yield of silacyclopentenes with attendant decrease in methylen-esilacyclobutanes, it appears that the latter are precursors to **4** and **6**. Supporting this interpretation is that pyrolysis of neat **1** with an equal volume of hexane as an inert internal standard at 421 °C in a fused salt bath produces **4** and **6** in nearly quantitative (>95%) yield.[12] Possible mechanisms for this novel transformation involve migration of either the vinylic silicon–carbon (path a) or vinylic carbon–carbon bond (path b) to the exocyclic methylene substituent of the silacyclobutane.
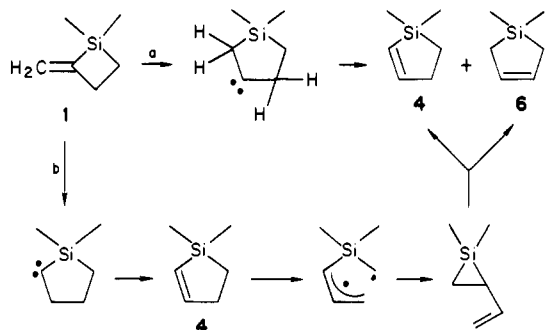
Although both paths are reasonable within the current context of mechanistic organosilicon reactions, especially in light of the surprisingly high strain enthalpy of silacyclopentane,[11] migration of the C–C bond requires a more circuitous and thermodynamically less reasonable sequence to the products.[12] Thus it is more likely that Si–C bond migration to the methylene substituent places the carbene center β to the Si atom. A hydrogen shift from either side of the divalent carbon would produce the silacyclopentene isomers.

(11) O'Neal, H. E.; Ring, M. A. J. Organomet. Chem. **1981**, 213, 419.
(12) No isomerization of **4** and **6** occurs under these conditions.

Chromatographic Resolution of Enantiomers Having Aromatic Groups by an Optically Active Clay–Chelate Adduct

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We have recently reported that a certain tris- or bischelated complex was adsorbed by a clay as a racemic pair rather than as a single enantiomer.[1] Racemic Ni(phen)$_3^{2+}$ (phen = 1,10-phenanthroline), for example, covered the surface of a clay completely with the alternating sequences of Δ- and Λ-enantiomers (d'   -am I), while enantiomeric Ni(phen)$_3^{2+}$ was adsorbed less
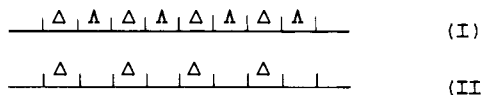
densely, resulting in only 50% coverage at saturated adsorption (diagram II). In both cases, Ni(phen)$_3^{2+}$ was adsorbed with its C_3 axis perpendicular to the surface.[2] In such configuration, the

(1) (a) Yamagishi, A.; Soma, M. J. Am. Chem. Soc. **1981**, 103, 4640. (b) Yamagishi, A. J. Phys. Chem. **1982**, 86, 2747. (c) Yamagishi, A.; Fujita, N. J. Colloid Interface Sci. **1984**, 100, 1778.

Table I. Adsorption of 2,2′-Binaphthol (**1**)^a by Δ-Ni(phen)$_3^{2+}$–Montmorillonite

vol % CH$_3$OH	**1** in soln		**1** on solid		
	R-1/10^{-7} mol	S-1/10^{-7} mol	R-1/10^{-7} mol	S-1/10^{-7} mol	K_R/K_S^{b}
66	21.0	24.0	5.0	2.0	2.9
44	14.0	20.0	12.0	6.4	3.4
33	5.4	14.6	18.0	9.4	5.1
21	1.8	7.2	22.0	16.0	5.2

^{a}6.0 × 10^{-6} mol of **1** was added to 20 mL of methanol–water mixture which contained 2.5 × 10^{-5} mol of Δ-Ni(phen)$_3^{2+}$–montmorillonite. The mixture was stirred at 0 °C for 3 h. The precipitate obtained by filtering the mixture was dispersed again in 20 mL of methanol. The amounts of free and adsorbed enantiomers of **1** were determined by analyzing the above methanol–water and methanol filtrates with the electronic and circular dichroism (CD) spectra. ^{b}Ratio of the binding constants of R-1 to S-1. R-1 and S-1 denote the two optical isomers of compound **1**.

**Table II.** Adsorption of Cyclohexyl Phenyl Sulfoxide (**2**)^a by Δ-Ni(phen)$_3^{2+}$–Montmorillonite

vol % CH$_3$OH	**2** in soln		**2** on solid		
	R-2/10^{-7} mol	S-2/10^{-7} mol	R-2/10^{-7} mol	S-2/10^{-7} mol	K_R/K_S
54	0.56	0.40	5.2	6.8	0.54
37	0.42	0.24	6.9	8.7	0.45
20	0.22	0.11	8.4	9.6	0.41
3.3	0.21	0.05	8.8	10.4	0.21

^{a}2.0 × 10^{-6} mol of **2** was added to 6 mL of methanol–water mixture which contained 2.0 × 10^{-5} mol of Δ-Ni(phen)$_3^{2+}$–montmorillonite. The succeeding procedures were the same as in case of **1** (Table I).

racemic chelates in state I had their ligands stacked in the so-called key-and-lock way. In contrast, the enantiomeric chelates in state II were not packed closely because the ligands in the adjacent chelates interfered sterically with each other.

As shown in the present communication, these findings have led to the chromatographic resolution of aromatic molecules on a column of an optically active clay–chelate adduct. As a result, important compounds for asymmetric syntheses, such as 2,2′-binaphthol, were obtained as pure enantiomers.

Comparing diagram I with diagram II, one can see that the void spaces in diagram II accepted exclusively the enantiomers opposite to the primarily adsorbed chelate (denoted by Δ in diagram II). Such recognition of chirality by surface II would be equally effective if a molecule of a different kind formed a diastereomeric pair with the primarily adsorbed chelate. This expectation prompted the author to study the adsorption of 2,2′-binaphthol (**1**) and cyclohexyl phenyl sulfoxide (**2**) by colloidally
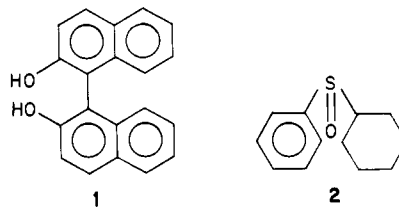
dispersed Δ-Ni(phen)$_3^{2+}$–montmorillonite. These molecules were selected because their two planar groups are twisted helically and would probably interact stereoselectively with the phenanthroline ligands in Δ-Ni(phen)$_3^{2+}$.

Δ-Ni(phen)$_3^{2+}$–montmorillonite was prepared by mixing Δ-Ni(phen)$_3$Cl$_2$ with sodium montmorillonite (Kunimine Ind. Co., Japan) dispersed in a methanol–water solution. Table 1 gives data

(2) These diagrams are simplified representations of the actual adsorbed states. A clay surface is actually a bidimensional silicate sheet.[1b] one site in the diagrams corresponds to three tetrahedral rings surrounded by six SiO$_4$$^{4-}$ tetrahedrons in the silicate sheet (see ref 1b for the details). These conclusions are different from the stereoselective adsorption or activation of a molecule by a clay as reported by other authors (e.g.: Jackson, T. A. Chem. Geol. **1971**, 7, 295).

Table III. Chromatographic Resolution of Racemic Compounds by an Optically Active M(phen)₃²⁺–Montmorillonite

| rac sample | column[a] | vol ratio of eluate[b] | capacity factor (config)[c] | | α[c] | Rₛ[c] |
			less retained	more retained		
2,2'-binaphthol	I	1:1	68 (S)	130 (R)	2.2	1.3
2,2'-binaphthol	II	1:2	8 (R)	16 (S)	2.3	1.1
2,2'-diaminobinaphtyl	I	1:1	46 (S)	100 (R)	2.5	1.3
2,2'-dimethylbinaphtyl	I	1:1	48 (S)	60 (R)	1.3	0.64
cyclohexyl phenyl sulfoxide	I	1:2	52 (R)	76 (S)	1.6	0.41
cyclohexyl phenyl sulfoxide	II	1:2	5.5 (S)	9.0 (R)	2.0	1.0
methyl phenyl sulfoxide	II	0:1	4.5 (S)	6.6 (R)	1.8	0.70
hydrobenzoin	I	1:2	24 (R)	34 (S)	1.7	0.75
1,2-diphenylethanol	I	1:2	31 (R)	41 (S)	1.5	0.40
1-phenylethanol	I	1:4	17	17	1	0
2,3-dihydro-2-methyl-5,6-diphenylpyrazine	I	1:1	21 (R)	36 (S)	2.1	0.60
2,3-dihydro-2-methyl-5,6-dimethylpyrazine	I	1:1	18	18	1	0
tris(acetylacetonato)cobalt(III)	I	0:1	29 (Λ)	45 (Δ)	1.9	1.0

[a] Column I was a 50 × 0.8 cm (i.d.) Δ-Ni(phen)₃²⁺–montmorillonite–silica gel. Column II was a 20 × 0.4 cm (i.d.) Λ-Ru(phen)₃²⁺–montmorillonite–silica gel. Dead volume (V_d) was 10 mL and 2 mL with water for I and II, respectively. Flow rate was 1 mL/min and 0.2 mL/min for I and II, respectively. The temperature was maintained at 0 and 23 °C for I and II, respectively. [b] Volume ratio of methanol–water in an eluate. [c] Capacity factor, α, and R_s were defined by V_1 (or V_2), $(V_2 - V_d)/(V_1 - V_d)$, and $(V_2 - V_1)/(\Delta V_2 + \Delta V_1)$, respectively. Subscripts 1 and 2 refer to the less and more retained enantiomers, respectively (see part b in Figure 1).

for adsorption of **1** from four kinds of mixed solvents. Racemic **1** was partially resolved because the R enantiomer of **1** (R-1) was adsorbed preferentially by Δ-Ni(phen)₃²⁺–montmorillonite. Such selectivity might arise from the association of R-1 with Δ-Ni-(phen)₃²⁺ on a clay surface. In fact, when R-1 was placed over Δ-Ni(phen)₃²⁺ with the C_2 axis of **1** perpendicular, it formed a well-matched molecular complex with its two naphthyl groups faced with the two phenanthroline ligands in Δ-Ni(phen)₃²⁺. Such steric matching was not achieved for a pair of S-1 and Δ-Ni-(phen)₃²⁺. Similar stereoselective adsorption was observed in case of **2** (Table II).

On the basis of the above experiments, an attempt was made to resolve **1** by liquid column chromatography. First, **1** was placed on a 5 × 1.0 cm (i.d.) clumn of Δ-Ni(phen)₃²⁺–montmorillonite prepared by pouring the clay–chelate adduct into a glass. Figure 1a shows the results obtained when the compound was eluted with 1:2 (v/v) methanol–water at 0 °C. At this temperature, the racemization of Δ-Ni(phen)₃²⁺ was negligible.[3] The chromatogram consisted of two peaks, the first and second peaks corresponding to S-1 and R-1, respectively, as determined from circular dichroism spectra. Thus, we concluded that **1** was at least partially resolved on the column.

We tried to improve the above results by means of high-performance liquid chromatography (HPLC). One difficulty in using the clay–chelate adduct as a packing material lies in the fact that the material is composed of particles of various sizes (ranging from 0.5 to 5 μm according to electric birefringence measurements[1b]). The inhomogeneity in particle size apparently disturbed the flow of an eluate, resulting in the tailing of a separated molecule. In fact, both S-1 and R-1 tailed strongly (Figure 1a). The problem was overcome by coating silica gel of uniform size with a thin film of clay–chelate adduct. The material was prepared as follows: 10 g of silica gel (230–400 mesh, Wako Pure Chem. Ind., Japan), 0.1 g of poly(vinyl alcohol) (Nakarai Chem. Ind., Japan), and 0.2 g of sodium montmorillonite were mixed in 200 mL of water. The mixture was boiled at 80 °C for about 6 h until the solvent was all evaporated. The solid was then ground to <200 mesh. When 1 × 10⁻⁴ mol of Δ-Ni(phen)₃Cl₂ was added to 100 mL of water containing the above material, the chelate was adsorbed by the solid completely to give a pinkish solid. The silica gel coated with Δ-Ni(phen)₃²⁺–montmorillonite was packed into a 50 × 0.8 cm (i.d.) stainless steel column as a slurry. The dead volume of the column, estimated with water, was 10 mL. HPLC was performed with a JASCO BIP-II chromatograph equipped with a JASCO UV-100 detector at 0 °C. The flow rate of eluent was 1 mL/min under a pressure of 50 kg/cm².

Figure 1b shows the results obtained when **1** was eluted with 1:1 (v/v) methanol–water. Note that the first peak due to S-1
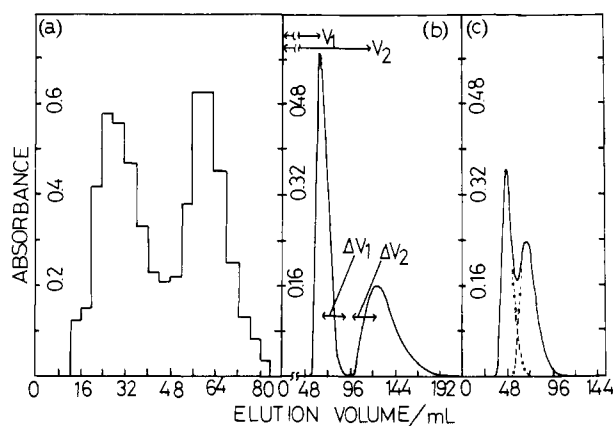

Figure 1. (a) Chromatogram obtained when 2.5 × 10⁻⁶ mol of 2,2'-binaphthol (**1**) was eluted with 1:2 (v/v) methanol–water on a column of 5 × 1 cm (i.d.) Δ-Ni(phen)₃²⁺–montmorillonite. Flow rate was 0.2 mL/min and temperature 0 °C. Wavelength was 335 nm. (b) Chromatogram obtained when 1.5 × 10⁻⁶ mol of 2,2'-binaphthol (**1**) was eluted with 1:1 (v/v) methanol–water on a column of 50 × 0.8 cm (i.d.) silica gel coated with Δ-Ni(phen)₃²⁺–montmorillonite. Flow rate was 1.0 mL/min and temperature 0 °C. Wavelength was 335 nm. (c) Chromatogram obtained when 1.2 × 10⁻⁶ mol of cyclohexyl phenyl sulfoxide (**2**) was eluted with 1:2 (v/v) methanol–water on the same column as in (b). Wavelength was 240 nm. The dotted curves were the elution curves of the enantiomers as determined by the circular dichroism measurements.

tailed to a much smaller extent so that the two peaks separated completely. It seems of vital significance that compound **1**, a key compound for the asymmetric reduction of ketones with LiAlH₄ and also for the preparation of an optically active crown ether,[4] was resolved completely on such a simply prepared column as this. Figure 1c shows the result obtained when **2** was eluted with 1:2 (v/v) methanol–water. The two peaks overlapped considerably with a corresponding lower resolution efficiency. When the eluted solvent was divided into two at an elution volume of 60 mL, the initial and final fractions contained R-2 and S-2 with optical purities of 85% and 80%, respectively.

Table III lists the chromatographic results, using a column of silica gel coated with either Δ-Ni(phen)₃²⁺–montmorillonite or Λ-Ru(phen)₃²⁺–montmorillonite. On the latter column, the HPLC was preformed at 23 °C because Λ-Ru(phen)₃²⁺ did not racemize at room temperature. According to the table, the type of column described was able to resolve a wide variety of aromatic molecules

(3) Lawrence, G. A.; Stranks, D. R. *Inorg. Chem.* **1978**, *17*, 1804.

(4) (a) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3179. (b) Sousa, L. R.; Hoffman, D. H.; Kaplan, L.; Cram, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 7100.

if they possessed two aromatic groups or one aromatic and one aliphatic ring group. Except for methyl phenyl sulfoxide, compounds with only one aromatic group per molecule could not be resolved.

In comparison to the known column materials, all of which have been naturally occurring and synthetic organic polymers,[5] the clay–chelate adducts have the following advantages: (i) The material is prepared simply by mixing silica gel coated with a clay and an optically active chelate. (ii) The material is not subject to chemical deterioration caused by oxidation and hydrolysis. (iii) The method is extremely versatile, as it can be varied indefinitely by changing the primarily adsorbed chelate.

Acknowledgment. Thanks are due to Prof. R. Noyori (Nagoya University, Japan) for his gift of compounds 2,2'-diaminobinaphthyl and 2,2'-dimethylbinaphthyl and also to Prof. K. Yagi (Hokkaido University, Japan) for his permission to use an instrument (a JASCO Model J-500 polarimeter).

(5) (a) Hesse, G.; Hagel, R. Liebigs Ann. Chem. 1976, 996. (b) Blaschke, G. Angew. Chem., Int. Ed. Engl. 1980, 19, 13. (c) Yuki, H.; Okamoto, Y.; Okamoto, I. J. Am. Chem. Soc. 1980, 102, 6358.

New Strategy for [3 + 2] Annulation: Applications to the Synthesis of Functionalized Di- and Triquinanes[1]

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Oxycyclopropanes, in particular those having an additional electron-withdrawing substituent, have become valuable intermediates in synthetic organic chemistry. Their best known reaction is the facile ring opening under acidic, basic, or thermal conditions, which has been extensively used to prepare γ-keto esters and lactones, β,γ-unsaturated ketones, cyclopentanones, and furans.[2] Less attention, however, has been placed upon the use of such a reaction for the formation of a carbon–carbon bond.[3] Recently, Reissig has described that 2-(silyloxy)cyclopropane carboxylate esters of general structure 1 react under equimolar amounts of a symmetrical ketone and titanium tetrachloride to afford γ-lactols in high yield.[4] This was the first report of the direct use of a "donor–acceptor-substituted cyclopropane" in the formation of a five-membered ring.

As part of our research program directed toward efficient pentannulations,[5] we envisioned that a (silyloxy)cyclopropane ester such as 1 could serve as a three-carbon synthon for cyclopentene syntheses. In particular, the fluoride-induced desilylation and concomitant ring opening should give rise to the elusive γ-oxo ester enolate system 2. The successful trapping of 2 in a Michael reaction with an activated alkene should provide access to intermediates such as 3 and, finally, to highly functionalized cyclopentenes 4 (Scheme I). This new strategy for [3 + 2] annulatiion would allow the introduction of the three-carbon synthon as a nucleophile, therefore complementing previous approaches to cyclopentenes involving electrophilic cyclopropanes.[5,6]

(1) A preliminary report of this work was presented: Marino, J. P.; Laborde, E. "Abstracts of Papers", 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 29, 1984; American Chemical Society: Washington, DC, 1984; ORGN 139.

(2) Reviews: (a) Wenkert, E. Acc. Chem. Res. 1980, 13, 27. (b) Wenkert, E. Heterocycles 1980, 14, 1703. (c) Conia, J. M. Pure Appl. Chem. 1975, 43, 317. (d) Schöllkopf, U. Angew. Chem., Int. Ed. Engl. 1968, 7, 588.
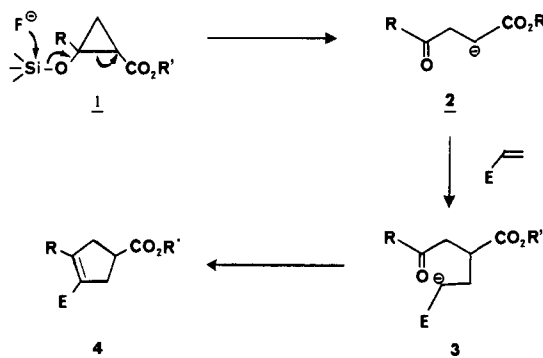
(3) For a former example, see: Makamura, E.; Kuwajima, I. J. Am. Chem. Soc. 1977, 99, 7360.

(4) Reissig, H.-U. Tetrahedron Lett. 1981, 22, 2981.

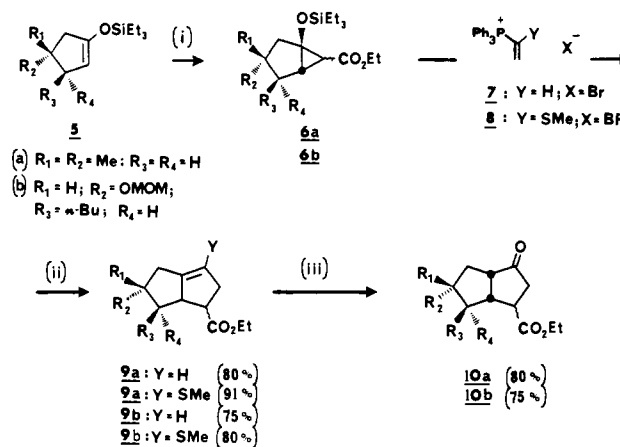(5) (a) Marino, J. P.; Landick, R. C. Tetrahedron Lett. 1975, 4531. (b) Marino, J. P.; Ferro, M. P. J. Org. Chem. 1981, 46, 1828.

(6) For a review, see: Danisefsky, S. Acc. Chem. Res. 1979, 12, 66.

Scheme I

Scheme II

(a) R₁ = R₂ = Me; R₃ = R₄ = H
(b) R₁ = H; R₂ = OMOM;
R₃ = n-Bu; R₄ = H

We wish to report the successful application of the above methodology to the synthesis of functionalized di- and triquinane systems. Our initial results focus on the use of (2-(silyloxy)-cyclopropane esters 6, derived from triethylsilyl enol ethers of cyclopentanones and ethyl diazoacetate. The specific activated alkenes are vinylphosphonium salts. These Michael acceptors were chosen because of their ability to generate in situ a Wittig reagent that could intramolecularly react with the incipient ketone.[7] Employment of 1-thio-substituted vinylphosphonium salt allowed for subsequent hydrolysis of the resulting vinyl sulfides to the corresponding bicyclooctanones. The overall sequence of reactions from the silyl enol ethers is shown in Scheme II.

In general, the reaction of silyl enol ether 5a[8] and 5b[9] with carbethoxycarbene (generated by the cupric sulfate catalyzed decomposition of ethyl diazoacetate) gave high yields of (silyloxy)cyclopropane esters 6. In the case of 6b, only one stereoisomer was formed at the ring fusion, while a 4:1 mixture of exo- and endo-carbethoxy isomers, respectively, was produced.[10] When the cyclopropanes 6 were treated with either vinylphosphonium salt 7[11] or 8,[12] in the presence of potassium fluoride and a catalytic

(7) For a related use of vinyl phosphonium salts, see: (a) Hewson, A. T. Tetrahedron Lett. 1978, 3267. (b) Hewson, A. T.; MacPherson, D. T. Ibid. 1983, 24, 5807. (c) Cameron, A. G.; Hewson, A. T. J. Chem. Soc., Perkin Trans. 1 1983, 2979.

(8) Exon, C.; Nobbs, M.; Magnus, P. Tetrahedron 1981, 37, 4515.

(9) Prepared by the sequence of reactions given below:
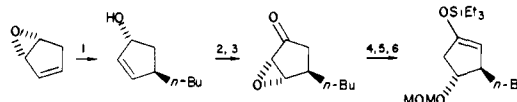
Reagents: (1) Li[CuCN-n-Bu], Et₂O, −40 °C; (2) t-BuOOH, VO(acac)₂, PhH, 40 °C; (3) CrO₃·pyr, CH₂Cl₂; (4) LDA, THF, −78 °C; then, Et₃SiCl; (5) LiAlH₄, Et₂O, room temperature; (6) MOMCl, i-Pr₂EtN, CH₂Cl₂

(10) The stereochemical assignments are based on the following ¹H NMR (360 MHz) data: For the exo isomer of 6b, $J_{3,4} = 0$ and $J_{2,3} = 4.0$ Hz; for the endo isomer of 6b, $J_{3,4} = 1.6$ and $J_{2,3} = 9.8$ Hz.