring system, and for this reason, the norbornene double bond is markedly more reactive in several types of reactions than would be predicted. For example, norbornene undergoes facile ring-opening metathesis polymerization while cyclohexene does not.[11,12] Similarly, the norbornene double bond takes part in free-radical-induced additions of thiols,[13] in cationic polymerizations,[14] and in hydrosilations[15] much more readily than cyclohexene. It was of some interest, therefore, to prepare a series of 2,3-epoxynorbornane monomers and to investigate and compare their reactivity in photoinduced cationic polymerization with monomers bearing the epoxycyclohexane moiety.

Experimental Section

Materials and Procedures. Reagent grade acetone, dichloromethane and toluene were purchased from Aldrich Chemical Co., Milwaukee, WI. Toluene was distilled over sodium metal. The other solvents were used as received. Norbornene (bicyclo[2.2.1]hept-2-ene, **I**), 5-(hydroxymethyl)-2-norbornene (5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene, **II**), 5-vinyl-2-norbornene (5-vinylbicyclo[2.2.1]hept-2-ene, **III**) (mixture of 80:20, 5-*endo*:5-*exo isomers),* dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine, tetra-*n*-butylammonium bromide, 1,4-dibromobutane, succinic acid, and oxone were also purchased from the above company. 1,1,3,3-Tetramethyldisiloxane (TMDS), 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS), methyltris(dimethylsiloxy)silane, and 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane were obtained from Hüls America., Bristol, PA. Phenylmethylsilane and phenyldimethylsilane were purchased from Silar Laboratories, Scotia, NY.

Routine infrared spectra were obtained using a MIDAC M1300 FTIR. Gas chromatographic (GC) analyses were performed using a Hewlett-Packard 5890 gas chromatograph equipped with a 10 m long, 5% OV-17 phenylsilicone capillary column and a flame ionization detector. ^{1}H and ^{13}C NMR experiments were performed on either a Varian XL-200 (200 MHz) or a Unity-500 (500 MHz) spectrometers at room temperature using $CDCl_3$ as the solvent containing 1% tetramethylsilane (TMS) as the internal standard. In the case of the epoxysilicone monomers, NMR spectra were obtained in

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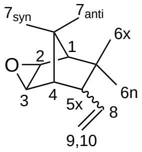
pure $CDCl_3$. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

Monomer Synthesis. Chemoselective Epoxidation of 5-Vinyl-2-norbornene. In a 3 L three-necked round-bottomed flask fitted with an efficient mechanical stirrer, Claisen adaptor, two pressure-equalizing addition funnels, and a thermometer were placed 39.6 g (0.33 mol) of **III**, 200 mL of dichloromethane, 200 mL of acetone, 1 L of phosphate buffer solution (pH 7.5), and 1.0 g of 18-crown-6. The flask was cooled to 0 °C using an ice/salt mixture, and 135.3 g of oxone ($2KHSO_5$, K_2SO_4, $KHSO_4$) as a 0.4 M clear, ice-cold aqueous solution, was added in small portions using one addition funnel. The pH of the solution was monitored using a narrow-range pH (7.2−8.8) paper and was maintained between 7.4−7.5 by adding 1 N sodium hydroxide from the other addition funnel. Upon completion of addition of oxone, the reaction mixture was stirred at 5 °C for an additional 5−6 h. The product was filtered to remove the precipitated solids, and the organic and aqueous layers were separated. The aqueous layer was extracted with four 100 mL aliquots of dichlormethane, and the combined organic layers were washed with four 100 mL aliquots of distilled water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator. The excess 5-vinyl-2-norbornene (bp 141 °C) was removed by distillation under reduced pressure. GC analysis of the resulting mixture showed that it was composed of 93% monoepoxide **IV**, 6% diepoxide **V**, and 1% starting material. A 2 g sample of this mixture was purified using column chromatography (200−400 mesh silica gel, 98:2 v/v hexane/ethyl acetate) to obtain 1.8 g of the pure *exo*-monoepoxide **IV**.



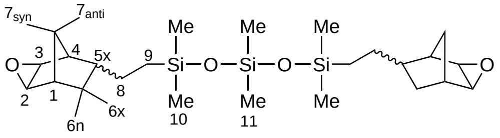
IV

The yield based on oxone was 95%: IR ν (cm^{-1}) 1640, 848; ^1H NMR ($Me_4Si/CDCl_3$) δ (ppm) 5.80−5.86 (m, H_8), 5.00−5.15 (m, H_9 and H_{10}), 3.17−3.22 (two d, H_2 and H_3), 2.65 (m, H_4), 2.50 (m, H_1 and H_{5x}), 1.77−1.82 (m, H_{6x}), 1.07−1.11 (m, H_{7anti}), 1.11−1.39 (m, H_{7syn}), 0.82 (m, H_{6n}); ^{13}C NMR ($Me_4Si/CDCl_3$) δ (ppm) 139.8 (C_8), 115.2 (C_9), 51.5 (C_2), 49.8 (C_3), 44.5 (C_4), 42.0 (C_1), 37.5 (C_5), 30.8 (C_7), 27.4 (C_6). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.03; H, 8.93.

Using a similar procedure, norbornene (**I**) was epoxidized to obtain 2,3-epoxynorbornane (**VI**) in 96% yield. **VI** was purified by column chromatography (70−230 mesh silica gel, 80:20 v/v hexane/ethyl acetate).

General Procedure for the Synthesis of Epoxynorbornane Functional Siloxanes. Described below is a typical procedure for the synthesis of monomer **VII** by the hydrosilation reaction of **IV** with HMTS. All the other epoxynorbornane functional siloxanes were prepared by an analogous procedure.

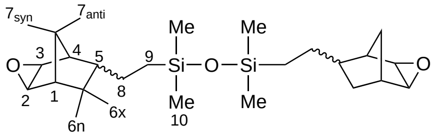
Synthesis of Monomer VII. Into a 5 mL round-bottom flask, containing a magnetic stirrer and fitted with a reflux condenser and a calcium chloride guard tube, were placed 0.82 g (6 mmol) of monoepoxide **IV**, 0.63 g (3 mmol) of HMTS, 0.55 mg of tris(triphenylphosphine)rhodium(I) chloride [$(PPh_3)_3RhCl$], and 2 mL of dry THF. The mixture was heated to 60 °C in an oil bath. An infrared spectrum of the reaction mixture after 3 h showed only a very small Si−H peak at 2130 cm^{-1}. The reaction was continued until this peak had completely disappeared from the IR spectrum. The total reaction time was 6 h. The THF and residual starting materials were removed using Krugeröhr distillation at 50 °C (0.01 mmHg). The product was obtained as a light yellow liquid and was purified by flash column chromatography (70−230 mesh silica gel; 97:3 v/v hexane/ethyl acetate). This process removed all the rhodium catalyst residues, and a clear, colorless liquid was obtained. The yield of the pure bisepoxide was 1.36 g (94%). Three fractions of enriched mixtures of diastereomers were obtained. The spectral data for the mixture containing the 5-*endo*, 5′-*endo* isomer as the major component are given below:



VII

^1H NMR ($Me_4Si/CDCl_3$) δ (ppm) 3.14 (d, J = 3.8 Hz, H_3 (5-*endo* isomer)), 3.10 (d, J = 3.7 Hz, H_2 (5-*endo* isomer)), 3.07 (d, J = 3.9 Hz, H_3 (5-*exo* isomer)), 3.03 (d, J = 3.8 Hz, H_2 (5-*exo* isomer)), 2.40−2.46 (m, H_4 and H_{5x}), 1.85−1.90 (m, H_1), 1.72−1.85 (m, H_{6x}), 1.35−1.55 (m, 2H, H_8), 1.20−1.32 (m, H_{7syn}), 1.02−1.06 (m, H_{7anti}), 0.72−0.82 (m, H_{6n}), 0.49−0.52 (m, 2H, H_9), 0.04 (m, 6H, H_{10}), 0.00 (m, 3H, H_{11}). Anal. Calcd for $C_{24}H_{44}O_4Si_3$: C, 59.95; H, 9.22. Found: C, 59.88; H, 8.94.

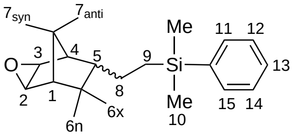
Monomer VIII. Monomer **VIII** (bp 50 °C (0.01 mmHg)) was prepared in 96% yield by the hydrosilation condensation of **IV** with TMDS. Purification was accomplished by column chromatography (70−230 mesh silica gel, 98:2 v/v hexane/ethyl acetate):



VIII

^1H NMR ($Me_4Si/CDCl_3$) δ (ppm) 3.16−3.14 (m, H_3), 3.14−3.10 (m, H_2), 2.43−2.46 (m, H_4 and H_{5x}), 1.85−1.90 (m, H_1), 1.72−1.85 (m, H_{6x}), 1.35−1.55 (m, 2H, H_8), 1.20−1.32 (m, H_{7syn}), 1.02−1.06 (m, H_{7anti}), 0.72−0.82 (m, H_{6n}), 0.49−0.52 (m, 2H, H_9), 0.04 (m, 6H, H_{10}). Anal. Calcd for $C_{22}H_{38}O_3Si_2$: C, 64.97; H, 9.42. Found: C, 64.43; H, 9.47.

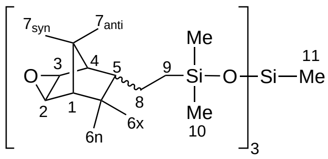
Monoepoxide IX. Monoepoxide **IX** was similarly obtained in 95% yield by the rhodium-catalyzed condensation of phenyldimethylsilane with **IV**. This monomer was purified by flash column chromatography (70−230 mesh silica gel, 96:4 v/v hexane/ethyl acetate):



IX

^1H NMR ($Me_4Si/CDCl_3$) δ (ppm) 7.49−7.52 (bm, H_{11} and H_{15}), 7.35−7.37 (bm, H_{12}, H_{14} and H_{13}), 3.00−3.08. (m, H_2 and H_3), 2.46−2.39 (m, H_4 and H_{5x}), 1.85−1.90 (m, H_1), 1.72−1.85 (m, H_{6x}), 1.35−1.55 (m, 2H, H_8), 1.20−1.32 (m, H_{7syn}), 1.02−1.06 (m, H_{7anti}), 0.76 (m, H_{6n}), 0.68−0.76 (m, 2H, H_9), 0.25−0.27 (m, 6H, two $SiCH_3$ groups). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 74.12; H, 8.33.

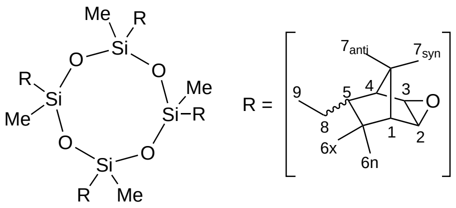
Synthesis of Trifunctional Monomer X. The yield of trifunctional monomer **X** after purification by flash column chromatography (70−230 mesh silica gel, 90:10 v/v hexane/ethyl acetate) was 1.61 g (95%).



X

^1H NMR ($Me_4Si/CDCl_3$) δ (ppm) 3.16. (m, H_3), 3.12 (m, H_2), 2.46−2.39 (m, H_4 and H_{5x}), 1.85−1.90 (m, H_1), 1.72−1.85 (m, H$_{6x}$), 1.35−1.55 (m, 2H, H$_8$), 1.20−1.32 (m, H$_{7syn}$), 1.02−1.06 (m, H$_{7anti}$), 0.76 (m, H$_{6n}$), 0.68−0.76 (m, 2H, H$_9$), 0.07−0.08 (2s, 6H, two SiCH_3 groups (H$_{10}$)), −0.01 (s, 3H, H$_{11}$). Anal. Calcd for $C_{34}H_{60}O_6Si_4$: C, 60.30; H, 8.93. Found: C, 60.06; H, 9.01.

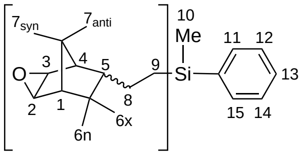
Synthesis of Tetrafunctional Monomer XI. The yield of tetraepoxide **XI** after purification by flash column chromatography (70−230 mesh silica gel, 84:16 v/v hexane/ethyl acetate) was 1.44 g (92%).



XI

^{1}H NMR (Me$_4$Si/CDCl$_3$) δ (ppm) 3.16 (m, H$_3$), 3.12 (m, H$_2$), 2.46−2.39 (m, H$_4$ and H$_{5x}$), 1.85−1.90 (m, H$_1$), 1.72−1.85 (m, H$_{6x}$), 1.35−1.55 (m, 2H, H$_8$), 1.20−1.32 (m, H$_{7syn}$), 1.02−1.06 (m, H$_{7anti}$), 0.76 (m, H$_{6n}$), 0.68−0.76 (m, 2H, H$_9$), 0.07−0.08 (bs, 3H, SiCH_3 (H$_{10}$)). Anal. Calcd for $C_{34}H_{60}O_6Si_4$: C, 61.18; H, 8.21. Found: C, 61.08; H, 8.29.

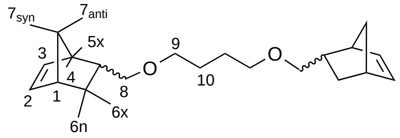
Preparation of Bisepoxide XII. The bisepoxide **XII** was prepared in 90% yield by the rhodium-catalyzed condensation of phenylmethylsilane with **IV**. This monomer was was purified by flash column chromatography (70−230 mesh silica gel, 92:8 v/v hexane/ethyl acetate):



XII

^{1}H NMR (Me$_4$Si/CDCl$_3$) δ (ppm) 7.49−7.52 (bm, H$_{11}$ and H$_{15}$), 7.35−7.37 (bm, H$_{12}$, H$_{14}$ and H$_{13}$), 3.02−3.08. (m, H$_2$ and H$_3$), 2.46−2.39 (m, H$_4$ and H$_{5x}$), 1.85−1.90 (m, H$_1$), 1.72−1.85 (m, H$_{6x}$), 1.35−1.55 (m, 2H, H$_8$), 1.20−1.32 (m, H$_{7syn}$), 1.02−1.06 (m, H$_{7anti}$), 0.76 (m, H$_{6n}$), 0.68−0.76 (m, 2H, H$_9$), 0.25−0.27 (m, 3H, SiCH_3 (H$_{10}$)). Anal. Calcd for $C_{17}H_{24}OSi$: C, 76.09; H, 8.68. Found: C, 75.57; H, 8.48.

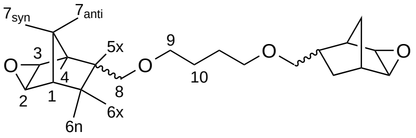
Synthesis of 1,6-[Bis[(bicyclo[2.2.1]hept-2-enyl)-6-methyl]]dioxyhexane (XIIIa). Into a round-bottom three-necked flask fitted with a mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet were placed 29.61 g (0.24 mol) of 5-(hydroxymethyl)-2-norbornene, 50 mL of distilled toluene, 14.28 g (0.36 mol) of sodium hydroxide, and 21.59 g (0.10 mol) of 1,4-dibromobutane. The solution was purged with nitrogen and then 3.84 g (5 mol % of the alcohol) of tetra-*n*-butylammonium bromide (TBAB) was added to the reaction mixture. An exotherm of 16−18 °C was observed over a period of 1 h. The reaction mixture was maintained at 80 °C. Small (1 g) portions of sodium hydroxide and (0.5 g) of TBAB were added at 6 h intervals in order to complete the reaction. GC analysis after 18 h of reaction indicated that all the 1,4-dibromobutane had disappeared, and a large peak was observed for the product. The reaction flask was cooled to room temperature, and the contents were poured into 500 mL of cold dilute hydrochloric acid. The mixture was taken up in 200 mL of fresh toluene and then washed with copious amounts of warm water to remove the phase transfer catalyst. The aqueous and the organic layers were separated, and the organic layer was dried over anhydrous sodium sulfate. The product was a clear, pale yellow liquid which distilled at 132 °C (0.05 mmHg). The yield of the crude product **XIIIa** was 24.16 g (80%), and the yield after purification by vacuum distillation was 23.0 g (76%):



XIIIa

IR ν (cm^{-1}) 3100, 1650; ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ (ppm) 5.95−6.15 (m, H$_2$ and H$_3$), 3.50 (bm, 2H, H$_8$), 3.20 (m, 2H, H$_9$), 2.90 (m, H$_4$), 2.80 (bm, H$_1$), 2.30 (bm, H$_{5x}$), 1.80 (m, H$_{6x}$), 1.65 (m, 2H, H$_{10}$), 1.40 (m, H$_{7syn}$), 1.20 (m, H$_{7anti}$), 0.82 (m, H$_{6n}$).

Synthesis of 1,6-[Bis(3-oxatricyclo[3.2.1.0^{2,4}]octyl-6-methyl)]-1,6-dioxahexane (XIIIb). In a three-necked round-bottom flask fitted with an efficient mechanical stirrer, a Claisen adaptor, two pressure-equalizing addition funnels, and a thermometer were placed 6.04 g (20 mmol) of **XIIIa**, 200 mL of dichloromethane, 200 mL of acetone, 600 mL of pH 7.5 phosphate buffer solution, and 0.75 g of 18-crown-6 ether. The flask was cooled to 0 °C using an ice/salt mixture and 77 g of oxone (2 $KHSO_5$, K_2SO_4, $KHSO_4$) as a 0.4 M ice-cold aqueous solution was added in small portions using one addition funnel. The pH of the solution was maintained between 7.4 and 7.5 by adding 1 N sodium hydroxide from the other addition funnel. Upon completion of addition of oxone, the reaction mixture was stirred at 5 °C for an additional 5−6 h. The product was filtered to remove the precipitated solids, and the organic and aqueous layers were separated. The aqueous layer was extracted with four 50 mL aliquots of dichloromethane, and the combined organic layers were washed with four 50 mL aliquots of distilled water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator. A 90% yield of a mixture of the bisepoxide product and 18-crown-6 ether was obtained. A 2 g mixture of the crude product was purified using column chromatography (200−400 mesh silica gel, 75:25 v/v hexane/ethyl acetate) to obtain 1.7 g of the pure bisepoxide **XIIIb**:

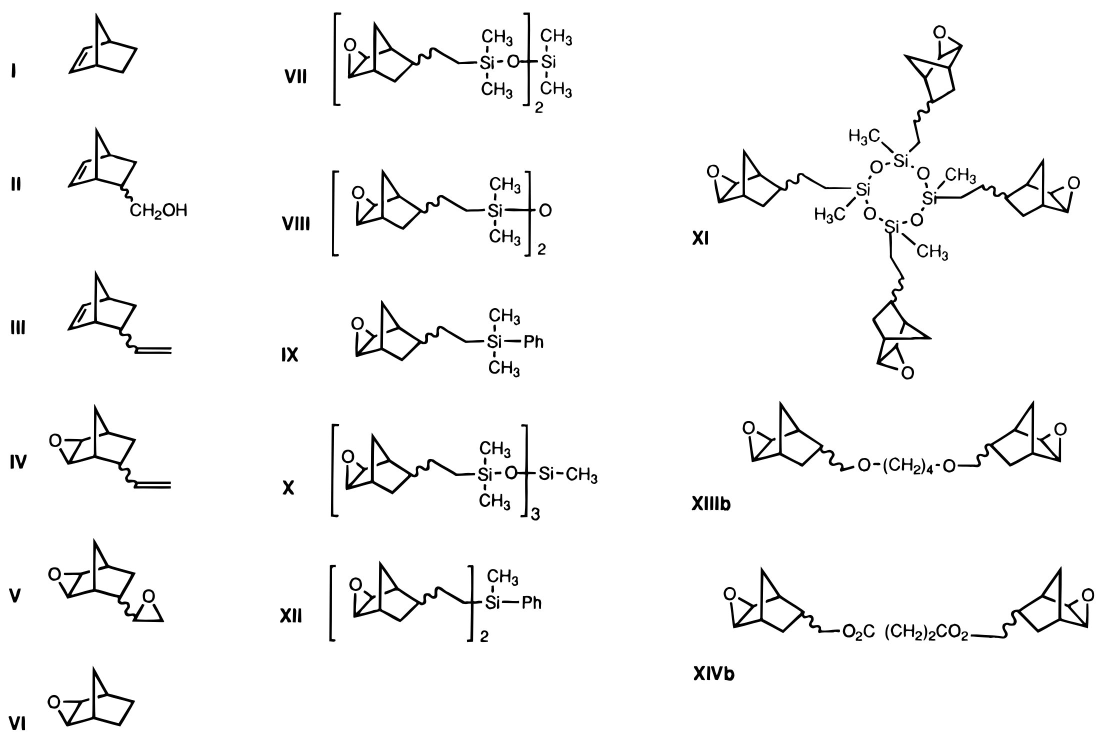


XIIIb

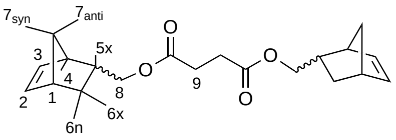
IR ν (cm^{-1}) 848, 3020; ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ (ppm) 3.50 (bm, 2H, H$_8$), 3.05−3.15 (two d, H$_2$ and H$_3$), 3.25 (m, 2H, H$_9$), 2.40−2.60 (m, H$_1$ and H$_4$), 2.30 (bm, H$_{5x}$), 1.75 (m, H$_{6x}$), 1.65 (m, 2H, H$_{10}$), 1.40 (m, H$_{7syn}$), 1.20 (m, H$_{7anti}$), 0.82 (m, H$_{6n}$).

Synthesis of (Bis[(bicyclo[2.2.1] hept-2-enyl)-6-methyl]) succinate (XIVa). In a 100 mL three-necked flask fitted with a nitrogen inlet, a magnetic stirrer, a thermometer, and a rubber septum were placed 12.44 g (100 mmol) of 5-(hydroxymethyl)-2-norbornene, 3.54 g (30 mmol) of succinic acid, 140 mg of 4-(dimethylamino)pyridine (DMAP), and 30 mL of dry DMF. The mixture was cooled to 0 °C and purged with dry N_2. A cold DMF solution of dicyclohexylcarbodiimide (12.8 g, 62 mmol) was added to the reaction mixture while the temperature was maintained at 0 °C. After 10 h, the precipitated urea was filtered off and the reaction mixture was taken up in 50 mL of dichloromethane. The DMAP was removed by the addition of 0.5 N hydrochloric acid (2 × 50 mL), and the unreacted acid was removed using an aqueous saturated sodium bicarbonate solution (2 × 50 mL). The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator. The crude product (7 g, 71%) was purified by column chromatography (200−400 mesh silica gel, 80:20 v/v hexane/EtOAc) to obtain 5.8 g of the pure

Table 1. Structures of Epoxynorbornane Starting Materials, Monomers, and Model Compounds



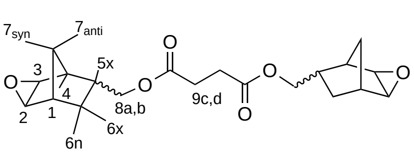
diester (**XIVa**) in 59% yield:



XIVa

IR ν (cm^{-1}) 1670, 1720, 3100; ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ (ppm) 5.90–6.15 (m, H$_2$ and H$_3$), 3.60–3.90 (m, 2H, H$_8$), 2.75–2.90 (bm, H$_1$ and H$_4$), 2.6 (t, 2H, H$_9$), 2.40 (bm, H$_{5x}$), 1.80 (m, H$_{6x}$), 1.40 (m, H$_{7syn}$), 1.20 (m, H$_{7anti}$), 0.60 (m, H$_{6n}$).

Synthesis of [Bis(3-oxatricyclo[3.2.1.0^{2,4}]octyl-6-methyl)] succinate (XIVb). An epoxidation procedure similar to the one described for monomer **XIIIb** was employed to obtain the bisepoxide **XIVb** in 98% yield. The crude product (2.0 g) was purified by column chromatography using silica gel (200–400 mesh, 80:20 v/v hexane/EtOAc) to obtain 1.9 g of the pure bisepoxide **XIVb** as a highly viscous oil:



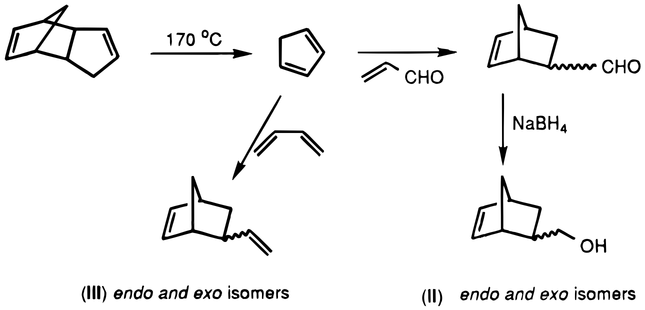
XIVb

IR ν (cm^{-1}) 3030, 1720, 848; ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ (ppm) 3.95–4.15 (m, 2H, H$_8$), 3.10–3.30 (m, H$_2$ and H$_3$), 2.6 (t, 2H, H$_9$), 2.40–2.50 (bm, H$_1$ and H$_4$), 2.30 (bm, H$_{5x}$), 1.80 (m, H$_{6x}$), 1.40 (m, H$_{7syn}$), 1.20 (m, H$_{7anti}$), 0.80 (m, H$_{6n}$).

Results and Discussion

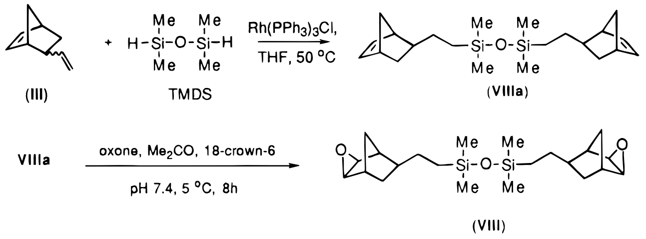
Monomer Design and Synthesis. Shown in Table 1 are the structures of the starting materials, model compounds, and monomers prepared during the course of this investigation. The basic strategy used for the preparation of the desired epoxynorbornane monomers was to employ precursors with either the norbornene or epoxynorbornane ring system bearing an additional functional group which could be further derivatized. Using this strategy, the synthesis of the desired monomers was achieved in one or two simple steps employing as the two basic starting materials: 5-hydroxymethyl-2-norbornene (**II**) and 5-vinyl-2-norbornene (**III**). Both of these precursors are easily prepared using the Diels-Alder reaction as shown in Scheme 1. **II** was obtained in high yields by the reaction of cyclopentadiene with acrolein, followed by reduction of the norbornene-5-carboxaldehyde with sodium borohydride, while **III** was obtained by the Diels–Alder reaction of cyclopentadiene with butadiene.

Scheme 1. Equations 1–4



Precursors **II** and **III** were carried forward in the synthesis of the desired monomers by selective reactions at the respective hydroxyl or vinyl groups. Then in a subsequent step, these unsaturated intermediates were subjected to epoxidation. As will be described, this strategy worked well for the synthesis of ethers and ester containing monomers from precursor **II**. Similarly, **III** could be hydrosilated with with a disilane such as 1,1,3,3-tetramethyldisiloxane to give the bisnorbornenyl derivative as shown in Scheme 2. Under mild conditions (60 °C), the hydrosilylation of **III** proceeded regioselectively (95%) at the 5-vinyl double bond. The remainder (5%) was the product of hydrosilation of the 2,3-disubstituted double bond of the norbornene ring.

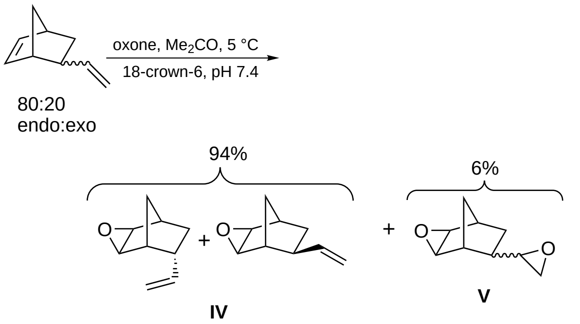
Scheme 2. Equations 5 and 6



Thus, this reaction appears to be under kinetic control with the most rapid hydrosilation taking place at the 5-vinyl double bond. The various hydrosilation products were separated by column chromatography to give pure **VIIIa**. Oxone epoxidation of **VIIIa** resulted in a quantitative yield of the bisepoxide **VIII**.

Epoxidation of III. While the reaction sequence shown in Scheme 2 is effective, the major difficulty is that careful and laborious purification was required to separate out the byproducts resulting from the Si−H addition to the norbornene double bond. Further, this procedure must be repeated for each monomer that is prepared. This can be a cumbersome process when a large number of different epoxynorbornane monomers of increasing complexity are to be synthesized. Accordingly, an alternate synthetic approach was sought. Previous research in this laboratory[16a] had shown that the hydrosilylation of 4-vinylcyclohexene oxide with the traditional platinum catalysts led to both hydrosilation and epoxide ring-opening polymerization. Subsequently, it was discovered that chemoselective hydrosilation a the double bond could be achieved using Wilkinson's catalyst without reaction at the epoxide ring.[16b]

With this information in hand, the epoxidation of **III** was attempted using several different reagents including *m*-chloroperbenzoic acid and peroxotungstophosphates.[17] It was found that **III** can be readily epoxidized in high yields using oxone ($2KHSO_5$, K_2SO_4, $KHSO_4$) at 0−5 °C with acetone as the solvent and reactant.[18,19] The epoxidation proceeds under nearly neutral conditions (pH 7.4) so that epoxide ring opening does not occur. Furthermore, we have observed that due to the much higher reactivity of the norbornene double bond, chemoselective epoxidation occurs preferentially at this site. Using an excess of **III** over the oxone (i.e., 1.3−1.5 mol of diolefin/equiv of oxone), it was possible to obtain the monoepoxide, **IV**, with a selectivity of 94%. The epoxidation was also diastereoselective giving only the *exo*-2,3-epoxy-5-vinyl-norbornane as depicted in eq 7. Given in Figure 1 is the ^{13}C NMR spectrum of **IV** together with assignments for each of the carbon atoms in the compound. The spectrum indicates that only one epoxide isomer is formed. These results can be explained by a combination of steric and stereoelectronic effects. It is known that the *exo* face of norbornene is somewhat richer in π-electrons than the *endo* face.[20] Since the epoxidation is formally an electrophilic addition reaction, there is a preference for the *exo* face over the *endo* face of the molecule. In addition, the *endo* hydrogen at C-6 and the vinyl substituent at C-5 are viewed as hindering the *endo* approach of the electrophile. In Figure 2 is presented the ^1H NMR spectrum of this key monoepoxide intermediate. The peak assignments were made using literature values for analogous model compounds.[21,22] The absence of *endo* epoxide was indicated by the lack of peaks respectively, at δ 3.4 and 62 ppm in the ^1H and the ^{13}C NMR spectra of the monoepoxide. The bisepoxide, **V**, was readily obtained in high yields by exhaustive epoxidation using excess oxone reagent.



(7)

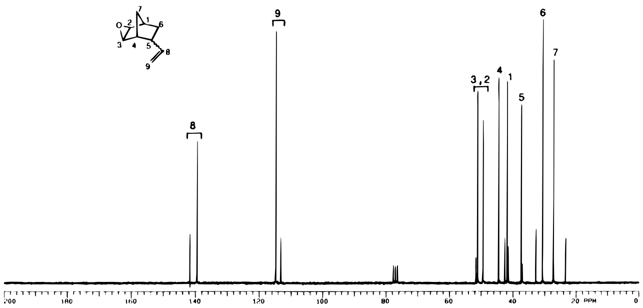


Figure 1. ^{13}C NMR spectrum of **IV** in $CDCl_3$.

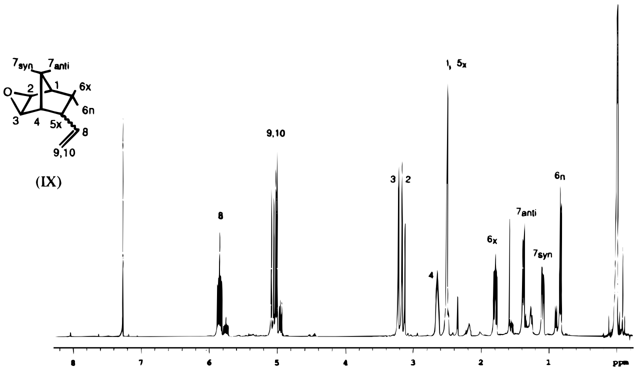
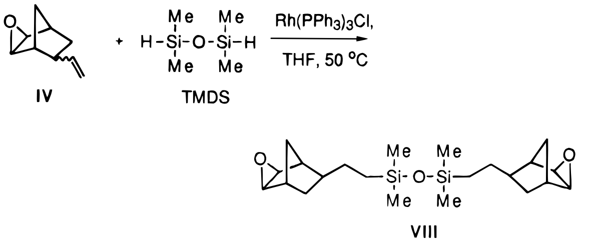


Figure 2. ^1H NMR spectrum of **IV** in $CDCl_3$.

Hydrosilylation of *exo*-2,3-Epoxy-5-vinylnorbornane (IV). A series of reactive epoxynorbornane monomers **VII**−**XII** were prepared in high yields via the hydrosilylation reaction. This reaction involved the rhodium catalyzed addition of a Si−H bond across the vinyl double bond of **IV**. Using mono-, di-, or multifunctional Si−H compounds as precursors, the corresponding epoxide containing monomers were obtained. A typical example is presented in eq 8.



(8)

Figure 3 shows the ^1H NMR spectrum of **VIII**. This spectrum indicates a complete absence of terminal vinyl proton peaks at δ 5.90 ppm and the presence of the characteristic epoxide and the $SiCH_3$ proton resonances at δ 3.00−3.15 and 0.04 ppm, respectively. Wilkinson's catalyst was specifically chosen for these hydrosilation

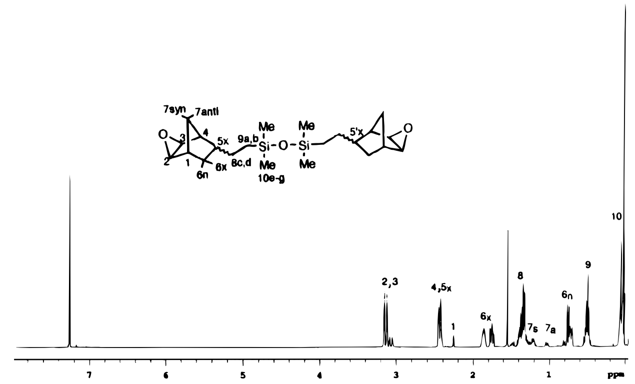
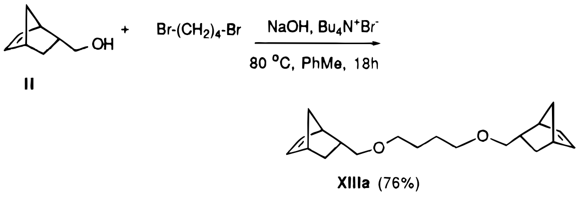


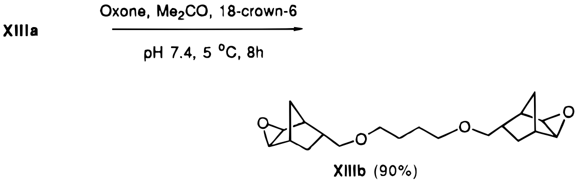
Figure 3. ^{1}H NMR spectrum of **VIII** in CDCl$_3$.

reactions to avoid the competing epoxide ring opening which is often observed with platinum catalysts.[23]

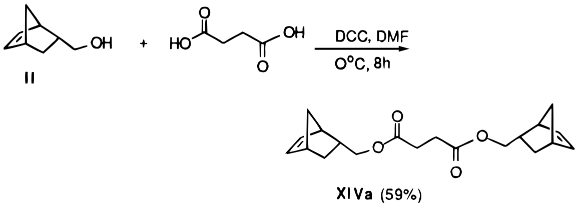
Synthesis of Epoxynorbornanes Containing Ether and Ester Linkages. Monomers **XIIIb** and **XIVb** were prepared by the two-step reaction sequences shown in eqs 9–12. **XIIIa** was prepared by the reaction



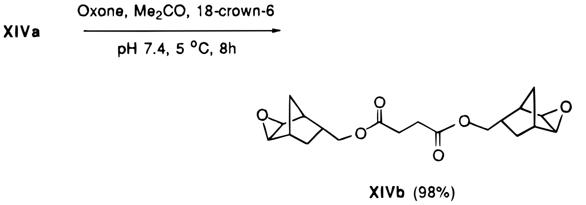
(9)



(10)



(11)



(12)

of **II** with 1,4-dibromobutane in the presence of sodium hydroxide and tetra-*n*-butylammonium bromide as a phase transfer agent. Subsequent oxone epoxidation of **XIIIa** provided the bisepoxide **XIIIb**. **XIVa** was prepared in fair yields by the direct esterification of 5-hydroxymethylnorbornene with succinic acid using dicyclohexylcarbodiimide as the condensing agent, followed by oxone epoxidation to yield monomer **XIVb** in near quantitative yield.

All the epoxynorbornane monomers were high-boiling colorless liquids. Higher functional monomers such as **X** and **XI** were viscous oils. With the exception of *exo*-2,3-epoxynorbornane (**VI**), all the other monomers were isolated as mixtures of the *endo* and *exo* isomers at the 5 position of the 2,3-*exo*-epoxynorbornane group. For example, monomer **XIVb** consists of a mixture of *endo*–*endo*, *endo*–*exo*, and *exo*–*exo* isomers. In preliminary screening tests, the monomers were found to be highly reactive in photoinitiated cationic polymerization. More detailed studies of the characterization and comparison of the reactivity of the monomers are reported in a companion paper.

Conclusions

A new series of highly reactive multifunctional monomers bearing the epoxynorbornane group were synthesized using straightforward methods. A key step in the syntheses was the chemoselective epoxidation of 5-vinyl-2-norbornene using oxone as the oxidant to obtain 5-vinyl-*exo*-2,3-epoxynorbornane in high yields. Employing the hydrosilation reaction, a series of epoxynorbornane functional monomers were prepared. Other monomers were prepared from 5-(hydroxymethyl)-2-norbornene by esterification and etherification reactions followed by oxone epoxidation. The epoxynorbornane monomers were fully characterized using IR, NMR spectroscopic, and elemental analysis techniques.

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