tion was prepared by mixing 0.2611 g (2.137 mmol) of (*S*)-(−)-1-(2-pyridyl)ethylamine [(*S*)-**1a**)] and 0.2838 (2.323 mmol) of salicylaldehyde in methanol. This solution was then diluted to 25.00 ml. After 3 hr it had $[\alpha]^{25}\mathrm{D}$ +140° (*c* 1.934, CH_3OH). The observed rotation of this solution remained unchanged for an additional 24 hr.

In a similar way, 0.266 g (2.18 mmol) of (*S*)-**1a** was boiled for 5 min with 0.280 g (2.29 mmol) of salicylaldehyde in methanol. Removal of the solvent and recrystallization of the residue from cyclohexane gave 0.260 g (53%) of partially racemic (*S*)-**1c**: flat, yellow prisms, mp 62–64°, $[\alpha]^{25}\mathrm{D}$ +66.4° (*c* 4.44, absolute C_2H_5OH). Removal of the cyclohexane from the mother liquors gave 0.040 g of partially racemic (*S*)-**1c**: fine, yellow plates, mp 58–60°, $[\alpha]^{25}\mathrm{D}$ +128° (*c* 4.20, absolute C_2H_5OH).

(*S*)-(−)- and (*R*)-(+)-1-(3-Pyridyl)ethylamine [(*S*)-2a and (*R*)-2a]. To 16.4 g (0.134 mol) of (±)-1-(3-pyridyl)ethylamine,[9] bp 119–121° (26 mm), in 250 ml of boiling ethanol was added a hot solution of 21.0 g (0.140 mol) of (+)-tartaric acid in 700 ml of 95% ethanol. On cooling to room temperature, there was deposited 34.7 g (190%) of fine, white prisms, $[\alpha]^{25}\mathrm{D}$ +17° (*c* 4.00, H_2O). Three recrystallizations of this salt from a 3:1 mixture of isopropyl alcohol–water gave 7.60 g (42%) of the (+)-acid tartrate salt of (*S*)-**2a**: fine, white prisms, mp 188–190° dec, $[\alpha]^{25}\mathrm{D}$ +21° (*c* 4.04, H_2O) [lit.[6] mp 193–194°, $[\alpha]^{20}\mathrm{D}$ +20.35° (*c* 4.01, H_2O)]. Decomposition of this salt as above gave 0.60 g (18%) of (*S*)-**2a**: colorless oil, bp 118° (25 mm), $[\alpha]^{25}\mathrm{D}$ −37.0° (*c* 4.00, absolute C_2H_5OH) [lit.[6] bp 99° (15 mm), $[\alpha]^{20}\mathrm{D}$ −39.4° (*c* 4.60, C_2H_5OH)].

Combination of the mother liquors from the resolution above, removal of the solvent, and decomposition of the (+)-acid tartrate salt gave 6.37 g (0.0521 mol) of partially racemic (*R*)-**2a**. The latter was combined with 7.40 g (0.0614 mol) of (−)-tartaric acid in 240 ml of boiling 3:1 isopropyl alcohol–water. On cooling to room temperature, there was obtained 5.30 g (29%) of (−)-acid tartrate salt of (*R*)-**2a**: fine, white prisms, mp 183–184° dec, $[\alpha]^{25}\mathrm{D}$ −20° (*c* 3.98, H_2O). This salt was decomposed as before, and there was obtained 0.63 g (8%) of (*R*)-**2a**: colorless oil, bp 118° (25 mm), $[\alpha]^{25}\mathrm{D}$ +35.7° (*c* 4.87, absolute C_2H_5OH).

(±)-1-(3-Pyridyl)ethylamine dihydrochloride [(±)-2b] was obtained as hygroscopic, fine, white prisms, mp 208–213° dec.

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.10.

(*R*)-(−)-1-(3-Pyridyl)ethylamine dihydrochloride [(*R*)-2b] was obtained as extremely hygroscopic, microscopic crystals, mp 191–194°, $[\alpha]^{25}\mathrm{D}$ −4.1° (*c* 4.09, H_2O).

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.16.

(*S*)-(+)-1-(3-Pyridyl)ethylamine dihydrochloride [(*S*)-2b] was in the form of extremely hygroscopic, fine, white prisms, mp 191–194°, $[\alpha]^{25}\mathrm{D}$ +4.5° (*c* 5.85, H_2O).

(*S*)-(−)-1-(4-Pyridyl)ethylamine [(*S*)-3a]. To 16.7 g (0.137 mol) of (±)-1-(4-pyridyl)ethylamine,[9] bp 80–85° (1–2 mm), in 400 ml of boiling methanol was added 20.6 g (0.137 mol) of (+)-tartaric acid in 350 ml of hot methanol. After cooling to room temperature, there was obtained 29.6 g (80%) of salt, $[\alpha]^{24}\mathrm{D}$ +22.3° (*c* 8.06, H_2O). The salt was recrystallized from methanol–water by mixing the salt with about 60 ml of boiling methanol per gram of salt and then adding water until solution was complete, usually about 20 ml of water per gram of salt. Three recrystallizations in this manner gave 10.6 g (57%) of the (+)-acid tartrate salt of (*S*)-**3a**: $[\alpha]^{25}\mathrm{D}$ +17.7° (*c* 8.19, H_2O) [lit.[6] $[\alpha]^{20}\mathrm{D}$ +18.15° (*c* 8.12, H_2O)]. Decomposition of 11.3 g (0.0415 mol) of salt, purified as above, in the usual way gave 3.66 g (79%) of (*S*)-**3a**: colorless oil, bp 89–91° (4 mm), $\alpha^{25}\mathrm{D}$ −33.2° (neat), $[\alpha]^{25}\mathrm{D}$ −28.0° (*c* 7.89, abs C_2H_5OH) [lit.[6] bp 95° (9 mm), $[\alpha]^{20}\mathrm{D}$ −27.9° (*c* 7.44, C_2H_5OH)].

(*S*)-(−)-1-(4-Pyridyl)ethylamine dihydrochloride [(*S*)-3b] was obtained as fine, white needles, mp 151–153° dec (sealed tube), $[\alpha]^{25}\mathrm{D}$ −4.2° (*c* 7.76, H_2O).

Anal. Calcd for $C_7H_{12}Cl_2N_2$: Cl, 36.35. Found: Cl, 36.46.

(*S*)-(+)-*N*-(5-Bromosalicylidine)-1-(4-pyridyl)ethylamine [(*S*)-3c]. To a boiling solution of 0.293 g (2.40 mmol) of (*S*)-(−)-1-(4-pyridyl)-ethylamine [(*S*)-**3a**] in 5 ml of methanol was added 0.489 g (2.43 mmol) of 5-bromosalicylaldehyde in 5 ml of hot methanol. Evaporation of the solvent and crystallization of the residue from cyclohexane gave 0.407 g (56%) of (*S*)-**3c**: microscopic, yellow needles, mp 101–102°, $[\alpha]^{25}\mathrm{D}$ +38° (*c* 1.25, absolute C_2H_5OH) [lit.[9] mp 89–90° for (±)-**3c** crystallized from ethanol–water]. After boiling this sample of (*S*)-**3c** in cyclohexane for 30 min and crystallization, its rotatory power was essentially unchanged.

Anal. Calcd for $C_{14}H_{13}BrN_2O$: C, 55.10; H, 4.29; Br, 26.19; N, 9.18. Found: C, 54.93; H, 4.25; Br, 25.99; N, 9.10.

Trimethylsilyl Migrations in the 5-Trimethylsilylbicyclo[2.1.0]pentanes[1]

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*Contribution from the Department of Chemistry, University of Michigan,
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Abstract: The rates and products of the thermal isomerization of *exo*- and *endo*-5-trimethylsilylbicyclo[2.1.0]-pentane are reported. The data suggest initial formation of a diradical followed by migration of a trimethylsilyl group to give the common product, 3-trimethylsilylcyclopentene.

Possibly the simplest purely thermal hydrogen migration occurs in the isomerization of cyclopropane to propylene.[3] Thermal sigmatropic migration of silicon has been observed preferentially to that of hydrogen in 5-trimethylsilylcyclopentadiene[4] and 1-trimethylsilylindene.[5] Thus the observation that trimethylsilylcyclopropane (1) is thermally converted to allyl trimethylsilane (2) suggests (but hardly demands) preferential silicon migration here as well.[6]

This paper reports an investigation of isomerization of trimethylsilyl substituted cyclopropanes and a determination of the relative rate of migration of silicon and hydrogen. The 5-trimethylsilylbicyclo[2.1.0]pen-

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(1) A preliminary account of this work is contained in the Abstracts of Papers, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971, p 43.

(2) Alfred P. Sloan Fellow, 1972–1974.

(3) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934). For a recent short review of this and related reactions, see R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

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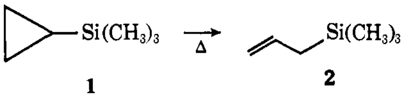
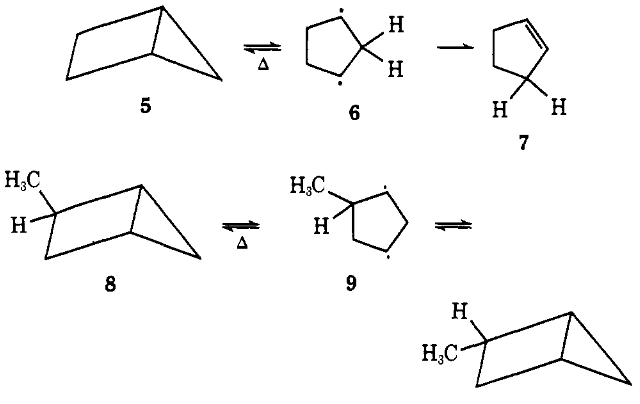
tane isomers (**3** and **4**) were selected for this study because the considerable data available for the parent hydrocarbon (**5**) could serve as a reference[7,8] and because the great ring strain of the system not only allows the reaction to occur at relatively low temperature but apparently also controls the direction of cleavage of the cyclopropane.[7,8]

Bicyclo[2.1.0]pentane (**5**) isomerizes cleanly to cyclopentene (**7**) either in the gas phase or in solution.[7,9] Formally a cleavage of the bond between the bridgehead atoms C_1 and C_4 with a migration of hydrogen from C_5 to C_1 must take place. Reversible scission of the C_1–C_4 bond occurs considerably more rapidly and independently of hydrogen migration. The stereoisomeric 2-methylbicyclo[2.1.0]pentanes (**8** and **10**) are interconverted 10^3 times more rapidly than **5** → **7**.[10] More highly substituted bicyclo[2.1.0]pentane derivatives undergo similar reactions.[11,12] Interconversion of **8** and **10** through diradical **9** is a plausible hypothesis.[7,11,13] Slower hydrogen from **6** would produce **7**.



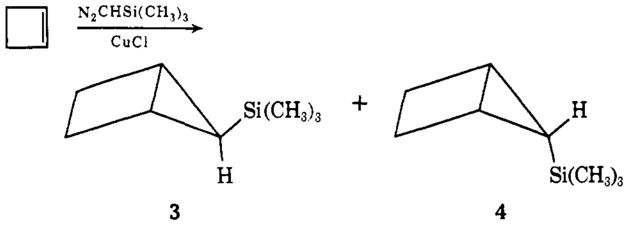
1 **2**



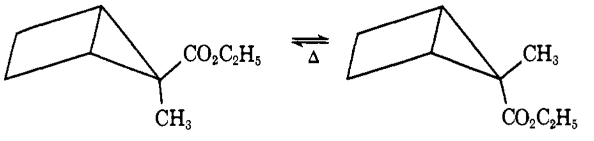
5 **6** **7** **8** **9** **10**

Results and Discussion

The cuprous chloride catalyzed addition of trimethylsilyldiazomethane to cyclobutene gave a 4:1 mixture of 5-trimethylsilylbicyclo[2.1.0]pentane isomers. Since it is known that catalyzed addition of diazo compounds to double bonds has a strong preference for exocyclic addition,[14] the predominate isomer was assigned the exo configuration. Additional evidence comes from the ^1H nmr spectrum.[15] Cis vicinal coupling constants of cyclopropanes are larger than trans.[16] The coupling constant of the C_5 proton to cis bridgehead protons is 6.5 Hz for **4**. Unfortunately the C_5 proton and the trimethylsilyl protons of **3** have the same chemical shift. Thus the corresponding coupling constant could not be observed. However, the width of the peak requires that J be less than 2.0 Hz. These values are close to those of the parent hydrocarbon (**5**) where J_{cis} = 6.0 Hz and J_{trans} = 1.5 Hz.[17]



3 **4**



14 **15**

exo-5-Trimethylsilylbicyclo[2.1.0]pentane (**3**) was converted exclusively to 3-trimethylsilylcyclopentene (**11**) by heating to 235° in benzene. The product derived from hydrogen migration from **3**, 1-trimethylsilylcyclopentene (**12**), could not be detected (<0.1%). Furthermore, **12** is stable under the reaction conditions and is thus excluded as an intermediate. Therefore trimethylsilyl migration is at least 10^3 faster than hydrogen.

The rate of disappearance of **3** in a dilute benzene solution was followed by glpc as described in the Experimental Section and summarized in Tables I and II. The rates were independent of concentration and ex-

Table I. Rate Data for Isomerization of 5-Trimethylsilylbicyclo[2.1.0]pentanes

Reaction	Temp, °C	Rate, sec^{-1}
3 → **11**	235.0 ± 0.2	12.2×10^{-4}
	204.9 ± 0.2	1.06×10^{-4}
4 → **11**	164.95 ± 0.2	1.76×10^{-4}
	195.15 ± 0.2	2.50×10^{-3}

Table II. Comparison of Rates and Activation Parameters

Reaction	Rate × 10^5 sec^{-1} at 195°	Log A	E_a, kcal/mol	Calcd from data in ref
3 → **11**	4.2	13.9	39.2	This work
4 → **11**	250	14.1	35.8	This work
5 → **7**	0.0069	14.1	45.6	7b
8 → **10**	7.6	13.9	38.7	8
14 → **15**	88	14.01	36.6	11

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(9) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(10) Calculated from data in ref 7 and 8.

(11) M. J. Jorgenson, T. J. Clark, and J. Corn, *J. Amer. Chem. Soc.*, **90**, 7020 (1968).

(12) W. R. Roth and K. Enderer, *Justus Liebigs Ann. Chem.*, **733**, 44 (1970).

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(15) The spectrum of the ring protons of the predominate isomer was virtually superimposable on that of *exo*-bicyclo[2.1.0]pentane-5-methanol, while the spectrum of the minor product resembled *endo*-bicyclo-[2.1.0]pentane-5-methanol: A. J. Ashe, III, Ph.D. Dissertation, Yale University, 1966; *Diss. Abstr.*, 27, 4298-B (1967).

(16) J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962).

(17) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967).

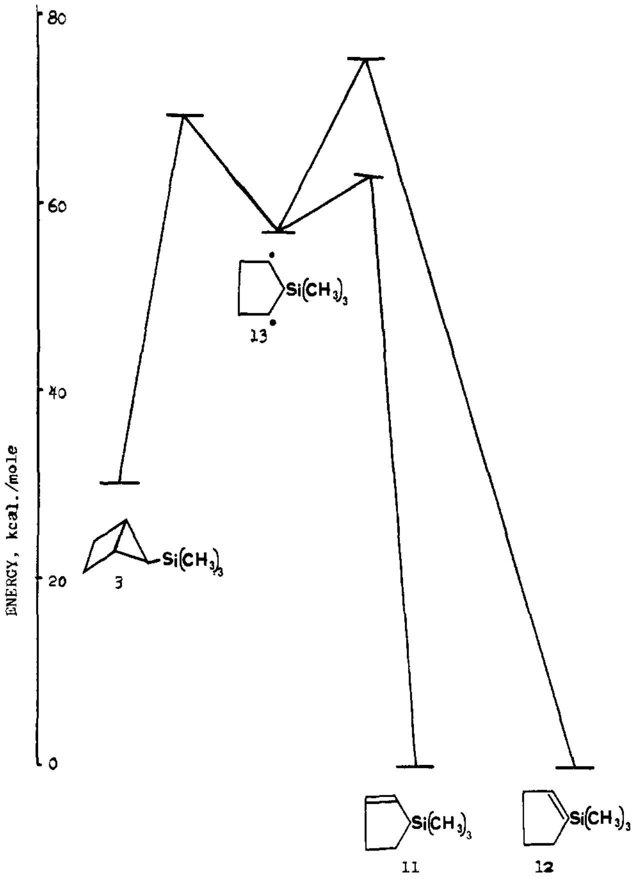
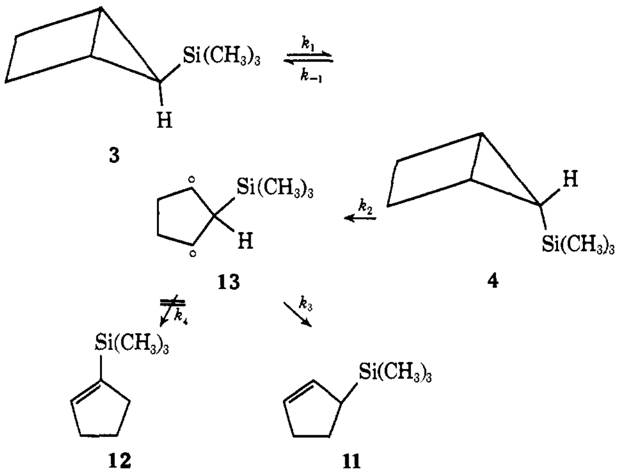


Figure 1. Relative energies of reactants, products, and activated complexes.



cellent linear first-order plots were obtained. The rates were also independent of solvent polarity since a change in solvents to both acetonitrile and cyclohexane made no difference in the rates. These data are consistent with a nonpolar unimolecular isomerization mechanism.

A comparison of the rate of **3** → **11** with the rate of **8** → **10** shows that both rates and activation parameters are virtually identical.[18] It is tempting to suppose that the activated complexes for the two processes are similar. The activated complex for **8** → **10** must involve partial breaking of the C_2–C_4 bond. Apparently the activated complex for **3** → **11** involves partial breaking of the C_1–C_4 bond, but does not involve migration of the $Si(CH_3)_3$ group. While this activated complex may not closely resemble **13** (or **9**), it is consistent with a process which leads to such a diradical.

4 rearranges to **11** 60 times faster than does **3**. Compared with **3** and **5**, **4** must incorporate additional strain owing to crowding of the large 5-*endo*-trimethylsilyl group. Initial rearrangement of **4** to **13** would predict some relief of this interaction in the transition state and predicts steric acceleration of rearrangement of **4**. Such steric acceleration has already been noted in C_1–C_4 bond scission of 5-*endo*-substituted bicyclo[2.1.0]pentanes such as **14** → **15**.[11] The larger rate of **4** is expected owing to the greater size of $(CH_3)_3Si$ *vs.* CH_3.

At 195° *endo*-trimethylsilylbicyclo[2.1.0]pentane gave none of its less reactive exo isomer within the estimated experimental limit of 0.25%. If one assumes the diradical **13** as an intermediate, the minimum product ratio **3**/**11** (>1/250) is the minimum ratio of the relative rates (k_{-1}/k_3) for reclosure of the diradical to give **3** and migration of the trimethylsilyl group to give **11**. The transition state for migration of a trimethylsilyl group from the diradical is at least 6 kcal/mol less than the transition state for **3** to **13**.

It is convenient to illustrate these data by constructing a reaction profile diagram (Figure 1). The heats of formation of reactants and products are unknown. However, the enthalpy difference between cyclopentene and bicyclo[2.1.0]pentane has been evaluated at 29.9 kcal/mol.[13] Using the plausible assumption that replacement of hydrogen by trimethylsilyl will cause an unknown but constant change in the heats of formation of **3** (but not the more crowded **4**) and **11** or **12**, the difference in enthalpy between **3** and **11** or **12** is assigned to be 29.9 kcal/mol. Thus the relative energy of reactants, products, and activated complexes may be assigned using **11** as an arbitrary reference. **13** has been placed at an arbitrary height, although it has been estimated that this intermediate is at least 11.4 kcal/mol lower in energy than the transition state for formation from **5** (and by analogy **3**).[13]

The path leading from **13** to **12** *via* an unobserved hydrogen transfer cannot be evaluated directly. However, a reasonable estimate can be made by examining the reaction **5** → **7**. This isomerization of course proceeds through a hydrogen transfer. It has already been pointed out that the formation of diradical **13** from **3** was energetically equivalent to the formation of **6** from **5**. Thus one might assume that hydrogen migration from **13** to **12** would be similar to hydrogen migration of **6** to **7**. The activated complex for **13** to **12** is assigned the same energy as that of the isomerization of **5** → **7**. This places the activated complex from **13** → **12** at least 13 kcal/mol higher in energy than that of **13** → **11**. At 195° the relative rate of trimethylsilyl *vs.* hydrogen migration (k_3/k_4) is greater than 10^6.

Experimental Section

General. Infrared spectra were recorded in dilute solutions of carbon tetrachloride with balanced 0.1-mm sodium chloride cells using a Perkin-Elmer 237 spectrometer. Proton magnetic

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[18] The comparison is made between rates in benzene solution and in the gas phase. Since solvents of greatly different polarity had no effect on the rate of disappearance of **3**, it is felt that gas-phase rates would be little different. For a comparison of rates of similar nonpolar processes in various media, see A. Wassermann, *Monatsh. Chem.*, 83, 543 (1952).

resonance spectra were taken in 20% carbon tetrachloride solution on a Varian T-60 spectrometer. The internal reference of TMS was added after recording the spectra so that it would not interfere with the trimethylsilyl peaks. A Varian Aerograph 90P chromatograph was employed for both analytical and preparative work. Two columns, (a) 10 ft × 0.25 in. diameter and (b) 25 ft × 0.25 in. diameter, were used. Each was packed with 20% Apiezon L on 60–80 mesh Chromosorb W. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

***endo*- and *exo*-5-Trimethylsilylbicyclo[2.1.0]pentanes.** A solution of 50 ml of cyclobutene[14,19] in 400 ml of cyclohexane and 3 g of cuprous chloride was placed in a 1-l. flask equipped with a mechanical stirrer, a cold-finger condenser containing Dry Ice, and an addition funnel. The solution was stirred at 45° while 20 g of trimethylsilyldiazomethane[11d] were added dropwise over 2 hr. After stirring and heating for an additional 2 hr, most of the solvent was removed leaving about 20 ml of an oil. Analysis by glpc (column a; 130°; 30 psi of He) showed in addition to residual solvent two major products in the ratio of 4:1. They had retention times of 2.0 and 2.5 min, respectively. Both were collected.

The major product was assigned the structure *exo*-5-trimethylsilylbicyclo[2.1.0]pentane: nmr (CCl_4) τ 7.6–8.0 (m, 2 H), 8.4–8.7 (m, 4 H), 10.1 (s, 10 H).

Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.39; H, 11.60.

The longer retention time peak was assigned the structure *endo*-5-trimethylsilylbicyclo[2.1.0]pentane: nmr (CCl_4) τ 7.8–8.0 (m, 2 H), 8.1–8.6 (m, 4 H), 9.8 (s, 9 H), 10.5 (t, J = 6.5 Hz, 1 H).

Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.55; H, 11.43.

1-Trimethylysilylcyclopentene. In a 500-ml three-neck flask equipped with an argon inlet tube, addition funnel, reflux condensor, and mechanical stirrer were placed 2.5 g (0.1 g-atom) of magnesium turnings and 25 ml of dry THF. A solution of 7.0 g (0.04 mol) of 1-bromocyclopentene[20] in 100 ml of THF was added dropwise; heat was applied and then removed as the mixture refluxed spontaneously. After 20 min of addition the mixture was heated for 30 min. After cooling, 5.0 g (0.047 mol) of chlorotrimethylsilane was added, and stirring for 30 min followed. Excess water was added and the mixture was extracted with pentane. The extracts were dried over 3A molecular sieves, and the solvent was removed, leaving 3.6 g of an oil. Glpc showed this to be essentially a single component: nmr (CCl_4) τ 4.2 (s, 1 H), 7.5–7.9 (m, 4 H), 8.0–8.4 (m, 2 H), 9.9 (s, 9 H). *Anal.* Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.42; H, 11.42.

3-Trimethylsilylcyclopentene. To 3.0 g (0.12 g-atom) of magnesium turnings was added a solution of 10.2 g (0.1 mol) of 3-chlorocyclopentene[21] and 10.8 g (0.1 mol) of chlorotrimethylsilane in 200 ml of THF. The solvent refluxed spontaneously during the addition and was heated to reflux for 20 min afterwards. After cooling, excess water was added and the mixture was extracted with pentane. The extracts were dried over 3A molecular sieves and distilled. The major product, bp 135–140°, showed essentially one peak on glpc: nmr (CCl_4) τ 4.3 (s, 2 H), 6.6–8.3 (m, 5 H), 10.0 (s, 9 H). *Anal.* Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.50; H, 11.50.

Thermal Isomerization Experiments. (1) Pure *exo*-5-trimethylbicyclo[2.1.0]pentane (50 μl) and 200 μl of benzene were sealed in an ampoule and heated to 235° for 10^4 sec. Analysis of glpc showed a single component which was identical in all respects with 3-trimethylsilylcyclopentene. No 1-trimethylsilylcyclopentene was detected.

(2) Pure 1-trimethylsilylcyclopentene (50 ml) was heated in 200 μl of benzene to 235° for 10^4 sec. Analysis by glpc showed no change.

(3) *endo*-5-Trimethylsilylbicyclo[2.1.0]pentene (50 μl) was heated in benzene to 235° for 10^4 sec. The product was identical in all respects with 3-trimethylsilylcyclopentene.

Kinetic Experiments. Solutions were prepared using 1.00 ml of benzene, 10 μl of toluene, and 50 μl of pure *endo*- or *exo*-5-trimethylsilylbicyclo[2.1.0]pentene. A 20-μl aliquot of this solution was placed in each of a series of melting point capillary tubes which were sealed. These tubes (at least ten per run) were placed in a constant temperature silicone oil bath maintained to ±0.2°. The temperature was determined using calibrated Anschutz thermometers. Individual tubes were removed at appropriate intervals.

The solutions were analyzed using column a at 175°, 50 psi of He pressure for exo runs and column b at 130°, 30 psi of He pressure for endo runs. In each case mixtures of the appropriate 5-trimethylsilylbicyclo[2.1.0]pentene isomer and 3-trimethylsilylcyclopentene were prepared. Solutions of these mixtures in benzene containing 1% toluene were subject to glpc analysis. It was found that the peak height of the appropriate 5-trimethylsilylbicyclo[2.1.0]pentane isomer relative to that of toluene was linear with concentration.

The observed rate constant was determined by a plot of the natural log of the relative peak height of **3** and **4** against time. Good first-order plots were obtained for at least 3 half-lives. At least two determinations were made at each temperature, the rate constants agreed to within 5%, and the reported rate constants are a mean of several runs. Runs were also made at different concentrations of **3** and **4** and using the solvents cyclohexane and acetonitrile in place of benzene. In all cases these rate constants agreed to within 10% of those reported.

Acknowledgment. We thank the Badische Anilin und Soda-Fabrik for a generous gift of cyclooctatetraene which was used to prepare cyclobutene. Support of this work by the Petroleum Research Fund (Grant No. 5241-AC3,4) of the American Chemical Society and by a Frederick Gardner Cottrell grant from the Research Corporation is gratefully acknowledged.

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