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Supplementary Material Available: Tables of crystallographic data for 6 and 10, positional parameters and temperature factor expressions for 6, and atomic coordinates and temperature factors for 10 (6 pages). Ordering information is given on any current masthead page.

Synthesis and Thermal Ring Expansion of 2-Methylene-1,1-dimethylsilacyclobutane

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Early studies of the degenerate rearrangement of methylenecyclobutane¹ provided new insight into the influence of substituents on the thermal isomerization² of four-membered rings. Difficulty with the synthesis of the analogous methylenesilacyclobutanes, however, has impeded progress toward understanding the role of a metal atom on the course of isomerizations of metallocyclobutanes. We report herein the first synthesis of a 2-methylenesilacyclobutane 1, which thermally isomerizes via an unexpected ring expansion to the isomeric silacyclopentenes.

Low-pressure flow pyrolysis³ of 1,1-dimethylsilacyclobutane in an eightfold excess of allene at 600 °C affords a 27% yield of 1^4 along with smaller amounts of six other products:⁵ 2, 3, 4, 5,⁶ 6, and the dimethylsilene dimer 7. When the pyrolysis tem-

$$S_{i} = + H_{2}C = C = CH_{2} \xrightarrow{\Delta}_{C_{2}H_{4}} = S_{i} + HC = C - CH + HC = C - CH$$

perature is raised from 600 to 670 °C, the combined yields of isomers 1 and 5 decrease from 31% to 5% while formation of 4

(1) Doering, W. v. E.; Gilbert, J. C. Tetrahedron, Suppl. 1966, No. 7, 397. (2) For a comprehensive review, see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

(5) Compounds 2, 3, 4, 6, and 7 were identified by comparison with authentic samples. Product yields were based on the quantity of decomposed

53 (20), 44 (20), 43 (76). Since base-line separation of 5 and 6 could be achieved only on a capillary GC column, an elemental analysis on the mixture of isomers was not obtained.

and 6 increases from 10% to 19%. With higher temperature and therefore higher concentration of dimethylsilene the yield of 7 increases as expected for dimerization. The ratio of total cyclic to acyclic silanes, 2.0 at 600 °C, however, shows little change at higher temperature, 1.8 at 670 °C.

The major product at the lower temperature is the previously unknown 2-methylene-1,1-dimethylsilacyclobutane (1). Predominant formation of the 2-isomer is consistent with initial approach of the silicon atom of the silene to C2 of allene with concomitant development of the allylic-type resonance in the carbon frame. Since there is good evidence in the literature that fragmentation of a silacyclobutane commences at a carbon-carbon bond,⁷ it is most likely that the reverse pathway, cycloaddition, starts with formation of a slightly stronger silicon-carbon bond8 as represented below by diyl 8. The symmetrical 3-methylenesilacyclobutane 5 is formed in lower yield (4.1% at 600 °C and 1.2% at 670 °C) than 1 presumably because formation of a somewhat weaker carbon-carbon bond in 9 is required in developing the transition state.



Other reaction pathways to be considered include those leading to 2 and 3. Both acyclic products were previously observed from the reaction of dimethylsilene and propyne9 where it was shown that 2 resulted from isomerization of a primary product, 3. The temperature dependence of the silene/allene reaction suggests a similar type of analysis. Since the ratio of the 2 to 3 increases from 0.3 to 0.7 as the pyrolysis temperature is lowered from 670 to 600 °C in the flow system, it is likely that 2 is a primary reaction product. The well-characterized, 1,3-trimethylsilyl shift converts the 2 to the thermodynamically more stable 3. At 670 °C the ratio of 2 to 3, 0.3, approaches the equilibrium value, 0.16, reported by Slutsky and Kwart.¹⁰

When propyne was the dimethylsilene trap, acyclic silanes 2 and 3 were the major products, formed in 5-7 times greater yield than the cyclic adduct 1,1,3-trimethylsilacyclobutene. In contrast, cycloadducts 1 and 4-6 are the major products of the silene/allene reaction. The acyclic products, 2 and 3, arising from the inter-



molecular silene ene reaction, are formed in lower yield with allene because vinylic C-H bonds are stronger and less reactive than the propargylic C-H bonds of propyne. Transfer of a vinylic hydrogen of allene to the methylene portion of the silene can be described by a concerted ene pathway.

The presence of dimethylsilacyclopentenes among the reaction products is without parallel for simple 2 + 2 cycloadditions in hydrocarbon chemistry. Since higher temperature increases the

(10) Slutsky, J.; Kwart, H. J. Am. Chem. Soc. 1973, 95, 8678.

⁽³⁾ For experimental conditions, see ref 9. (4) 1: ¹H NMR (neat) δ -0.19, (s, 6 H, (CH₃)₂Si), 0.50 (br t, J = 8.5 Hz, CH₂Si), 2.25 (m, 2 H, CCH₂C), 4.90 (m, 1 H, =-CH), 4.68 (m, 1 H, =-CH); CH₃51), 2.25 (m, 2 H, CCH₂C), 4.50 (m, 1 H, -CH₃, 5.06 (m, 1 H, -CH₃), ¹³C NMR (neat) δ -1.11 (q), 10.68 (t), 31.73 (t), 118.42 (t), 157.11 (s); GC/MS, m/e (% rel intensity) 112 (9), 97 (50), 85 (12), 84 (100), 83 (13), 72 (25), 71 (18), 68 (16), 58 (19), 58 (80); mass spectrum, calcd for SiC₆H₁₂ 112.0709, m/e found 112.0709.

⁽⁷⁾ Barton, T. J.; Marquardt, G.; Kilgour, J. A.; J. Organomet. Chem. 1974, 85, 317. Golino, C. M.; Bush, R. D.; On, P.; Sommer, L. H. J. Am. Chem. Soc. 1975, 97, 8678. Valkovich, P. B.; Ito, T. I.; Weber, W. P. J. Org. Chem. 1974, 24, 3543.

⁽⁸⁾ Walsh, R. Acc. Chem. Res. 1981, 14, 246.

⁽⁹⁾ Conlin, R. T.; Kwak, Y.-W.; Huffaker, H. B. Organometallics 1983, 2. 343.

yield of silacyclopentenes with attendant decrease in methylenesilacyclobutanes, 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 $421 \,^{\circ}$ 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.

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(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)₃²⁺ (phen = 1,10phenanthroline), 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)₃²⁺ was adsorbed less

densely, resulting in only 50% coverage at saturated adsorption (diagram II). In both cases, Ni(phen)₃²⁺ was adsorbed with its C_3 axis perpendicular to the surface.² In such configuration, the

Table I. Adsorption of 2,2'-Binaphthol $(1)^a$ by Δ -Ni(phen)₃²⁺-Montmorillonite

vol % CH₃OH	1 in soln		1 on solid		
	<i>R</i> -1/10 ⁻⁷ mol	S-1/10 ⁻⁷ mol	<i>R</i> -1/10 ⁻⁷ mol	S-1/10 ⁻⁷ mol	$K_{\rm R}/K_{\rm S}^{b}$
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)₃²⁺-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 enantimers of 1 were determined by analyzing the above methanol-water and methanol filtrates with the electronic and circular dichroism (CD) spectra. ^bRatio 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)₃²⁺-Montmorillonite

vol % CH₃OH	2 in soln		2 on solid		
	<i>R</i> -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)₃²⁺-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)₃²⁺-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)₃²⁺.

 Δ -Ni(phen)₃²⁺-montmorillonite was prepared by mixing Δ -Ni(phen)₃Cl₂ with sodium montmorillonite (Kunimine Ind. Co., Japan) dispersed in a methanol-water solution. Table 1 gives data

 ^{(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.

⁽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 SiO₄⁴⁻ 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).