Journal of Organometallic Chemistry, 133 (1977) 7—17

ACETOLYSIS OF 4,4-DISUBSTITUTED 4-SILACYCLOHEXYL TOSYLATES: EFFECT OF REMOTE SILICON SUBSTITUTION ON ORGANIC REACTIVITY *

STEPHEN S. WASHBURNE * and RAM R. CHAWLA

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122 (U.S.A.)

(Received November 30th, 1976)

Summary

4,4-Dimethyl-(Ia), 4,4-diphenyl-(Ib), and phenyl-methyl-substituted 4-silacyclohexyl tosylates (Ic—Id) were compared with isosteric 4,4-disubstituted cyclohexyl tosylates. The rates of acetolysis of the silatosylates were three to five times greater than those of the carbocyclic analogs. With the exception of Ia, which largely fragmented to di-4-pentenyltetramethyldisiloxane, the acetolysis products of compounds I were acetates and olefins in proportions similar to that observed for cyclohexyl tosylates. It is concluded that the kinetic and product-determining effect of a γ-silyl substituent on a tosylate is slight, although where a stabilized β-silylcarbonium ion can form by rearrangement, such as with Ia, fragmentation products will predominate.

Introduction

While substitution of a metal into the α- or β-position of an organic substrate has a profound effect on reactivity, succinctly examined by Traylor [1], the effect of remote metal substitution by Group IV elements has not been well documented. Solvolytic rate enhancements ranging from dramatic: 1-trimethylstannyl-methyl-2-*exo*-*p*-nitrobenzoyloxynorbornane solvolyses 600000 times faster than 1-methyl-2-*exo*-*p*-nitrobenzoyloxynorbornane [2], to moderate: γ-trimethylstannyl- and γ-trimethylsilyl-propyl mesylates undergo acetolysis respectively, 1425 and 14 times faster than propyl mesylate [3], to slight in the $R_3Sn—C—C—C^+$ series [4] have been observed. An approach to understanding the stereochemical effect of γ-trimethyltin substitution has been made by an elegant solvolysis study of four trimethylstannylnorbornyl mesylates [6]. Since we had observed fragmentation of 4,4-dimethyl-4-silacyclohexyl tosylate into

* Preliminary communication, ref. 5; taken in part from the Ph.D. Dissertation of R.R.C., April 1973, Temple University.

di-4-pentenyl-tetramethyldisiloxane (IV) upon acetolysis [5], the title series seemed an ideal one to probe the effect of a γ-silicon atom relative to the corresponding carbocyclic system, in terms of both kinetics and product distribution. Both experimentally [7] and theoretically [8] the silacyclohexane ring is known to exist in a flattened chair conformation with an inversion barrier (5.5 kcal/mol) about half that of cyclohexane, so the title series was expected to be stereochemically closely related to the cyclohexyl tosylates (VI). A fixed silicon γ-carbon distance (from molecular mechanics calculations [8] estimated at 4.1 Å for 4-silacyclohexanol), and the limited range of conformations available to a cyclohexyl system provide further simplification by limiting parameters that must be considered.

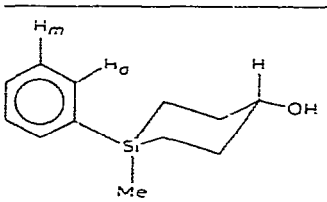
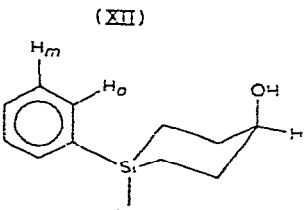
Preparation of tosylates

Synthetic design strategy applied to I suggests use of a 3-functionalized 1,5-dimetallopentane which would allow introduction of an R′RSi≺ fragment at a late stage. Despite Märkl's recent success in silacyclohexane synthesis by this route [9], our attempts toward realization of eq. 1 failed, and we turned to the well established Benkeser—Bennett scheme [10] illustrated in eq. 2, which gave Ia—Id in straight-forward fashion.
(For all compounds, a refers to R = R′ = CH_3, b to R = R′ = C_6H_5; c to R = C_6H_5, R′ = CH_3 (*trans*); d to R = CH_3, R′ = C_6H_5 (*cis*))

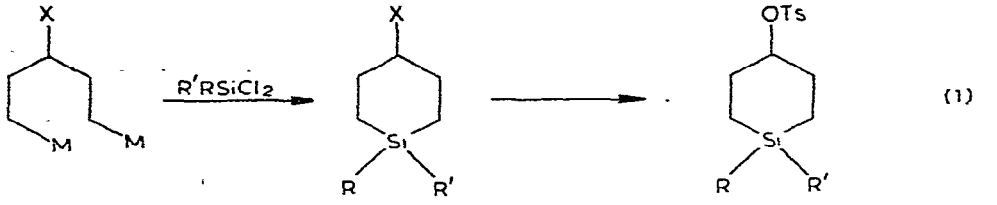
Sodium borohydride reduction of the R = CH_3, R′ = Ph ketone yielded an alcohol fraction exhibiting two Si—CH_3 resonances (of nearly equal intensity) in

TABLE 1

MOLAR SHIFT VALUES OF 4-METHYL-4-PHENYL-4-SILACYCLOHEXANOLS WITH Eu(dpm)$_3$

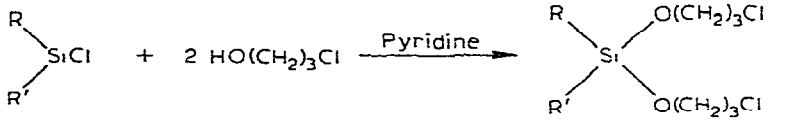
Compound	ΔEu for various protons [a]				
	OH	H(1)	Si—Me	*o*-H	*m*-H
 (XII)	87.1	25.6	3.5	2.38	1.10
 (XIII)	83.3	25.8	2.57	3.10	1.06

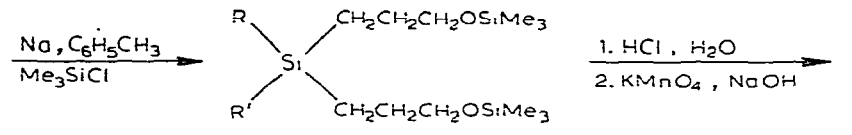
[a] ΔEu = difference in resonance position (ppm) for a given proton in the presence of an equimolar quantity of Eu(dpm)$_3$.



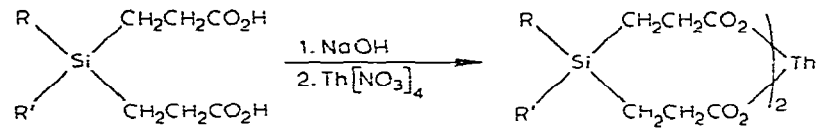
(1)

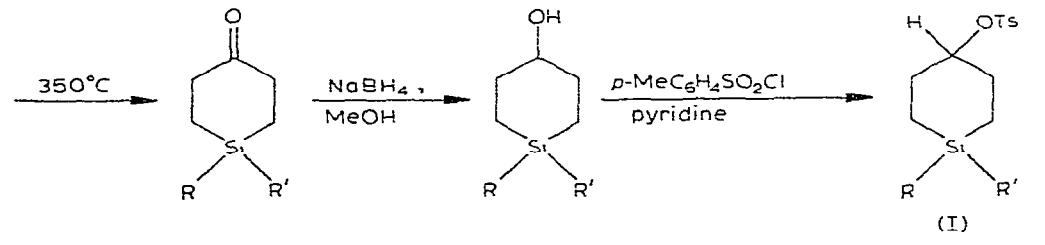
(Ia) R = R′ = CH_3
(Ib) R = R′ = C_6H_5
(Ic) R = C_6H_5, R′ = CH_3
(Id) R = CH_3, R′ = C_6H_5





(2)





(I)

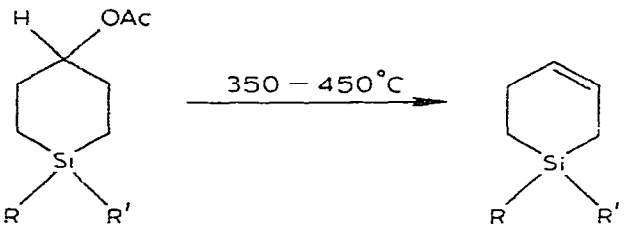
the NMR spectrum, implying non-stereospecific production of *trans*- and *cis*-4-methyl-4-phenyl-4-silacyclohexanols *. This mixture could not be resolved by GLPC, nor could the corresponding silyl ethers (from treatment with Me_3SiCl/pyridine) be separated. Although a mixture of tosylates Ic and Id could be mechanically separated into needles (m.p. 75°C) and octahedrons (m.p. 65°C), this Pasteurean procedure was less convenient than fractional crystallization from ether of a mixture of *p*-nitrobenzoates prepared by the Dauben technique [11]. Potassium hydroxide hydrolysis afforded the pure alcohols XII and XIII.

Assignment of configuration was made by analysis of the effects produced on the NMR spectra by addition of $Eu(dpm)_3$ **, use of shift reagents for confor-

* *Trans* and *cis* referring to the relative configuration of the methyl group and the alcohol function.
** dpm = dipivaloylmethane.

mational analysis of metallocycloalkanols being well established [12]. From Table 1 it is clear that the Si—CH_3 resonance of *cis* alcohol XII shift downfield faster than the resonance of XIII; while the *ortho*-H resonance of XIII shifts faster than the *ortho*-H of XII. Given the known chair conformation of the silacyclohexane ring [7,8], the structural assignments shown can be made with confidence.

Passage of the acetates IIIa—IIId through a glass-bead-packed tube at 350—400°C gave a clean pyrolysis leading to 1,1-disubstituted 1-silacyclohex-3-enes IIa—IIc in 80—88% yield (eq. 3). As the traditional route to 1-silacyclohex-3-enes involves vigorous conditions, hot quinoline on a mixture of chlorosilacyclohexanes [13], this route can be considered an excellent source of this valuable class of allylsilanes.



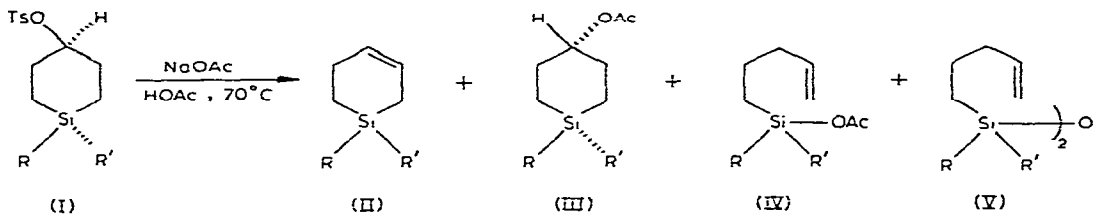
(3)

(III) (II)

Possession of the silacyclohexanols, the tosylates I, acetates III, and silacyclohexenes II gave us the substrates and the expected acetolysis products for a kinetic study of the effect of γ-silicon substitution in a cyclohexyl tosylate.

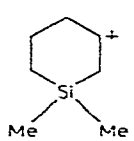
Acetolysis products

Solvolysis of tosylates Ia—Id and VIa in buffered acetic acid (eq. 4), gave the results shown in Table 2. Only for the dimethyl derivative Ia was any fragmentation observed. For tosylates Ib—Id our GLPC technique for product analysis might have allowed a maximum of 2% of fragmentation product to pass undetected. Products were characterized by spectral comparison with authentic materials, or in the case of V, by IR spectroscopy.



(I) (II) (III) (IV) (V)

(4)



(XI)

TABLE 2

SOLVOLYSIS OF 4,4-DISUBSTITUTED CYCLOHEXYL TOSYLATES IN BUFFERED ACETIC ACID [a]

TsO—⬡—X, X =	Temperature (°C)	Time (h)	Yield (%) ⬡=X	AcO—⬡—X	X—OAc	(⬡—X)$_2$O
Ia $(CH_3)_2Si$	70	13	28	24	7	41
	90	7	23	34	29	14
Ib $(C_6H_5)_2Si$	70	48	70	30	--	--
	70	15	62	26	--	-- [d]
Ic $(C_6H_5)(CH_3)Si$ (trans)	70	24	69.5	30.5	--	--
Id $(C_6H_5)(CH_3)Si$ (cis)	70	24	66	34	--	--
VIa $(CH_3)_2C$	70	48	68	32	--	--
$(CD_3)(CH_3)C$ cis [b]	65	--	83	14.8 [c]	--	--

[a] 0.05 *M* NaOAc in HOAc containing 1% Ac_2O. [b] Ref. 14. [c] Also 2.2% of 3,3-dimethylcyclohexyl acetate observed. [d] 22% unreacted Ib recovered.

In accord with results in the 4,4-dimethylcyclohexyl [14] and cyclohexyl [15] series, the acetate formed from Ic and Id was of inverted configuration, i.e. Ic → IIId, Id → IIIc.

To determine the origin of IV and V, tosylate Ia was subjected to various con-

TABLE 3

RATES OF ACETOLYSIS OF TsO—⬡—SiRR' and TsO—⬡—CRR' AT 70°C

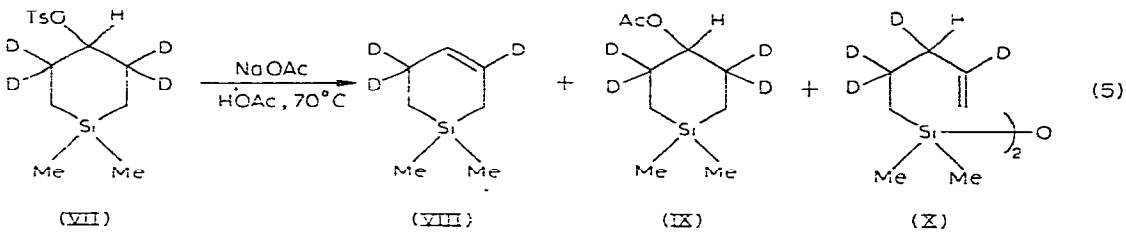
Tosylate		$k \times 10^4$ s^{-1}	$k \times 10^4$ s^{-1}	Tosylate	
TsO, H, Si(Me)(Me)	(Ia)	1.05	0.275 [a]	TsO, H, C(Me)(Me)	(VIa)
TsO, H, Si(Ph)(Ph)	(Ib)	0.313			
TsO, H, Si(Ph)(Me)	(Ic)	0.613	0.201	TsO, H, C(Ph)(Me)	(VIc)
TsO, H, Si(Me)(Ph)	(Id)	0.587	0.136	TsO, H, C(Me)(Ph)	(VId)

a Lit. value 0.271 [18]

trol experiments: Ia was recovered unchanged after heating in dry dimethylformamide for 18 h at 70°C, and after heating at reflux in dry acetone for 17 h. Thus fragmentation products do not arise from thermal reactions of Ia. Likewise, silacyclohexene IIa was recovered unchanged after 16 h of treatment under the solvolysis conditions. To verify the migration of a hydrogen atom from an adjacent carbon, solvolysis of tetradeuteriotosylate VII under the conditions of eq. 4 gave rise to VIII, IX and X in yields of 23, 31, and 46% respectively. Thus the hydrogen in the 3-position of 4-pentylsiloxane V arises from the 2-position of tosylate Ia.

Kinetics

The rates of acetolysis of tosylates Ia—Id and VIa—VIc were measured at 70°C by the standard Winstein—Grunwald procedure [16], and are tabulated in Table 3. All tosylates displayed good first order-behavior. The striking factor to emerge from these data is that isosteric substitution of silicon for carbon produces only a 3- to 5-fold rate enhancement, which is minute when it is remembered that cycloheptyl tosylate solvolyzes thirty times faster than cycloheptyl tosylate [17].



(VII) (VIII) (IX) (X) (5)

Discussion

The small rate enhancements observed for silicon substitution at the γ-position must be reconciled with the observed 14-fold rate enhancement of $Me_3SiCH_2CH_2CH_2OMs$ relative to $CH_3CH_2CH_2OMs$ * [3], and also with the observation of fragmentation for Ia, but not Ib—d. Concerning the former, it should be noted that the present substitution is an isosteric one. The rate difference between $Me_3SiCH_2CH_2CH_2OMs$ and $Me_3CCH_2CH_2CH_2OMs$ is not known, but is probably not a factor of fourteen.

Without descending into the sea of controversy surrounding solvolysis mechanisms in cyclohexyl systems, it can be assumed that distortions (principally angle strain in the present case) of a cyclohexane ring increase solvolysis rate by destabilizing the ground state relative to the transition state, i.e. cyclopentyl and cycloheptyl tosylates [17] both solvolyse faster than cyclohexyl, hence a three- to five-fold rate increase in the silacyclohexyl system can be explained on conformational effects alone. It is noteworthy that Benseker and Bennett found the dissociation constant of 4,4-dimethylsilacyclohexanone cyanohydrin to be

* Ms = mesyl = methylsulfonyl.

five times greater than that of 4,4-dimethylcyclohexanone cyanohydrin [10]. Both cyanohydrin dissociation and the present acetolysis presumably are governed by the decreased activation energy required to convert the 4-position of the ring from tetrahedral to trigonal geometry.

As it is not accompanied by a significant rate effect, fragmentation of Ia is probably not a concerted process. That it involves 1,2-hydride shift and that IV and V are formed at the expense of IIa imply that a stabilized β-silyl carbonium ion [1] such as XI is involved. Evidence for XI was found in the trityl fluoborate-induced fragmentation of dimethylsilacyclohexane to pentenyldimethylsilyl fluoride [19], and the 15% yield of the Si—Br analog of IVa observed in the dibromocyclopropanation of 1,1-dimethyl-1-silacyclohex-2-ene [20] may arise from XI or a closely related species. Hydride shift in the cyclohexyl tosylate series is known (3,3-dimethylcyclohexyl acetate was formed in acetolysis of VIa [14]) but depends on subtle factors: the percentage of rearrangement product in solvolysis of cyclohexyl tosylate increases as the solvent is changed from acetic to formic to trifluoroacetic acid [15]. Probably, fragmentation products from Ib—Id are not observed because β-silyl carbonium ions are not as well stabilized by phenyl as by methyl substituents on silicon (as implied by σ^+ values CH_2SiMe_3, —0.62 vs. CH_2SiPh_3, —0.4 [21]), hence hydride shift to species like XI can not compete with collapse to normal acetolysis products. Although no hydride shift products were observed in acetolysis of $Me_3SiCH_2CH_2CH_2OMs$ [3], the "minor quantity" of $(Ph_3Si)_2O$ produced in formolysis of $Ph_3SiCH_2CH_2CH_2OTs$ [22] may arise by hydride shift to $Ph_3SiCH_2CH^+—CH_3$ followed by elimination. Alternatively, this siloxane may arise from a 1,3-fragmentation of the tosylate, which has a W-conformation [6] available.

It should be pointed out in conclusion that the lack of substantial effect from silicon substitution in this work does not imply that all remote silicon substitution will be without effect. Since such effects have a stereochemical component [1], and rate-accelerated deoxymetallation of γ-substituted tins proceeds through a W-conformation [6], the very factors that make the present system amenable to study, rigidity and readily available carbon analogs, may limit manifestation of the effects of silicon substitution. It is safe to conclude that small changes in substrate structure or reaction media may produce large changes in product distribution without significant effect on rate. With a solvent of greater ionizing power, fragmentation of Ib—Id via rearrangement might be observable and our present studies are directed towards this end.

Experimental

General comments. IR spectra were determined on a Perkin—Elmer 137 Spectrophotometer, ^1H NMR spectra, determined as ca. 15% solutions on Varian A60A and XL-100-15 spectrometers, are reported in ppm downfield (δ) from tetramethylsilane. Benzene, TMS, or methylene chloride was used as internal standard according to whether the compound contained CH_3—Si, Ph—Si, or both CH_3—Si and Ph—Si groups, respectively. GLPC was performed on a Hewlett—Packard 5751 Chromatograph, using one of the following: Column A: $\frac{1}{4}''$ × 6′, 10% diethyleneglycol succinate; Column B: $\frac{1}{4}''$ × 6′, 10% DC-200 silicone oil. Melting points are uncorrected. Microanalyses were carried out by

Galbraith Laboratories, Knoxville, TN and Schwarzkopf Microanalytical Laboratories, Woodside, NY.

4,4-Dimethyl-4-silacyclohexanol. Reduction of 11.0 g of 4,4-dimethyl-4-silacyclohexanone [10] with 1.5 g of $NaBH_4$ afforded 10.1 g (90%) of alcohol, b.p. 55—57°C/3 mmHg (lit. [10] b.p. 70—71°C/5 mmHg); IR (neat) 3400 and 1250 cm^{-1}; NMR ($CDCl_3$) δ 3.6 (s, 1, OH), 3.45 (tt, 1, C<u>H</u>OH), 1.7 (m, 4), 0.56 (m, 4), 0.03 (s, 3), and 0.0 (s, 3) ppm. The tosylate Ia, obtained by the method of Tipson [23] in 90% yield, had m.p. 60°C; IR (KBr) 1350, 1250, 1170 cm^{-1}; NMR (CCl_4) δ 7.75 (d, 2), 7.30 (d, 2), 3.45 (m, 1), 1.9 (q, 4), 0.67 (m, 4), 0.04 (s, 3), and 0.00 (s, 3) ppm. (Found: C, 56.62; H, 7.56; S, 10.80. $C_{14}H_{22}O_3SSi$ calcd.: C, 56.38; H, 7.38; S, 10.73%.)

4,4-Dimethyl-4-silacyclohexyl acetate (IIIa). A mixture of 750 mg (5 mmol) of alcohol, 1.0 g of acetic anhydride, and 60 mg of pyridine was heated at 80°C for 4 h., then poured into 10 ml of ice water and extracted with ether. The ether layer was washed, dried ($MgSO_4$), and distilled to give 800 mg (85% yield) of acetate IIIa, b.p. 110°C/0.5 mmHg; IR (neat) 1745, 1380, 1250, 1030 cm^{-1}; NMR (CCl_4) δ 4.65 (m, 1, C<u>H</u>OC), 2.0 (s, 3, C<u>H</u>$_3$C), 1.75 (m, 4), 0.69 (m, 4), 0.09 (s, 3), and 0.05 (s, 3) ppm. (Found: C, 57.75; H, 9.47. $C_9H_{18}O_2Si$ calcd.: C, 58.06; H, 9.67%.)

1,1-Dimethyl-1-silacyclohex-3-ene (IIa). A vertically mounted 350 × 25 mm pyrex pyrolysis column packed with 5 mm o.d. glass beads was heated at 450°C and swept with a nitrogen stream while 500 mg (2.7 mmol) of acetate IIIa was dropped onto the beads. The effluent vapors, condensed in a trap at —78°C, were treated with 10 ml of ether, poured into ice water, and neutralized with $NaHCO_3$. The ether layer, combined with 3 × 20 ml ether extracts of the aqueous layer, was washed, dried, and evaporated to give 300 mg (88% yield) of olefin IIa, which was purified by GLPC (Column A, 75°C). IR (CCl_4) 1645, 1260 cm^{-1}; NMR (CCl_4) δ 5.75 (m, 2), 2.33 (m, 2), 1.25 (m, 2), 0.72 (t, 2), and 0.10 (s, 6) ppm. (Found: C, 66.87; H, 11.18. $C_7H_{14}Si$ calcd.: C, 66.70; H, 11.10%.)

Bis(2-carboxyethyl)diphenylsilane. A modification of the Benkeser—Bennett method [10] for preparation of the dimethylsilyl derivative was employed. Bis-(3-chloropropoxy)diphenylsilane (90% from Ph_2SiCl_2, $ClCH_2CH_2CH_2OH$, and pyridine), b.p. 158—162°C/0.05 mmHg; IR (neat) 1605, 1440, 1120, and 1080 cm^{-1}; NMR (CCl_4) δ 7.1—7.6 (m, 10), 3.85 (t, 4), 3.52 (t, 4), 1.9 (quint, 4), was mixed with Me_3SiCl, then added to sodium sand in toluene. Work-up by the Benkeser—Cunico procedure [24], gave 44% of bis(3-hydroxypropyl)diphenylsilane, m.p. 83—84° (from PhH); IR (KBr) 3450, 1430, 1115, 1060 cm^{-1}; NMR ($CDCl_3$) δ 7.2—7.65 (m, 10), 3.50 (t, 4), 2.65 (s, 2, O<u>H</u>), 1.35—1.85 (m, 4), and 0.9—1.3 (m, 4) ppm. Potassium permanganate oxidation [10] in 1/1 (v/v) H_2O/t-BuOH gave 70% of diacid, m.p. 132—133°C. The yield using water as solvent was only 24%. IR (KBr) 3475—2775, 1710, 1430, 1110 cm^{-1}; NMR (DMSO-d_6) δ 7.6 (m, 10), 2.2 (m, 4), and 1.50 (m, 4) ppm. (Found: C, 65.63; H, 6.11; $C_{18}H_{20}O_4Si$ calcd.: C, 65.85; H, 6.09%.).

4,4-Diphenyl-4-silacyclohexanone. Pyrolysis [10] of 30 g (34 mmol) of the thorium salt of the above diacid gave 5.3 g (30% yield) of ketone, m.p. 94—95°C (from Et_2O); IR (KBr) 1715, 1430, 1115 cm^{-1}; NMR ($CDCl_3$) δ 7.3—7.9 (m, 10), 2.5—2.85 (m, 4), and 1.35—1.7 (m, 4) ppm. (Found: C, 76.51; H, 7.00. $C_{17}H_{18}OSi$ calcd.: C, 76.69; H, 6.76%.)

4,4-Diphenyl-4-silacyclohexanol. Sodium borohydride reduction of 5.6 g (21 mmol) of the above ketone gave 88% of alcohol, m.p. 123°C (*p*-nitrobenzoate m.p. 125°C); IR (KBr) 3420, 1425, 1105 cm^{-1}; NMR ($CDCl_3$) δ 7.2—7.6 (m, 10), 3.70 (tt, 1, CHOH), 0.85—2.25 (m, 9) ppm. The tosylate Ib (88% yield [23]) had m.p. 99—100°C; IR (KBr) 1605, 1440, 1360, 1120 cm^{-1}; NMR ($CDCl_3$) δ 7.3—7.8 (m, 14), 4.70 (m, 1), 2.42 (s, 3), 1.85—2.15 (m, 4), and 1.0—1.5 (m, 4) ppm. (Found: C, 68.02; H, 6.02; S, 7.48. $C_{24}H_{26}O_3SSi$ calcd.: C, 68.24; H, 6.14; S, 7.58%.)

4,4-Diphenyl-4-silacyclohexyl acetate (IIIb). By the procedure used to prepare IIIa, IIIb was obtained in 91% yield, m.p. 61—62°C (from Et_2O); IR (KBr) 1740, 1440, 1390, and 1120 cm^{-1}; NMR ($CDCl_3$) δ 7.2—7.8 (m, 10), 4.9 (m, 1), 1.8—2.2 (m + s, 7), and 1.15—1.50 (q, 4) ppm. (Found: C, 73.67; H, 7.15. $C_{19}H_{22}O_2Si$ calcd.: C, 73.55; H, 7.09%).

1,1-Diphenyl-1-silacyclohex-3-ene (IIb). Pyrolysis of IIIb by the method used to prepare IIa gave IIb (80% yield), a viscous oil purified by GLPC (Column B, 150°C); IR (neat) 1650, 1430, and 1105 cm^{-1}; NMR ($CDCl_3$) δ 7.3—7.7 (m, 10), 5.9 (m, 2), 2.2—2.6 (m, 2), 1.8 (broad s, 2), and 1.25 (t, 2) ppm. (Found: C, 81.85; H, 7.41. $C_{17}H_{18}Si$ calcd.: C, 81.60; H, 7.20%.)

Bis(2-carboxyethyl)methylphenylsilane. Following the above procedure, the diacid was obtained in 33% overall yield from $PhMeSiCl_2$, m.p. 56—57°C (from CCl_4); IR (KBr) 3500—2900, 1730, 1430, 1255, and 1110 cm^{-1}; NMR ($CDCl_3$) δ 11.7 (s, 2, CO_2H), 7.4—7.7 (m, 5), 2.2—2.6 (m, 4), 0.95—1.35 (m, 4), and 0.31 (s, 3), ppm. (Found: C, 58.78; H, 6.92. $C_{13}H_{18}O_4Si$ calcd.: C, 58.64; H, 6.76%.)

4-Methyl-4-phenyl-4-silacyclohexanone. Pyrolysis [10] of the thorium salt of the above diacid gave ketone (33% yield), b.p. 105—107°C/0.25 mmHg; IR (neat) 1710, 1425, 1255, 1105 cm^{-1}; NMR ($CDCl_3$) δ 7.4—7.7 (m, 5), 2.56 (t, 4), 1.20 (dt, 4), 0.35 (s, 3) ppm. The 2,4-DNP derivative had m.p. 135—136°C. (Found: C, 55.96; H, 5.29; N, 14.18. $C_{18}H_{20}N_4O_4Si$ calcd.: C, 56.25; H, 5.21; N, 14.58%.)

4-Methyl-4-phenyl-4-silacyclohexanols (XII + XIII). An alcohol mixture was obtained in 92% yield by sodium borohydride reduction of the above ketone, b.p. 112°C/0.2 mmHg; IR (neat) 3480, 1430, 1260, and 1115 cm^{-1}. The tosylate mixture (85% yield [23]) could be mechanically separated (tweezers) or less conveniently, fractionally crystallized from petr. ether, into two crops: Id, needles m.p. 75°C and Ic, octahedrons m.p. 65°C, which showed substantially identical spectra (Id given, Ic in parentheses where different): IR (KBr): 1605, 1440, 1350 (1360), 1255 (1260), 1120 cm^{-1}; NMR (CCl_4) δ 7.2—7.8 (m, 9), 4.55 (4.52) (quint, 1), 2.45 (2.47) (s, 3), 1.95 (q, 4), 0.7—1.2 (m, 4), and 0.25 (0.30) (s, 3) ppm. The mixture of *p*-nitrobenzoates [11] was resolved by crystallization from ether into two crops: needles m.p. 112—113°C and plates m.p. 102—103°C. Hydrolysis of the latter with Claisen's alkali afforded XIII as a viscous oil; GLPC Column B, 150°C); IR (CCl_4) 3580, 3325, 1420, 1250, 1110, and 1030 cm^{-1}; NMR (CCl_4) δ 7.35 (m, 5), 3.61 (tt, 1), 2.15 (m, 2), 1.75 (m, 2), 1.65 (s, 1, OH), 0.8—1.2 (m, 4), and 0.30 (s, 3) ppm. The former *p*-nitrobenzoate afforded XII, m.p. 46—47°C; (GLPC Column B, 150°C); IR (CCl_4) 3580, 3320, 1420, 1260, 1110, and 1030 cm^{-1}; NMR (CCl_4) δ 7.40 (m, 5), 3.68 (tt, 1), 1.45—2.30 (m, 4), 1.48 (s, 1, OH), 0.7—1.38 (m, 4), and 0.26 (s, 3) ppm. (ana-

lysis of a mixture of XII and XIII: Found: C, 69.52; H, 8.62. $C_{12}H_{18}OSi$ calcd.: C, 69.90; H, 8.73%.)

trans-4-Methyl-4-phenyl-4-silacyclohexyl acetate (IIIc). By the procedure for IIIa (87% yield); IR (KBr) 1745, 1430, 1255, and 1115 cm^{-1}; NMR (CCl_4) δ 7.45 (m, 5), 4.7 (m, 1), 2.02 (s, 3), 1.86 (m, 4), 1.00 (t, 4), and 0.34 (s, 3) ppm.

cis-4-Methyl-4-phenyl-4-silacyclohexyl acetate (IIId). By the same procedure (89% yield); IR (CCl_4) 1745, 1430, 1245, and 1110 cm^{-1}; NMR (CCl_4) δ 7.4 (m, 5), 4.7 (m, 1), 1.95 (s, 3), 1.80 (m, 4), 1.20 (m, 2), 0.75 (m, 2), and 0.25 (s, 3) ppm; (Found: C, 67.98; H, 8.26. $C_{14}H_{20}O_2Si$ calcd.: C, 67.74; H, 8.06%.) Saponification of IIIc and IIId produced XIII and XII, respectively.

1-Methyl-1-phenyl-1-silacyclohex-3-ene (IIc). Pyrolysis of a mixture of IIIc and IIId (or either independently) by the procedure used to prepare IIa gave IIc (81% yield), pyrified by GLPC (Column B, 195°C); IR (neat) 1650, 1440, 1255, 1120 cm^{-1}; NMR (CCl_4) δ 7.4 (m, 5), 5.75 (m, 2), 2.30 (m, 2), 1.46 (m, 2), 0.9 (broad s, 2), and 0.3 (s, 3) ppm. (Found: C, 76.70; H, 8.60. $C_{12}H_{16}Si$ calcd.: C, 76.60; H, 8.51%.)

Other tosylates (VIa [18] and VIc—VId [25]. These were prepared by literature techniques. Deuterated tosylate VII was obtained from 4,4-dimethyl-4-silacyclohexanone [10] by exchange (NaOMe, D_2O, reflux), reduction and tosylation [23]; m.p. 60°C; IR (KBr) 2210, 1605, 1360, 1255, 1175 cm^{-1}; NMR (CCl_4) δ 7.48 (m, 4), 4.48 (s, 1), 2.55 (s, 3), 0.75 (m, 4), and 0.14 (s, 6) ppm. (Found: C, 55.60; H + D, 7.77; S, 10.84. $C_{14}H_{18}D_4O_3SSi$ calcd.: C, 55.59; H + D, 7.43; S, 10.60%.)

Acetolysis experiments

The general procedure is illustrated for tosylate VII. A solution of 1.5 g (5 mmol) of VII in 125 ml of 0.05 *M* sodium acetate in glacial acetic acid containing 1% [w/v] of acetic anhydride was heated in a thermostat at 70°C for 13 h. The mixture was poured into 300 ml of ice/water, and continuously extracted with pentane for 16 h. The pentane extract was washed with cold water, dried, and evaporated to leave 700 mg (72% yield) of residue which was analysed by GLPC (Column A, 85°C). Eluted were (ret. time, rel. yield): VIII (1.5 min, 23%), X (13 min, 46%), and IX (17 min, 31%). A peak eluting at 7.5 min (5% yield), presumably Va-d_4, upon collection and reinjection was identical with X. VIII had NMR (CCl_4) δ 5.6 (s, 1), 1.25 (broad s, 2), 0.75 (broad s, 2), and 0.14 (s, 6) ppm. X had NMR (CCl_4) δ 4.9 (broad s, 4), 2.0 (s, 2), 0.47 (s, 4), and 0.01 (s, 12) ppm. IX had IR (neat) 2220, 1755, 1380 and 1255 cm^{-1}; NMR (CCl_4) δ 4.61 (s, 1), 1.91 (s, 3), 0.70 (s, 4), 0.05 (s, 3), and 0.01 (s, 3) ppm.

Results for other tosylates are reported in Table 2. Olefins IIa—IId, 4,4-dimethylcyclohex-1-ene [18]; acetates IIIa—IIId; and siloxane IVa [5,20] were identified by comparison with authentic samples.

Kinetic experiments

Following the procedure of Winstein and Grunwald [16], 750 mg of the appropriate tosylate was dissolved in 0.0595 *M* sodium acetate in glacial acetic acid containing 1% of acetic anhydride to give a final volume of 50 ml. Ampoules (4.0 ml each) of the above solution were sealed and hung in a thermostat at 70°C. At suitable times ampoules were removed, cooled, opened, and titrated

with 0.0254 *N* perchloric acid to a bromophenol blue end point. The time of the first analysis was called zero time. Typically reactions were followed to at least three half lives. Results are summarized in Table 3, each point of which is the average of two runs which differed by 3% or less. Complete data and plots are found in the Ph.D. dissertation of R.R. Chawla.

Acknowledgement

The assistance of Mssrs. William Cox and Gerson Stauber in the preparation of starting materials made this work possible, as did the generosity of Union Carbide Corporation, who donated chlorosilanes.

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