Tetrahedron Vol. 39, No. 6, pp 913 to 924, 1983
Printed in Great Britain.

0040-4020/83/060913-12$03.00/0
Pergamon Press Ltd

SILICON IN ORGANIC SYNTHESIS—17

CYCLOPENTANNULATION BY THERMOLYSIS OF (1-TRIMETHYLSILYLCYCLOPROPYL)ETHYLENES—THE 1-TRIMETHYLSILYLCYCLOPROPYL ANION[1]

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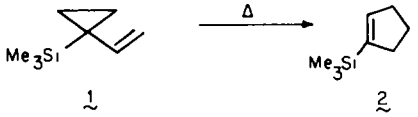
(*Received in U.S.A.* 14 *May* 1982)

Abstract—Several alternatives for preparing (1-trimethylsilylcyclopropyl)ethylenes have been examined. Although 1-lithio-1-(trimethylsilyl)ethylene does add satisfactorily to carbonyl compounds and the subsequent Simmons–Smith cyclopropanation provides the desired cyclopropyl carbinols, shorter routes involving the 1-trimethylsilylcyclopropyl anion were sought. The sequence based upon reductive lithiation of 1-(trimethylsilyl)-1-phenylthiocyclopropane proved less than satisfactory. In contrast, metalation of 1-bromo-1-(trimethylsilyl)cyclopropane leads efficiently to the desired carbinols which dehydrate without rearrangement. Pyrolysis of the resulting (1-trimethylsilylcyclopropyl)ethylenes affords silyl substituted cyclopentenes in high yield. Subsequent reaction of these products with varied electrophiles forms the basis of a new and versatile 5-ring annulation sequence. An intramolecular competitive study of the vinylcyclopropane rearrangement is documented as are other attempts to induce ring expansion of the Si-substituted 3-membered ring by ionic pathways.

Although the thermal rearrangement of vinylcyclopropane derivatives constitutes a most powerful method for the annulative formation of functionalized cyclopentenes,[3] no Si-substituted compounds appear to have been subjected to such pyrolytic treatment.[4] One incentive for the study of (1-trimethylsilylcyclopropyl)ethylenes (e.g. **1**) is provided by the vinylsilane character of the products (**2**) which should allow for



1 **2**

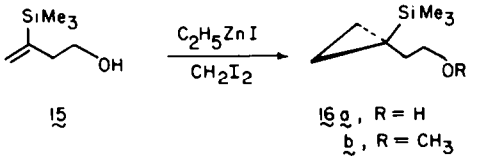
extensive subsequent functionalization.[5] The possible broad adaptation of this methodology requires, of course, that there be no shortage of efficient synthetic routes to higher and more complex homologues of **1**. Herein, we disclose the full details of our investigation involving various means of producing strained molecules of this type and detail their response to thermal activation. Also developed in the course of this work is a particularly expedient method for the generation of the 1-trimethylsilylcyclopropyl anion, a versatile heteroatom stabilized organometallic which has the potential for becoming a highly useful instrument in synthetic organosilicon chemistry.

Indirect preparation of (1-trimethylsilylcyclopropyl)ethylenes. Because α-bromovinyltrimethylsilane (**3**) can be conveniently prepared in large quantities[6] and readily coaxed into halogen–metal exchange with t-BuLi in ether at −78°,[7] we began by assessing the viability of this organometallic reagent (**4**) in providing 1-(trimethylsilyl)cyclopropyl carbinols. Although the addition of **4** to

3

4

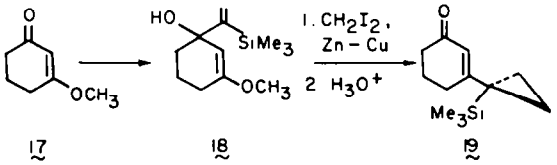
carbonyl compounds proceeded uneventfully (Table 1), we did note that the use of 1.25–1.5 equiv. of t-BuLi generally delivered the carbinols in best yield. These products smoothly underwent Simmons–Smith cyclopropanation when the modified form of this procedure which utilizes EtZnI[8] was applied. Strikingly, no methyl ether formation was observed. This was not the case when the OH group is primary in nature as in **15**. Under



15 **16a**, R = H; **b**, R = CH_3

the usual experimental conditions which make use of 1.2 equiv. of CH_2I_2, mixtures of **16a**, **16b**, and starting alcohol **15** were obtained. Aliquot analysis showed **16b** to be present even at low conversion. In the presence of excess CH_2I_2, no **16a** was obtained and **16b** was the primary product. When recourse was made to Zn–Cu couple instead of EtZnI, a 5.5:1 mixture of **16a** and **16b** was produced.

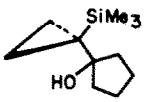
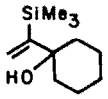
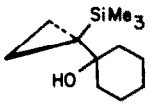
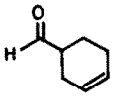
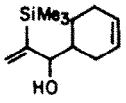
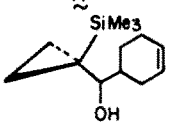
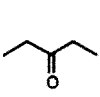
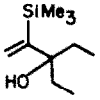
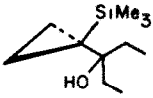
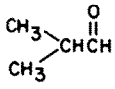
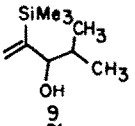
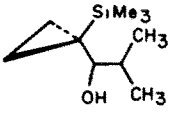
Expectedly, the acid lability of the carbinol resulting from cyclopropanation of **18** led to the direct formation of enone **19** on workup.



17 **18** **19**

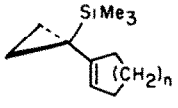
Carbinols **10** and **11** were directly dehydrated *without rearrangement* in yields of 52–75% upon exposure to catalytic amounts of *p*-toluenesulfonic acid in benzene at 20°. No evidence was found for the occurrence of ring expansion or cleavage processes under these mild con-

Table 1. Preparation of (1-trimethylsilylcyclopropyl)carbinyl alcohols by reaction of 4 with ketones and aldehydes followed by Simmons–Smith cyclopropanation

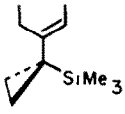
Carbonyl compd	Vinyl alcohol	Yield, %	Cyclopropylcarbinyl alcohol	Yield, %
	 **5**	67	 **10**	65[a]
	 **6**	76	 **11**	98
	 **7**	50	 **12**	—
	 **8**	75	 **13**	—
	 **9**	80	 **14**	92

[a]Some dehydration was encountered during the reaction and workup.

ditions. Where **13** was concerned, an *ca.* 1:1 mixture of the *E*- and *Z*-isomers was formed. This pair of allylsilanes (**21** and **22**) was conveniently separated by vapor phase chromatography and their individual structural assignments confirmed by their thermal behavior (see below).



20 a, n = 1
b, n = 2



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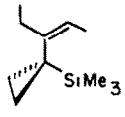
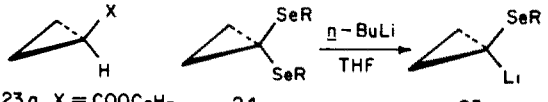


22

Methods for generation of the 1-*trimethylsilylcyclopropyl anion.* Notwithstanding the reasonable efficiency of the standard methodology just described, the feasibility of a more direct route mediated by the 1-trimethylsilylcyclopropyl anion now had to be considered. Recourse to 3-membered organometallic intermediates has been made with ever-increasing frequency in recent years, although their generation has on occasion presented complications. Thus, while attempts to produce the anions of **23a** and **23b** by deprotonation have not been successful,[9-11] cyclopropyl phenyl sulfide (**23c**) under-

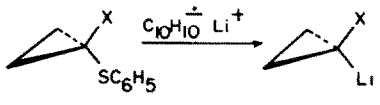


23 a, X = $COOC_2H_5$
b, X = NO_2
c, X = SC_6H_5
d, X = COOH

24

25

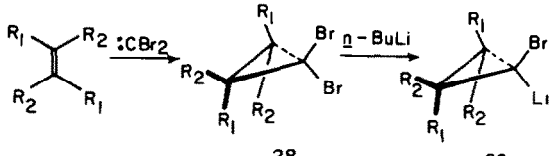
goes rapid and efficient proton abstraction with n-BuLi at 0°.[12-14] The dianion of **23d** is likewise readily formed upon exposure to 2.2 equiv. of lithium diisopropylamide in THF at 0°.[15] Krief and Reich have established that cyclopropanone diselenoketals such as **24** enter rapidly into reaction with n-BuLi in THF to produce the corresponding selenocarbanions **25** in high yield.[16] More recently, Cohen and Matz have shown that cyclopropyl sulfides of type **26** are subject to reductive lithiation with lithium naphthalenide or lithium 1-dimethylamino-



26 a, X = SC_6H_5
b, X = OCH_3

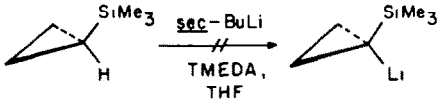
27

naphthalenide.[17] Reaction sequences involving dibromocarbene addition to alkenes followed by transmetalation of **28** with n-BuLi to give α-lithiocyclopropyl bromides **29** can be utilized conventionally without serious complication from carbenoid formation.[18,19]

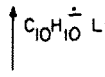


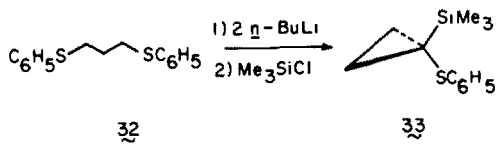
28 **29**

No comparable attention has been paid to silylcyclopropanes.[20] Quite unlike **23c** and **23d**, trimethylsilylcyclopropane (**30**) does not undergo deprotonation at its α-cyclopropyl[21] site under a variety of conditions, including prolonged exposure to sec-BuLi and TMEDA in THF solution.[22] Accordingly, recourse was made to deprotonation of **23c** and condensation of the resulting anion (**27a**) with trimethylsilyl chloride to give **33**. A considerably more convenient synthetic entry to this bifunctional cyclopropane can be realized by sequential treatment of **32** with 2 equiv. of n-BuLi[13] and Me_3SiCl. With **33** in hand, it proved an easy matter to overcome the lack of proton acidity in **30** and arrive at **31** by reductive cleavage of the phenylthio substituent with lithium naphthalenide.



30 **31**



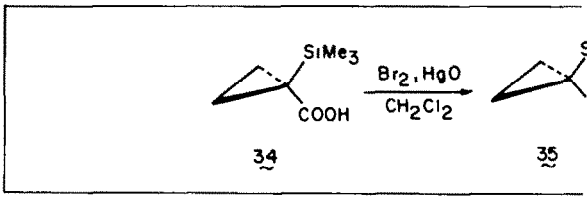


32 **33**

The addition of **31** prepared in this manner to carbonyl compounds suffered from two annoying drawbacks. Firstly, chromatography was necessary to separate naphthalene from the resulting carbinols which often suffered dehydration under these conditions. Because the polarities of the (1-trimethylsilylcyclopropyl)ethylenes formed *in situ* on the column differed little from that of the aromatic by-product, drastically lowered yields of pure products had to be tolerated. Secondly, the reductive lithiations themselves proved problematical, even failing totally on occasion for unknown reasons. When the use of 1-dimethylaminonaphthalenide did not resolve either complication, this approach was abandoned.

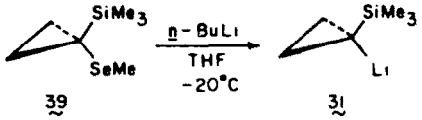
While the preparation of 1,1-dibromocyclopropane from ethylene has been described,[23] autoclave conditions and the expensive dibromocarbene source $PhHgCBr_3$ must be utilized. These requirements seriously detract from the attractiveness of this precursory molecule.

Alternatively, **34** is conveniently available in large quantity by reaction of thd dianion of **23d** with trimethylsilyl chloride.[15] Hunsdiecker degradation of **34** in dichloromethane solution was found to occur spontaneously, to be mildly exothermic, and to proceed to completion within 2 hr. Fractional distillation to separate small amounts (5–10%) of bromodichloromethane which is formed concomitantly provides the low melting solid bromide **35** in 50–60% isolated yield. We have thus far noted that **35** undergoes lithiation with n-BuLi in THF at −78° and condensation with carbonyl compounds routinely in high yield, except in the case of cyclopentanone where enolate anion formation is somewhat competitive. Generally, dehydration of the carbinols was effected without purification. The overall yields provided in Table 2 are illustrative of the efficiency of the method which has repeatedly shown itself to be superior to the other alternatives described herein.

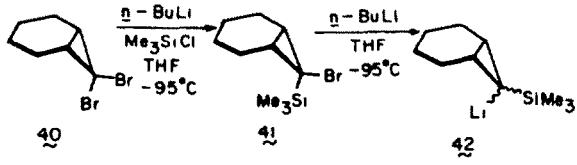


34 **35** **31**

Following upon these developments in this laboratory, Krief has disclosed his independent findings that **39** (obtained by condensation of **25** with Me_3SiCl) can be effectively converted to **31** upon reaction with n-BuLi.[24] They and the group headed by Nozaki[25] also reported recently that more highly substituted 1,1-dibromocyclopropanes (e.g. **40**) can be transformed via silyl bromides such as **41** to 1-trimethylsilylcyclopropyllithium reagents (**42**). Thus, a broadly general synthetic entry to 1-trimethylsilylcyclopropyl anions is now available.



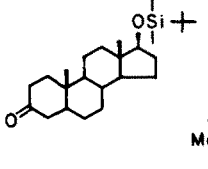
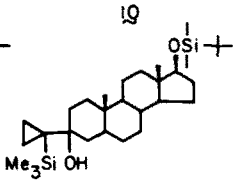
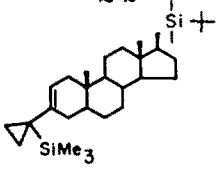
39 **31**

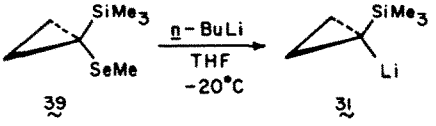


40 **41** **42**

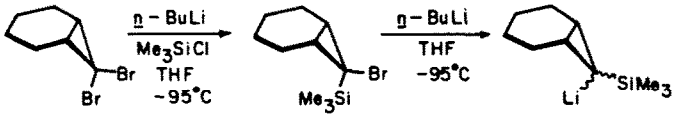
Thermal isomerization studies. The long-range goal of this research program was to effect the thermal rear-

Table 2. Preparation of (1-trimethylsilylcyclopropyl)ethylenes by reaction of **31** (prepared from bromide **35**) with ketones followed by dehydration

Carbonyl compd	Cyclopropylcarbinyl alcohol	(1-Trimethylsilyl-cyclopropyl)ethylene	Overall Yield, %
3-Pentanone	13	21/22	60
Cyclohexanone	11	20b	51
Cyclopentanone	10	20a	20
			60
36	37	38	

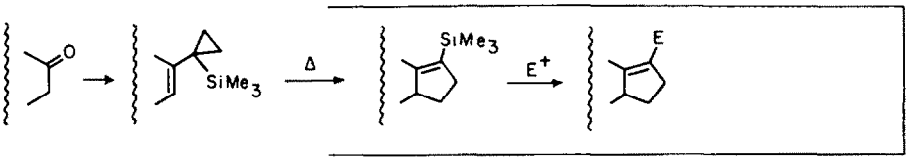


39 31



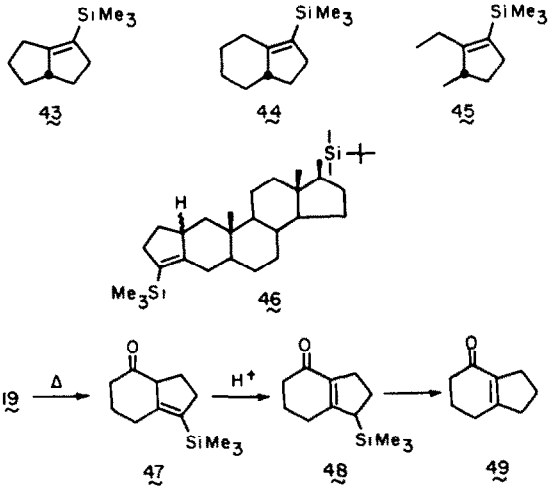
40 41 42

rangement of silicon functionalized vinylcyclopropanes in order to achieve a new 5-ring annulation procedure of androstanolone **38** delivered **46**. Incorporation of the double bond into a cyclic enone moiety as in **19** did not disrupt the bond relocation process, although somewhat more elevated temperatures (660°) were now required.



rich diversity based ultimately upon electrophilic substitution of the resulting cyclopentenyl silanes. As the result of extensive kinetic investigation by several groups, it is now widely recognized that heteroatoms positioned on vinylcyclopropane moieties and other strained ring systems capable of thermal rearrangement exert a powerful influence on rate (Table 3). Although this effect is understandably closely related to the location of the substituent, electro-negative atoms such as O and N are generally seen to give rise to a rate enhancement effect. Although the kinetic consequences of pendant silyl groups had not been examined, we surmised that the electropositive character of Si relative to C would likely be adequate to deter the thermal rearrangement of **20** and **21**, particularly since the Me_3Si residue was bonded to C-1 in these compounds.

This assumption was soon proven to be correct. Passage of **20a**, **20b** and **21** in the gas phase at 30–40 torr (N_2 as carrier gas) through a quartz chip-packed tube (30 m long) required heating to 570° to achieve useful levels of conversion to **43** (89%), **44** (85%) and **45** (71%), respectively. Comparable treatment of the functionalized

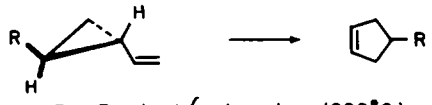


43 44 45 46

19 47 48 49

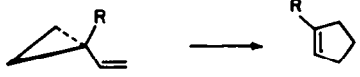
Table 3. Activation energy and relative rate data for the thermal rearrangement of selected strained ring systems

A. 2-Substituted Vinylcyclopropanes



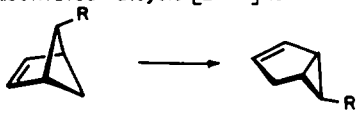
R	E_a, kcal/mol	k_{rel} (200°C)	ref
H	49.7	1	a
OCH_3	38.7	10^4	b
NMe_2	31.2	3×10^5	c

B. 1-Substituted Vinylcyclopropanes



R	E_a, kcal/mol	ref
H	49.7	a
CH_3	49.4	d
OCH_3	44.7	b

C. 5-Substituted Bicyclo[2.1.1]hexanes



R	E_a, kcal/mol	k_{rel} (100°C)	ref
H	35.2	1	e
OAc	28.2	10^3	f
OCH_3	25.1	10^5	g

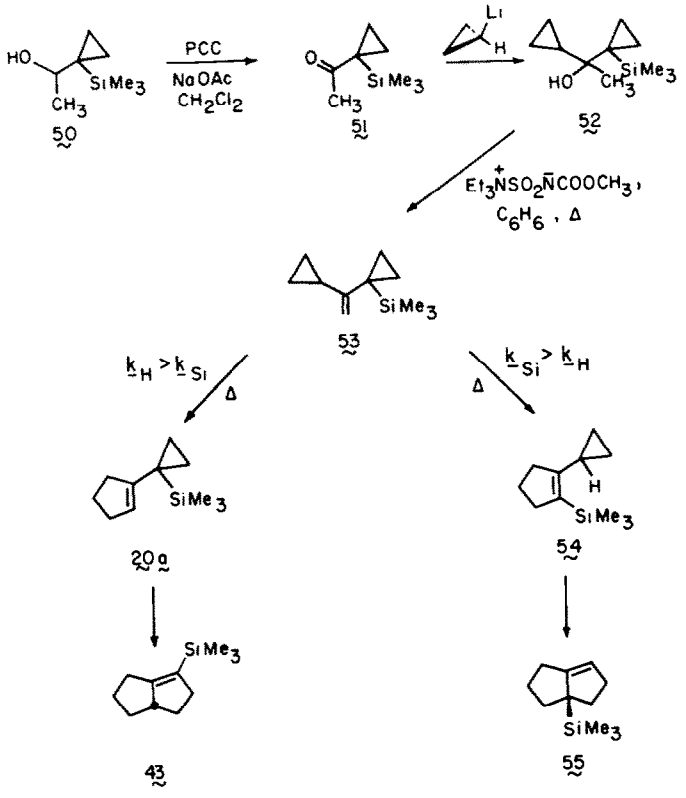
D. 7-Substituted Bicyclo[3.2.0]hept-2-enes

R	E_a, kcal/mol	k_{rel} (240°C)	ref
H	49.6	1	h
OCH_3	46.3	23	i
NMe_2	41.0	2×10^3	i

[a]M. C. Flowers and H. M. Frey, *J. Chem. Soc.* 3547 (1961); C. A. Wellington, *J. Phys. Chem.* 66, 1671 (1962); [b]J. M. Simpson and H. G. Richey, Jr., *Tetrahedron Letters* 2545 (1973); [c]H. G. Richey, Jr. and D. W. Shull, *Ibid.* 575 (1976); [d]R. J. Ellis and H. M. Frey, *J. Chem. Soc.* 959 (1964); [e]H. M. Frey and G. R. Hopkins, *J. Chem. Soc. B.* 1410 (1970); [f]S. Masamune, S. Takada, N. Nakatsuka, R. Vukov and E. N. Cain, *J. Am. Chem. Soc.* 91, 4322 (1969); [g]F. Scheidt and W. Kirmse, *J. Chem. Soc. Chem. Commun.* 176 (1972); [h]A. T. Cocks and H. M. Frey, *J. Chem. Soc. A.* 2564 (1971); [i]W. Kirmse and B. P. Kampmann, unpublished; B. P. Kampmann, Dissertation, Univ. Bochum 1979.

Compound **47** is particularly prone to prototropic shift. Because the trimethylsilyl group in **48** now happens to be allylic, desilylation also occurs readily during the chromatographic purification process.

A competition study. The thermal rearrangements just described may well proceed by a stepwise pathway wherein the Si-substituted C atom acquires odd-electron character during formation of an intermediate biradical. Since α-silyl free radicals are known to lack stabilization,[26] the $-SiMe_3$ group would be expected to exert an untoward kinetic effect. Although the somewhat elevated temperatures required can be construed to be an indication of rate retardation, we sought to acquire additional evidence. Kinetic studies of vinylcyclopropane rearrangements abound.[27] Interestingly, however, no intramolecular competition version of this process has been documented. Although quantitative information is not usually obtained from experiments of this type, a qualitative appreciation of kinetic ordering can be gained with certainty, frequently with minimal expenditure of effort. For these reasons, we prepared the dicyclopropylethylene **53**.



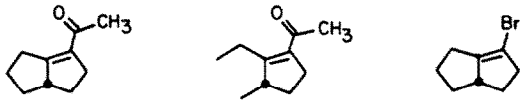
Secondary alcohol **50** was synthesized from acetaldehyde in conventional fashion and oxidized with pyridinium chlorochromate. Following the additions of cyclopropyllithium to ketone **51**, the resulting tertiary alcohol (**52**) proved to be most efficiently dehydrated through use of the Burgess reagent.[28]

As is illustrated, kinetically favored involvement of the unsubstituted 3-membered ring will lead initially to **20a** and ultimately to **43**. To the extent that the silylcyclopropane moiety enters first into isomerization, vinylsilane **54** will result initially. Continued thermal rearrangement of **54** would lead to allylsilane **55**. Experimentally, we found that pyrolysis of **53** under the predescribed conditions results in clear conversion uniquely to **43**. Clearly, therefore, $k_H \gg k_{Si}$.

Electrophilic additions to the cyclopentannulated vinylsilanes. We emphasize here that the present procedure delivers mono- and bicyclic vinylsilanes having the double bond invariably positioned at the more highly substituted site. This regiochemistry is not attainable through application of the Shapiro reaction which leads via kinetically controlled proton abstraction to the lesser substituted vinylsilane[29] (e.g. **56**→**57**). As a result, the methodologies are usefully complementary.

56 **57**

In the course of selected experiments involving **43** and **45**, it was noted that these vinylsilanes conform to the usual pattern of regioselectivity wherein the Si-substituent directs the entry of electrophiles to the Si-bonded C. However, conditions had to be controlled more strictly than normal, perhaps as a consequence of the tetrasubstituted nature of their double bonds. Thus, acetylation by means of acetyl chloride in dichloromethane at −78° afforded **58** and **59**, while bromination led to the isolation of **60**. Through reaction with *m*-chloroperbenzoic acid, **43** was efficiently transformed into a 60:40 mixture of the epimers of **61**, and **45** gave rise to a 1:1 mixture of **62a** and **62b**. The individual stereochemistries of these isomers was not revealed unambiguously by lanthanide shifting experiment.



58 **59** **60**

61 a, β−H
b, α−H

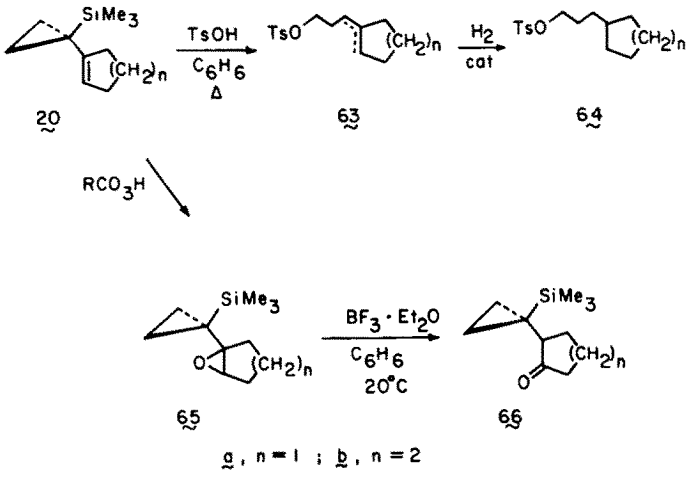
62 a, β−H
b, α−H

Response of (1-*trimethylsilylcyclopropyl*)*ethylenes to electrophilic agents.* It will be recalled that cyclopropyl ring expansion was not observed during the dehydration of carbinols such as **10–14** and **37**. Nor was rearrangement considered to be particularly likely under carbocationic conditions, since a positive charge would be required to reside α to the trimethylsilyl group at least temporarily. The energetic costs of this substitution plan

in carbonium ions are generally recognized to be rather substantial.[30] However, these disadvantages would well be outweighted by the imminent possibilities for strain relief. In order to acquire an appreciation of the extent to which these factors are counterbalanced, we subjected the (1-trimethylsilylcyclopropyl)ethylenes **20a** and **20b** to certain informative experiments.

When **20a** was heated at the reflux temperature with 1 equiv. of *p*-toluenesulfonic acid in benzene, cyclopentylidene tosylate **63a** possessing only an exocyclic double bond was isolated in 87% yield. Cyclohexenyl analog **20b** behaved comparably, except that a mixture of exo- and endocyclic isomers of **63b** was formed. The tenets summarized in the Brown–Brewster–Shechter rule[31] are unquestionably at work here. Structural confirmation in both examples was achieved by catalytic hydrogenation to **64** and direct comparison with authentic samples. Although several mechanisms can be advanced to account for these transformations, cyclopropane ring expansion is not one of them.

Exposure of epoxides **65a** and **65b** to boron trifluoride etherate in benzene solution at 20° resulted in isomerization to ketones **66**. Although cyclopropylcarbinyl cations presumably again intervene here, prototropic shifting clearly has taken precedent over ring enlargement.



EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian T-60, Varian EM-360, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were recorded with a Bruker WP-80 or HX-90 spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on Varian Aerograph Model A-90-P3 instruments equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Laboratory, Herlev, Denmark.

1-Hydroxy-1-(1-trimethylsilylethenyl)cyclopentane (**5**)

To a cold (−78°) soln of α-bromovinyltrimethylsilane[6] (7.0 g, 40 mmol) in dry ether (100 mL) under argon was added 27 mL of 1.87 *M* t-BuLi (50.5 mmol). The resulting clear yellow soln was stirred at −78° for 1 hr and treated dropwise during 10 min with a soln of freshly distilled cyclopentanone (3.36 g, 40 mmol) in ether (20 mL). The mixture was allowed to warm slowly to room temp. during 3 hr. After an additional hr, 5% HClaq. was added and the organic layer was washed with water (2 × 5 mL). The combined aqueous phases were back-extracted with ether. The ether solns were dried and concentrated to give 7.29 g of a yellow oil, distillation of which at 3.5 torr afforded 4.93 (67%) of **5**, b.p. 76–77°; IR (cm^{-1}, neat) 3440, 3060, 2960, 2867, 1450, 1408, 1250, 1185, 1000, 935, 861, 842, 765, and 690; ^{1}H NMR (δ, $CDCl_3$) 5.8 (d, J = 2 Hz, 1 H), 5.42 (d, J = 2 Hz, 1 H), 2.02–1.70 (m, 8 H), and 0.23 (s, 9 H); *m/e* Calc. (M$^+$): 184.1283, Obsd: 184.1277.

(Found: C, 65.45; H, 10.84. Calc. for $C_{10}H_{20}OSi$: C, 65.21; H, 10.86%.)

1-Hydroxy-1-(1-trimethylsilylethenyl)cyclohexane (**6**)

Reaction of 7.0 g (0.04 mol) of **3** with 30 mL of 2.0 *M* t-BuLi (0.06 mol) and 3.8 g (0.039 mol) cyclohexanone as previously described gave 6.80 g (76%) of **6** after distillation at 3.5 torr; ^{1}H NMR (δ, $CDCl_3$) 5.70 (d, J = 2 Hz, 1 H), 5.40 (d, J = 2 Hz, 1 H), 1.80–1.35 (m, 10 H), and 0.15 (s, 9 H); *m/e* Calc. (M$^+$) 212.1496, Obsd: 212.1602.

4-(1-Hydroxy-2-trimethylsilyl-2-propenyl)cyclohexene (**7**)

Reaction of **3** (4.47 g, 0.025 mol) with 12.3 mL of 2.03 *M* t-BuLi in pentane and 2.75 g (0.025 mol) 1,2,3,6-tetrahydrobenzaldehyde in the predescribed manner gave 5.28 g of clear yellow oil. Vacuum distillation furnished **7** (2.6 g, 50%), b.p. 111–119°/3.5 torr; IR (cm^{-1}, neat) 3440, 3024, 2960, 2920, 2840, 1650, 1435, 1400, 1250, 1170, 1137, 1040, 1020, 965, 930, 835, 755, and 685; ^{1}H NMR (δ, $CDCl_3$) 5.72 (d, J = 3 Hz, 1 H), 5.65 (m, 1 H), 5.45 (d, J = 3 Hz, 1 H), 4.05 (m, 1 H), 2.15–1.35 (m, 8 H), and 0.1 (s, 9 H); *m/e* Calc. (M$^+$): 192.1334, Obsd: 192.1329. (Found: C, 68.33; H, 10.45. Calc. for $C_{12}H_{22}OSi$: C, 68.56; H, 10.47%.)

3-Hydroxy-3-ethyl-2-(trimethylsilyl)-1-pentene (**8**)

Reaction of **3** (5.0 g, 28 mmol) with 19.94 mL of 1.82 *M* t-BuLi in hexane (36 mmol) followed by 3-pentanone (2.65 g, 31 mmol) gave 391 g (75%) of **8** as a colorless liquid, b.p. 62–65° (3.5 torr); ^{1}H NMR (δ, $CDCl_3$) 5.55 (d, J = 2 Hz, 1 H), 5.45 (d, J = 2 Hz, 1 H), 1.7–1.4 (q, J = 7 Hz, 4 H), 1.35 (s, 1 H), 1.0–0.75 (t, J = 7 Hz, 6 H), and 0.0 (s, 9 H); *m/e* Calc. (M$^+$): 168.1334, Obsd: 168.1339. (Found: C, 64.18; H, 11.89. Calc. for $C_{10}H_{22}OSi$: C, 64.43; H, 11.92%.)

3-Hydroxy-4-methyl-2-(trimethylsilyl)-1-pentene (**9**)

Reaction of **3** (12.4 g, 69.3 mmol) with 50 mL of 1.77 *M* t-BuLi (88.5 mmol) and 5.0 g (69.3 mmol) isobutyraldehyde as above afforded 9.59 g (80%) of **9**, b.p. 90–92° (8 torr); ^{1}H NMR (δ, $CDCl_3$) 5.75 (m, 1 H), 5.50 (m, 1 H), 4.1 (br s, 1 H), 2.0–1.5 (m, 2 H), 1.05 (d, J = 6 Hz, 6 H), and 0.30 (s, 9 H).

1 - (1 - *Trimethylsilylcyclopropyl)cyclopentanol* (**10**)

An ethereal soln of EtZnI (90 mL of 1.0 *M*) was blanketed with N_2 and CH_2I_2 (5.65 g, 21.1 mmol) was added. The resulting soln was heated at reflux for 1 hr, cooled to 0° in an ice bath while **5** (3.4 g, 18.5 mmol) dissolved in anhyd. ether (20 mL), and stirred overnight at room temp. After the volume was reduced to *ca.* 50 mL by distillation, the mixture was cooled and quenched with sat. NH_4Claq. Following the addition of ether (50 mL), the organic phase was washed with sat NH_4Claq and water prior to drying and solvent evaopration. There was obtained 2.38 g (65%) of **10** as a pale yellow oil which underwent facile dehydration upon attempted chromatographic purification; IR (cm^{-1}, neat) 3470, 3070, 2980, 1250, 1025, 1000, 920, 840, 760, and 690; NMR (δ, $CDCl_3$) 1.93–1.52 (m, 8 H), 0.62–0.45 (m, 4 H), and 0.08 (s, 9 H).

1 - (1 - *Trimethylsilylcyclopropyl)cyclohexanol* (**11**)

From 270 mL of 1.0 *M* EtZnI, 4.0 g (14.99 mmol) CH_2I_2, and 2.63 g (13.3 mmol) of **6**, there was obtained 3.09 g (98%) of **11** which also was dehydrated upon attempted chromatographic purification; ^1H NMR (δ, $CDCl_3$) 1.9–1.35 (m, 10H), 0.78–0.6 (m, 2 H), 0.50–0.35 (m, 2 H), and 0.15 (s, 9 H); *m/e* Calc. (M^+): 212.1596, Obsd: 212.1602.

1 - (1 - *Hydroxy* - 2 - *methylpropyl*) - 1 - (*trimethylsilyl)cyclopropane* (**14**)

From 25 mL of 1.2 *M* EtZnI, 1.8 g (6.7 mmol) of CH_2I_2, and 1.0 g (5.8 mmol) of **9**, there was obtained 0.99 g (91.6%) of **14** as a colorless oil. An analytically pure sample was prepared by preparative VPC at 112° (5 ft × 0.25 in. 5% SE-30); IR (cm^{-1}, neat) 3500, 3070, 2960, 1460–1430, 1410–1365, 1265, 1255, 1030, 985, 960, 950, 930, 895, 840, and 755; ^1H NMR (δ, $CDCl_3$) 2.35 (d, J = 9 Hz, 1 H), 2.09–1.69 (m, 1 H), 1.40 (br s, 1 H), 0.99 (d, J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 0.48–0.25 (m, 4 H), and 0.05 (s, 9 H); *m/e* 171 ($M^+ - CH_3$), 168 ($M^+ - H_2O$), and 153 ($M^+ - CH_3$ and H_2O).

1 - (2 - *Hydroxyethyl*) - 1 - (*trimethylsilyl)cyclopropane* (**16a**)

Zn dust (3.0 g) and cuprous chloride (450 mg) were slurried in 7 mL dry ether under argon and heated at reflux for 30 min. To the resulting couple was added 1.8 mL (22.8 mmol) CH_2I_2 and 1.0 g (6.3 mmol) of **15**, and this mixture was heated at reflux for 24 hr and stirred at room temp. for an additional 24 hr. Following the addition of sat. NH_4CHaq., the mixture was filtered through Celite and the residue was rinsed with ether. The filtrate was washed with water (2 ×), dried, and concentrated *in vacuo*. There was obtained 1.09 g of a 5.5:1 mixture of **16a** and **16b** as a colorless oil. Chromatography on silica gel (elution with 8% EtOH in pentane) gave 820 mg (75%) of **16a**; IR (cm^{-1}, neat) 3320, 3060, 2990, 2950, 1429, 1245, 1050, 1020, 950, 870, 830, 740, and 680; ^1H NMR (δ, $CDCl_3$) 3.70 (t, J = 7 Hz, 2 H), 1.57 (t, J = 7 Hz, 2 H), 1.37 (br s, 1 H), 0.45 (m, 2 H), 0.32 (m, 2 H), and 0.00 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 62.7, 41.2, 9.1, 2.5, and −2.4; *m/e* Calc. (M^+): 143.0892, Obsd: 143.0836. (Found: C, 60.56; H, 11.59. Calc. for $C_8H_{18}OSi$: C, 60.69; H, 11.46%.)

1 - (2 - *Methoxyethyl*) - 1 - (*trimethylsilyl)cyclopropane* (**16b**)

From 90 mL of 1.0 *M* EtZnI, 16.63 g (62 mmol) CH_2I_2, and 3.0 g (20.8 mmol) of **15**, there was isolated 3.10 g (95%) of **16b** after purification by medium pressure liquid chromatography (MPLC) on silica gel (elution with 7% ether in hexane); IR (cm^{-1}, neat) 3060, 2900, 1445, 1385, 1249, 1180, 1117, 1012, 937, 907, 857, 830, 740, and 680; ^1H NMR (δ, $CDCl_3$) 3.45 (t, J = 7 Hz, 2 H), 3.40 (s, 3 H), 1.60 (t, J = 7 Hz, 2 H), 0.55–0.30 (m, 4 H), and 0.08 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 72.7, 58.5, 38.0, 9.3, 3.0, and −2.5; *m/e* Calc. (M^+): 157.1049, Obsd: 157.1045. (Found: C, 62.60; H, 11.73. Calc. for $C_9H_{20}OSi$: C, 62.79; H, 11.62%.)

3 - *Methoxy* - 1 - (1 - *trimethylsilylethenyl*) - 2 - *cyclohexen* - 1 - *ol* (**18**)

To a −78° ethereal soln (20 mL) of α-bromovinyltrimethylsilane (1.8 g, 10 mmol) was added t-BuLi (7 mL of 1.82 *M*) over 2 min. The mixture was stirred for 1.5 hr at −78° and subsequently warmed to 0°. A soln of 3-methoxy-2-cyclohexenone (630 mg, 5.0 mmol) in dry ether (15 mL) was added dropwise during 1 min and the mixture was stirred at 0° for 15–20 min before being allowed to warm to room temp. After 15 min, the soln was cooled to −78° and treated with 10 mL water. The organic phase was separated and the aqueous layer was extracted with ether (3 ×). Following solvent evaporation, there was isolated 1.1 g (95%) of **18**; IR (cm^{-1}, neat) 3500, 3040, 2980, 1660, 1620, 1250, and 1225; ^1H NMR (δ, CCl_4) 5.5 (d, J = 2 Hz, 1 H), 5.25 (d, J = 2 Hz, 1 H), 4.4 (s, 1 H), 3.4 (s, 3 H), and 2.05–1.45 (m, 7 H).

3 - (1 - *Trimethylsilylcyclopropyl*) - 2 - *cyclohexenone* (**19**)

(a) *Simmons–Smith cyclopropanation of* **18**. A mixture of **18** (4.5 g, 20 mmol), CH_2I_2 (16.08 g, 60 mmol) and Zn–Cu couple (6.5 g) in dry ether (80 mL) was heated at reflux for 24 hr. Following cooling to 0°, sat. NH_4Claq. was added slowly and the separated organic phase was washed with sat. $NaHCO_3$aq. and $NaHSO_3$aq., and water prior to drying. Solvent evaporation and chromatography of the residue on silica gel (elution with hexane–ether, 6:1) gave 3.6 g (81%) of **19**; IR (cm^{-1}, neat) 3080, 2980, 1670, 1620, and 835; ^1H NMR (δ, CCl_4) (δ, CCl_4) 5.6 (br s, 1 H), 2.4–1.8 (m, 6 H), 0.6 (s, 4 H), and −0.3 (s, 9 H); *m/e* Calc. (M^+): 208.1283, Obsd: 208.1278. (Found: C, 68.94; H, 9.66. Calc. for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67%.)

(b) *Direct addition of* 1 - (*trimethylsilyl*) - 1 - *lithiocyclopropane*. A 3.6 g (16.2 mmol) sample of **33** was added via syringe to a soln of lithium naphthalenide (32.4 mmol) in ether at −78° over 5 min. During the addition, the deep blue color faded and a red color appeared. The mixture was stirred for 20 min at −78° and allowed to warm to 0° at which point a soln of **17** (1.7 g, 13.5 mmol) in anhyd. THF (10 mL) was introduced dropwise. Following 15 min at 0° and 4 hr at 25°, the soln was poured into a separatory funnel containing ice-cold 2 N HCl (50 mL) and ether (250 mL). Intermittent agitation of this mixture (15 min) followed by the usual workup and chromatography furnished 2.56 g (91%) of **18** with spectral properties identical to those described above.

1 - (1 - *Trimethylsilylcyclopropyl)cyclopentene* (**20a**)

To a soln of **10** (1.0 g, 4.7 mmol) in dry benzene (75 mL, distilled from CaH_2) was added 150 mg *p*-toluenesulfonic acid monohydrate. The mixture was stirred at room temp. for 4.5 hr, treated with sat. $NaHCO_3$aq, and washed twice more with the same soln prior to drying and careful solvent evaporation. There was obtained 0.90 g (99%) of **20a** as a colorless oil which was purified for analysis by preparative VPC (6 ft × 0.25 in. 5% SE-30, 105°); IR (cm^{-1}, neat) 3070, 3050, 3000, 2960, 2850, 1633, 1430, 1320, 1295, 1250, 1200, 1015, 930, 910, 830, 745, and 680; ^1H NMR (δ, $CDCl_3$) 5.25 (t, J = 1.5 Hz, 1 H), 2.32–2.02 (m, 4 H), 1.95–1.58 (m, 2 H), 0.50 (s, 4 H), and −0.05 (s, 9 H); *m/e* Calc. (M^+): 180.1334, Obsd: 180.1340. (Found: C, 73.01; H, 11.06. Calc. for $C_{11}H_{20}Si$: C, 73.31; H, 11.10%.)

L - (1 - *Trimethylsilylcyclopropyl)cyclohexene* (**20b**)

Chromatography of 5.72 g of crude **11** on silica gel (80 g) with hexane as eluant gave 4.99 g of **20b** as a colorless oil which was pruified by VPC as above (170°); IR (cm^{-1}, neat) 3070, 3000, 2940, 2860, 2840, 1650, 1440, 1405, 1365, 1345, 1280, 1252, 1210, 1140, 1080, 1030, 970, 920, 910, 845, 755, and 690; ^1H NMR (δ, $CDCl_3$) 5.45–5.30 (m, 1 H), 2.10–1.80 (m, 4 H), 1.65–1.40 (m, 4 H), 0.45 (s, 4 H), and −0.05 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 141.5, 123.0, 29.7, 25.5, 23.4, 22.9, 15.5, 9.0 and −2.5; *m/e* 194 (M^+) and 179 (M^+-CH_3). (Found: C, 74.31; H, 11.47. Calc. for $C_{12}H_{22}Si$: C, 74.21; H, 11.33%.)

(E)- *and* (Z) - 3 - (1 - *Trimethylsilylcyclopropyl)pentene* (**21** *and* **22**)

A soln of EtZnI in ether (13.4 mL of 2 *M*) was treated with CH_2I_2 (1.58 g, 5.9 mmol) and heated at reflux for 1 hr. The contents were cooled to 0° and diluted with ether (35 mL) prior to the addition of **8** (1.0 g, 5.36 mmol). The mixture was heated at the reflux temp. for 20 hr and quenched with water. The organic phase was washed with 10% Na_2SO_3aq. and water, dried, and concentrated. The residue was distilled to give 510 mg (51%) of a mixture of **21** and **22**, b.p. 55–58° at 3.6 torr. The isomers were

separated by preparative VPC (10 ft × 0.25 in. 10% Carbowax on Chromosorb G, 80°).

For compound **21**: ^{1}H NMR (δ, $CDCl_3$) 5.20 (q, J = 7 Hz, 1 H), 2.15 (q, J = 8 Hz, 2 H), 1.60 (d, J = 7 Hz, 3 H), 1.05 (t, J = 8 Hz, 3 H), 0.55 (m, 4 H), and 0.05 (s, 9 H); *m/e* Calc. (M^+) 182.1491, Obsd 182.1497.

For compound **22**: ^{1}H NMR (δ, $CDCl_3$) 5.20 (q, J = 8 Hz, 1 H), 2.0 (q, J = 8 Hz, 2 H), 1.65 (d, J = 7 Hz, 3 H), 1.0 (t, J = 8 Hz, 3 H), 0.60 (m, 4 H), and 0.05 (s, 9 H); *m/e* Calc. (M^+) 182.1491, Obsd 182.1497. (Found: C, 72.64; H, 12.13. Calc. for $C_{11}H_{22}Si$: C, 72.42; H, 12.18%.)

1 - *Phenylthio* - 1 - (*trimethylsilyl*)*cyclopropane* (**33**)

(a) *Silylation to* **23c**. To a cold (0°) soln of phenylcyclopropyl sulfide (510 mg, 3.4 mmol) in dry THF (10 mL) under N_2 was added 3.0 mL of 1.37 *M* n-BuLi. The dark yellow soln was stirred at 0° for 2.5 hr, treated with 0.8 mL freshly distilled trimethylsilyl chloride, stirred at room temp. for 10 min, diluted with pentane (10 mL), and quenched with water (2 mL) and sat. NH_4Claq. (2 mL). The organic layer was separated, washed with water, and dried prior to solvent evaporation. Kugelrohr distillation (105° and 0.1 torr) of the residue afforded 670 mg (88%) of **33** as a clear colorless oil; IR (cm^{-1}, neat) 3060, 3000, 2955, 1580, 1475, 1435, 1245, 1210, 1085, 1020, 895, 830, 730, and 680; ^{1}H NMR (δ, $CDCl_3$) 7.42–6.95 (m, 5 H), 1.05–0.85 (m, 4 H), and 0.0 (s, 9 H); *m/e* Calc. (M^+) 222.0898, Obsd 222.0904. (Found: C, 64.92; H, 8.23. Calc. for $C_{12}H_{18}SSi$: C, 64.84; H, 8.10%.)

(b) *Cyclization of* **32**. To a cold (0°) soln of 1,3-bisphenylthiopropane (50 g, 0.19 mol) in dry THF (250 mL) was added 350 mL of 1.2 *M* n-BuLi dropwise over 1 hr. Following 2 hr at 0°, freshly distilled trimethylsilyl chloride (45 g, 0.41 mol) was added. The mixture was stirred for 10 min and quenched by the addition of water (100 mL) and sat. NH_4Claq. (200 mL). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic solns were washed with 10% NaOHaq and water prior to drying and solvent evaporation. Vacuum distillation of the residue afforded 36.2 g (85%) of **33**, b.p. 73–83° (0.1 torr).

Reductive lithiation of **33**

(a) *Preparation of* **11**. To a cold (−78°) soln of **33** (317 mg, 1.43 mmol) in dry THF (5 mL) under N_2 was added a soln of lithium naphthalenide (from 400 mg naphthalene and 50 mg Li) in 10 mL THF. Following 30 min at −78°, cyclohexanone (150 μl) was added dropwise by syringe and the mixture was stirred at room temp. for 2 hr. Sat. NH_4Claq. was added and the organic phase was extracted with 5% NaOHaq. (2 × 15 mL) and water prior to drying and solvent evaporation. Mplc of the residue (elution with 10% ether in hexane) yielded 109 mg (36%) of **11**, whose spectra were identical to those reported earlier.

(b) *Preparation of* **13**. A magnetically stirred soln of naphthalene (2.62 g, 20.4 mmol) in dry THF (100 mL) was treated with Li wire (142 mg, 20.4 g-at). After 10 hr at room temp., the resulting green soln was cooled to −78° while 2.22 g (10 mmol) of **33** in 10 mL of the same solvent was added over 10 min. After an additional 10 min, a soln of 3-pentanone (860 mg, 10 mmol) in THF (10 mL) was introduced. Workup in the predescribed manner gave 4.59 g of crude semi-solid, chromatography of which on silica gel to remove naphthalene lead directly to **21/22** because of dehydration. There was isolated 320 mg (15%) of this vinylsilane mixture.

(c) *Preparation of* **14**. To 45 mL of 0.21 *M* lithium naphthalenide in THF at −78° under N_2 was added 1.0 g of **33** in 10 mL dry THF during 15 min. After an additional 5 min, 325 mg (4.5 mmol) isobutyraldehyde in 10 mL of the same solvent was added dropwise over 10 min. Processing as above afforded 650 mg (78%) of **14**; IR (cm^{-1}, neat) 3500, 3070, 2960, 1460–1430, 1410–1365, 1265, 1255, 1030, 985, 960, 950, 930, 895, 840, and 755; ^{1}H NMR (δ, $CDCl_3$) 2.35 (d, J = 9 Hz, 1 H), 2.09–1.69 (series of m, 1 H), 1.40 (br s, 1 H), 0.99 (d, J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 0.48–0.25 (m, 4 H), and 0.05 (s, 9 H); *m/e* 171 (M^+-CH_3), 168 (M^+-H_2O), and 153 (M^+-CH_3 and H_2O).

1 - *Bromo* - 1 - (1 - *trimethylsilyl*)*cyclopropane* (**35**)

To a stirred mixture of **34** (500 mg, 3.16 mmol) and red mercuric oxide (520 mg, 2.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise a soln of Br_2 (500 mg, 3.16 mmol) in the same solvent (10 mL) during 15–20 min. Following 2 hr stirring, the ppt was separated by filtration and the solvent was carefully removed by careful distillation through a Vigreux column at atmospheric pressure. Distillation of the residue at 100 torr provided 0.33 g (55%) of **35**, b.p. 123–125°, as a colorless solid, m.p. 24–27°; ^{1}H NMR (δ, $CDCl_3$) 1.0 (m, 2 H), 0.7 (m, 2 H), and 0.0 (s, 9 H); *m/e* Calc. (M^+): 191.9970, Obsd: 191.9975. (Found: C, 37.42; H, 6.81. Calc. for $C_6H_{13}BrSi$: C, 37.30; H, 6.80%.)

Lithiation–carbonyl condensation–dehydration reactions of **35**

General procedure. Into a cold (−78°) soln of **35** (1.1 equiv.) in dry (5 mL) was syringed 1.2 equiv. of n-BuLi in hexane. The resulting light yellow soln was stirred for 3 hr before addition of 1.0 equiv. of the ketone. The mixture was allowed to warm to room temp., treated with a little water, diluted with CH_2Cl_2, and washed with sat. $NaHCO_3$aq. prior to drying. Solvent evaporation afforded the crude carbinols which were directly dehydrated by stirring with 0.2 equiv. of *p*-toluenesulfonic acid in benzene (3–5 mL) at room temp. for 2–4 hr. The vinyl-cyclopropanes were isolated after washing with sat. $NaHCO_3$aq., drying, careful removal of solvent, and column chromatography on silica gel (elution with pentane).

(a) *Cyclopentanone*: 20% yield of **20a**. (b) *Cyclohexanone*: 51% yield of **20b**. (c) 3-*Pentanone*: 60% yield of **21/22**.

(d) *Androstanolone* t-*butyldimethylsilyl ether* (**36**)

A 60% yield of **38**; m.p. 134–137°; ^{1}H NMR (δ, $CDCl_3$) 5.35 (m, 1 H), 3.65 (m, 1 H), 1.9–0.85 (series of m, 20 H), 1.05 (s, 9 H), 0.85 (s, 6 H), 0.60 (s, 4 H), 0.05 and 0.02 (s, 15 H); ^{13}C NMR (ppm, $CDCl_3$) 140.07, 121.91, 82.07, 50.84, 43.31, 42.27, 40.47, 37.37, 35.84, 34.72, 34.68, 31.58, 31.02, 28.83, 25.93, 23.61, 20.76, 18.16, 14.93, 11.83, 11.39, 9.07, −2.34, −4.44, and −4.74: *m/e* Calc. (M^+) 500.3870, Obsd 500.3884.

Thermolysis of **20a**. A 314 mg (1.74 mmol) sample of **20a** was passed slowly through a 30 cm long quartz chip packed tube at 570° in stream of N_2 (6 ml/min) at 35 torr. The pyrolysate was collected in a U-tube immersed in a dry ice–i-PrOH bath. There was obtained 280 mg (89%) of **43** which was purified by preparative VPC at 125° (12 ft × 0.25 in. 5% SE-30); IR (cm^{-1}, neat) 2920, 2825, 1625, 1445, 1245, 1080, 1030, 890, 830, 743, and 680; ^{1}H NMR (δ, $CDCl_3$) 3.03–2.45 (m, 3 H), 2.31–1.65 (m, 6 H), 1.50–0.82 (m, 2 H), and 0.02 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 165.40, 128.41, 55.68, 42.23, 32.43, 31.70, 29.32, 24.80, and −1.06; *m/e* Calc. (M^+): 180.1334, Obsd: 180.1338. (Found: C, 73.15; H, 11.22. Calc. for $C_{11}H_{20}Si$: C, 73.31; H, 11.10%.)

Thermolysis of **20b**. Pyrolysis of **20b** (245 mg, 1.26 mmol) as described above furnished 208 mg (85%) of **43** which was further purified by VPC; IR (cm^{-1}, neat) 2930, 2859, 1620, 1448, 1408, 1328, 1250, 1080, 1055, 1040, 965, 932, 900, 870, 840, 758, and 690; ^{1}H NMR (δ, $CDCl_3$) 2.9–1.0 (series of m, 13 H) and 0.30 (s, 9 H); *m/e* Calc. (M^+): 194.1491, Obsd: 194.1496.

Thermolysis of **21/22**. A 1:1 mixture of **21** and **22** (90 mg, 0.50 mmol) was pyrolyzed in the manner described above to give 71 mg (78%) of a yellowish liquid. The two major components (ratio *ca.* 1:1) were separated by preparative VPC at 120° (6 ft × 0.25 in. 5% SE-30). The first component proved to be unrearranged **22**. The second peak was identified as **45**; ^{1}H NMR (δ, $CDCl_3$) 2.3–2.0 (m, 5 H), 1.4–1.2 (m, 2 H), 1.0–0.7 (m, 6 H), and 0.0 (s, 9 H); *m/e* Calcd (M^+) 182.1491, Obsd 182.1495. (Found: C, 72.46; H, 12.11. Calc. for $C_{11}H_{22}Si$: C, 72.42; H, 12.18%.)

When pure samples of **21** and **22** were individually pyrolyzed under comparable conditions, only **21** was found to isomerize to **45** (71% isolated).

Thermolysis of **38**. a 60 mg (0.12 mmol) sample of **38** was pyrolyzed in the same manner as before to give 53 mg (88%) of **46** as a light yellow viscous oil; ^{1}H NMR (δ, $CDCl_3$) 3.60 (m, 1 H), 2.45–0.70 (series of m, 23 H), 0.95 (s, 9 H), 0.75 (s, 6 H), 0.10 and 0.50 (s, 15 H); *m/e* Calc. (M^+): 500.3870, Obsd: 500.3884.

Thermolysis of **19**. Pyrolysis of **19** (100 mg) in the apparatus described above at 600–610° (argon as carrier gas) afforded 80 mg

of a pale yellow pyrolysate; ^{1}H NMR (δ, $CDCl_3$) 3.3–1.7 (m, ring protons), 0.9 (s due to **47**), and 0.4 (s due to **48**).

Purification of this material by chromatography on silica gel or basic alumina, or by preparative VPC led to the isolation of ketone **49**; IR (cm^{-1}, neat) 2980, 1670, and 1630; ^{1}H NMR (δ, CCl_4) 2.7–1.5 (series of m, 12 H); *m/e* Calc. (M^+): 136.0888, Obsd: 136.0882.

Its 2,4-dinitrophenylhydrazone was obtained as a red solid, m.p. 245–247°.

2-(Trimethylsilyl)buten-3-ol

Reaction of **3** (15.0 g, 83.7 mmol) with 49.5 mL of 2.2 *M* t-BuLi (1.07 mmol) in pentane followed by acetaldehyde (4.8 g, 109 mmol) in the predescribed manner afforded 6.91 g (57%) of the alcohol as a colorless liquid, b.p. 60–62° (10 torr); ^{1}H NMR (δ, $CDCl_3$) 5.8 (br s, 1 H), 5.35 (br s, 1 H), 4.6–4.3 (q, J = 7 Hz, 1 H), 1.9 (s, 1 H), 1.3 (d, J = 7 Hz, 3 H), and 0.2 (s, 9 H); *m/e* Calc. (M^+): 129.0736, Obsd: 120.0740. (Found: C, 58.52; H, 11.15. Calc. for $C_7H_{16}OSi$: C, 58.25; H, 11.12%.)

1 - (1 - *Trimethylsilylcyclopropyl)ethanol* (**50**)

From 40 mL 1.4 *M* EtZnI in ether (55.4 mmol), 4.3 g (16.0 mmol) CH_2I_2, and 2.0 g (13.9 mmol) of the preceding allylic alcohol, there was obtained 980 mg (45%) of **50** after silica gel chromatography to remove the vinylcyclopropane (900 mg, 90% combined yield); ^{1}H NMR (δ, $CDCl_3$) 3.2 (q, J = 7 Hz, 1 H), 1.6 (br s, 1 H), 1.2 (d, J = 7 Hz, 3 H), 0.4 (br s, 4 H), and 0.1 (s, 9 H).

1 - *Acetyl* - 1 - (*trimethylsilyl)cyclopropane* (**51**)

To a stirred slurry of sodium acetate (1.51 g, 18.4 mmol) and pyridinium chlorochromate (2.77 g, 12.8 mmol) in 50 mL of dry dichloromethane was added a solution of **50** (1.27 g, 8.02 mmol) in 10 mL of the same solvent dropwise over several minutes. The reaction mixture was stirred at room temp. for 3 h when ether (100 mL) was added to precipitate the chromium salts. The dark brown solution was filtered through Celite and evaporated. The residue was taken up in ether and washed several times with water prior to drying. Solvent evaporation left 810 mg (65%) of **51** as a clear oil. This material was eluted through a short plug of silica gel (ether elution) and distilled in a Kugelrohr apparatus at 110° and 10 torr. There was obtained 790 mg (54%) of pure product; ^{1}H NMR (δ, $CDCl_3$) 1.9 (s, 3 H), 1.2–0.7 (series of m, 4 H), and 0.0 (s, 9 H); *m/e* Calc. (M^+) 141.0736, Obsd 141.0739. (Found: C, 61.43; H, 10.31. Calc. for $C_8H_{16}OSi$: C, 61.46; H, 10.34%.)

1 - *Cyclopropyl* - 1 - (*trimethylsilylcyclopropyl)ethanol* (**52**)

A solution of cyclopropyl bromide (1.16 g, 9.6 mmol) in dry ether (15 mL) was treated with 133 mg (19.2 mg-at) of lithium wire cut in small pieces. The mixture was stirred at room temp. for 90 min whereupon a solution of **51** (750 mg, 4.8 mmol) in a few mL of anhyd. ether was introduced dropwise via syringe. The solution was stirred at room temp. for 90 min and quenched by the careful addition of 10% ammonium chloride solution. The organic phase was separated, washed with brine, dried, and evaporated. Silica gel chromatography of the residue (elution with 5% ethyl acetate in hexane) furnished 680 mg (70%) of **52** as a colorless oil; ^{1}H NMR (δ, $CDCl_3$) 1.1 (s, 3 H), 0.9–0.3 (m, 9 H), and 0.1 (s, 9 H); *m/e* Calc. (M^+-H_2O) 180.1334, Obsd 180.1341.

1 - *Cyclopropyl* - 1 - (*trimethylsilylcyclopropyl)ethylene* (**53**)

To a stirred solution of **52** (600 mg, 3.02 mmol) in benzene (distilled from CaH_2) at room temp. was added 940 mg (3.93 mmol) of the Burgess reagent.[28] Following a 7 hr reflux period, an additional 300 mg of this reagent was added and heating was resumed for a further 2 hr. The cooled reaction mixture was poured into a separatory funnel, diluted with benzene, and washed with brine prior to drying. Solvent evaporation and silica gel chromatography (elution with petroleum ether) afforded 135 mg (25%) of **53** as a clear oil; ^{1}H NMR (δ, $CDCl_3$) 4.5 (d, J = 8 Hz, 2 H), 0.8–0.5 (br s, 8 H), and 0.05 (s, 9 H); *m/e* Calc. (M^+) 180.1334, Obsd 180.1341. (Found: C, 73.61; 11.13. Calc. for $C_{11}H_{19}Si$: C, 73.23; H, 11.20%.)

Pyrolysis of **53**. Pyrolysis of **53** at 570° as described earlier gave an 80% material recovery on two separate trials. VPC analysis indicated the presence of a major product (90+%) in both instances, the spectra of which showed it to be **43**.

General acetylation procedure

A slurry of anhyd. aluminum chloride (3.0 mmol) in dry dichloromethane (5 mL) was blanketed under nitrogen and stirred while freshly distilled acetyl chloride (1.5 mmol) was introduced via syringe. This mixture was stirred at room temp. for 15 min, cooled to −78°, and treated dropwise with 1.0 mmol of **43** or **45** during 30 min. After an additional hr, sat. $NaHCO_3$aq. was added and the organic phase was separated and washed with 10% H_2SO_4aq. and $NaHCO_3$aq. prior to drying and concentration. A 90–95% recovery of light yellow oil was achieved. Isolation of the pure adducts was achieved by preparative tlc on silica gel (elution with 20% ether in hexane) to give a 30% yield of **58** and 61% yield of **59**.

For compound **58**: IR (cm^{-1}, neat) 2950, 2860, 1710, 1660, 1445, 1420, 1365, 1290, 1265, and 1180; ^{1}H NMR (δ, $CDCl_3$) 2.8–1.1 (series of m, 11 H) and 2.2 (s, 3 H); m/e Calc. (M^+) 150.1045, Obsd 150.1039. (Found: C, 79.88; H, 9.43. Calc. for $C_{10}H_{14}O$: C, 79.94; H, 9.41%.)

For compound **59**: IR (cm^{-1}, neat) 2950, 2860, 1685, 1609, 1450, 1415, 1350, 1280, and 1190; ^{1}H NMR (δ, $CDCl_3$) 3.0–1.3 (series of m, 5 H), 2.2 (s, 3 H), 1.3–0.9 (m, 8 H); *m/e* Calc. (M^+) 152.1266, Obsd 152.1267. (Found: C, 78.82; H, 10.62. Calc. for $C_{10}H_{16}O$: C, 78.88; H, 10.61%.)

2 - *Bromobicyclo*[3.3.0]*oct* - 1 - *ene* (**60**)

Br_2 (44 mg, 0.28 mmol) dissolved in CH_2Cl_2 (2 mL) was added dropwise over several min to a cold (−78°) stirred soln of **43** (50 mg, 0.28 mmol) in 3 mL of the same solvent. The mixture was allowed to warm to room temp., poured into a separatory funnel containing 10 mL 10% $Na_2S_2O_3$aq., and diluted with additional CH_2Cl_2 (25 mL). The organic phase was washed with brine, dried, and concentrated to leave a dark oil. Chromatography on neutral alumina afforded 16 mg (30%) of pure **60** as a pale yellow oil; ^{1}H NMR (δ, $CDCl_3$) 4.7–4.4 (m, 1 H), 3.1–2.8 (m, 1 H), 2.4–1.7 (series of m, 6 H), and 1.7–1.2 (m, 3 H); *m/e* Calc. (M^+): 187.0123, Obsd: 187.0128.

Epoxidation of **43** *and* **45**

General procedure. A cold (0°) magnetically stirred mixture of **43** or **45** (1.0 mmol) and $NaHCO_3$ (1.5 mmol) in CH_2Cl_2 (2 mL) was treated dropwise with a soln of *m*-chloroperbenzoic acid (1.1 mmol) in 6 mL of the same solvent. After 20 min, the mixture was washed with sat. $NaHCO_3$aq., dried, and evaporated. The residual oil was subjected to chromatography on silica gel (elution with 5% ether in hexane) to separate the isomers (1:1 for **43** and 3:2 for **45**). The overall yield was 65% in both cases.

For compounds **61a** *and* **61b**: High R_f isomer; ^{1}H NMR (δ, $CDCl_3$) 2.3–1.0 (series of m, 11 H) and 0.1 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 83.01, 59.52, 48.30, 35.44, 27.91, 25.39, 23.98, 19.90, and −2.96; *m/e* Calc. (M^+): 196.1283, Obsd: 196.1288.

Low R_f isomer; ^{1}H NMR (δ, $CDCl_3$) 2.4–2.1 (m, 1 H), 1.9–1.4 (m, 10 H), and 0.1 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 82.09, 67.14, 44.17, 29.95, 28.64, 26.41, 24.17, 23.10 and −2.86; *m/e* Calc. (M^+): 196.1283; Obsd: 196.1281.

For compounds **62a** *and* **62b**: High R_f isomer; ^{1}H NMR (δ, $CDCl_3$) 1.7–0.7 (series of m, 13 H) and 0.1 (s, 9 H); *m/e* Calc. (M^+) 198.1440, Obsd: 198.1445.

Low R_f isomer; ^{1}H NMR (δ, $CDCl_3$) 1.7–0.6 (series of m, 13 H) and 0.1 (s, 9 H); *m/e* Calc. (M^+) 198.1440, Obsd: 198.1445.

3 - *Cyclopentylidene* - 1 - (p - *toluenesulfonyloxy)propane* (**63a**)

A soln of **20a** (211 mg, 1.09 mmol) and *p*-toluenesulfonic acid monohydrate (248 mg) in dry benzene (15 mL) was heated at reflux for 30 min, cooled, and stirred over 5 mL of sat. $NaHCO_3$aq.. for 15 min. The organic phase was separated, washed twice with sat. $NaHCO_3$aq., dried, and concentrated. There was isolated 269 mg (87%) of **63a** (exocyclic double bond only) after mplc on silica gel (elution with 10% ether in hexane); IR (cm^{-1}, neat) 3030, 2930, 2850, 1595, 1490, 1440, 1350, 1285, 1170, 1090, 915, 805, and 650; ^{1}H NMR (δ, $CDCl_3$) 7.78 (d, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 5.23 (m, 1 H), 4.05 (t, J = 5 Hz, 2 H), 2.45 (s, 3 H), and 2.41–1.53 (m, 10 H); ^{13}C NMR (ppm, $CDCl_3$) 144.63, 142.64, 133.41, 129.82, 127.93, 124.48, 70.25, 34.91, 32.38, 26.99, 26.80, 23.35, and 21.60. (Found: C, 64.13; H, 7.21. Calc. for $C_{15}H_{20}O_3S$: C, 64.29; H, 7.14%.)

3 - *Cyclopentyl* - 1 - (p - *toluenesulfonyloxy*)*propane* (**64a**)

A soln of **63a** (93.1 mg) in EtOAc (10 mL) was treated with 10% Pd–C (24.5 mg) and hydrogenated in a Parr apparatus for 5 hr. Filtration of the mixture through Celite and solvent evaporation afforded 89.1 mg (95%) of **64a**. Mplc on silica gel (elution with 5% ether in hexane) afforded pure saturated tosylate; ^{1}H NMR (δ, $CDCl_3$) 7.75 (d, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 4.01 (t, J = 6 Hz, 2 H), 2.42 (s, 3 H), and 1.90–0.72 (series of m, 13 H). (Found: C, 63.91; H, 7.90. Calc. for $C_{15}H_{22}O_3S$: C, 63.84; H, 7.80%.)

Ozonolysis of **63a**

The ozonolysis was carried out using the procedure of Pappas and Keaveney.[32] A sample of **63a** (140.5 mg, 0.5 mmol) was dissolved in a mixture of CH_2Cl_2 (1.5 mL) and MeOH (0.5 mL) and ozonized at −78°. Following purging with O_2 at −78°, freshly distilled Me_2S (0.4 mL) was introduced and the resulting soln was stirred at 0° for 1.5 hr and at room temp. for 30 min. The solvent volume was concentrated to 0.5 mL and the residue was subjected to preparative VPC (8 ft × 0.25 in. 5% SE-30, 95°). The only two substances present proved to be cyclopentanone and dimethyl sulfoxide.

Heating of **20b** *with* p-*toluenesulfonic acid*

A soln of **20b** (163.2 mg, 0.84 mmol) and *p*-toluenesulfonic acid monohydrate (192 mg, 1.0 mmol) in dry benzene was heated at the reflux temp. for 2 hr and worked up in the predescribed manner to give 204 mg of a light yellow oil. Preparative tlc on silica gel (elution with 8% EtOAc in hexane) afforded 145 mg (59%) of **64** as a 1:1 mixture of exo- and endocyclic double bond isomers; ^{1}H NMR (δ, $CDCl_3$), 7.78 (d, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 5.34–5.15 (m, 1 H), 3.98 (two overlapping t's, J = 6 Hz, 2 H), 2.42 (s, 3 H), and 2.10–1.32 (series of m, 12 H).

Hydrogenation of **63b**

3 - *Cyclohexyl* - 1 - (p - *toluenesulfonyloxy*)*propane* (**64b**). Hydrogenation of **63b** (104.5 mg, 0.35 mmol) over 10% Pd–C (25 mg) in EtOAc soln (15 mL) as before afforded 97.1 mg (93%) of **64b** whose spectra were identical to those of an authentic sample prepared as previously outlined.[33]

1 - (1 - *Trimethylsilylcyclopropyl*) - 6 - *oxabicyclo*[3.1.0]*hexane* (**65a**)

A cold (0°), magnetically stirred soln of **20a** (101 mg, 0.56 mmol) in CH_2Cl_2 containing 94 mg powdered Na_2CO_3 was treated with 106 mg (0.60 mmol) *m*-chloroperbenzoic acid which had previously been washed with phosphate buffer. This slurry was stirred at 0° for 40 min and concentrated. The residue was dissolved in ether, washed sequentially with water, $Na_2S_2O_3$aq, and water, dried, and concentrated. There was obtained 114 mg (100%) of **65a** as a colorless oil; IR (cm^{-1}, neat) 3060, 2945, 1410, 1300, 1245, 1008, 920, 830, and 740; ^{1}H NMR (δ, $CDCl_3$) 3.18 (s, 1 H), 2.08–1.35 (series of m, 6 H), 0.65–0.38 (m, 4 H), and 0.04 (s, 9 H); *m/e* Calc. (M^+): 196.1283, Obsd: 196.1288.

1 - (1 - *Trimethylsilylcyclopropyl*) - 7 - *oxabicyclo*[4.1.0]*heptane* (**65b**)

Epoxidation of **20b** (1.0 g, 5.15 mmol) in the predescribed manner afforded 1.3 g of colorless oily residue. Kugelrohr distillation at 80–100° and 0.5 mm yielded 900 mg (83%) of **65b**; IR (cm^{-1}, neat) 3080, 3060, 2940, 2860, 1449, 1437, 1360, 1300, 1250, 1215, 1080, 1040, 1030, 990, 950, 915, 890, 840, 778, 755, 715, and 690; ^{1}H NMR (δ, $CDCl_3$) 2.78 (t, J = 2 Hz, 1 H), 1.92–1.17 (series of m, 8 H), 0.56–0.07 (m, 4 H), and 0.0 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 55.24, 54.08, 25.63, 25.09, 20.00, 19.56, and −4.27; *m/e* Calc. (M^+): 210.1440, Obsd: 210.1445. (Found: C, 68.50; H, 10.57. Calc. for $C_{12}H_{22}OSi$: C, 68.56; H, 10.47%.)

2 - (1 - *Trimethylsilylcyclopropyl*)*cyclopentanone* (**66a**)

To a soln of **65a** (40.6 mg, 0.207 mmol) in dry benzene (2 mL) was added BF_3–etherate (18 mg, 0.13 mmol). The light brown soln was stirred at room temp. for 3.75 hr, diluted with ether (6 mL), and quenched with water. The organic phase was dried and concentrated to give 41 mg (100%) of **66a** which was further purified by preparative VPC (8 ft × 0.25 in. 5% Se-30, 130°); IR (cm^{-1}, neat) 3060, 2920, 1740, 1445, 1400, 1240, 1135, 925, 830, and 740; ^{1}H NMR (δ, $CDCl_3$) 2.41–1.50 (series of m, 7 H), 0.50–0.38 (m, 4 H), and 0.0 (s, 9 H); *m/e* Calc. (M^+): 196.1283, Obsd: 196.1288.

2 - (1 - *Trimethylsilylcyclopropyl*)*cyclohexanone* (**66**)

Exposure of **65b** (231 mg, 1.25 mmol) in benzene (15 mL) to BF_3-etherate (89 mg, 0.63 mmol) at room temp. for 2 hr, followed by the identical workup as above, afforded 113 mg (49%) of **66b** after mplc on silica gel (elution with 7% ether in hexane); IR (cm^{-1}, neat) 3070, 2940, 2865, 1712, 1455, 1320, 1295, 1250, 1225, 1130, 1073, 1025, 950, 922, 903, 880, 860, 840, 690, and 660; ^{1}H NMR (δ, $CDCl_3$) 2.40–1.33 (series of m, 9 H), 0.69–0.0 (m, 4 H), and −0.1 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 211.2, 61.9, 42.3, 33.1, 27.2, 25.9, 11.0, 8.7, 5.8, and −0.8; *m/e* Calc. (M^+): 210.1440, Obsd: 210.1445. (Found: C, 68.32; H, 10.54. Calc. for $C_{12}H_{22}OSi$: C, 68.56; H, 10.47%.)

Acknowledgement—The financial support of the National Science Foundation and the National Institutes of Health made possible this research.

REFERENCES

[1]Part 16. T.-H. Yan and L. A. Paquette, *Tetrahedron Letters* 3227 (1982).

[2]National Institutes of Health Postdoctoral Fellow (1980–1981).

[3a]B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.* **95**, 289, 5298, 5311 (1973); [b]E. Piers, C. K. Lau and I. Nagakura, *Tetrahedron Letters* 3233 (1976); [c]E. Piers, and E. H. Ruediger, *J. Chem. Soc. Chem. Commun.* 166 (1979); [d]E. Piers and J. Banville, *Ibid.* 1138 (1979); [e]E. Piers, I. Nagakura and H. E. Morton, *J. Org. Chem.* **43**, 3630 (1978); [f]P. A. Wender and M. P. Filosa, *Ibid.* **41**, 3490 (1976); [g]J. P. Marino and L. J. Browne, *Tetrahedron Letters* 3241, 3245 (1976); [h]E. Piers and I. Nagakura, *Ibid.* 3237 (1976); [i]E. Piers and C. K. Lau, *Synth. Commun.* **7**, 495 (1977); [j]D. Brule *et al.*, *Bull. Soc. Chim. Fr.* II-57 (1981); [k]T. Hudlicky *et al.*, *J. Org. Chem.* **45**, 5020 (1980); **46**, 2911 (1981).

[4a]L. A. Paquette, K. A. Horn and G. J. Wells, *Tetrahedron Letters* 259 (1982); [b]L. A. Paquette, G. J. Wells, K. A. Horn and T.-H. Yan, *Ibid.* 263 (1982). Excluding, of course, our preliminary communications on this subject.

[5]See, for example: L. A. Paquette, W. E. Fristad, D. S. Dime and T. R. Bailey, *J. Org. Chem.* **45**, 3017 (1980); W. E. Fristad, T. R. Bailey and L. A. Paquette, *Ibid.* **45**, 3028 (1980) and refs cited.

[6]T. H. Chan, W. Mychajlowskij, B. S. Ong and D. N. Harpp, *J. Org. Chem.* **43**, 1526 (1978).

[7a]B.-T. Gröbel and D. Seebach, *Angew. Chen.* **86**, 102 (1974); [b]T. H. Chan and W. Mychajlowskij, *Tetrahedron Letters* 3479 (1974).

[8]S. Sawada and Y. Inoue, *Bull. Chem. Soc. Japan* **42**, 2669 (1969).

[9]H. W. Pinnick, Y.-H. Chang, S. C. Foster and M. Govindan, *J. Org. Chem.* **45**, 4505 (1980).

[10]Y. Kai, P. Kuschel, S. Kwiatkowski, J. D. Dunitz, J. F. M. Oth, D. Seebach and H.-O. Kalinowski, *Helv. Chim. Acta* **65**, 137 (1982).

[11]cf: [a]I. Böhm, E. Hirsch and H.-U. Reissig, *Angew. Chem.*, Int. Ed. Engl. **20**, 574 (1981); [b]H.-U. Reissig, I. Böhm, *J. Am. Chem. Soc.* **104**, 1735 (1982).

[12a]B. M. Trost, D. E. Keeley, H. C. Arndt, J. H. Rigby and M. J. Bogdanowicz, *J. Am. Chem. Soc.* **99**, 3080 (1977); [b]B. M. Trost, D. E. Keeley, H. C. Arndt and M. J. Bogdanowicz, *Ibid.* **99**, 3088 (1977); [c]B. M. Trost and L. M. Jungheim, *Ibid.* **102**, 7910 (1980).

[13]K. Tanaka, H. Uneme, S. Matsui, R. Tanigaka and A. Kaji, *Chem. Lett.* 287 (1980).

[14]T. Cohen and J. R. Matz, *Tetrahedron Letters* 2455 (1981).

[15a]P. M. Warner and D. Le, *J. Org. Chem.* **47**, 893 (1982); [b]C. Ainsworth and Y. N. Kuo, *J. Organometal. Chem.* **46**, 73 (1973).

[16a]S. Halazy, J. Lucchetti and A. Krief, *Tetrahedron Letters* 3971 (1978); [b]S. Halazy and A. Krief, *Ibid.* 1829, 1833 (1981); [c]A.

Krief, *Proc. Int. Symp. Org. Selenium Tellurium Compd.* 3*rd* 13 (1981). [d]H. J. Reich, S. K. Shah and F. Chow, *J. Am. Chem. Soc.* **101**, 6648 (1979).

[17a]T. Cohen and J. R. Matz, *J. Am. Chem. Soc.* **102**, 6900 (1980); [b]*Tetrahedron Letters* 2455 (1981); [c]J. R. Matz and T. Cohen, *Ibid.* 2459 (1981).

[18a]M. Braun and D. Seebach, *Angew. Chem.*, Int. Ed. Engl. **13**, 277 (1974); [b]M. Braun, R. Dammann and D. Seebach, *Chem. Ber.* **108**, 2368 (1975); [c]R. Dammann, M. Braun and D. Seebach, *Helv. Chim. Acta* **59**, 2821 (1976); [d]R. Dammann and D. Seebach, *Chem. Ber.* **112**, 2167 (1979); [e]D. Seebach, R. Dammann, H. J. Lindner and B. Kitschke, *Helv. Chim. Acta* **62**, 1143 (1979); [f]R. Hässig, H. Siegel and D. Seebach, *Chem. Ber.* 115 (1982).

[19a]A. Schmidt and G. Köbrich, *Tetrahedron Letters* 2561 (1974); [b]K. Kitatani, T. Hiyama and H. Nozaki, *J. Am. Chem. Soc.* **97**, 949 (1975); [c]E. Piers, C. K. Lau and I. Nagakura, *Tetrahedron Letters* 3233 (1976); [d]E. Piers and I. Nagakura, *Ibid.* 3237 (1976); [e]J. P. Marino and L. J. Browne, *Ibid.* 3241, 3245 (1976).

[20]Review: L. A. Paquette, *Israel J. Chem.* **21**, 128 (1981).

[21]Prof. R. F. Cuncio has informed us of similar negative experiments in his laboratory.

[22]This reagent/solvent combination is highly preferred for the deprotonation of allyltrimethylsilane: E. Ehlinger and P. D. Magnus, *J. Am. Chem. Soc.* **102**, 5004 (1980).

[23]D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Trieber and S. R. Dows, *J. Am. Chem. Soc.* **87**, 4529 (1965).

[24]S. Halazy, W. Dumont and A. Krief, *Tetrahedron Letters* 4737 (1981).

[25]T. Hiyama, A. Kanakura, Y. Morizawa and H. Nozaki, *Tetrahedron Letters* 1279 (1982).

[26]For example: L. H. Sommer, E. Dorfman, G. M. Goldberg and F. G. Whitmore, *J. Am. Chem. Soc.* **68**, 488 (1946).

[27]B. M. Trost and P. H. Scudder, *J. Org. Chem.* **46**, 506 (1981), and Refs. cited.

[28]E. M. Burgess, H. R. Penton Jr. and E. A. Taylor, *J. Org. Chem.* **38**, 26 (1973).

[29a]R. T. Taylor, C. R. Degenhardt, W. P. Melega and L. A. Paquette, *Tetrahedron Letters* 159 (1977); [b]L. A. Paquette, W. E. Fristad, D. S. Dime and T. R. Bailey, *J. Org. Chem.* **45**, 3017 (1980); [c]T. H. Chan, A. Baldassare and D. Massuda, *Synthesis* 801 (1976); [d]A. R. Chamberlin, J. E. Stenke and F. T. Bond, *J. Org. Chem.* **43**, 147 (1978).

[30]Compare R. G. Daniels and L. A. Paquette, *J. Org. Chem.* **49**, 2901 (1981).

[31]H. C. Brown, J. H. Brewster and H. Schechter, *J. Am. Chem. Soc.* **76**, 467 (1954).

[32]J. J. Pappas and W. P. Keaveney, *Tetrahedron Letters* 4273 (1966).

[33]K. B. Becker, A. F. Boschung and C. A. Grob, *Helv. Chim. Acta* **56**, 2733 (1973).