20. Silicon-Directed *Nazarov* Cyclizations

Part VI

The Anomalous Cyclization of Vinyl Dienyl Ketones

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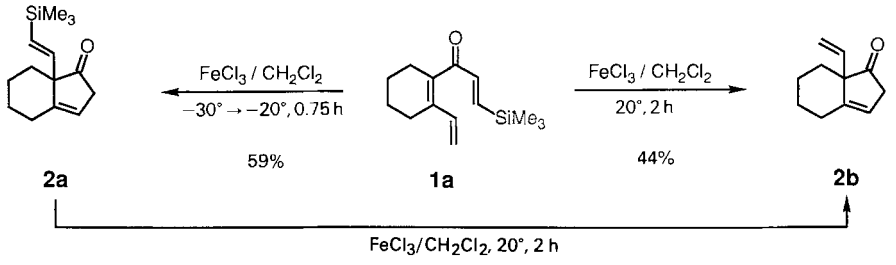
Reactions of various vinyl dienyl ketones (see **1a–e**, **1i**) with $FeCl_3$ give rise to β,γ-unsaturated α-vinyl-cyclopentenones (see **2a–e**, **2i**, *Table 2*). The reaction succeeds for vinyl dienyl ketones with substituents on either double bond. Aryl dienyl and alkyl dienyl ketones (see **1f–h**) do not cyclize cleanly. The effects of substituents on the rate of reaction is discussed in terms of the mechanism of the rearrangement. A ^{13}C-labeling study establishes the pathway as an unusual 1-hydroxypentadienyl-cation electrocyclization to a cyclopentenyl cation which collapses *via* a pinacol rearrangement to the α-vinyl ketone.

Introduction. – In the preceding paper, we described the general compatibility of olefins to the conditions of the silicon-directed *Nazarov* cyclization (SDNC). In some substrates with double bonds directly attached to the divinyl ketone, no involvement of the alkene was observed. However, one system bearing a β-vinyl appendage, **1a**, cyclized under normal reaction conditions to give the unexpected α-vinyl-cyclopentenone isomer **2b** (*Scheme 1*). We describe in this paper studies on the mechanism and synthetic generality of this interesting process.

Scheme 1



Mechanistic Studies. – That the major product obtained from treatment of **1a** with $FeCl_3$ was not the expected cyclopentenone could be immediately discerned from its lack of UV activity and greater mobility on TLC. High-resolution mass spectrometry showed it to be an isomer of the expected product. However, it contained only 4 olefinic ^1H-NMR signals (3 of which were diagnostic for the vinyl group), and it was clearly a non-conju-

[1]) Taken in part from the M.S. Thesis of *G. A. H.*, University of Illinois, Urbana, IL, 1987.

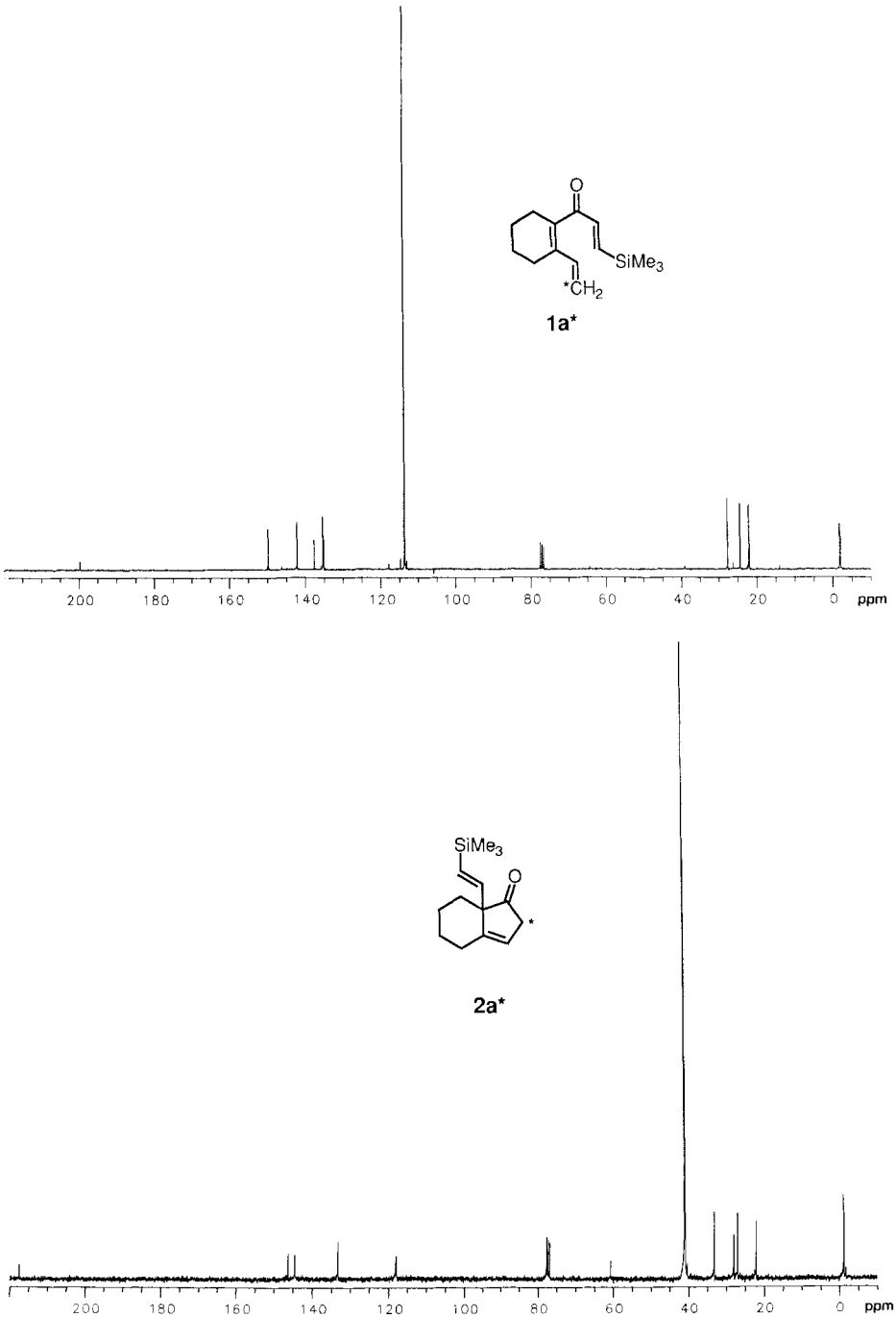


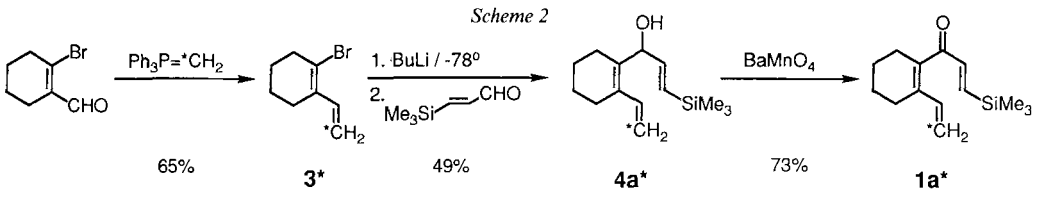
Figure. ^{13}C-*NMR spectra of labeled* **1a*** *and* **2a***

gated cyclopentanone (ν(CO) 1748 cm^{-1}). The most interesting and useful information came from homonuclear $^1H/^1H$ decoupling experiments which showed that the pair of *m* at 3.00 and 2.72 ppm were strongly coupled to each other (J = 22.7 Hz) and weakly coupled to the unassigned vinyl proton at 5.71 ppm. This suggested the presence of a β,γ-unsaturated cyclopentenone with diastereotopic methylene H-atoms. The vinyl group displayed a first-order splitting pattern with no additional couplings, suggesting its attachment to a quaternary center. Structure **2b** seemed to fit the available data and was corroborated in the mechanistic experiments below.

In an attempt to increase the yield of **2b**, the reaction was run at −30 to 0°, and in this case, a different product, **2a**, was isolated in 59% yield. By spectroscopic analysis, **2a** was clearly related to **2b**, but had retained the trimethylsilyl group. Treatment of **2a** with $FeCl_3$ at 20° did induce protiodesilylation to **2b** suggesting the vinylsilane as a common source for the vinyl groups in **2a** and **2b**.

The fate of the original vinyl unit in **1a** was established by a ^{13}C-labeling experiment. The preparation of **1a**[2]) was easily modified to specifically incorporate a ^{13}C-label in the terminal C-atom of the vinyl group as outlined in *Scheme 2*. Methylenation of 2-bromo-1-cyclohexenecarboxaldehyde with ^{13}C-enriched (methylidene)triphenylphosphorane (10% ^{13}C) produced **3*** in 65% yield which, *via* **4a***, was carried through to the divinyl ketone **1a*** as described in the preceding paper. The enrichment of ^{13}C in **1a*** was measured to be 7.44 times natural abundance[3]). Cyclization of **1a*** at −30 to −20°/0.75 h afforded **2a*** in which C(2) has exclusively incorporated the ^{13}C-label (see *Figure*). The ^{13}C enrichment at C(2) was measured to be 7.42 times natural abundance by the method described above. Thus, transfer of the label was quantitative.

Scheme 2



* = ^{13}C

Scope and Limitations. – From mechanistic considerations *(vide infra)*, it was clear that the silylvinyl unit was undergoing a cationic 1,2-shift during the reaction. To investigate the generality of this process, we prepared three types of substrates, substrates 1) with non-vinyl migrating groups, 2) with substituted vinyl migrating groups, and 3) with dienyl-substituted groups.

Preparation of Substrates. All but one of the dienyl ketones were prepared by the general route shown in *Scheme 3*. The yields for the corresponding alcohols **4a–h** and ketones **1a–h** are collected in *Table 1*. The substrate **1i** was prepared by a minor modification which employed (benzylidene)triphenylphosphorane as the olefinating reagent *(Scheme 3)*. After addition and oxidation, the ketone was obtained as a mixture of

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[2]) For details, see preceding paper in this issue.

[3]) This was done by measuring the ratio of peak heights of the labeled peak to a reference peak in the ^{13}C-NMR spectrum of **1a*** and then comparing it to the ratio of the heights of the same peaks in the ^{13}C-NMR spectrum of unlabeled **1a**. The same method was used for **2a***/**2a**.

Scheme 3

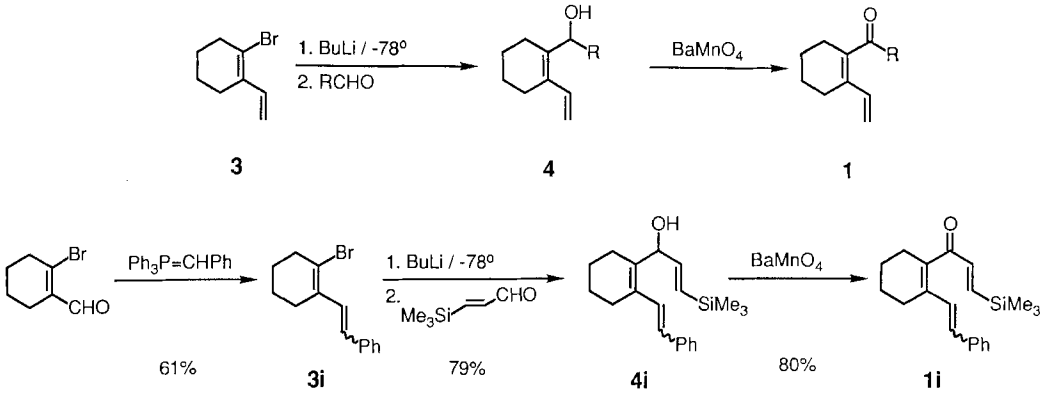


Table 1. *Preparation of Dienyl Ketones* 1

R	Product **4**	Yield [%][a])	Product **1**	Yield [%][a])
$Me_3SiCH=CH$	**4a**	53	**1a**	82
$CH_2=CH$	**4b**	60	**1b**	59
$CH_2=C(CH_3)$	**4c**	68	**1c**	82
$CH_3CH=CH$	**4d**	86	**1d**	68
$PhCH=CH$	**4e**	77	**1e**	60
C_6H_5	**4f**	90	**1f**	85
$(CH_3)_3C$	**4g**	80	**1g**	36
CH_3	**4h**	99	**1h**	16[b])

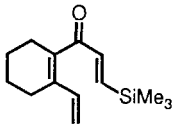
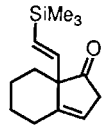
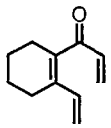
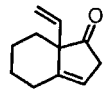
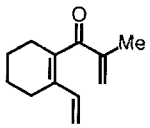
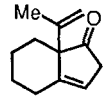
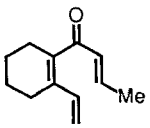
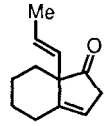
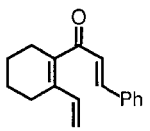
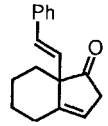
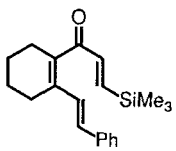
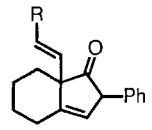
[a]) Yield after chromatography.
[b]) Low yield due to volatility.

geometrical isomers from which the isomer *(E,E)*-**1i** crystallized and was used in pure form. The isomer *(E,Z)*-**1i** could be obtained in pure form after repeated chromatography of the mother liquors. A ^{1}H-NMR spectrum (300 MHz) could be obtained. However, due to a facile isomerization, cyclization experiments were done with mixtures containing varying amounts of *(E,E)*-**1i**. Nonetheless, these cyclizations provided important mechanistic information.

Cyclizations. We first tested the phenyl (**1f**), *t*-butyl (**1g**), and methyl (**1h**) dienyl ketones for their ability to participate in the cyclization. Under no conditions with several *Lewis* acids could any tractable materials be isolated. Reaction mixtures were highly colored and showed destruction of the reactants.

Retaining a vinyl migrating group seemed necessary, so we next examined the effects of substituents on the migrating group. The results of these cyclizations are compiled in *Table 2*. Compound **1a** is included for comparison. In all cases, the *Lewis* acid $FeCl_3$ and the solvent CH_2Cl_2 were used, at a starting temperature of −30°. The beneficial effect of the Me_3Si group was demonstrated in the low yield for cyclization of **1b**. Placement of a Me group on the migrating center had little effect on the outcome of the reaction giving the poorest yield of all cyclizations. In striking contrast, the 1-propenyl ketone **1d** with a Me group in the *β*-position to the migrating C-atom cyclized in 61% yield. In a similar fashion, the styryl ketone **1e** provided 65% of the cyclization product **2e**. The products

Table 2. *Cyclizations of Vinyl Dienyl Ketones* **1**[a])

Substrate		Time [min]	Temp. [°]	Product		Yield [%]
1a		30	−10		**2a**	59
1b		30	−15		**2b**	19
1c		30	−15		**2c**	16
1d		30	0		**2d**	61
1e		30	0		**2e**	65
(*E,E*)-**1i**		5	0		**2i**[c])R = Me_3Si **2j**[c])R = H	34 44

[a]) All reactions were run at 0.08M in CH_2Cl_2 with 1.05 equiv. of $FeCl_3$.
[b]) Yields after chromatography.
[c]) For configuration, see text.

2d, **2e** as well as **2a** were formed as single geometrical isomers (capillary GC) of *(E)*-configuration as judged by the large ^3J (16–18 Hz) in the ^{1}H-NMR spectra.

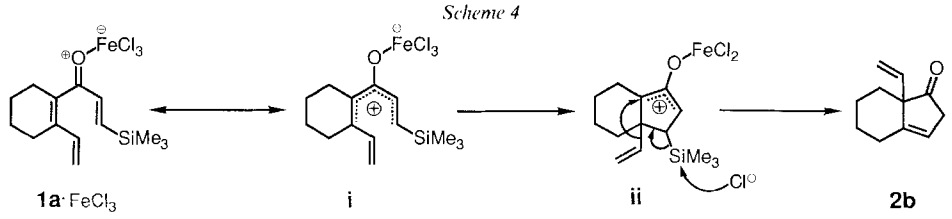
Cyclization of the ketone *(E,E)*-**1i** proceeded rapidly at 0° to provide a mixture of the 'expected' cyclopentenone **2i** and its protiodesilylated congener **2j** in 78% combined yield. Interestingly, both products were formed as single diastereoisomers. While the relative configuration at C(2) and C(7a) could not be assigned with certainty, some of the spectroscopic data are suggestive. Most notable is the similarity in chemical shift for the protons on the angular vinyl group in **2a** (5.79 and 5.72 ppm) compared to **2i** (*s* at 5.78 ppm), and **2b** (5.67, 5.24, and 5.07 ppm) compared to **2j** (5.67, 5.19, and 5.09 ppm). Based on analysis of the lowest-energy conformations for **2j** generated by *Allinger*'s MM2 force

field[4]), these ^{1}H-NMR data are most consistent with a *trans* isomer. In the *cis* isomer, the vinyl and phenyl groups are held at *ca.* 4-Å separation by the relatively rigid and flat cyclopentenone ring. A significant change in some of the resonances would be expected due to anisotropy of the phenyl ring [1]. This assignment is supported by results of the cyclization of a 3:2 mixture of *(E,E)*-**1i** and *(E,Z)*-**1i**. Analysis of the ^{1}H-NMR spectrum of the crude reaction mixture revealed the presence of *trans*-**2i** (H–C(2) at 4.02 ppm) along with another, related product assigned as *cis*-**2i** (H–C(2) at 4.20 ppm) in a 2:1 ratio.

A pure sample of *cis*-**2i** was obtained from a larger-scale (60 mg) reaction[5]) of **1i** (*(E,E)*/*(E,Z)* 7:3). The ^{1}H-NMR spectrum of pure *cis*-**2i** provided three useful pieces of information. First, H–C(2) appears at 4.20 ppm as a narrow *dd* (J = 1.2, 4.2 Hz) compared to the *t* (J = 2.3 Hz) for this proton in *trans*-**2i**. Second, the chemical shift of the protons on the angular vinyl group (5.90 and 5.85 ppm) are > 0.1 ppm downfield compared to *trans*-**2i**. Finally, the aromatic protons are far more split showing fine structure from 7.46 to 7.17 ppm. We feel that these data, while supportive, are not unambiguous. Nevertheless, it should be appreciated that the production of distinct stereoisomeric products from geometrical isomers of starting materials has important mechanistic implications, whatever the actual structural assignments may be.

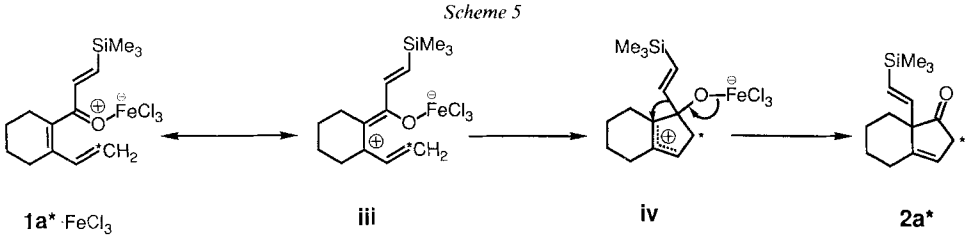
Discussion. – From the results of our initial experiments, we envisioned the formation of **2b** from **1a** by the process shown in *Scheme 4*. Conrotatory cyclization in the normal sense [2] produces, *via* **i**, cation **ii** which suffers a facile 1,2-vinyl migration [3] with

Scheme 4



Si-assistance to the observed product. This picture, however, is not consistent with the formation of **2a** from **1a** at lower temperature. To explain the persistence of the vinylsilane in the product, the mechanism in *Scheme 5* is suggested. The electrocyclic closure is proposed to involve a linearly conjugated dienyl ketone (instead of the cross-conjugated

Scheme 5



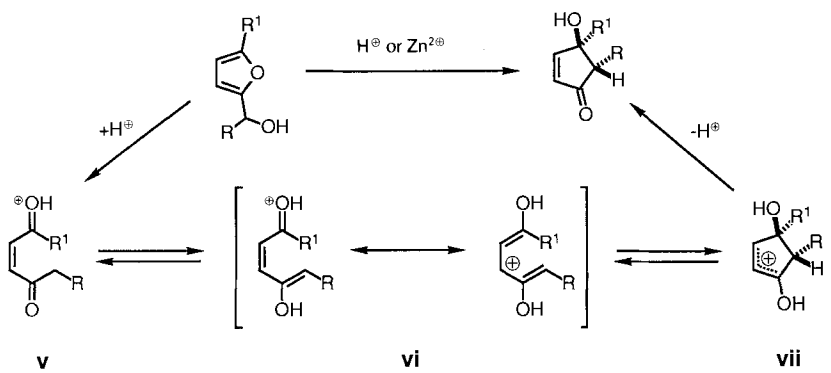
[4]) Minimized strain energies: *cis*-**2j** 19.22 kcal/mol, *trans*-**2j** 18.14 kcal/mol.

[5]) In this larger-scale experiment, a significant amount of *cis*-**2i** suffered protiodesilylation to *cis*-**2j** (H–C(2) at 4.25 ppm *(dd)*) which could not be separated from *trans*-**2j**.

divinyl ketone). The $FeCl_3$-complexed, pentadienyl-cation precursor **iii** undergoes conrotatory closure to the cyclopentenyl caton **iv** which is spontaneously disposed for an extremely facile 1,2-vinyl migration (pinacol rearrangement [4]). As shown by the ^{13}C-isotopic marker and variously substituted starting materials *(Table 2)*, the latter mechanism is more consistent with available data. Furthermore, the conversion of **2a** to **2b** with $FeCl_3$ at r.t. demonstrates the feasibility of this pathway.

A thorough search of the literature on the *Nazarov* cyclization failed to reveal a direct precedent for this type of electrocyclic closure. The closest analogy was found in the work of *Piancatelli* [5] who has studied the acid-catalyzed rearrangements of furylcarbinols to substituted cyclopentenones *(Scheme 6)*. Mechanistically, this can be understood in terms of an electrocyclization of the 1,4-dihydroxypentadienyl cation **vi** which bears an obvious relationship with cation **iii** and is obtained *via* **v** *(Scheme 6)*. No products derived from migration of R^1 = H or Me were reported. This is understandable, since the intermediate cyclopentenyl cation **vii** (*cf.* **iv**) is directly converted to the product enone by proton loss. *Hiyama* and coworkers have reported abnormal products in divinyl-ketone cyclizations in which the carbonyl group has apparently migrated [6a]. These workers have correctly interpreted these products as arising from capture of the normal cyclopentenyl cation by H_2O followed by proton transfer and dehydration[6]). *Noyori et al.* have obtained 5-vinyl-2-cyclopentenones from the irradiation of cycloheptadienones in acid media [7a]. The formation of these products can also be understood as 'normal', since they may arise from a thermal closure of 4-hydroxytrienyl cations generated photochemically. *Wagner-Meerwein* rearrangements have been documented in *Nazarov* cyclizations in the damascenone series of *Ohloff et al.* [8] as well as in the photochemistry of protonated cyclononadienones by *Noyori et al.* [7b]. Finally, in the recently reported Sn-directed *Nazarov* cyclization, *Peel* and *Johnson* [9] obtain the 'normal' *Nazarov* products from acyclic vinyl dienyl ketones. This observation is best explained by the all-*E* geometry of the double bonds in this case. For the 'anomalous' pathway to compete, the dienyl unit must contain a *Z* double bond next to the ketone. In our case, this situation is enforced by incorporation into a ring. In *Piancatelli*'s work that double bond is initially created in the *Z* configuration from the furan ring (**v**, *Scheme 6*).

Scheme 6



Based on our mechanistic considerations, we envisioned the possibility of a general process which could deliver α-substituted cyclopentenones from dienyl ketones **1f**, **1g**, and **1h**. The failure of these ketones to undergo an analogous cyclization was both disappointing and perplexing. Most surprising was the failure of **1f**, since phenyl migrations in pinacol rearrangements are well documented [10]. We can only speculate that either cation **iv** is not formed from these substrates or that other, non-productive pathways can compete.

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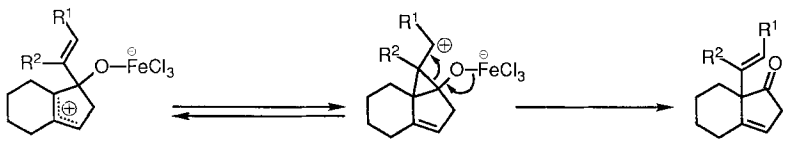
[6]) *Shoppee* and *Cooke* have reported the isolation of such a nucleophile-captured cyclopentenyl cation [6b].

The propensity of the vinyl group to migrate is most certainly related to the ability of the π-electrons to participate in stabilizing the transition state for migration. In the limit, this stabilization may be written as the cyclopropylcarbinyl cation **viii** *(Scheme 7)*[7]). This picture provides a reasonable explanation of the trends observed in the migration of substituted vinyl derivatives **1a–e**. The poorest results were obtained from **1b** and **1c** in which the cyclopropylcarbinyl cation would be primary (R^1 = H), and thus migration is just barely able to compete with other pathways. Interestingly, Me substitution at the migrating C-atom (**1c**, R^2 = Me) had no effect on the reaction. However, substitution at the β-position with Me (**1d**) or Ph (**1e**) groups led to better yields. We can logically speculate that the improvements derive from stabilization of **viii** resulting in a more competitive rearrangement rate. Similar arguments have been used by *Servis* and *Roberts* to explain the effects of Me and Ph substituents in the formolysis of homoallylic tosylates [12]. The case of **1a** (R^1 = Me_3Si) is intriguing[8]). Recent experimental [14a][14b] and theoretical [14c] studies indicate that for carbenium-ion centers, a Me_3Si group is stabilizing with respect to H but destabilizing with respect to Me. Based on comparison of solvolysis rates of tertiary 4-nitrobenzoates, *Apeloig* and *Stanger* [14a] estimated a 12–14 kcal/mol stabilization compared to H and a 6–8 kcal/mol destabilization compared to Me. Our results qualitatively agree in the closer similarity of **1a** and **1d** than **1a** and **1b**. An alternative explanation is the manifestation of the β-effect of silicon on the migrating center [15]. This explanation is less attractive, since we observed that **1c**, which is capable of direct cation stabilization, rearranged no better than **1a**.

Scheme 7



iv **viii** **2**

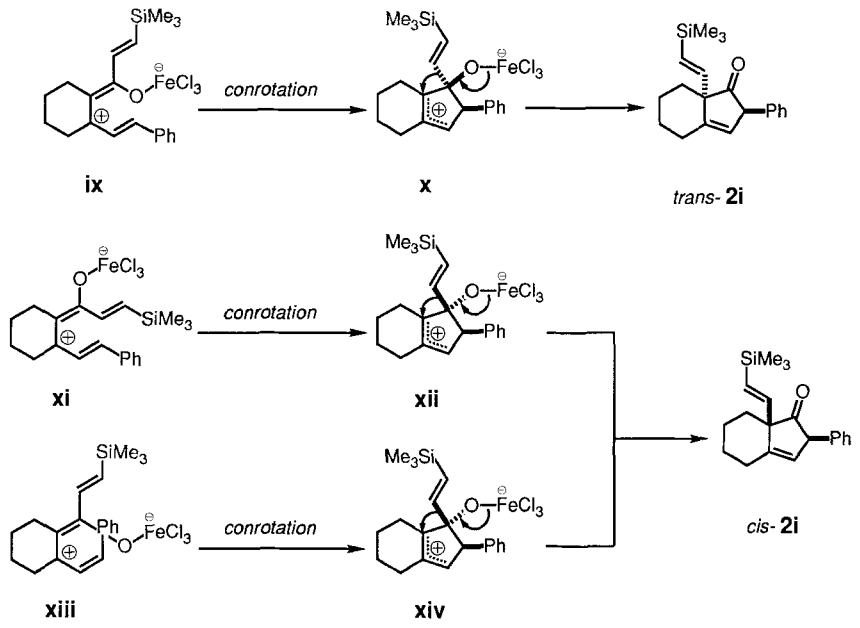
Ketone **1i** is the only precursor bearing a substituent on the dienyl moiety. Cyclization occurred in 78% combined yield of products **2i** and **2j**. Using *(E,E)*-**1i**, both *trans*-**2i** and *trans*-**2j** were formed as single diastereoisomers. Assuming that the closure of **iii** to **iv** is conrotatory and that vinyl migration occurs suprafacially from **iv**, this requires that the reacting pentadienyl cation is a single geometrical isomer. Thus, cation **ix** leads to a *trans*-**2i** *via* **x**, while cation **xi** would lead to *cis*-**2i** *via* **xii** *independent of the sense of conrotation (Scheme 8)*. Thus, we can rule out **xi** as a contributing intermediate cation. Furthermore, the observation that *(E,Z)*-**1i** produced *cis*-**2i**, necessarily implies that the reaction is operating under kinetic control[9]). The geometry of the reacting cation (**xiii**, *Scheme 8*) must differ only at the styryl double bond for another diastereoisomer of **2i** to

[7]) The experimental and theoretical literature on the structure and reactivity of the homoallyl carbenium ion family is vast. The exact nature of the intermediates is beyond the scope of the present discussion. For excellent reviews of the area, see [3][11].

[8]) *Danheiser* and *Fink* have reported an example of a *Wagner-Meerwein* shift involving a β-silylvinyl unit [13].

[9]) It is indeed unlikely that **2i** would be obtained at all if the reaction were under thermodynamic control due to the preference for the 2-cyclopentenone tautomer [16].

Scheme 8



arise by the same two-step process. Our tentative, spectroscopic assignment of *trans*-**2i** and *cis*-**2i** is also consistent with this picture. The preferential cyclization of **ix** compared to **xi** is reasonable on the basis of steric effects.

In summary, we have described a new variant of the *Nazarov* cyclization which involves a 1-hydroxypentadienyl cation. The success of the reaction rests on the facility of a subsequent pinacol rearrangement which generates a cyclopentenone. While at present the reaction seems to be limited to vinyl migrating groups, the unique angular substitution and versatility of the vinyl group to synthetic manipulation provide interesting opportunities for applications in synthesis. These avenues as well as further aspects of stereocontrol occupy our current efforts.

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Experimental Part

1. General. – For the general experimental procedures and specifications, see preceding paper. The 1-bromo-2-ethenyl-1-cyclohexene and 1-bromo-2-(2'-phenylethenyl)-1-cyclohexene were prepared by literature methods [17]. ^{13}C-Enriched CH_3I was purchased from *Cambridge Isotopes*.

2. Preparation of Dienylmethanols 4. – All alcohols **4** were prepared from the dienyl bromide **3** or **3i** and RCHO (see *Table 1*) by the same procedure. The preparation of **4a** is provided as representative.

(E)-1-(2'-Ethenyl-1'-cyclohexenyl)-3-(trimethylsilyl)-2-propen-1-ol (**4a**). A soln. of *1-bromo-2-ethenyl-1-cyclohexene* (**3**) (0.165 g, 0.882 mmol) in 2.7 ml of THF under N_2 at −78° was treated dropwise with BuLi (0.65 ml of a 1.5M soln. in hexane, 0.97 mmol). After stirring for 15 min, 3-(trimethylsilyl)-2-propenal (0.124 g, 0.97 mmol) was added. After stirring for 1h, the mixture was allowed to warm to 0° and quenched with 15 ml of 4% NH_4Cl soln. The mixture was extracted with Et_2O (3 × 35 ml), and the org. layers were washed with H_2O (20 ml) and brine (2 × 20 ml). The combined extracts were dried (K_2CO_3), evaporated, and chromatographed to afford **4a**. Yield 0.111 g (53%). B.p. 95°/0.05 Torr. R_f 0.28 (hexane/AcOEt 8:1). IR: 3353*m*, 3090*w*, 2930*s*, 2859*m*, 2840*m*, 1615*w*, 1437*w*, 1418*w*, 1306*w*, 1275*w*, 1248*s*, 1198*w*, 1055*w*, 992*m*, 897*m*, 866*s*, 837*s*, 750*m*, 731*w*, 693*m*. ^1H-NMR (300 MHz): 6.89 (*dd*, J = 17.2, 11.0, CH_2=C*H*); 6.02 (*dd*, J = 19.0, 3.7, H–C(2)); 5.91 (*dd*, J = 18.9, 1.3, H–C(3)); 5.36 (*t*, J = 3.3, H–C(1)); 5.22 (*d*, J = 17.5, H_Z–C(8')); 5.04 (*d*, J = 11.0, H_E–C(8')); 2.25–1.92 (*m*, 2 H–C(3'), 2 H–C(6')); 1.69–1.48 (*m*, 2 H–C(4'), 2 H–C(5'), OH); 0.07 (*s*, Me_3Si). MS: 236 (2, M^+), 144 (11), 131 (15), 129 (12), 118 (10), 91 (18), 75 (67), 73 (100), 59 (11), 45 (14), 41 (12), 31 (10). Anal. calc. for $C_{14}H_{24}OSi$: C 71.13, H 10.22; found: C 70.77, H 10.19.

1-(2'-Ethenyl-1'-cyclohexenyl)-2-propen-1-ol (**4b**). Yield 60%. R_f 0.28 (hexane/AcOEt 5:1). IR: 3366*m*, 3090*w*, 3019*w*, 2930*s*, 2859*m*, 2840*m*, 1632*w*, 1595*w*, 1451*w*, 1437*w*, 1418*w*, 1275*w*, 1250*w*, 1138*w*, 1115*w*, 1071*w*, 988*s*, 957*w*, 920*s*, 897*m*, 758*w*. ^1H-NMR (300 MHz): 6.88 (*dd*, J = 17.2, 11.0, H–C(7')); 5.89 (*ddd*, J = 17.2, 10.5, 4.9, H–C(2)); 5.38 (*t*, J = 3.7, H–C(1)); 5.28 (*d*, J = 17.2, H_Z–C(3)); 5.22 (*d*, J = 17.6, H_Z–C(8')); 5.15 (*d*, J = 10.7, H_E–C(3)); 5.04 (*d*, J = 11.0, H_E–C(8')); 2.22–2.00 (*m*, 2 H–C(3'), 2 H–C(6')); 1.68–1.31 (*m*, OH, 2 H–C(4'), 2 H–C(5')). MS: 164 (2, M^+), 149 (20), 146 (11), 135 (35), 133 (64), 132 (10), 131 (19), 122 (12), 121 (23), 120 (12), 188 (13), 117 (17), 109 (42), 108 (12), 107 (38), 105 (20), 95 (15), 94 (21), 93 (25), 92 (16), 91 (100), 81 (20), 79 (51), 67 (56), 57 (40), 55 (17). HR-MS: 164.1198 ($C_{11}H_{16}O$, calc. 164.1201).

1-(2'-Ethenyl-1'-cyclohexenyl)-2-methyl-2-propen-1-ol (**4c**). Yield 68%. R_f 0.34 (hexane/AcOEt 5:1). IR: 3349*m*, 3088*w*, 3021*w*, 2928*s*, 2859*m*, 2840*w*, 1653*w*, 1630*w*, 1593*w*, 1449*w*, 1375*w*, 1265*w*, 1136*w*, 1075*w*, 944*m*, 990*w*, 951*w*, 897*s*, 764*w*. ^1H-NMR (300 MHz): 6.95 (*dd*, J = 17.2, 11.0, H–C(7')); 5.26 (*s*, H_Z–C(3)); 5.23 (*d*, J = 17.0, H_Z–C(8')); 5.10 (*s*, H_E–C(3)); 5.04 (*d*, J = 11.1, H_E–C(8')); 4.94 (*m*, H–C(1)); 2.32–2.04 (*m*, 2 H–C(3'), 2 H–C(6')); 1.94–1.53 (*m*, OH, 2 H–C(4'), 2 H–C(5')); 1.61 (*s*, CH_3). MS: 178 (4, M^+), 163 (25), 150 (24), 149 (100), 147 (41), 145 (19), 136 (12), 135 (39), 133 (14), 131 (12), 122 (16), 121 (49), 119 (17), 117 (15), 109 (25), 108 (11), 107 (31), 105 (65), 95 (14), 94 (12), 93 (36), 91 (46), 81 (25), 79 (42), 69 (22), 67 (48), 55 (11). HR-MS: 178.1355 ($C_{12}H_{18}O$, calc. 178.1358).

1-(2'-Ethenyl-1'-cyclohexenyl)-2-buten-1-ol (**4d**). Yield 86%. R_f 0.28 (hexane/AcOEt 5:1). IR: 3349*m*, 3088*w*, 3023*w*, 2930*s*, 2859*s*, 1632*w*, 1597*w*, 1449*m*, 1418*w*, 1377*w*, 1275*w*, 1240*w*, 1136*w*, 1115*w*, 1073*m*, 967*s*, 895*s*, 801*w*. ^1H-NMR (300 MHz): 6.88 (*dd*, J = 17.2, 11.0, H–C(7')); 5.74–5.54 (*m*, H–C(2), H–C(3)); 5.29 (*d*, J = 5.5, H–C(1)); 5.20 (*d*, J = 17.1, H_Z–C(8')); 5.02 (*d*, J = 11.0, H_E–C(8')); 2.28–2.04 (*m*, 2 H–C(3'), 2 H–C(6')); 1.70 (*s*, CH_3); 1.69–1.50 (*m*, OH, 2 H–C(4'), 2 H–C(5')). MS: 178 (18, M^+), 163 (26), 150 (18), 149 (67), 147 (43), 145 (13), 135 (25), 133 (13), 131 (21), 122 (12), 121 (38), 120 (31), 119 (14), 117 (11) 109 (27), 108 (12), 107 (34), 105 (43), 95 (15), 94 (12), 93 (26), 91 (32), 86 (12), 81 (20), 79 (32), 71 (70), 69 (100), 68 (10), 67 (30), 55 (12). HR-MS: 178.1354 ($C_{12}H_{18}O$, calc. 178.1358).

(E)-1-(2'-Ethenyl-1'-cyclohexenyl)-3-phenyl-2-propen-1-ol (**4e**). Yield 77%. R_f 0.28 (hexane/AcOEt 5:1). IR: 3374*m*, 3085*w*, 3061*w*, 3027*m*, 2930*s*, 2859*m*, 1630*w*, 1599*w*, 1405*w*, 1277*w*, 1134*w*, 1059*w*, 968*m*, 899*w*, 754*m*, 693*m*. ^1H-NMR (300 MHz): 7.46–7.20 (*m*, Ph); 6.95 (*dd*, J = 17.2, 11.0, CH_2=CH); 6.62 (*d*, J = 15.8, H–C(3)); 6.26 (*dd*, J = 16.1, 5.2, H–C(2)); 5.56 (*d*, J = 5.2, H–C(1)); 5.25 (*d*, J = 17.3, H_Z–C(8')), 5.08 (*d*, J = 11.0, H_E–C(8')); 2.48–2.11 (*m*, 2 H–C(3'), 2 H–C(6')); 1.82–1.32 (*m*, OH, 2 H–C(4'), 2 H–C(5')). MS: 240 (4, M^+), 218 (10), 190 (17), 149 (19), 148 (50), 134 (13), 133 (100), 132 (14), 131 (45), 130 (32), 129 (12), 121 (24), 120 (32), 117 (25), 115 (20), 108 (12), 107 (26), 105 (50), 104 (17), 94 (19), 92 (12), 91 (59), 85 (29), 84 (13), 79 (15), 57 (24), 55 (31), 49 (22). HR-MS: 240.1507 ($C_{17}H_{20}O$, calc. 240.1514).

α-(2'-Ethenyl-1'-cyclohexenyl)benzyl Alcohol (**4f**). Yield 90%. R_f 0.32 (hexane/AcOEt 5:1). IR: 3364*m*, 3087*w*, 3061*w*, 3027*w*, 2928*s*, 2859*m*, 2838*m*, 1639*w*, 1601*w*, 1493*w*, 1449*m*, 1418*w*, 1323*w*, 1277*w*, 1242*w*, 1181*w*, 1138*w*, 1082*w*, 1014*s*, 957*w*, 899*m*, 762*w*, 712*s*, 700*s*. ^1H-NMR (300 MHz): 7.37–7.22 (*m*, Ph); 7.06 (*dd*, J = 17.1,

11.0, H–C(7')); 6.08 (*d*, *J* = 3.7, H–C(1)); 5.30 (*d*, *J* = 17.1, H_Z–C(8')); 5.11 (*d*, *J* = 11.0, H_E–C(8')); 2.27 (*m*, 2 H–C(3'), 2 H–C(6')); 1.80 (*d*, *J* = 3.8, OH); 1.76–1.51 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 214 (7, M^+), 197 (17), 196 (100), 183 (11), 168 (12), 105 (12), 74 (11), 59 (11). HR-MS: 214.1354 ($C_{15}H_{18}O$, calc. 214.1358).

1-(2'-Ethenyl-1'-cyclohexenyl)-2,2-dimethyl-1-propanol (**4g**). Yield 80%. R_f 0.26 (hexane/AcOEt 8:1). IR: 3409*m*, 3090*w*, 2932*s*, 2861*m*, 1626*w*, 1590*w*, 1480*m*, 1464*m*, 1449*w*, 1393*w*, 1364*w*, 1279*m*, 1233*w*, 1075*w*, 1038*m*, 999*s*, 955*w*, 895*m*. ^{1}H-NMR (300 MHz): 6.88 (*dd*, *J* = 17.2, 11.0, H–C(7')); 5.15 (*d*, *J* = 17.3, H_Z–C(8')); 4.96 (*d*, *J* = 11.0 H_E–C(8')); 4.61 (*d*, *J* = 4.0, H–C(1)); 2.39–2.23 (*m*, 2 H); 2.20–2.05 (*m*, 2 H); 1.75–1.46 (*m*, 2 H–C(4'), 2 H–C(5')); 1.45 (*d*, *J* = 4.3, OH); 0.95 (*s*, $(CH_3)_3C$). MS: 194 (5, M^+), 138 (10), 137 (84), 120 (17), 119 (62), 105 (10), 95 (14), 93 (26), 92 (12), 91 (75), 87 (42), 86 (16), 81 (12), 79 (25), 77 (15), 69 (93), 67 (35), 57 (43), 56 (15), 55 (17), 45 (13), 44 (28), 43 (39), 41 (66), 40 (100), 39 (21). HR-MS: 194.1671 ($C_{13}H_{22}O$, calc. 194.1671). Anal. calc. for $C_{13}H_{22}O$: C 80.35, H 11.41; found: C 79.99, H 11.77.

1-[2'-(E and Z)-(2'-Phenylethenyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-ol (**4i**). Yield 79%. R_f 0.28 (hexane/AcOEt 12:1). IR: 3372*m*, 3025*w*, 2932*s*, 2859*m*, 1615*w*, 1597*w*, 1493*w*, 1448*m*, 1248*s*, 1198*w*, 1055*m*, 994*m*, 953*m*, 866*s*, 839*s*, 775*w*, 750*s*, 693*s*. ^{1}H-NMR (300 MHz): 7.46–7.22 (*m*, Ph, H–C(8') of both); 6.61 (*d*, *J* = 16.0, 0.75 H, H–C(7') of *(E)*); 6.43 (*d*, *J* = 12.1, 0.25 H, H–C(7') of *(Z)*); 6.10 (*dd*, *J* = 18.5, 3.8, H–C(2) of both); 6.00 (*d*, *J* = 18.5, H–C(3) of both); 5.50 (br. *d*, *J* = 2.9, 0.75 H, H–C(1) of *(E)*); 5.08 (br. *d*, *J* = 1.7, 0.25 H, H–C(1) of *(Z)*); 2.41–1.89 (*m*, 2 H–C(3'), 2 H–C(6')); 1.78–1.61 (*m*, OH, 2 H–C(4'), 2 H–C(5')); 0.10 (*s*, 6.75 H, Me_3Si of *(E)*); 0.01 (*s*, 2.25 H, Me_3Si of *(Z)*). MS: 312 (14, M^+), 222 (11), 221 (23), 131 (14), 127 (10), 91 (13), 75 (12), 73 (100). HR-MS: 312.1907 ($C_{20}H_{28}OSi$, calc. 312.1909).

3. Preparation of Dienyl Ketones (1). – *General Procedure.* A stirred soln. of the dienylmethanol **4** in dry CH_2Cl_2 (0.1M) was cooled to 0° and treated with 10 equiv. of $BaMnO_4$. The mixture was warmed to r.t. Upon completion (usually *ca.* 12 h; TLC monitoring) the mixture was filtered through *Celite* and the solids were washed with CH_2Cl_2. The filtrate was evaporated, chromatographed, and distilled.

(E)-1-(2'-Ethenyl-1'-cyclohexenyl)-3-(trimethylsilyl)-2-propen-1-one (**1a**). Yield 82%. B.p.: 100°/0.05 Torr. R_f 0.37 (hexane/AcOEt 12:1). IR: 3090*w*, 2980*w*, 2934*s*, 2861*m*, 2836*m*, 1653*s*, 1584*m*, 1449*w*, 1435*w*, 1366*w*, 1279*m*, 1248*s*, 1215*m*, 1175*m*, 1036*w*, 995*m*, 901*m*, 862*s*, 754*m*, 696*w*. ^{1}H-NMR (300 MHz): 7.04 (*d*, *J* = 19.1, H–C(2)); 6.56 (*d*, *J* = 19.0, H–C(3)); 6.43 (*dd*, *J* = 17.3, 10.9, H–C(7')); 5.24 (*d*, *J* = 17.2, H_Z–C(8')); 5.02 (*d*, *J* = 11.0, H_E–C(8')); 2.28 (br. *d*, *J* = 6.0, 2 H–C(3'), 2 H–C(6')); 1.70 (*m*, 2 H–C(4'), 2 H–C(5')); 0.14 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 199.7 (C(1)); 149.8 (C(2)); 142.1 (C(3)); 137.7 (C(2')); 135.4 (C(7')); 135.2 (C(1')); 113.6 (C(8')); 27.7; 24.3; 22.1; 22.0; –1.9 (Me_3Si). MS: 234 (15, M^+), 219 (14), 127 (30), 107 (19), 99 (12), 91 (11), 85 (11), 79 (27), 75 (40), 73 (100), 59 (11), 58 (13), 57 (13), 45 (19), 43 (35), 41 (19). HR-MS: 234.1439 ($C_{14}H_{22}OSi$, calc. 234.1440). Anal. calc. for $C_{14}H_{22}OSi$: C 71.33, H 9.46; found: C 71.26, H 9.35.

1-(2'-Ethenyl-1'-cyclohexenyl)-2-propen-1-one (**1b**). Yield 59%. B.p. 50°/0.35 Torr. R_f 0.27 (hexane/AcOEt 12:1). IR: 3092*w*, 2932*s*, 2861*m*, 2836*m*, 1657*s*, 1601*m*, 1449*w*, 1435*w*, 1399*m*, 1366*w*, 1283*m*, 1252*m*, 1188*w*, 1173*w*, 1022*w*, 984*m*, 907*m*, 789*w*. ^{1}H-NMR (300 MHz): 6.45 (*dd*, *J* = 17.2, 11.1, H–C(7') and *dd*, *J* = 17.7, 10.2, H–C(2)); 6.20 (*dd*, *J* = 17.2, 0.9, H_Z–C(3)); 5.97 (*dd*, *J* = 10.4, 1.3, H_E–C(3)); 5.26 (*d*, *J* = 17.2, H_Z–C(8')); 5.04 (*d*, *J* = 10.9, H_E–C(8')); 2.28 (*m*, 2 H–C(3'), 2 H–C(6')); 1.71 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 162 (100, M^+), 161, (99.8), 147 (72), 134 (24), 133 (28), 120 (11), 119 (22), 107 (16), 105 (24), 92 (17), 91 (63), 79 (39), 55 (14). HR-MS: 162.1039 ($C_{11}H_{14}O$, calc. 162.1045). Anal. calc. for $C_{11}H_{14}O$: C 81.44, H 8.70; found: C 81.19, H 8.81.

1-(2'-Ethenyl-1'-cyclohexenyl)-2-methyl-2-propen-1-one (**1c**). Yield 82%. R_f 0.32 (hexane/AcOEt 12:1). IR: 3090*w*, 2928*s*, 2859*m*, 2838*m*, 1655*s*, 1597*w*, 1449*m*, 1435*m*, 1372*m*, 1316*m*, 1275*w*, 1233*w*, 1157*w*, 1024*m*, 984*m*, 965*m*, 939*m*, 903*m*, 810*w*, 789*w*. ^{1}H-NMR (300 MHz): 6.23 (*dd*, *J* = 17.2, 10.9, H–C(7')); 5.93 (*s*, H_Z–C(3)); 5.91 (*s*, H_E–C(3)); 5.19 (*d*, *J* = 17.4, H_Z–C(8')); 4.97 (*d*, *J* = 10.9, H_E–C(8')); 2.24 (*m*, 2 H–C(3'), 2 H–C(6')); 1.92 (*s*, CH_3); 1.71 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 177 (13, $M^+ + 1$), 176 (100, M^+), 175 (46), 161 (53), 148 (14), 147 (14), 135 (15), 133 (25), 119 (11), 107 (36), 106 (11), 105 (26), 91 (27), 79 (30). Anal. calc. for $C_{12}H_{16}O$: C 81.77, H 9.15; found: C 81.77, H 9.23.

(E)-1-(2'-Ethenyl-1'-cyclohexenyl)-2-buten-1-one (**1d**). Yield 68%. B.p. 60°/0.05 Torr. R_f 0.26 (hexane/AcOEt 8:1). GC: column *A* (120° (2 min) 10°/min, 280° (20 min)), t_R 8.42 min (93%, *(E)*-isomer) and 9.26 min (7%, *(Z)*-isomer). IR: 3090*w*, 3017*w*, 2932*s*, 2861*m*, 2836*m*, 1649*s*, 1617*s*, 1439*m*, 1368*w*, 1283*m*, 1252*m*, 1173*m*, 1044*w*, 972*m*, 901*m*, 764*w*. ^{1}H-NMR (300 MHz): 6.80 (*dq*, *J* = 15.6, 6.9, H–C(3)); 6.42 (*dd*, *J* = 17.3, 10.9, H–C(7')); 6.17 (*dd*, *J* = 16.0, 1.2, H–C(2)); 5.22 (*d*, *J* = 17.1, H_Z–C(8')); 5.00 (*d*, *J* = 10.9, H_E–C(8')); 2.17 (*m*, 2 H–C(3'), 2 H–C(6')); 1.92 (*dd*, *J* = 6.7, 1.2, CH_3); 1.68 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 176 (100, M^+), 161 (52), 148 (20), 147 (26), 133 (25), 120 (18), 119 (15), 107 (12), 105 (28), 91 (39), 79 (18), 69 (28). Anal. calc. for $C_{12}H_{16}O$: C 81.77, H 9.15; found: C 81.73, H 9.26.

(E)-1-(2'-Ethenyl-1'-cyclohexenyl)-3-phenyl-2-propen-1-one (**1e**). Yield 60%. B.p. 150°/0.05 Torr. R_f 0.24 (hexane/AcOEt 8:1). IR: 3061*w*, 3029*w*, 2932*s*, 2861*m*, 2836*w*, 1634*s*, 1599*s*, 1576*m*, 1495*w*, 1449*m*, 1368*w*, 1327*m*, 1306*m*, 1281*m*, 1254*m*, 1202*m*, 1169*m*, 1134*w*, 1073*w*, 1042*w*, 1030*m*, 982*m*, 955*w*, 907*m*, 764*s*, 689*m*. ^{1}H-NMR (300 MHz): 7.58–7.54 (*m*, 2 H_o); 7.49 (*d*, *J* = 16.2, H–C(3)); 7.40 (*m*, 2 H_m, 1 H_p); 6.82 (*d*, *J* = 16.4, H–C(2)); 6.54 (*dd*, *J* = 17.3, 10.9, H–C(7')); 5.28 (*d*, *J* = 17.5, H_Z–C(8')); 5.04 (*d*, *J* = 10.8, H_E–C(8')); 2.35 (*m*, 2 H–C(3'), 2 H–C(6')); 1.75 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 238 (8, $M^{+\cdot}$), 188 (7), 167 (8), 146 (55), 132 (11), 131 (100), 119 (28), 103 (25), 91 (18). HR-MS: 238.1350 ($C_{17}H_{18}O$, calc. 238.1358. Anal. calc. for $C_{17}H_{18}O$: C 85.67, H 7.61; found: C 85.56, H 7.57.

(2'-Ethenyl-1-cyclohexenyl) Phenyl Ketone (**1f**). Yield 85%. M.p. 42°. R_f 0.30 (hexane/AcOEt 8:1). IR: 3063*w*, 3021*w*, 2934*s*, 2859*m*, 2836*m*, 1663*s*, 1595*m*, 1580*m*, 1449*m*, 1366*w*, 1312*m*, 1279*s*, 1250*s*, 1175*m*, 1071*w*, 1015*m*, 984*m*, 924*m*, 804*m*, 789*m*, 712*s*. ^{1}H-NMR (300 MHz): 7.90 (*m*, 2 H_o); 7.57 (*m*, 1 H_p); 7.46 (*m*, 2 H_m); 6.27 (*dd*, *J* = 17.2, 10.8, H–C(7')); 5.23 (*d*, *J* = 17.1, H_Z–C(8')); 4.93 (*d*, *J* = 10.9, H_E–C(8')); 2.34 (*m*, 2 H–C(3'), 2 H–C(6')); 1.77 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 213 (12, $M^{+\cdot}$ + 1), 212 (76, $M^{+\cdot}$), 211 (38), 197 (14), 184 (31), 183 (21), 169 (13), 155 (11), 142 (13), 141 (37), 128 (10), 115 (15), 105 (70), 91 (28), 79 (23), 78 (14), 77 (100), 65 (11), 51 (18), 43 (15), 41 (12). Anal. calc. for $C_{15}H_{16}O$: C 84.87, H 7.60; found: C 84.98, H 7.45.

1-(2'-Ethenyl-1'-cyclohexenyl)-2,2-dimethylpropanone (**1g**). Yield 36% (2 days, refluxing benzene). B.p. 60°/0.1 Torr. R_f 0.34 (hexane/AcOEt 12:1). IR: 3092*w*, 2934*s*, 2867*m*, 2838*w*, 1682*s*, 1634*w*, 1597*w*, 1478*m*, 1462*m*, 1393*w*, 1364*m*, 1279*w*, 1258*w*, 1233*w*, 1162*m*, 1132*w*, 1011*w*, 986*m*, 943*m*, 897*m*, 833*w*, 783*w*, 752*w*. ^{1}H-NMR (300 MHz): 6.15 (*dd*, *J* = 17.2, 10.9, H–C(7')); 5.18 (*d*, *J* = 17.1, H_Z–C(8')); 4.99 (*d*, *J* = 10.9, H_E–C(8')); 2.21 (*m*, 2 H–C(3'), 2 H–C(6')), 1.68 (*m*, 2 H–C(4'), 2 H–C(5')); 1.19 (*s*, $(CH_3)_3C$). MS: 192 (13, $M^{+\cdot}$), 135 (52), 107 (100), 91 (6), 79 (23). Anal. calc. for $C_{15}H_{20}O$: C 81.20, H 10.48; found: C 81.14, H 10.25.

1-(2'-Ethenyl-1'-cyclohexenyl)propanone (**1h**). Yield 16%. B.p. 50°/0.4 Torr. R_f 0.28 (hexane/AcOEt 8:1). IR: 3092*w*, 2932*s*, 2860*m*, 2838*m*, 1684*s*, 1619*w*, 1580*w*, 1424*m*, 1350*m*, 1279*m*, 1235*s*, 1219*s*, 1179*w*, 1136*w*, 1046*w*, 990*m*, 911*m*. ^{1}H-NMR (300 MHz): 6.74 (*dd*, *J* = 17.4, 11.0, H–C(7')); 5.33 (*d*, *J* = 17.2, H_Z–C(8')), 5.12 (*d*, *J* = 11.0, H_E–C(8')); 2.32–2.28 (*m* and *s*, 2 H–C(3'), 2 H–C(6'), CH_3); 1.67 (*m*, 2 H–C(4'), 2 H–C(5')). MS: 150 (82, $M^{+\cdot}$), 149 (100), 135 (52), 122 (24), 121 (12), 107 (30), 91 (20), 79 (44). Anal. calc. for $C_{10}H_{14}O$: C 79.96, H 9.39; found: C 79.76, H 9.31.

(E,E)-1-[2'-(2''-Phenylethenyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-one ((*E,E*)-**1i**). Yield 80%. M.P. 49°. R_f 0.24 (hexane/Et_2O 20:1). IR: 3027*w*, 2938*s*, 2862*m*, 1651*s*, 1583*w*, 1449*w*, 1281*w*, 1250*s*, 1219*m*, 995*m*, 961*w*, 843*s*, 750*m*, 693*s*. ^{1}H-NMR (300 MHz): 7.38–7.22 (*m*, Ph); 7.14 (*d*, *J* = 19.0, H–C(2)); 6.98 (*d*, *J* = 16.1, H–C(2'')); 6.71 (*d*, *J* = 19.0, H–C(3)); 6.63 (*d*, *J* = 16.1, H–C(1'')); 2.48 (*m*, 2 H); 2.39 (*m*, 2 H); 1.77 (*m*, 2 H–C(4'), 2 H–C(5')); 0.15 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 199.0; 149.2; 142.5; 138.1; 137.3; 136.2; 128.63; 128.57; 127.8; 127.6; 126.5; 27.95; 25.4; 22.2; −1.8. MS: 311 (27, $M^{+\cdot}$ + 1), 310 (100, $M^{+\cdot}$), 309 (17), 295 (31), 281 (13), 237 (14), 233 (20), 221 (12), 220 (11), 219 (41), 211 (25), 141 (15), 113 (11), 91 (14), 75 (30), 73 (59). Anal. calc. for $C_{20}H_{26}OSi$: C 77.36, H 8.44; found: C 77.32, H 8.54.

(E,Z)-1-[2'-(2''-Phenylethenyl)-1'-cyclohexenyl]-3-(trimethylsilyl)-2-propen-1-one ((*E,Z*)-**1i**). A 0.58-g sample of crude **1i** ((*E,E*)/(*E,Z*) 10:1) was purified by medium-pressure LC to provide 60 mg of pure *(E,Z)*-**1i**. R_f 0.19 (hexane/Et_2O 20:1). ^{1}H-NMR (300 MHz): 7.38–7.22 (*m*, Ph); 6.97 (*d*, *J* = 18.8, H–C(2)); 6.76 (*d*, *J* = 18.8, H–C(3)); 6.37 (*d*, *J* = 12.1, H–C(2'')); 6.25 (br. *d*, *J* = 12.1, H–C(1'')); 2.35 (*m*, 2 H); 2.17 (*m*, 2 H); 1.66 (*m*, 2 H–C(4'), 2 H–C(5')); 0.08 (*s*, Me_3Si). After storage for 2 days, this sample isomerized to a 7:3 (*E,E*)/(*E,Z*) mixture.

4. Cyclization of Dienyl Vinyl Ketones (1→2). – *General Procedure.* Reaction times and temp. are listed in *Table 2*. The dienyl vinyl ketone was dissolved in CH_2Cl_2 (0.08M) and cooled to the stated temp. (0° for r.t. cases). Then, 1.05 equiv. of 98% $FeCl_3$ were added and the reaction was followed by TLC.

*1,4,5,6,7,7a-Hexahydro-7a-[2'-(trimethylsilyl)ethenyl]-2*H*-inden-1-one* (**2a**). Yield 69%. B.p. 70°/0.05 Torr. R_f 0.37 (hexane/AcOEt 12:1). IR: 2934*s*, 2857*m*, 1746*s*, 1597*w*, 1447*w*, 1404*w*, 1248*s*, 1200*w*, 1154*w*, 1128*w*, 994*m*, 882*m*, 862*s*, 839*s*, 797*w*, 723*w*, 692*w*. ^{1}H-NMR (300 MHz): 5.79 (*d*, *J* = 18.6, Me_3SiCH=C*H*); 5.78 (*m*, H–C(3)); 5.72 (*d*, *J* = 18.6, Me_3SiCH=CH); 2.96 (*ddd*, *J* = 22.4, 4.5, 1.5, 1 H–C(2)); 2.69 (*dt*, *J* = 22.4, 2.3, 1 H–C(2)); 2.30 (*m*, 1 H); 2.11 (*m*, 2 H); 1.78 (*m*, 1 H); 1.66 (*m*, 1 H); 1.46–1.10 (*m*, 3 H); 0.04 (*s*, Me_3Si). ^{13}C-NMR (75.5 MHz): 217.3 (C(1)); 146.1 (C(3a)); 144.3; 133.1; 117.9; 60.5 (C(7a)); 40.7 (C(2)); 33.0; 27.9; 26.9, 22.0; −1.3. MS: 234 (29, $M^{+\cdot}$), 233 (15), 220 (19), 219 (100), 206 (35), 191 (15), 177 (25), 145 (26), 132 (26), 117 (11), 104 (38), 91 (27), 75 (20), 73 (97). Anal. calc. for $C_{14}H_{22}OSi$: C 71.33, H 9.46; found: C 71.44, H 9.45.

*7a-Ethenyl-1,4,5,6,7,7a-hexahydro-2*H*-inden-1-one* (**2b**). Yield 44%. B.p. 100°/0.1 Torr. R_f 0.33 (hexane/AcOEt 8:1). IR: 3050*w*, 2934*s*, 2857*m*, 1748*s*, 1649*w*, 1628*m*, 1445*m*, 1402*m*, 1321*w*, 1260*m*, 1192*m*, 1154*m*, 1127*m*, 1061*m*, 1005*m*, 992*m*, 976*m*, 920*m*, 866*w*, 841*w*, 797*m*, 689*m*, 652*m*, 635*m*. ^{1}H-NMR (300 MHz): 5.77 (*d*, *J* = 1.9, H–C(3)); 5.67 (*dd*, *J* = 17.5, 10.3, H–C(8)); 5.24 (*d*, *J* = 10.2, H_E–C(9)); 5.07 (*d*, *J* = 17.0, H_Z–C(9)); 3.00

(*ddd, J* = 22.7, 4.4, 1.3, 1 H–C(2)); 2.72 (*dt, J* = 22.6, 2.3, 1 H–C(2)); 2.37–2.30 (*m*, H–C(7)); 2.20–2.04 (*m*, 2 H–C(4)); 1.82–1.64 (*m*, 2 H); 1.55–1.10 (*m*, 3 H). MS: 162 (21, $M^{+\cdot}$), 134 (38), 119 (27), 106 (25), 105 (30), 93 (11), 92 (41), 91 (100), 79 (17), 78 (17), 77 (20), 65 (12), 51 (13), 41 (18), 39 (23), 32 (12). HR-MS: 162.1048 ($C_{11}H_{14}O$, calc. 162.1045).

*1,4,5,6,7,7a-Hexahydro-7a-(1'-methylethenyl)-2*H*-inden-1-one* (**2c**). Yield 16%. B.p. 40°/0.05 Torr. R_f 0.38 (hexane/AcOEt 8:1). IR: 3050*w*, 2932*s*, 2857*m*, 1740*s*, 1649*w*, 1632*m*, 1445*m*, 1404*w*, 1374*w*, 1321*w*, 1264*m*, 1204*w*, 1173*w*, 1150*w*, 1127*m*, 1073*w*, 1059*w*, 978*m*, 922*w*, 897*m*, 801*w*, 706*w*, 683*w*, 625*m*. ^{1}H-NMR (300 MHz): 5.76 (*t, J* = 1.8, H–C(3)); 5.03 (*s*, 1 H, CH_2=C(Me)); 4.85 (*s*, 1 H, CH_2=C(Me)); 3.00 (*ddd, J* = 22.5, 4.4, 1.6, C(2)); 2.71 (*dt, J* = 22.5, 2.3, H–C(2)); 2.33 (br. *s*, 1 H); 2.29 (br. *s*, 1 H); 2.16 (*m*, 1 H); 1.78 (*s*, CH_3); 1.65 (*m*, 1 H); 1.42–1.12 (*m*, 4 H). MS: 176 (58, $M^{+\cdot}$), 149 (11), 148 (87), 134 (18), 133 (100), 120 (32), 119 (44), 107 (12), 106 (52), 105 (96), 92 (13), 91 (75). Anal. calc. for $C_{12}H_{16}O$: C 81.77, H 9.15; found: C 81.76, H 9.20.

*(E)-1,4,5,6,7,7a-Hexahydro-7a-(2-propenyl)-2*H*-inden-1-one* (**2d**). Yield 61%. B.p. 61°/0.4 Torr. R_f 0.29 (hexane/AcOEt 8:1). IR: 3020*w*, 2932*s*, 2855*m*, 1744*s*, 1649*w*, 1445*w*, 1404*m*, 1323*w*, 1260*m*, 1190*w*, 1156*w*, 1129*w*, 1061*w*, 976*m*, 932*w*, 797*m*. ^{1}H-NMR (300 MHz): 5.69 (*d, J* = 1.8, H–C(3)); 5.43 (*dq, J* = 15.6, 6.3, MeC*H*=CH); 5.25 (*dd, J* = 15.5, 1.1, MeCH=C*H*); 2.96 (*ddd, J* = 22.4, 4.3, 1.6, 1 H–C(2)); 2.68 (*dt, J* = 22.5, 2.3, 1 H–C(2)); 2.27 (*m*, 1 H); 2.13 (*m*, 1 H); 1.97 (br. *d, J* = 12.7, 1 H); 1.79–1.13 (*m*, 5 H); 1.66 (*dd, J* = 6.0, 1.1, Me). MS: 176 (37, $M^{+\cdot}$), 149 (10), 148 (76), 133 (53), 120 (19), 119 (54), 106 (43), 105 (63), 92 (15), 91 (100), 79 (11). HR-MS: 176.1198 ($C_{12}H_{16}O$, calc. 176.1201). Anal. calc. for $C_{12}H_{16}O$: C 81.77, H 9.15; found: C 82.08, H 9.36.

*(E)-1,4,5,6,7,7a-Hexahydro-7a-(2-phenylethenyl)-2*H*-inden-1-one* (**2e**). Yield 65%. B.p. 120°/0.1 Torr. R_f 0.29 (hexane/AcOEt 8:1). IR: 3058*w*, 3025*w*, 2932*s*, 2855*m*, 1743*s*, 1692*w*, 1653*w*, 1611*w*, 1576*w*, 1495*w*, 1447*m*, 1402*w*, 1262*m*, 1204*w*, 1183*w*, 1154*w*, 1129*w*, 1067*w*, 970*m*, 951*w*, 916*w*, 799*m*, 747*s*, 693*m*. ^{1}H-NMR (300 MHz): 7.41–7.20 (*m*, Ph); 6.34 (*d, J* = 16.2, PhC*H*=CH); 6.06 (*d, J* = 16.2, PhCH=C*H*); 5.85 (*t, J* = 1.8, H–C(3)); 3.07 (*ddd, J* = 22.5, 4.5, 1.5, H–C(2)); 2.77 (*dt, J* = 22.5, 2.4, 1 H–C(2)); 2.43–2.15 (*m*, 2 H–C(4), H–C(7)); 1.86–1.21 (*m*, 2 H–C(5), 2 H–C(6), H–C(7)). MS: 238 (32, $M^{+\cdot}$), 21 (16), 210 (100), 197 (10), 196 (63), 195 (10), 182 (12), 181 (16), 169 (11), 168 (53), 167 (51), 119 (63), 118 (19), 91 (57), 86 (35), 84 (56), 51 (23), 49 (70). HR-MS: 238.1357 ($C_{17}H_{18}O$, calc. 238.1358). Anal. calc. for $C_{17}H_{18}O$: C 85.67, H 7.61; found: C 85.64, H 7.67.

trans-*1,4,5,6,7,7a-Hexahydro-2-phenyl-7a-[2'-(trimethylsilyl)ethenyl]-2*H*-inden-1-one* (*trans*-**2i**). R_f 0.30 (hexane/Et_2O 8:1). IR: 3031*w*, 2932*s*, 2855*m*, 1746*s*, 1649*w*, 1601*m*, 1493*m*, 1447*m*, 1318*w*, 1248*s*, 1225*w*, 1179*w*, 1127*w*, 1059*w*, 1030*w*, 995*m*, 939*w*, 889*m*, 862*s*, 839*s*, 765*w*, 721*m*, 696*s*. ^{1}H-NMR (300 MHz): 7.34–7.19 (*m*, Ph); 5.99 (*t, J* = 2.0, H–C(3)); 5.78 (*s*, Me_3SiCH=C*H*); 4.01 (*t, J* = 2.3, H–C(2)); 2.45 (*m*, 1 H); 2.36–2.25 (*m*, 1 H); 2.15 (*m*, 1 H); 1.87 (*m*, 1 H); 1.70–1.23 (*m*, 4 H); −0.04 (*s*, Me_3Si). MS: 311 (20, $M^{+\cdot}$ + 1), 310 (75, $M^{+\cdot}$), 295 (28), 282 (14), 221 (10), 220 (13), 219 (59), 209 (45), 208 (72), 203 (20), 180 (15), 167 (20), 132 (13), 91 (9), 73 (100). HR-MS: 310.1747 ($C_{20}H_{26}OSi$, calc. 310.1751).

cis-*1,4,5,6,7,7a-Hexahydro-2-phenyl-7a-[2'-(trimethylsilyl)ethenyl]-2*H*-inden-1-one* (*cis*-**2i**). R_f 0.34 (hexane/Et_2O 20:1). IR: 2940*s*, 2855*m*, 1740*s*, 1605*s*, 1495*w*, 1450*m*, 1260*m*, 1250*s*, 1220*w*, 1180*w*, 1150*w*, 1130*w*, 1090*m*, 1070*m*, 1060*m*, 1030*m*. ^{1}H-NMR (300 MHz): 7.46–7.17 (*m*, Ph); 5.91 (*t, J* = 1.7, H–C(3)); 5.90 (*d, J* = 18.8, Me_3SiCH=CH); 5.85 (*d, J* = 18.8, Me_3SiCH=C*H*); 4.20 (*dd, J* = 1.2, 4.2, H–C(2)); 2.42 (*m*, 1 H); 2.25 (*m*, 1 H); 2.15 (br. *d, J* = 6.2, 1 H); 1.9 (*m*, 1 H); 1.7 (*m*, 1 H); 1.55–1.25 (*m*, 3 H); 0.09 (*s*, Me_3Si).

trans-*7a-Ethenyl-1,4,5,6,7,7a-hexahydro-2-phenyl-2*H*-inden-1-one* (*trans*-**2j**). R_f 0.30 (hexane/AcOEt 8:1). IR: 3031*w*, 2936*s*, 2859*m*, 1746*s*, 1630*w*, 1601*w*, 1495*m*, 1449*m*, 1061*w*, 1032*w*, 995*w*, 930*w*, 862*m*, 841*w*, 818*w*, 766*w*, 723*m*, 696*s*. ^{1}H-NMR (300 MHz): 7.31–7.20 (*m*, Ph); 5.98 (*t, J* = 2.1, H–C(3)); 5.67 (*dd, J* = 17.4, 10.5, CH_2=C*H*), 5.19 (*d, J* = 18.1, H_Z–C(9)); 5.09 (*d, J* = 10.2, H_E–C(9)); 4.05 (*t, J* = 2.4, H–C(2)); 2.46 (*m*, 1 H); 2.42–2.25 (*m*, 1 H); 2.13 (*m*, 1 H); 1.88 (*m*, 1 H); 1.71–1.25 (*m*, 4 H). MS: 238 (15, $M^{+\cdot}$), 211 (17), 210 (100), 196 (44), 181 (14), 168 (40), 167 (42), 120 (13), 119 (51), 118 (14), 91 (43). HR-MS: 238.1355 ($C_{17}H_{18}O$, calc. 238.1358).

REFERENCES

[1] L. M. Jackman, S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', 2nd edn., Pergamon Press, Oxford, 1969, pp. 94–98.

[2] R. B. Woodward, R. Hoffmann, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1971, pp. 38–64.

[3] M. Hanack, H.-J. Schneider, *Angew. Chem., Int. Ed.* **1967**, *6*, 666.

[4] a) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', 2nd edn., Cornell University Press, Ithaca, 1969, pp. 724–730; b) Y. Pocker in 'Molecular Rearrangements', Ed. P. de Mayo, Interscience, New York, 1963, Vol. 1, pp. 15–25.

[5] a) G. Piancatelli, A. Scettri, S. Barbadoro, *Tetrahedron Lett.* **1976**, 3555; b) G. Piancatelli, A. Scettri, *ibid.* **1977**, 1131; c) G. Piancatelli, A. Scettri, *Tetrahedron* **1977**, *33*, 69; d) G. Piancatelli, A. Scettri, G. David, M. D'Aunia, *ibid.* **1978**, *34*, 2775; e) G. Piancatelli, *Heterocycles* **1982**, *19*, 1735; f) E. Castagnino, M. D'Auria, A. DeMico, F. D'Onofrio, G. Piancatelli, *J. Chem. Soc., Chem. Commun.* **1987**, 907.

[6] a) S. Hirano, S. Takagi, T. Hiyama, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 169; b) C. W. Shoppee, B. J. A. Cooke, *J. Chem. Soc., Perkin Trans. 1* **1972**, 2271.

[7] a) R. Noyori, Y. Onishi, M. Kato, *J. Am. Chem. Soc.* **1972**, *94*, 5105; b) R. Noyori, Y. Onishi, M. Kato, *ibid.* **1975**, *97*, 928.

[8] G. Ohloff, K. H. Schulte-Elte, E. Demole, *Helv. Chim. Acta* **1971**, *54*, 2913.

[9] M. R. Peel, C. R. Johnson, *Tetrahedron Lett.* **1986**, *27*, 5947.

[10] a) W. E. Bachmann, J. W. Ferguson, *J. Am. Chem. Soc.* **1934**, *56*, 2081; b) J. R. Owen, W. H. Saunders, *ibid.* **1966**, *88*, 5809; c) R. L. Heidke, W. H. Saunders, *ibid.* **1966**, *88*, 5816.

[11] a) P. R. Story, B. C. Clark, in 'Carbonium Ions', Eds. G. A. Olah and P. v. R. Schleyer, Wiley, New York, 1972, Vol. III, Chapt. 23; b) K. B. Wiberg, A. H. Hess, A. J. Ashe, in 'Carbonium Ions', Eds. G. A. Olah and P. v. R. Schleyer, Wiley, New York, 1972, Vol. III, Chapt. 26; c) M. Saunders, J. Chandrasekhar, P. v. R. Schleyer, in 'Rearrangements in Ground and Excited States', Ed. P. de Mayo, Academic Press, New York, 1980, Vol. 1, pp. 1–53; d) P. Ahlberg, G. Jonsall, C. Engdahl, *Adv. Phys. Org. Chem.* **1983**, *19*, 223.

[12] K. L. Servis, J. D. Roberts, *J. Am. Chem. Soc.* **1965**, *87*, 1331.

[13] R. L. Danheiser, D. M. Fink, *Tetrahedron Lett.* **1985**, *26*, 2513.

[14] a) Y. Apeloig, A. Stanger, *J. Am. Chem. Soc.* **1985**, *107*, 2806; b) G. A. Olah, A. L. Berrier, L. D. Field, G. K. S. Prakash, *ibid.* **1982**, *104*, 1349; c) A. C. Hopkinson, M. H. Lien, *J. Org. Chem.* **1981**, *46*, 998.

[15] A. W. P. Jarvie, *Organomet. Chem. Rev. A* **1970**, *6*, 153.

[16] a) S. E. Denmark, K. L. Habermas, G. A. Hite, T. K. Jones, *Tetrahedron* **1986**, *42*, 2821; b) I. U. Khand, P. L. Pauson, *J. Chem. Res. (S)* **1977**, 9.

[17] a) I. R. Robertson, J. T. Sharp, *Tetrahedron* **1984**, *40*, 3095; b) R. A. S. Chandraratna, A. L. Bayerque, W. H. Okamura, *J. Am. Chem. Soc.* **1983**, *105*, 3588.