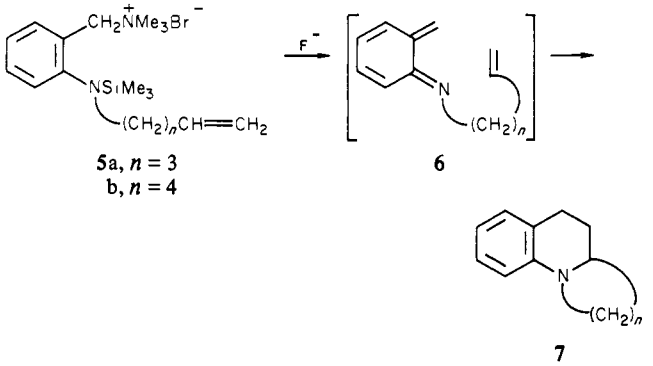
However, attempts to trap the *o*-quinone methide imine (**2a**) with dienophiles such as acrylate, fumarate, acetylenedicarboxylate, and *N*-phenylmaleimide all failed, resulting in the formation of **4** as the sole isolable product. However, intramolecular Diels–Alder reaction of *o*-quinone methide *N*-alkenylimine intermediates (**6**) provided a useful synthetic method for construction of nitrogen-containing polycycles as shown in the following scheme.



5a, $n = 3$
b, $n = 4$

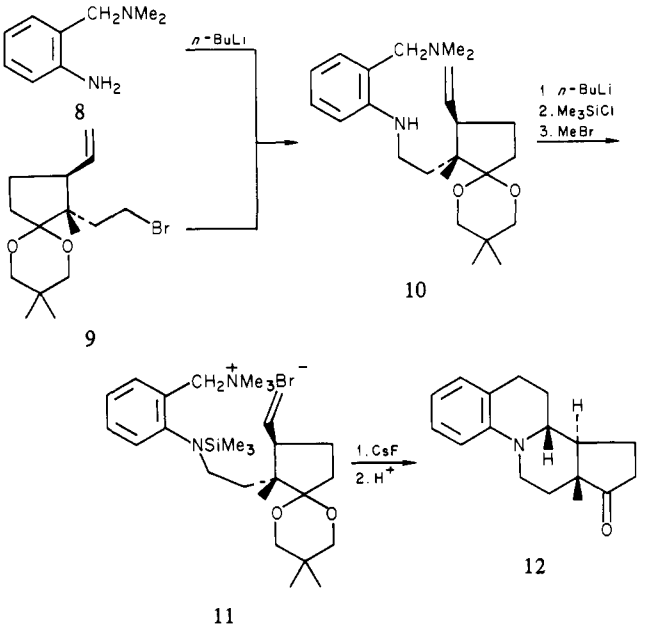
6

7

A representative procedure for the intramolecular Diels–Alder reaction of *o*-quinone methide *N*-alkenylimine intermediate (**6**) is exemplified by the synthesis of benzo[*c*]quinolizidine (**7b**). To a refluxing suspension of 304 mg (2 mmol) of CsF in 10 mL of acetonitrile, a solution of 400 mg (1 mmol) of [*o*-[(trimethylsilyl)hex-5-enylamino]benzyl]trimethylammonium bromide (**5b**)[7] in 10 mL of acetonitrile was added dropwise over 1 h and then heated at reflux for 1 h. The reaction mixture was filtered to remove insoluble materials and evaporated in vacuo. The residue was subjected to preparative thin layer chromatography on silica gel with benzene solvent to furnish benzo[*c*]quinolizidine (**7b**)[9] as a yellow liquid (R_f = 0.66) in 58% yield[10] [**7b**: ^{1}H NMR ($CDCl_3$ with Me_4Si) δ 1.1–2.2 (m, 8 H), 2.3–3.3 (m, 4 H), 3.89 (dm, 1 H, J_{H-H} = 12.2 Hz), 6.4–7.7 (m, 4 H); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 24.43, 25.69, 26.95, 30.23, 33.29, 47.94, 56.70, 112.62, 117.12, 124.62, 126.78, 128.80, 146.78].

Similarly, the fluoride anion induced intramolecular Diels–Alder reaction of [*o*-[(trimethylsilyl)pent-4-enylamino]benzyl]trimethylammonium bromide (**5a**) afforded benzo[*e*]indolizidine (**7a**)[11] in 53% isolated yield.

Finally, the successful synthesis of nitrogen-containing polycycles mentioned above has been extended to the stereoselective synthesis of 9-azaestra-1,3,5(10)-trien-17-one (**12**). The requisite precursor (**11**) for construction of **12** was prepared by the reaction of (*o*-aminobenzyl)dimethylamine (**8**) and bromide (**9**)[2] followed by N-silylation and quaternization. On treatment of **11** with CsF in a refluxing acetonitrile according to the procedure described above, 8,14-*anti*-13,14-*trans*-9-azaestra-1,3,5(10)-trien-17-one (**12**)[12] was selectively produced in 60% yield based on **10** after preparative thin layer chromatography on silica gel with hexane–ethyl acetate (2:1) (R_f = 0.63) [**12**: mp 122.5–123 °C; IR (KBr disk) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$ with Me_4Si) δ 0.94 (s, 3 H), 0.5–2.6 (m, 9 H), 2.6–3.4 (m, 4 H), 3.70 (ddd, 1 H, J_{H-H} = 12.8, 5.1, 2.6 Hz), 6.4–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 12.52, 20.70, 26.86 (2C), 31.35, 35.35, 42.36, 45.96, 48.88, 54.86, 112.49, 117.52, 123.81, 127.10, 129.25, 146.47, 219.20]. The stereochemistry and stereochemical homogeneity of **12** were established by the coupling constant of the ^{1}H NMR signal at 3.70 ppm and from the set of ^{13}C NMR absorptions (16 different C, thus one degeneracy).



Further studies of stereoselective synthesis of heterocyclic natural products on the basis of the present methodology are now in progress in our laboratory.

Acknowledgment. We are grateful to Shin-etsu Chemical Industry Co., Ltd., for a generous gift of trimethylchlorosilane.

(7) **5b** was prepared by the reaction of [*o*-[(trimethylsilyl)hex-5-enylamino]benzyl]dimethylamine [bp 95–100 °C (0.1 mmHg)], which was prepared by N-lithiation and subsequent silylation of [*o*-(hex-5-enylamino)-benzyl]dimethylamine,[8] with methyl bromide in acetonitrile at 0–15 °C for 5 h [**5b**: NMR (CD_3CN with Me_4Si) δ 0.01 (s, 9 H), 0.9–2.2 (m, 6 H), 3.20 (s, 9 H), 2.9–3.4 (m, 2 H), 4.71 (s, 2 H), 4.6–5.9 (m, 3 H), 6.8–7.8 (m, 4 H)].

(8) Attempts to generate *o*-quinone methide imine intermediate (**6b**) by the reaction of [*o*-(hex-5-enylamino)benzyl]trimethylammonium bromide with *n*-BuLi have not led to the formation of **7b**.

(9) Fozard, A.; Davies, L. S.; Bradsher, C. K. *J. Chem. Soc. C* **1971**, 3650. **7b**: mass spectrum, *m/e* (relative intensity) 187 (M^+, 97), 186 (100), 172 (45), 158 (51), 146 (35), 144 (45), 131 (75), 130 (79), 117 (24), 91 (31), 77 (35). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.19; H, 9.17; N, 7.48.

(10) The yield based upon [*o*-[(trimethylsilyl)hex-5-enylamino]benzyl]-dimethylamine was not optimized.

(11) **7a**: ^{1}H NMR ($CDCl_3$ with Me_4Si) δ 0.9–2.3 (m, 6 H), 2.5–3.6 (m, 5 H), 6.2–7.2 (m, 4 H); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 24.02, 27.57, 28.29, 33.28, 46.99, 58.14, 110.06, 114.91, 121.38, 127.32, 128.58, 145.03. Mass spectrum, *m/e* (relative intensity) 174 (13), 173 (M^+, 100), 172 (78), 145 (13), 144 (7), 117 (6). Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.41; H, 8.60; N, 7.99.

(12) **12**: Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.12; H, 8.35; N, 5.53.

Effect of the Silicon Site on the Cyclization of Sila-5-hexen-1-yl Radicals. The Unusual Effect of α-Silicon

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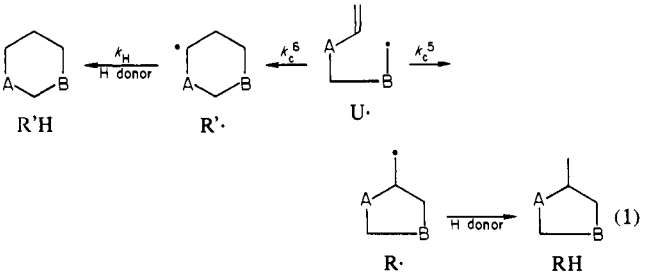
The cyclization of 5-hexen-1-yl radicals to cyclopentylcarbinyl and cyclohexyl radicals (reaction 1, A = B = CH_2) is one of the best-known radical rearrangements. It is very well documented



and examples abound even in heteroatom analogues.[1] The process

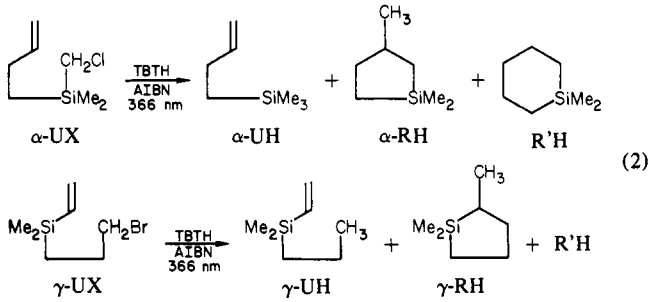
(1) For a recent and comprehensive review, see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1. I thank Professor Beckwith and Dr. Ingold for a preprint of their chapter.

0002-7863/81/1503-5251$01.25/0

is actually used as a probe for mechanisms,[2] being diagnostic in rate[3] and regioselectivity[4] for the radical but not for the ionic species.[5]

In our continuing investigation of α-silyl radicals,[6] it has now been observed that this cyclization is unusual with the α-silyl analogue (α-U·, A = CH_2, B = Me_2Si) but not with the γ-silyl analogue (γ-U·, A = Me_2Si, B = CH_2). The behavior of α-U· is exceptional both in the *reduced rate* and in the *reversed regioselectivity* of its cyclization. Contrariwise, the cyclization of γ-U· is quite comparable to that of all-carbon analogues.

(Chloromethyl)dimethyl-3-butenylsilane (α-UX) was synthesized by the procedure of Connolly and Fryer.[7] (3-Bromopropyl)dimethylvinylsilane (γ-UX) was prepared by treatment of vinylmagnesium bromide in ether with 1 equiv of (3-bromopropyl)trichlorosilane followed by methylation with 2 equiv of methylmagnesium bromide in ether:[8] bp 88–90 °C (2 mm); ^{1}H NMR δ ($CDCl_3$) 6.3–5.4 (m, $CH{=}CH_2$), 3.37 (t, $J \sim 7$ Hz, CH_2Br), 2.1–1.55 (m, CCH_2C), 0.9–0.4 (m, $Si{-}CH_2$), and 0.13 (s, $SiMe_2$); IR ν (neat) 3100, 3050, 1600, 1010, 960 ($CH{=}CH_2$), 1260, 820 ($SiMe_2$) cm^{-1}. Anal. Calcd: C, 4058; H, 7.30. Found: C, 40.07; H, 7.20. Reduction of these halides was studied, using tri-*n*-butyltin hydride (TBTH) as the reducing agent and in varying ratios of reactants.[9] Both halides were readily reduced in hexadecane solvent at 25 °C at 366 nm using azobis(isobutyronitrile) (AIBN) as an initiator. The course of the reduction is shown in reaction 2. The products were identified by comparison with known samples, which were independently synthesized.[10] Product composition was established by gas chromatography with calibration via concomitantly determined response factors for the reaction components. Rearrangement (cyclization) data are gathered in Table I.



(2)

The data in Table I show an increase in rearrangement with decreasing TBTH(D) concentration, as expected for a reduction of this type.[11] The noteworthy data are the low values of *S* and *r* for α-UX. Normally the regioselectivity for 5-hexen-1-yl radical cyclizations is overwhelmingly toward exo cyclization,[12] with cyclopentylcarbinyl product predominating over cyclohexyl product by factors of 15–20 or more.[13] Halide γ-UX behaved in this normal fashion. Consequently, the anomalous behavior of α-UX is not caused simply by the *presence* of silicon but rather by its *position*. Evaluation of the cyclization constants k_c^5 and k_c^6 (reaction 1) was possible, using a value 1.05×10^6 M^{-1} s^{-1} for the value of k_H, the rate constant for hydrogen abstraction from TBTH.[14] These data are shown in Table II. The significant

Table I. Rearrangement (Cyclization) Data[a]

[halide]: [TBTH]	$[TBTH]_0$, M	% RH[b]	% R'H	*S*[c]	$10^3 r$,[d] M
		α-UX			
1:1.85	1.063	0.6	1.4	0.46 ± 0.02	1.1
1:1.00	0.643	0.7	1.4		
1:0.48	0.347	1.0	2.3		
1:0.25	0.189	1.8	3.8		
1:0.14	0.103	3.5	6.5		
1:0.46[e]	0.359[e]	1.5	3.0	0.46 ± 0.02	1.7
1:0.25[e]	0.191[e]	2.1	4.7		
1:0.11[e]	0.087[e]	5.3	10.7		
		γ-UX			
1:1.89	2.089	3.8	0.2	15 ± 2	33
1:0.87	0.948	12.1	0.8		
1:0.61	0.557	16.4	1.4		
1:0.28	0.261	22.7	1.7		
1:0.15	0.151	42.5	2.9		
1:0.55[e]	0.522[e]	21.7	1.7	13 ± 3	56
1:0.31[e]	0.254[e]	31.2	1.7		
1:0.19[e]	0.158[e]	38.8	4.2		

[a] Reactions empolyed 0.42–0.55 mmol of halide, the appropriate amount of TBTH (or tri-*n*-butyltin deuteride, TBTD), 0.44–0.53 mmol of nonane (internal standard), and 0.02–0.05 mmol of AIBN. The solvent was hexadecane, added to bring all reaction volumes to 0.5 mL. The reactants were placed into NMR tubes, purged with nitrogen, and capped. Irradiation was carried out at 25 °C for 3 h at 366 nm in a mini photoreactor carousel (Rayonet). The solutions were then immediately chromatographed on a Gow-Mac Model 550 thermal conductivity chromatograph using an SE-30 column (4 ft × 1/4 in.) at 95 °C. Products were those shown in reaction 2. Yields based upon consumed halide were essentially quantitative. Mass balances were theoretical ±3%. [b] α-RH from α-UX; γ-RH from γ-UX. The uncertainties in the percentages ranged from 0.5–7.0% of the listed values. [c] Regioselectivity, determined by the ratio % RH/% R'H. [d] Competitive cyclization constant, $r = k_c/k_H$, where k_c is the summed cyclization rate constant ($k_c^5 + k_c^6$) and k_H is the rate constant for the reaction of α- and γ-U· with TBTH or TBTD. The constant *r* was calculated by using an iterative computer program from the expression [α- or γ-RH] + [R'H] = $r \ln [([S_0] + r)/r]$, where $[S_0]$ is the initial concentration of TBTH or TBTD. The data from those experiments wherein excess TBTH was employed were not included in the determination of *r* because this equation is inapplicable to such cases. The iteration was continued until a correspondence of ±2% between found and calculated rearrangement was found. [e] TBTD was used.

Table II. Estimated Cyclization Constants[a] (25 °C, s^{-1})

radical	$10^{-5} k_c^5$	$10^{-5} k_c^6$
α-U·	0.0038	0.008
γ-U·	0.328	0.022
5-hexen-1-yl[b]	1.1	<0.005

[a] Calculated from the *S* and *r* values of Table I, using 1.05×10^6 M^{-1} s^{-1} for k_H. [b] Data (at 40 °C) from: Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* 1972, *94*, 6059.

(2) Recent use of this probe was reported by: Chung, S.-K.; Chung, F. *Tetrahedraon Lett.* **1979**, 2473. Newcomb, M.; Courtney, A. R. *J. Org. Chem.* **1980**, *45*, 1707. Kitching, W.; Olszowy, H.; Harvey, K. *Ibid.* **1981**, *46*, 2423.

(3) At 25 °C, the cyclization rate constant for the parent 5-hexen-1-yl radical is $\sim 1 \times 10^5$ s^{-1}. Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

(4) Cyclization to R· is usually favored over cyclization to R'· by considerable factors in sterically unencumbered 5-hexen-1-yl radicals. Cf. ref 1.

(5) The anion cyclizes slowly but preferentially to the cyclopentylcarbinyl product; Kossa, W. C., Jr.; Rees, T. C.; Richey, H. G., Jr. *Tetrahedron Lett.* **1971**, 3455. The analogous cation cyclizes only to the cyclohexyl cation. Bartlett, P. D.; Closson, W. D.; Cogdell, T. J. *J. Am. Chem. Soc.* **1965**, *87*, 1308.

(6) Wilt, J. W.; Aznavoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285.

(7) Connolly, J. W.; Fryer, P. F. *J. Organomet. Chem.* **1971**, *30*, 315.

(8) The vinyl and methyl Grignard reagents were purchased from Alfa and Aldrich, respectively. The silane was obtained from Petrarch.

(9) α-Chlorosilanes are easily reduced under these conditions. Cf. ref 6. Because γ-chlorosilanes are far less reactive in this radical chain process (manuscript in preparation with F. G. Belmonte), a bromide was chosen to generate γ-U·.

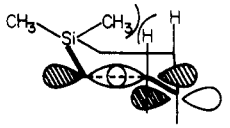
(10) Prepared as reported. α-UH: ref 7. γ-UH: Nametkin, N. S.; Durgar'yan, S. G.; Chemyatkov, I. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 1181. α-RH: Araki, T.; Terunuma, D.; Fuse, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 293. γ-RH and R'H; Swisher, J. V.; Chen, H.-H. *J. Organomet. Chem.* **1974**, *69*, 83. The physical properties, including IR and NMR spectra, were in agreement with those either reported or otherwise expected for the structures.

(11) Walling, C.; Cooley, J. H.; Ponaras, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361.

(12) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

(13) For some "guidelines" for such radical reactions, see: Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. Two exceptions to such regioselectivity are found with radicals substituted at the vinyl group or radicals bearing stabilizing groups at the radical center.

difference among the radicals is the low value of k_c^5 for α-U·.[15] Otherwise, the radicals are, by and large, comparable to the parent 5-hexen-1-yl radical. The low k_c^5 value for α-U· explains the unusual regioselectivity in its cyclization. It is diminished exo cyclization and not enhanced endo cyclization which is responsible. Explanation of the diminished exo cyclization must be somewhat speculative, because the factors involved in exo vs. *endo* cyclization are complex. Certainly a stereoelectronic rationale involving better orbital overlap for exo cyclization seems to be important.[16] Examination of molecular models (FMO) indicated that such overlap appeared to be more difficult in α-U· then in γ-U·. However, overlap for endo cyclization in α-U· appeared from the models to be equally effective as that for exo cyclization in γ-U·. Such stereoelectronic equivalence should make k_c^6 for α-U· comparable to R_c^5 for γ-U·. This is not the case, possibly because axial repulsion is developed in the endo cyclization of α-U· as shown.



Other factors might be mentioned, as well. Because one molecular orbital view of radical addition to a double bond ascribes cationic character to the radical,[17] it is possible that polar effects are also involved. The presence of silicon α to cationic centers is apparently destablizing, contrary to expectations.[18] If such an effect were operating in the present case, however, it would add to the difficulty of *any* cyclization of α-U·, a result in contrast to its "normal" k_c^6 value. Furthermore, the possibility that α-silyl radicals (such as α-U·) are stabilized relative to related carbon radicals,[6] which in turn would decrease their cyclization propensity, does not appear to be substantiated. Such stabilization could conceivably result in reversibility of the cyclizations of α-U·, especially via R_c^5 where the cyclized radical R· is primary. But the "normal" value of k_c^6 and the response of total rearrangement to dilution of TBTH, as exemplified by the constancy of the *r* value for α-U·, indicates that reversibility is not involved.[19] Nevertheless, reversibility in the cyclization of α-U· via k_c^5 would indeed lower both its *r* and *S* values relative to γ-U·, as observed. This possibility will be directly checked in future work.

At present the results are best explained, although not entirely satisfactorily, in terms of a stereoelectronic factor coupled with steric effects. Nonetheless, α-U· appears to be the first 5-hexen-1-yl-type radical bearing neither substituents on the vinyl group nor known radical stabilizing groups at the radical center which shows such decreased exo cyclization. This unusual result adds to others noted[20] for α-silyl radicals and makes one suspect that some deeper explanation for their behavior exists.

Lastly, comparison of the *r* values for TBTH vs. TBTD reduction allows the determination of k_H/k_D values for α- and γ-U·, 1.5 and 1.7, respectively. These values (which may be the same, considering experimental error) are somewhat lower than that reported for all-carbon cases (~3).[3] The interpretation of this difference as well as a better understanding of α-silyl radical cyclization (and other rearrangements) must await the results of further studies presently under way.[21]

Acknowledgment. I thank the Loyola University Research Committee and the Dow-Corning Copr. for grants in support of this work.

(14) Obviously the individual values of k_c^5 and k_c^6 (but *not* their ratio) depend upon the value used for k_H. The value chosen is taken from: Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* 1980, 1083. It represents the preferred value over a close range. Different values of k_H for α-U· and γ-U· would obviously affect the *r* values and possibly show comparable cyclization reactivities for the two systems. But the *S* values would remain as a glaring difference.

(15) A better comparison would involve α-±· vs. 2,2-dimethyl-5-hexen-1-yl radical and γ-U· vs. 4,4-dimethyl-5-hexen-1-yl radical. No published data on the latter have appeared, although the 2,2-dimethyl analogue has been reported to cyclize exclusively vis k_c^5 and about 10 times more rapidly at 80 °C than the parent (Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1535). Both observations only magnify the anomaly of α-U·.

(16) This view has been developed largely by A. L. J. Beckwith. Cf. ref 1 and references therein. For a recent theoretical treatment of this subject using MINDO/3-UHF calculations, see: Bischof, P. *Helv. Chim. Acta* **1980**, *63*, 1434.

(17) Fujimoto, H.; Yamabe, S.; Minato, T.; Fukui, K. *J. Am. Chem. Soc.* **1972**, *94*, 9205. Other (contrary) views are held. Cf. ref 1.

(18) Eaborn, C. "Organosilicon Compounds"; Butterworths: London, 1960; pp 431–434.

(19) For a situation involving reversibility and the thereby revised mathematical approach to obtain a constant *r* value, see: Wilt, J. W., Chwang, W. K., Dockus, C. F.; Tomiuk, N. M. *J. Am. Chem. Soc.* **1978**, *100*, 5534.

(20) For example, absence of 1,2-aryl shift: Wilt, J. W.; Kolewe, O.; Kraemer, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 2624. Ease of formation from α-chlorosilanes.[6]

(21) Among other efforts, attempts to synthesize a chloride precursor to a β-U· analogue of α-±· have recently succeeded. Investigation of its cyclization, and, as mentioned in the text, studies on the possible reversibility of the cyclization of α-U· are in progress and will be reported subsequently. Another aim, the study of the unencumbered 1-sila analogue of the 5-hexen-1-yl radical, would appear to be quite difficult owing to the probable instability of its precursors. Such radicals substituted at silicon with phenyl, chloro, isopropyl, and methyl groups have been cyclized, though in low yield. Sakurai, H. *Free Radicals* **1973**, *2*, 793.

Silica-Bound Rhodium Hydride Catalysts for Arene Hydrogenation

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Received April 13, 1981

We have recently described the synthesis of a family of silica-bound rhodium hydride complexes including [Si]-ORh(allyl)H (**1**).[1] In contrast to conventional nonsoluble heterogeneous catalysts, these complexes can be characterized on the molecular level, and aspects of their chemistry can be elucidated readily as for their soluble counterparts. For example, the stoichiometric ligation of olefins or phosphine ligands to **1** could be explained by employing coordination number arguments for the Rh(III) center, which suggested the metal could behave as a formally four-coordinate species. We have observed that **1** is an efficient catalyst for olefin hydrogenation and have described a sequence, on the molecular level, which accounts for this catalytic behavior. Similar logic suggested that substrates requiring more than one site on a metal (for example, an arene) could be coordinated to **1**; activation of H_2 by the resulting species would provide a pathway for the catalytic hydrogenation of the substrate. Indeed, we found that **1** does catalyze arene hydrogenation under mild conditions.[3] In the course of these studies we have also discovered an unusual exchange process which takes place under the hydrogenation reaction conditions.

Hydrogenation of benzene catalyzed by **1** proceeded smoothly (to give cyclohexane) with essentially no decrease in rate even after >3000 turnovers. Naphthalene hydrogenation, however, took quite a different course; under the reaction conditions (500-psi H_2; 22 °C) the initial rate of hydrogenation (60 turnovers/h) was not maintained; rather, hydrogenation activity slowly decreased over ca. 300 turnovers and eventually approached a new, *constant* rate (7.7 turnovers/h). In this time period propane (0.7 equiv) was evolved.[4] Alkaline hydrolysis (1 M MeO^-/MeOH) of the

(1) Ward, M. D.; Schwartz, J. *J. Mol. Catal.* **1981**, *11*, 397. **1** was prepared by the sequence

$$[Si]\text{-}OH + Rh(allyl)_3{}^2 \rightarrow [Si]ORh(allyl)_2 \xrightarrow[1\ atm]{H_2} \mathbf{1}$$

(2) Powell, J.; Shaw, B. L. *Chem. Commun.* **1966**, 323.

(3) Catalytic hydrogenations were performed in a modified Parr minireactor equipped with a glass liner and nylon stirrer in order to preclude contact of the reaction mixture with the autoclave stainless steel surface. For conditions see Table I.

0002-7863/81/1503-5253$01.25/0