ISSN 0018-019X

Erscheint 9mal jährlich - Paraît 9 fois par an

236. Silicon-Directed *Nazarov* Reactions II. Preparation and Cyclization of β-Silyl-substituted Divinyl Ketones

by **Todd K. Jones** and **Scott E. Denmark***

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, IL 61801

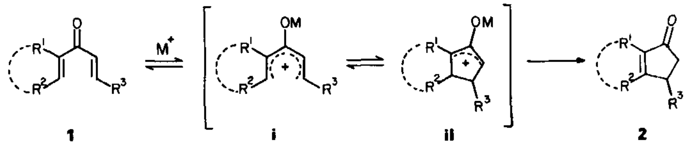
(27.VI.83)

Summary

Two general methods for the preparation of β-silyl-substituted divinyl ketones have been developed starting from either α,β-unsaturated aldehydes or simple ketones. Anhydrous $FeCl_3$ induces the cyclization to cyclopentenones under mild conditions and in good yields with predictable and complete control over the position of the double bond in the five-membered ring. The observed effects of substituents on rate can be explained by a rate-determining cationic electrocyclization. Silyl substitution has been shown to retard the reaction.

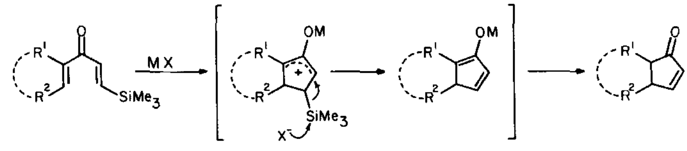
Introduction. - The incorporation into organic synthesis of reagents and methods based on organosilicon chemistry has been an area of enormous activity over the last 10-15 years [1]. The ability of silicon (suitably placed) to stabilize organic reactive intermediates has been put to good use to develop solutions to difficult or low yielding transformations. Of the two most important properties (stabilization of α-anions and β-cations) it is the latter, commonly termed the β-effect, [2] which has dominated the application of organosilicon-based methodology in synthesis [3]. As part of a program on the use of Si to control and direct electrocyclic reactions of cations [4] we selected, as point of entry, the well-known *Nazarov* cyclization [5] [40] *(Scheme 1)*.

Scheme 1



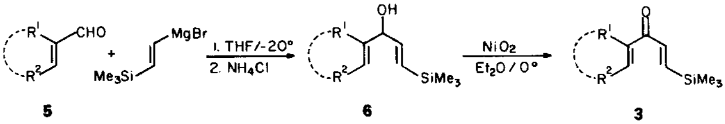
Treatment of divinyl ketones, **1**, (or their equivalent) with protic [6a-c] or *Lewis* acids [6d,c] results in the formation of cyclopentenones **2** in moderate yields. While it is clear that the bulk of the charge in cations **i** resides on the O-atom, nonetheless they behave like oxypentadienylic cations and undergo conrotatory cyclization [7] [8] to cyclopentenylic cations **ii**. It is here where problems with the *Nazarov* reaction arise; hydride and alkyl migrations have been observed [6c,e] [9]

Scheme 2



and the loss of a proton is unselective resulting in mixtures of olefin isomers. We reasoned that strategic placement of a silyl group as shown in *Scheme 2* could provide a solution to these problems¹). Thus, cyclization of β-silyl-substituted divinyl ketones, **3**, should produce cyclopentenylic cation **iii** wherein it was hoped that the rapid loss of the silicon electrofuge followed by protonation of the resulting enolate **iv** would produce a different cyclopentenone **4**. The advantages of such a process are *1*) suppression of undesirable side reactions, *2*) production of the thermodynamically less stable double-bond isomer, *3*) introduction of functionality based on the double bond, and *4*) potential iterative nature of the annelation. Despite the considerable effort in the development of penta-annelation methods [11] there still exists a need for reactions which not only create a five-membered ring, but also exercise regiocontrol in the introduction of functionality and stereocontrol in the formation of new chiral centers associated with the annelation process²). We recently communicated [13] the successful realization of the reaction in *Scheme 2* and elaborate in this paper the preparation and cyclization of ketones **3**. In the accompanying paper³), we describe experiments which defined the stereochemical course of the cyclization and which provided insights into the nature of intermediates **iii** and **iv**.

Scheme 3



Preparation of β-Silyl-substituted Divinyl Ketones. – 1. From Enals. – In our earlier communication the only method described for the preparation of β-silyl-substituted divinyl ketones **3** was that shown in *Scheme 3*. This method is very reliable and gives good yields (39–85%). The diallyl alcohols **6** are stable to chromatography (silica gel) and distillation, and should be purified for best results in the oxidation. *Table 1* summarizes the yields for the ketones **3** that we have prepared by this method. The stereochemistry at the silyl-substituted double bond was in each case >90% (*E*) by GC and ^{1}H-NMR analysis. This reflects the ratio of isomers

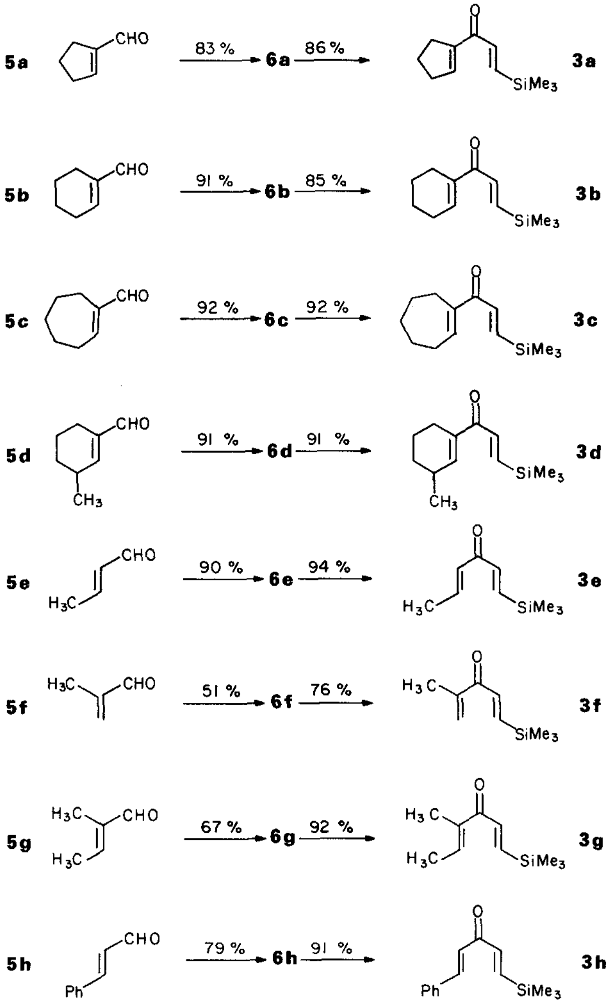
---

¹) A similar rationale has led to the development of a S-substituted penta-annelation procedure [10].

²) Indeed, *Heathcock et al.* has recently pointed out that of the four conceptual approaches to the hydroazulene skeleton of pseudoguaianolides there are not examples which employ a penta-annelation method [12].

³) *T. K. Jones & S. E. Denmark*, following paper in this issue.

Table 1. *Divinyl Ketones from Enals*



in the readily available reagent (*E*)-(2-bromoethenyl)trimethylsilane[4]) [14]. The only limitation in this approach is the availability of enals. Preliminary experiments using α,β-unsaturated acids and acid chlorides with the corresponding Li- [15] and Cd-reagents [16] suggested little hope for this route[5]). Thus, we explored an alternative bond-connection scheme.

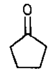
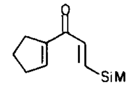
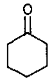
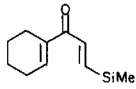
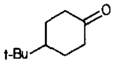
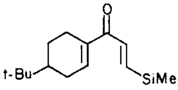
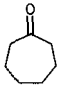
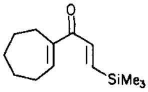
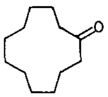
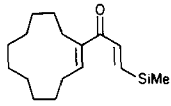
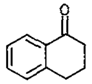
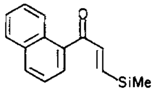
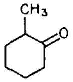
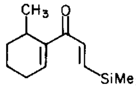
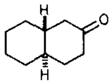
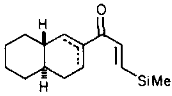
---

[4]) GC analysis (Column A (see *Exper. Part*), 35°, isothermal) indicated as much as 13% of the (*Z*)-isomer was present.

[5]) Based on *Calas'* observation that ketones, 3, can be formed from the appropriate acid chlorides and 1,2-bis(trimethylsilyl)ethene, we explored unsuccessfully, the possibility of a one-pot annelation procedure [17]. *J. P. Germanas*, unpublished results from these laboratories.

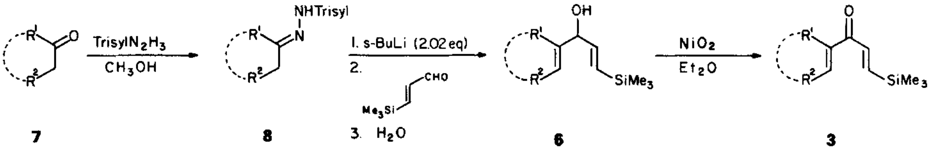
2. From Ketones. – The second method involved formation of the other olefin-carbonyl bond by way of a *Shapiro* reaction [18]. We employed the modification of *Bond et al.* [19] in the use of (2,4,6-triisopropylbenzenesulfonyl)hydrazones. Two advantages of this modification are noteworthy: *1*) stoichiometric amounts of Li-base and electrophile can be used and *2*) trisylhydrazone dianions decompose at lower temperatures (–20° → 0 °C) than do their Ts-counterparts. Thus, we successfully employed 2.02 equiv. of *s*-BuLi (*n*-BuLi doesn't work) in hexane/TMEDA 1:1 to generate the vinyl anion, followed by addition of (*E*)-3-(trimethyl-

Table 2. *Cyclic Divinyl Ketones from Ketones*a)

7a		62 % →	22 % →	86 % →		**3a**
7b		80 % →	69 % →	85 % →		**3b**
7i		83 % →	78 % →	100 % →		**3i**
7c		85 % →	66 % →	97 % →		**3c**
7j		85 % →	72 % →	78 % →		**3j**
7k		94 % →	86 % →	78 % →		**3k**
7l		84 % →	73 % →	80 % →		**3l**
7m		35 % →	53 % →	58 % →		**3m**b)

a) Yields for conversion ketones **7** to hydrazones **8** to alcohols **6** to dienones **3**.
b) An inseparable 2:1 mixture of isomers.

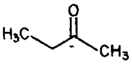
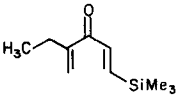
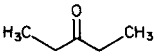
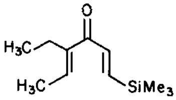
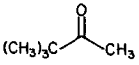
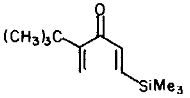
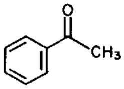
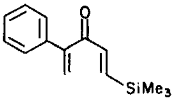
Scheme 4



silyl)propenal [20] to produce the familiar alcohols **6** which were smoothly oxidized with NiO_2 as before (*Scheme 4*). *Tables 2* and *3* summarize the yields for each step in the preparation of 12 divinyl ketones by this route. The procedure works well for both cyclic (*Table 2*) and acyclic (*Table 3*) ketones (42-65% overall) with the exceptions of cyclopentanone (unstable vinyl anion), 2-decalone (unstable hydrazone), and acetophenone (alcohol **6q** polymerized upon oxidation). The *Shapiro* reaction offers the additional advantage of regiocontrol in the formation of the vinyl anion with unsymmetrically substituted ketones **7l-n**[6]). A third, as yet unexplored approach involves the Pd-catalyzed carbonylation of iodoalkenes [22].

Cyclization of Ketones 3. - In addition to the *Lewis* acids examined in our earlier report ($AlCl_3$, $BF_3 \cdot OEt_2$, $SnCl_4$, $TiCl_4$, $ZnCl_2$, Me_3SiOTF, Me_3SiI) we have

Table 3. *Acyclic Divinyl Ketones from Ketones*

7n		80 %	90 %	84 %		**3n**
7o		59 %	73 %	93 %		**3o**
7p		83 %	72 %	84 %		**3p**
7q		69 %	70 %	17 %		**3q**

---

[6]) The minimal regiocontrol in the formation of the vinyl lithium species from *trans*-2-decalone is surprising [21].

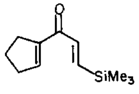
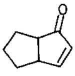
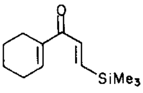
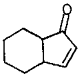
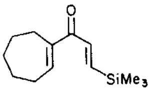
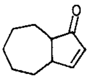
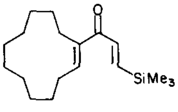
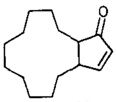
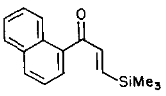
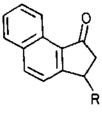
Table 4. *Effects of Varying Amounts of* $FeCl_3$ *on the Cyclization of* **3b**[a])

Equiv. $FeCl_3$ (based on **3b**)	Temp. [°C]	Time [h]	Comments
2.0	0°	3	complete
1.05	0°	4	84% yield
0.4	0°	1.5	no reaction
0.4	20°	1.5	78% yield
0.5	0°	1.0	no reaction
0.5	20°	1.0	84% yield
0.1	0°	0.5	no reaction
0.1	20°	days	incomplete

[a]) All reactions were done in CH_2Cl_2, 0.08 M in **3b**.

tested CuCl, $AgBF_4$ and $Ce(NH_4)_2(SO_4)_3$, which were essentially ineffective in producing a reaction. The reagent of choice is by far anhydrous $FeCl_3$ (*Aldrich* or *Alfa* 98%) in dry CH_2Cl_2 or dichloroethane[7]). In all experiments 1.05 equiv. of $FeCl_3$ were used. We have briefly examined the effects of varying amounts of $FeCl_3$ on the reaction. The results, summarized in *Table 4*, show that as little as 0.4 equiv.

Table 5. *Cyclization of Cyclic Divinyl Ketones* **3**[a])

Substrate	Solvent	Time [h]	Temp. [°C]	Product	*cis/trans*	Yield [%]
3a 	$(CH_2Cl)_2$	2.5	20	 **4a**	100/0	52
3b 	CH_2Cl_2	4	0	 **4b**	100/0	84
3c 	CH_2Cl_2	1	0	 **4c**	85/15	74
3j 	CH_2Cl_2	2	0	 **4j**	46/54	78
3k 						
	$(CH_2Cl)_2$	12	20	**4k′** R = $SiMe_3$		70
	toluene	48	20	**4k** R = H		60

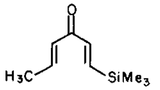
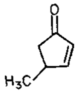
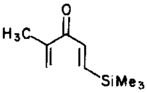
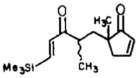
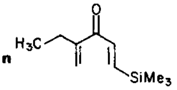
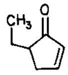
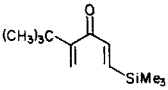
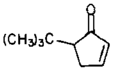
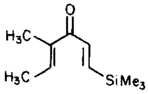
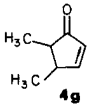
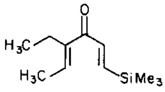
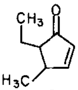
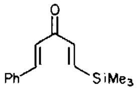
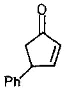
[a]) All reactions were 0.08 M in ketone.

---

[7]) $CHCl_3$ and toluene can be used with some success. CCl_4, trichloroethylene, chlorobenzene and nitromethane are unsatisfactory.

of reagent were sufficient to bring about complete reaction albeit at reduced rate while 0.1 equiv. were not. To simplify discussion of the results we have divided the experiments into three structural categories, *1*) simple cyclic systems, *2*) acyclic systems and *3*) cyclic systems with chiral centers. The third category is discussed in the accompanying paper. Simple cyclic systems *(Table 5)* reacted under mild conditions to give good yields of 4,5-annelated-2-cyclopentenones uncontaminated by double-bond isomers (GC analysis). In general the *cis*-ring-fusion isomer is formed to an extent greater than that found at equilibrium[8]). Ketone **3k** provides

Table 6. *Cyclization of Acyclic Divinyl Ketones* **3**[a])

Substrate		Solvent	Time [h]	Temp. [°C]	Product		*cis/trans*	Yield [%]
3e		CH_2Cl_2	12	20		**4e**	–	54
3f		CH_2Cl_2	6	-20		**4f**		42
3n		CH_2Cl_2	2	0		**4n**	–	–[b])
		0.02M	8	0			–	33
		0.004M	48	0			–	51
3p		CH_2Cl_2	1	0		**4p**	–	97
3g		CH_2Cl_2	0.5	-10		**4g**	59/41	95
3o		CH_2Cl_2	1	0		**4o**	43/57	70
3h		toluene	12	20		**4h**	–	27

[a]) All reactions were 0.08 M in ketone unless otherwise noted.

[b]) Only dimers were detected.

---

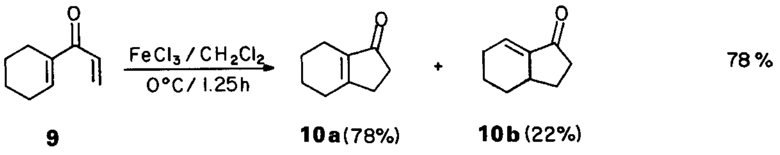
[8]) This was vigorously proven only for **4j** where ring fusion epimerization was possible directly on the enone (100% *trans* at equilibrium). Enones **4b** and **4c** had to be hydrogenated prior to equilibration to obviate rapid shifting of the double bond. Equilibrium ratios for saturated ketones: H_2-**4b** (*cis/trans* 75:25), H_2-**4c** (*cis/trans* 24:76).

an example of the competitive loss of a proton from intermediate **iii** *(Scheme 2)*, obviously tempered by the rearomatization energy of the naphthalene nucleus.

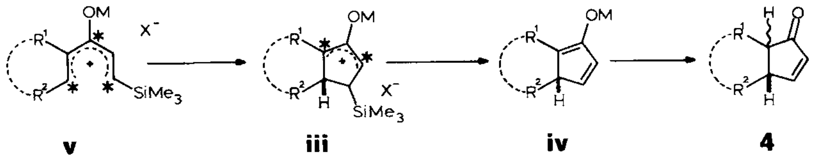
The ability to produce 4- and 5-substituted 2-cyclopentenones is another advantage of this method. This is a difficult process which succeeds only in highly substituted cases under classical conditions or not at all with more modern variants. *Table 6* summarizes our results to date. The yields are good, and in some cases, excellent. Reaction rate varies markedly: α- (**3f, n, p**) or α,β- (**3g, o**) substituted systems reacting much faster than β- (**3e, h**) substituted only. In α-substituted ketones **3f** and **3n** a competing *Michael* addition consumed starting materials faster than cyclization to produce dimers (*e.g.* **4f**). In the case of **3n**, however, we could suppress dimerization by dilution and obtain **4n** in 51% yield. Further dilution led to impractically slow reactions. Dimerization was also inhibited by steric hindrance in the 5-position as demonstrated by the remarkably successful production of 5-*tert*-butyl-2-cyclopentenone **4p** in 97% yield. 4,5-Disubstituted systems were produced in very good yield with a surplus of the *cis*-isomer with respect to equilibrium composition⁹).

The striking success of $FeCl_3$ in inducing the cyclization made us wonder whether the silicon was necessary at all. We therefore prepared the Si-free substrate **9** by standard procedures and subjected it to the usual reaction conditions¹⁰). Within the limits of GC detection, none of the indenone **4b** was formed, but instead a 78:22 mixture of tetra- and trisubstituted isomers (**10a** and **10b**) in 78% yield *(Scheme 5)*. Further, it was demonstrated that **4b** is indeed stable under the reaction conditions by its recovery in 97% yield.

Scheme 5



Scheme 6



---

⁹) Equilibrium ratios: **4q** (*cis/trans* 10:90), **4o** (*cis/trans* 4:96).

¹⁰) *J. D. Clark*, unpublished observations in these laboratories.

Discussion. – It is interesting to note that the rate of undirected cyclization (0 °C/1.25 h) is *greater* than the Si-directed reaction (0 °C/4 h) under identical conditions. While this behavior appears contradictory at first glance it is consistent with the mechanism shown in *Scheme 6* wherein the conrotatory cyclization of the pentadienylic cation is the rate-determining step and subsequent loss of the electrofuge (R_3Si^+ or H^+) is rapid [23]. This hypothesis explains the observed substituent effects in the acyclic systems. In the cyclization, positive charge is transferred from the positions marked with asterisks in the pentadienylic cation **v** to those similarly marked in the cyclopentenylic cation **iii**. Substituents in the β-position which stabilize positive charge (R^2 = alkyl, phenyl) will selectively stabilize the educt cation and thus raise the activation energy. Contrariwise, cation-stabilizing substituents in the α-position (R^1 = alkyl) selectively stabilize the product cation (and to whatever extent this effect is present in the transition state) thereby lowering the transition state energy resulting in rapid reactions. The observed rate depression resulting from β-silyl substitution may be due to steric and/or electronic effects. We have observed that increasing the size of ligands on silicon dramatically decreases the reaction rate. Further, if the cyclization is the rate-determining step, then the concentration of the [divinyl ketone · $FeCl_3$] complex is important. The well-documented destabilization of adjacent cationic charge by silicon [24] (*cf.* cation **v**) may act to decrease the equilibrium concentration of reactive complexes[11]).

Also illustrated in *Scheme 6* is a simple, steric-approach-based explanation for the production of *cis*-fused and *cis*-substituted cyclopentenones. Clearly a proton will (kinetically) prefer to approach the cross-conjugated dienolate **iv** from the face containing a H-atom rather than a substituent or ring residue R^2.

The modified *Nazarov* reaction described herein appears to have general utility in the annelation and construction of cyclopentenones. The versatility in preparation of precursors, mildness of conditions and predictability of regiochemical outcome make this a very attractive reaction for use in cyclopentanoid natural product synthesis. Detailed discussion of secondary stereochemical control and the nature of proposed intermediates is found in the accompanying paper.

Acknowledgment is made to the donors of the *Petroleum Research Fund*, administered by the *American Chemical Society* for support of this research. This work was supported in part by the University of Illinois *NSF* Regional Instrumentation Facility (*NSF* CHE 79-16100). High-resolution and gas chromatographic mass spectra were obtained in the Mass Spectrometry Laboratory, University of Illinois, supported in part by a grant from the *National Institutes of General Medical Sciences* (GM 27029). *T.K.J.* thanks the University of Illinois for a Fellowship.

Experimental Part

1. General. – Melting points (m.p.) were determined on a *Thomas-Hoover* capillary melting point apparatus and are corrected. Bulb-to-bulb distillations were done on a *Buchi GKR-50* Kugelrohr, boiling points (b.p.) refer to air bath temperatures and are uncorrected. Analytical TLC was performed on *Merck* silica gel plates with *QF-254* indicator. Visualization was accomplished with UV light,

---

[11]) If the cationic complex **v** is formed *irreversibly*, this hypothesis would predict an *enhanced* reaction rate for the β-silyl-substituted systems.

phosphomolybdic acid, I_2, H_2SO_4 and/or 2,4-DNP solution. R_f-data is given in the following solvent systems hexane/EtOAc or pentane/Et_2O. Column chromatography was performed by the method of *Still* [25] (32–36-μm silica gel, woelm) or *Taber* [26] (*Merck*, TLC alumina). Anal. GC was performed on a *Varian 3700* chromatograph fitted with a flame ionization detector. (N_2 carrier gas for packed columns (30 ml/min), H_2 for capillary column (1 ml/min)). Columns: A) 11% QF-1 on *60-80 Chromosorb G* (6 ft. × ⅛ in.), B) 10 or 23 m *OV-101 WCOT*, split ratio 30:1. Retention times (t_R) and integrals were obtained from a *Hewlett Packard 3390* recorder. High-performance liquid chromatography (HPLC) was performed on a *Perkin-Elmer* Series 1 chromatograph with a *Perkin-Elmer LC-75* detector using a 25 × 4.5 mm column of silica gel (5 μM). THF and Et_2O were distilled from sodium benzophenone. CH_2Cl_2 and dichloroethane were either distilled from CaH_2 or passed through basic *Alox* activity I prior to use. Benzene, toluene, hexane and tetramethylethylene diamine (TMEDA) were distilled from CaH_2. MeOH was distilled from $Mg(OCH_3)_2$. *n*BuLi and *s*-BuLi were titrated by the method of *Gilman*. Nickel peroxide was prepared and titrated according to *Nakata* [27]. Anh. 98% $FeCl_3$ was used as supplied by *Aldrich* or *Alfa*. All other chemicals were used as obtained or purified by distillation as needed. All reactions were performed in oven (140°) or flame dried glassware under an atmosphere of dry N_2. IR spectra were obtained on either a *Perkin-Elmer 237B* or a *Nicolet 7199C FT* IR spectrophotometer in $CHCl_3$-solutions unless otherwise stated. Peaks are reported in cm^{-1} with the following relative intensities: *s* (strong, 66–100%), *m* (medium 33–66%), *w* (weak, 0–33%). ^1H-NMR spectra were recorded on either *Varian EM-390* (90 MHz), *HR-220* (220 MHz) or *Nicolet NTC-360* (360 MHz) spectrometers in $CDCl_3$ with $CHCl_3$ as an internal standard (δ 7.26) unless otherwise stated. Chemical shifts are given in ppm (δ); multiplicities indicated by *s* (singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *m* (multiplet), br. (broadened). Mass spectra were obtained on a *Varian MAT CH-5* spectrometer with ionization voltages of 10 and 70 eV. Data are reported in the form *m/z* (intensity relative to base = 100). High-resolution mass spectra were obtained on a *Varian MAT-731* spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

2. Starting Materials. – 1-Cyclopentenecarbaldehyde [28], 1-cyclohexenecarbaldehyde [29], 1-cycloheptenecarbaldehyde [19], trisylhydrazine [30], (*E*)-(2-bromoethenyl)trimethylsilane [14], (*E*)-3-trimethylsilylpropenal [20], and 3-methyl-1-cyclohexenecarbaldehyde [31] were prepared by published procedures.

3. Preparation of Diallyl Alcohols 6 from Enals. – *General Procedure.* Mg-powder (1.8 equiv.) and dry THF (1 ml/0.1 g Mg) were placed in a 3-necked flask fitted with a condenser, addition funnel and magnetic stir bar. A solution of (*E*)-(2-bromoethenyl)trimethylsilane (1.8 equiv.) in dry THF (8 ml/g bromide) was added dropwise to the refluxing suspension over 0.5 h. After complete addition the mixture was refluxed 1 h further. The resulting yellow-green solution was cooled to −30° and a solution of the enal (1.0 equiv.) in dry THF (10 ml/g enal) was delivered dropwise through the addition funnel. After stirring for 10 min the colorless mixture is warmed to 0° and quenched with 4% NH_4Cl-solution (20 ml/g bromide). The reaction mixture was extracted with Et_2O (3 × 25 ml/g bromide) and the extracts washed individually with H_2O (30 ml/g bromide) and brine (40 ml/g bromide). The combined Et_2O-layers were dried (K_2CO_3) and evaporated to afford the crude product which was chromatographed on silica gel. Analytical data were obtained from a distilled sample.

*(*E*)-1-(1-Cyclopentenyl)-3-trimethylsilyl-2-propen-1-ol* (**6a**). Yield 83%, b.p. 70°/0.03 Torr, R_f 0.30 (hexane/EtOAc 6:1). IR: 3650*w* (OH), 3050*s*, 3020*m*, 2975*m*, 1600*w* (C=C), 1400*w*, 1225*s*, 1160*w*, 1040*m*, 940*m*. ^1H-NMR (90 MHz): 6.07–5.93 (*m*, 2 H, H–C(2), H–C(3)); 5.67–5.60 (*m*, 1 H, H–C(2')); 4.77–4.67 (*m*, 1 H, H–C(1)); 2.53–2.23 (br. *m*, 4 H, 2 H–C(3') and 2 H–C(5')); 2.13–1.83 (*m*, 2 H, 2 H–C(4')); 1.80–1.60 (br. *m*, 1 H, OH); 0.23 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 196 (2, M^+), 179 (10), 123 (13), 105 (13), 95 (13), 91 (27), 79 (12), 78 (20), *75* (100), 73 (95), 67 (26), 59 (11).

$C_{11}H_{20}OSi$ (196.40) Calc. C 67.28 H 10.27% Found C 66.82 H 9.90%

*(*E*)-1-(1-Cyclohexenyl)-3-trimethylsilyl-2-propen-1-ol* (**6b**). Yield 91%, b.p. 120°/0.05 Torr, R_f 0.32 (hexane/EtOAc 6:1). IR: 3520*m* (OH), 3000*m*, 2940*s*, 2850*m*, 1620*w*, 1220*m*, 1140*w*, 1055*m*, 990*m*. ^1H-NMR (220 MHz): 6.00 (*dd*, *J* = 18.6, 4.4, 1 H, H–C(2)); 5.88 (*d*, *J* = 18.6, 1 H, H–C(3)); 5.69 (br. *m*, 1 H, H–C(2')); 4.42 (*d*, *J* = 4.4, 1 H, H–C(1)); 2.02–1.91 (br. *m*, 4 H, 2 H–C(3') and 2 H–C(6')); 1.65–1.54 (br. *m*, 5 H, 2 H–C(4'), 2 H–C(5') and OH); 0.05 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 210 (3, M^+), 105 (15), 92 (34), 91 (28), 79 (18), 75 (83), *73* (TMS, 100), 67 (16).

$C_{12}H_{22}OSi$ (210.43) Calc. C 68.51 H 10.54% Found C 68.17 H 10.50%

(E)-1-(1-Cycloheptenyl)-3-trimethylsilyl-2-propen-1-ol (**6c**). Yield 92%, b.p. 95°/0.05 Torr, R_f 0.30 (hexane/EtOAc 6:1). IR: 3600*m* (OH), 2930*s*, 2880*m*, 1250*m*, 975*w*, 850*w*. ^{1}H-NMR (220 MHz): 5.98 (*dd*, J= 18.8, 3.4, 1 H, H–C(2)); 5.85 (*d*, J= 18.8, 1 H, H–C(2)); 5.87–5.82 (*m*, 1 H, H–C(2′)); 4.47 (*d*, J= 3.4, 1 H, H–C(1)); 2.14–2.00 (*m*, 4 H, 2 H–C(3′) and 2 H–C(7′)); 1.72–1.65 (*m*, 5 H, 2 H–C(4′), OH and 2 H–C(6′)); 1.49–1.40 (*m*, 2 H, 2 H–C(5′)); 0.04 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 224 (2, M^+), 151 (14), 119 (12), 106 (13), 105 (13), 93 (13), 92 (15), 91 (27), 81 (13), 79 (13), 75 (73), *73* (100), 67 (10), 59 (16), 55 (11).

$C_{13}H_{24}OSi$ (224.46) Calc. C 69.58 H 10.78% Found C 69.18 H 10.71%

(E)-1-(3-Methyl-1-cyclohexenyl)-3-trimethylsilyl-2-propen-1-ol (**6d**). Yield 91%, b.p. 105°/0.02 Torr, R_f 0.32 (hexane/EtOAc 9:1). IR: 3600*w* (OH), 3020*s*, 2940*m*, 2870*w*, 1645*s*, 1532*w*, 1455*w*, 1263*m*, 1250*s*, 1230*s*, 1210*s*, 992*m*. ^{1}H-NMR (220 MHz): 6.02 (*dd*, J= 18.8, 3.4, 1 H, H–C(2)); 5.90 (*d*, J= 18.8, 1 H, H–C(3)); 5.56 (*m*, 1 H, H–C(2′)); 4.45 (*m*, 1 H, H–C(1)); 2.20 (*m*, 1 H, H–C(3′)); 1.93–1.50 (br. *m*, 6 H, 2 H–C(4′), 2 H–C(5′) and 2 H–C(6′)); 1.18–0.97 (*m*, 1 H, OH); 0.98 (*d*, J= 6, 3 H, CH_3–C(3′)); 0.07 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 224 (2, M^+), 119 (24), 105 (12), 95 (34), 91 (21), 81 (13), 75 (61), *73* (100), 59 (17).

$C_{13}H_{24}OSi$ (224.46) Calc. C 69.58 H 10.78% Found C 69.42 H 10.74%

(1E,4E)-1-Trimethylsilyl-1,4-hexadien-3-ol (**6e**). Yield 90%, b.p. 125°/20 Torr, R_f 0.30 (pentane/Et_2O 10:1). IR (neat): 3550 br. *s* (OH), 3100*s*, 3020*m*, 3000*m*, 1655*w*, 1610*m*, 1500*m*, 1420*s*, 1300*m*, 1190*m*, 1100*m*, 1090*m*, 1050*m*, 1020*m*, 975*s*, 950*s*, 910*s*, 850*s*. ^{1}H-NMR (90 MHz): 6.07–5.95 (*m*, 2 H, H–C(1) and H–C(2)); 5.86–5.33 (*m*, 2 H, H–C(4) and H–C(5)); 4.67–4.30 (*m*, 1 H, H–C(3)); 1.76 (*d*, J= 4.0, 3 H, 3 H–C(6)); 1.67 (*s*, 1 H, OH); 0.17 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 170 (0.65, M^+), 155 (14), 79 (16), 78 (32), 75 (81), *73* (100), 59 (13). This alcohol was very unstable. Satisfactory combustion data could not be obtained, it was oxidized immediately after chromatography.

(E)-4-Methyl-1-trimethylsilyl-1,4-pentadien-3-ol (**6f**). Yield 51%. This alcohol was extremely unstable and could not be distilled or stored. It was oxidized immediately after chromatography: ^{1}H-NMR (90 MHz): 6.08–6.02 (*m*, 2 H, H–C(1) and H–C(2)); 5.08 (br. *s*, 1 H, H–C(5)); 4.95 (br. *s*, 1 H, 1 H–C(5)); 4.65–4.57 (br. *m*, 1 H, H–C(3)); 1.87 (br. *s*, 1 H, OH); 1.80 (*s*, 3 H, H_3C–C(4)); 0.20 (*s*, 9 H, $(CH_3)_3Si$).

(1E,4E)-4-Methyl-1-trimethylsilyl-1,4-hexadien-3-ol (**6g**). Yield 67%, b.p. 125°/25 Torr, R_f 0.29 (hexane/EtOAc 6:1). IR: 3600*m* (OH), 2950*m*, 2850*w*, 1600*w*, 1430*w*, 1245*s*, 1175*w*, 1055*m*, 980*m*. ^{1}H-NMR (90 MHz): 6.1–5.96 (*m*, 2 H, H–C(1) and H–C(2)); 5.86–5.43 (*m*, 1 H, H–C(5′)); 4.59 (br. *s*, 1 H, H–C(3)); 1.74 (br. *s*, 1 H, OH); 1.65 (br. *s*, 6 H, CH_3–C(4) and 3 H–C(6)); 0.17 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 184 (1, M^+), 169 (13), 153 (10), 111 (15), 85 (18), 79 (48), 75 (89), *73* (100), 59 (10).

$C_{10}H_{20}OSi$ (184.39) Calc. C 65.15 H 10.94% Found C 65.32 H 10.72%

(1E,4E)-5-Phenyl-1-trimethylsilyl-1,4-pentadien-3-ol (**6h**). Yield 79%, b.p. 155°/0.09 Torr, R_f 0.30 (hexane/EtOAc 5:1). IR: 3650*w* (OH), 3000*w*, 2950*m*, 2880*w*, 1650*m*, 1600*w*, 1500*w*, 1480*w*, 1240*w*, 1100*m*, 1050*m*, 970*s*, 945*s*, 845*s*. ^{1}H-NMR (220 MHz): 7.45–7.26 (*m*, 5 H, arom. H); 6.63 (*d*, J= 15.9, 1 H, H–C(5)); 6.24 (*dd*, J= 15.9, 6.5, 1 H, H–C(4)); 6.12 (*dd*, J= 19.5, 4.5, 1 H, H–C(2)); 6.04 (*d*, J= 19.5, 1 H, H–C(1)); 4.77 (*m*, 1 H, H–C(3)); 1.54 (*m*, 1 H, OH); 0.12 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 232 (3, M^+), 160 (15), 159 (12), 143 (21), 142 (18), 116 (20), 92 (14), 76 (42), *74* (100), 60 (10).

$C_{14}H_{20}OSi$ (232.43) Calc. C 72.36 H 8.67% Found C 72.49 H 8.43%

1-(1-Cyclohexenyl)-2-propen-1-ol [32]. This was prepared by an analogous procedure using vinyl magnesium bromide, and used in the next step without further purification. Yield 94%, R_f 0.34 (hexane/EtOAc 3:1). IR: 3425*m* (OH), 2920*s*, 2875*m*, 1470*m*, 980*m*, 920*s*. ^{1}H-NMR (220 MHz, TMS): 6.05–5.65 (br. *m*, 1 H, H–C(2)); 5.30 (*m*, 1 H, H–C(3)); 5.15 (*m*, 1 H, H–C(3)); 5.05 (*m*, 1 H, H–C(2′)); 4.40 (*d*, J=4.5, 1 H, H–C(1)); 2.40–1.90 (br. *m*, 4 H, 2 H–C(3′) and H–C(6′)); 1.70–1.50 (br. *m*, 5 H, 2 H–C(4′), 2 H–C(5′) and OH).

4. Preparation of Diallyl Alcohols 6 from Ketones. – 4.1. *Preparation of (2,4,6-Triisopropylbenzenesulfonyl)hydrazones.* All of the (triisopropylbenzenesulfonyl)hydrazones used in this work were prepared according to the method of *Bond et al.* [19]. The trisylhydrazones of the following ketones have not been previously reported with analytical data.

Cyclopentanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8a**): yield 62%, m.p. 158–163° d.

Calc. C 65.89 H 8.85 N 7.68 S 8.80%
Found C 65.82 H 8.84 N 7.73 S 8.69%

Cycloheptanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8c**): yield 85%, m.p. 145–146° d.

Calc. C 67.30 H 9.24 N 7.14 S 8.17%
Found C 67.38 H 9.24 N 7.03 S 8.07%

*4-*tert*-Butylcyclohexanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone* (**8i**): yield 83%, m.p. 116–117°.

Calc. C 69.08 H 9.74 N 6.44 S 7.38%
Found C 69.05 H 9.70 N 6.43 S 7.64%

Cyclododecanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8j**): yield 85%, m.p. 137–138° d.

Calc. C 70.08 H 10.02 N 6.05 S 6.93%
Found C 69.94 H 10.08 N 6.04 S 6.93%

1-Tetralone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8k**): yield 94%, m.p. 150–152° d.

Calc. C 70.38 H 8.03 N 6.57 S 7.52%
Found C 70.50 H 8.11 N 6.69 S 7.57%

2-Methylcyclohexanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8l**): yield 84%, m.p. 116–117°d.

Calc. C 67.30 H 9.24 N 7.14 S 8.17%
Found C 67.15 H 9.34 N 7.13 S 8.30%

trans-*2-Decalone (2,4,6-triisopropylbenzenesulfonyl)hydrazone* (**8m**): yield 35%, m.p. 127–128° d.

Calc. C 69.40 H 9.32 N 6.47 S 7.41%
Found C 69.17 H 9.20 N 6.23 S 7.37%

2-Butanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8n**): yield 80%, m.p. 132–133°.

Calc. C 64.73 H 9.15 N 7.95 S 9.10%
Found C 65.01 H 9.22 N 8.07 S 9.23%

3-Pentanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8o**): yield 59%, m.p. 123–125°.

Calc. C 65.53 H 9.35 N 7.64 S 8.75%
Found C 65.75 H 9.44 N 7.74 S 8.68%

3,3-Dimethyl-2-butanone (2,4,6-triisopropylbenzenesulfonyl)hydrazone (**8p**): yield 83%, m.p. 160–161° d.

Calc. C 66.27 H 9.53 N 7.36 S 8.42%
Found C 66.15 H 9.70 N 7.50 S 8.28%

4.2. *Shapiro Reaction. – General Procedure.* To a magnetically stirred suspension of the hydrazone in 1:1 TMEDA/hexane (10 ml/g hydrazone) at –78° was added 2.02 equiv. of *s*-BuLi. The resulting orange-red solution was stirred at –78° for 2 h, then warmed to 0° and held there for 10 min. The resulting clear, yellow solution was cooled to –40° and then treated dropwise with a solution of (*E*)-3-(trimethylsilyl)-2-propenal (1.02 equiv.) in hexane (10 ml/g aldehyde). The mixture was immediately warmed to 0°, stirred for 2 min and quenched with H_2O (10 ml/g hydrazone). The reaction mixture was extracted with Et_2O (3 × 20 ml/g hydrazone) and the individual Et_2O-extracts were washed with H_2O (20 ml/g hydrazone) until the washings were neutral to litmus (4–5 X). The Et_2O-phases were washed with brine (20 ml/g hydrazone), combined, dried (K_2CO_3) and concentrated to a colorless oil which was chromatographed on silica gel. Analytical data were obtained from a distilled sample.

*(*E*)-1-(4-*tert*-Butyl-1-cyclohexenyl)-3-trimethylsilyl-2-propen-1-ol* (**6i**). Yield 78%, b.p. 135°/0.04 Torr, R_f 0.35 (hexane/EtOAc 5:1). IR: 3550*w* (OH), 2900*s*, 1625*w*, 1480*w*, 1360*s*, 1310*m*, 1240*s*, 1060*m*,

990*s*, 915*m*, 870*s*. ^{1}H-NMR (220 MHz): 6.02 (*dd*, *J* = 19.1, 3.6, 1 H, H–C(2)); 5.88 (*d*, *J* = 19.1, 1 H, H–C(1)); 5.72 (*m*, 1 H, H–C(2′)); 4.48 (*d*, *J* = 3.6, 1 H, H–C(3)); 2.12–0.96 (br. *m*, 8 H, 2 H–C(3′), H–C(4′), 2 H–C(5′), 2 H–C(6′) and OH); 0.87 (*s*, 9 H, $(CH_3)_3C$); 0.08 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 266 (17, M^+), 209 (12), 194 (20), 193 (12), 161 (13), 153 (10), 133 (14), 127 (28), 126 (12), 123 (15), 120 (42), 119 (67), 117 (10), 107 (10), 106 (12), 105 (20), 93 (14), 92 (33), 91 (30), 75 (82), *73* (100), 57 (79).

$C_{16}H_{30}OSi$ (266.55) Calc. C 72.11 H 11.35% Found C 72.06 H 11.46%

*(*E*)-1-(1-Cyclododecenyl)-3-trimethylsilyl-2-propen-1-ol* (**6j**). Yield 72%, b.p. 160°/0.03 Torr, R_f 0.36 (hexane/EtOAc 8:1). IR: 3600*w* (OH), 3010*m*, 2930*s*, 2860*m*, 1615*w*, 1468*m*, 1448*w*, 1248*s*, 1210*m*, 1070*w*, 990*m*, 868*s*, 840*s*. ^{1}H-NMR (220 MHz): 6.04 (*dd*, *J* = 18.7, 3.4, 1 H, H–C(2)); 5.97 (*d*, *J* = 18.7, 1 H, H–C(1)); 5.50 (*t*, *J* = 7.9, 1 H, H–C(2′)); 4.55 (*m*, 1 H, H–C(3)); 2.23–2.02 (br. *m*, 4 H, 2 H–C(3′) and 2 H–C(12′)); 1.59–1.16 (br. *m*, 16 H); 0.07 (*s*, 9 H, $(CH_3)_3Si$). MS (10 eV): *73* (100).

$C_{18}H_{34}OSi$ (294.61) Calc. C 73.40 H 11.63% Found C 73.57 H 11.41%

*(*E*)-1-(3,4-Dihydro-1-naphthyl)-3-trimethylsilyl-2-propen-1-ol* (**6k**). Yield 84%, b.p. 135°/0.10 Torr, R_f 0.31 (hexane/EtOAc 6:1). IR: 3550*m* (OH), 2900*s*, 1625*m*, 1485*m*, 1445*m*, 1305*m*, 1250*s*, 1230*w*, 1075*m*, 995*s*, 925*s*, 850*s*. ^{1}H-NMR (220 MHz): 7.36 (*d*, *J* = 3.4, 1 H, H–C(8′)); 7.16–7.05 (*m*, 3 H, arom. H); 6.15 (*dd*, *J* = 19.0, 4.0, 1 H, H–C(2)); 6.04 (*t*, *J* = 5.5, 1 H, H–C(2′)); 6.00 (*d*, *J* = 19.0, 1 H, H–C(1)); 5.06 (br. *s*, 1 H, H–C(3)); 2.67 (*t*, *J* = 8.0, 2 H, 2 H–C(4′)); 2.27–2.18 (*m*, 2 H, 2 H–C(3′)); 1.78 (br. *s*, 1 H, OH); 0.00 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 258 (22, M^+), 168 (29), 167 (45), 153 (25), 129 (27), 128 (15), 115 (11), 75 (57), *73* (100), 60 (12).

$C_{16}H_{20}OSi$ (258.47) Calc. C 74.36 H 8.58% Found C 74.16 H 8.52%

*(*E*)-1-(6-Methyl-1-cyclohexenyl)-3-trimethylsilyl-2-propen-1-ol* (**6l**). Data for both diastereomers. Yield 73%, b.p. 120°/0.15 Torr, R_f 0.30 (hexane/EtOAc 9:1). IR: 3680*w* (OH), 3600*w*, 3020*s*, 2958*s*, 2935*m*, 1620*w*, 1520*w*, 1435*w*, 1425*w*, 1250*s*, 1215*s*, 1050*w*, 990*m*, 930*w*, 868*s*, 840*s*. ^{1}H-NMR (360 MHz): 6.12–5.62 (*m*, 3 H, H–C(3), H–C(2) and H–C(2′)); 5.3 (*m*, 1 H, H–C(1)); 2.40–1.20 (*m*, 8 H, 2 H–C(3′), 2 H–C(4′), 2 H–C(5′), H–C(6′) and OH); 1.05 (*m*, 3 H, CH_3–C(6′)); 0.06 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 224 (3, M^+), 119 (35), 106 (15), 105 (15), 95 (13), 93 (15), 92 (15), 91 (27), 81 (17), 79 (11), 75 (90), *73* (100), 67 (10), 59 (13), 55 (13).

$C_{13}H_{24}OSi$ (224.46) Calc. C 69.58 H 10.78% Found C 69.45 H 10.90%

*(*E*)-4-Ethyl-1-trimethylsilyl-1,4-pentadien-3-ol* (**6n**)[12]. Yield 90%, b.p. 140°/40 Torr, R_f 0.3 (hexane/Et_2O 5:1, Al_2O_3). IR: 3600*w* (OH), 3020*m*, 2960*m*, 2900*w*, 1650*w*, 1618*w*, 1438*w*, 1250*s*, 1222*m*, 1075*w*, 990*m*, 908*m*, 868*s*, 842*s*. ^{1}H-NMR (220 MHz): 6.00 (*dd*, *J* = 18.5, 4.0, 1 H, H–C(2)); 5.90 (*d*, *J* = 18.5, 1 H, H–C(1)); 5.09 (*s*, 1 H, H–C(5)); 4.89 (*s*, 1 H, H–C(5)); 4.57 (br. *m*, 1 H, H–C(3)); 2.05 (*q*, *J* = 7.4, 2 H, 2 H–C(1′)); 1.80 (br. *s*, 1 H, OH); 1.06 (*t*, *J* = 7.4, 3 H, *CH*$_3$CH$_2$); 0.08 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 184 (1, M^+), 169 (14), 95 (11), 79 (33), *75* (100), 73 (98), 71 (19), 61 (10), 59 (14).

$C_{10}H_{20}OSi$ (184.39) Calc. C 65.15 H 10.94% Found C 65.28 H 11.10%

*(1*E*,4*E*)-4-Ethyl-1-trimethylsilyl-1,4-hexadien-3-ol* (**6o**). Yield 93%, b.p. 135°/20 Torr, R_f 0.35 (hexane/Et_2O 5:1). IR: 3690*w* (OH), 3600*w*, 3010*m*, 2960*m*, 1620*w*, 1468*w*, 1455*w*, 1375*w*, 1249*s*, 1218*m*, 1210*m*, 1060*w*, 992*m*, 868*s*, 840*s*. ^{1}H-NMR (220 MHz): 6.02 (*dd*, *J* = 18.7, 4.1, 1 H, H–C(2)); 5.90 (*d*, *J* = 18.7, 1 H, H–C(1)); 5.52 (*q*, *J* = 6.8, 1 H, H–C(5)); 4.52 (*m*, 1 H, H–C(3)); 2.07 (*q*, *J* = 7.5, 2 H, 2 H–C(1′)); 1.64 (*d*, *J* = 6.8, 3 H, 3 H–C(6)); 1.61 (*s*, 1 H, OH); 0.98 (*t*, *J* = 7.5, 3 H, *CH*$_3$CH$_2$–C(4)); 0.07 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 198 (1, M^+), 125 (10), 99 (10), 93 (39), 75 (81), *73* (100), 59 (12).

$C_{11}H_{22}OSi$ (198.42) Calc. C 66.60 H 11.80% Found C 66.38 H 11.53%

*(*E*)-4-*tert*-Butyl-1-trimethylsilyl-1,4-pentadien-3-ol* (**6p**). Yield 72%, b.p. 150°/20 Torr, R_f 0.28 (hexane/Et_2O 6:1, Al_2O_3). IR: 3600*m* (OH), 3015*m*, 2910*m*, 2875*m*, 1618*w*, 1482*w*, 1465*m*, 1405*w*, 1388*m*, 1365*m*, 1250*s*, 1210*s*, 1150*w*, 1068*m*, 992*s*, 915*m*, 870*s*, 842*s*. ^{1}H-NMR (360 MHz): 6.04 (*dd*, *J* = 18.7, 4.2, 1 H, H–C(2)); 5.96 (*d*, *J* = 18.7, 1 H, H–C(1)); 5.10 (br. *s*, 1 H, H–C(5)); 5.09

---

[12] Contains 8% of **6g** by GC analysis.

(br. *s*, 1 H, H–C(5)); 4.74 (br. *s*, 1 H, H–C(3)); 1.52 (br. *s*, 1 H, OH); 1.13 (*s*, 9 H, $(CH_3)_3C$); 0.08 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 197 (18), 107 (39), *75* (100), *73* (100), 59 (12), 57 (37).

$C_{12}H_{24}OSi$ (212.45) Calc. C 67.86 H 11.39% Found C 68.12 H 11.50%

5. Preparation of Divinyl Ketones 3. – *General Procedure.* A magnetically stirred solution of the alcohol **6** in dry Et_2O (0.1M) was cooled to 0° and treated with 1.5–1.8 equiv. of nickel peroxide in one portion. The mixture was warmed to r.t. after 30 min and the progress monitored by TLC (*ca.* 2 H). The nickel peroxide was filtered off and washed three times with acetone. Evaporation of the filtrate afforded the crude ketone which was usually distilled directly. Cases in which chromatography was necessary are indicated by R_f-data.

(E)-1-(1-Cyclopentenyl)-3-trimethylsilyl-2-propen-1-one (**3a**). Yield 86%, b.p. 85°/0.03 Torr. IR: 3010*m*, 2985*s*, 2825*m*, 1650*s* (C=O), 1615*s*, 1590*s*, 1430*s*, 1395*s*, 1315*s*, 1250*s*, 1125*w*, 1050*m*, 990*s*, 950*m*, 850*s*. ^{1}H-NMR (220 MHz): 7.07 (*d*, J = 17.6, 1 H, H–C(2)); 6.98 (*d*, J = 17.6, 1 H, H–C(3)); 6.78 (*m*, 1 H, H–C(2′)); 2.73–2.47 (*m*, 4 H, 2 H–C(3′) and 2 H–C(5′)); 2.17–1.80 (*m*, 2 H, 2 H–C(4′)); 0.15 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 194 (5, M^+), 179 (50), 151 (11), 120 (13), 95 (51), 75 (56), *73* (67), 67 (16), 28 (100).

$C_{11}H_{18}OSi$ (194.38) Calc. C 67.96 H 9.34% Found C 67.96 H 9.43%

(E)-1-(1-Cyclohexenyl)-3-trimethylsilyl-2-propen-1-one (**3b**). Yield 85%, b.p. 110°/0.1 Torr. IR: 3010*w*, 3000*m*, 2990*m*, 2880*w*, 1645*s* (C=O), 1580*m*, 1500*w*, 1455*w*, 1390*m*, 1350*m*, 1285*m*, 1200*s*, 1195*s*, 1180*w*, 1000*s*, 920*w*. ^{1}H-NMR (220 MHz): 7.08 (*d*, J = 19, 1 H, H–C(2)); 7.07 (*d*, J = 19, 1 H, H–C(3)); 6.96 (*m*, 1 H, H–C(2′)); 2.32–2.25 (br. *m*, 4 H, 2 H–C(3′) and 2 H–C(6′)); 1.71–1.60 (br. *m*, 4 H, 2 H–C(4′) and 2 H–C(5′)); 0.15 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 208 (15, M^+), 193 (27), 135 (19), 134 (15), 118 (32), 117 (25), 109 (55), 81 (52), 75 (54), *73* (100), 59 (14), 53 (13).

$C_{12}H_{20}OSi$ (208.41) Calc. C 69.17 H 9.67% Found C 69.17 H 9.96%

(E)-1-(1-Cycloheptenyl)-3-trimethylsilyl-2-propen-1-one (**3c**). Yield 92%, b.p. 110°/0.05 Torr. IR: 2954*m*, 2850*s*, 2830*s*, 2750*m*, 1640*s* (C=O), 1575*m*, 1430*m*, 1370*w*, 1200*m*, 1130*m*, 985*s*, 960*w*, 850*s*. ^{1}H-NMR (220 MHz): 7.21–6.97 (*m*, 3 H, H–C(2), H–C(3) and H–C(2′)); 2.68–2.57 (*m*, 2 H); 2.47–2.40 (*m*, 2 H); 1.96–1.77 (*m*, 2 H); 1.67–1.45 (*m*, 4 H); 0.20 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 222 (13, M^+), 207 (20), 179 (22), 149 (25), 132 (18), 123 (27), 117 (14), 95 (32), 91 (12), 75 (31), *73* (100), 67 (15), 59 (12), 55 (11).

$C_{13}H_{22}OSi$ (222.44) Calc. C 70.21 H 9.97% Found C 70.14 H 10.18%

(E)-1-(3-Methyl-1-cyclohexenyl)-3-trimethylsilyl-2-propen-1-one (**3d**). Yield 91%, b.p. 105°/0.02 Torr, R_f 0.24 (hexane/EtOAc 18:1). IR: 3020*s*, 2960*s*, 2940*m*, 2870*w*, 1645*s* (C=O), 1585*m*, 1520*m*, 1485*w*, 1432*w*, 1385*w*, 1370*w*, 1325*w*, 1262*m*, 1250*s*, 1230*s*, 1220*s*, 1210*s*, 1158*w*, 1132*w*, 992*m*, 930*w*, 875*s*, 845*s*. ^{1}H-NMR (220 MHz): 7.12 (*d*, J = 18.5, 1 H, H–C(2)); 7.02 (*d*, J = 18.5, 1 H, H–C(3)); 6.74 (*m*, 1 H, H–C(2′)); 2.45–1.09 (br. *m*, 7 H, H–C(3′), 2 H–C(4′), 2 H–C(5′) and 2 H–C(6′)); 1.11 (*d*, J = 6.9, CH_3–C(3′)); 0.15 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 222 (11, M^+), 207 (30), 206 (24), 191 (26), 149 (11), 127 (22), 123 (30), 117 (18), 99 (10), 95 (62), 75 (43), *73* (100), 67 (21), 59 (11), 55 (14).

$C_{13}H_{22}OSi$ (222.44) Calc. C 70.21 H 9.97% Found C 70.10 H 10.03%

The corresponding (*Z*)-isomer (**3d′**) was isolated by chromatography (2% from the oxidation of **6d**) and was characterized by its ^{1}H-NMR spectrum. R_f 0.32 (hexane/EtOAc 18:1). ^{1}H-NMR (220 MHz): 7.34 (*d*, J = 14.3, 1 H, H–C(2)); 6.78 (*m*, 1 H, H–C(2′)); 6.37 (*d*, J = 14.3, 1 H, H–C(1)); 1.86–1.16 (br. *m*, 7 H, H–C(3′), 2 H–C(4′), 2 H–C(5′) and 2 H–C(6′)); 1.08 (*d*, J = 7.2, 3 H, CH_3–C(3′)); 0.14 (*s*, 9 H, $(CH_3)_3Si$).

(1E,4E)-1-Trimethylsilyl-1,4-hexadien-3-one (**3e**). Yield 94%, b.p. 125°/18 Torr. IR: 3000*w*, 2950*m*, 2900*w*, 1665*m*, 1650*s* (C=O), 1630*s*, 1600*m*, 1450*m*, 1380*w*, 1340*w*, 1320*w*, 1300*w*, 1200*m*, 1160*m*, 1105*m*, 1010*m*, 970*m*, 875*s*. ^{1}H-NMR (90 MHz, CCl_4, $(CH_2Cl)_2$): 7.12 (*d*, J = 18.8, 1 H, H–C(2)); 6.93 (*dq*, J = 15.0, 6.8, 1 H, H–C(5)); 6.72 (*d*, J = 18.8, 1 H, H–C(1)); 6.43 (*dm*, J = 15.0, 1 H, H–C(4)); 2.03 (*dd*, J = 6.8, 1.5, 3 H, 3 H–C(6)); 0.33 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 168 (2, M^+), 154 (14), *153* (100), 109 (13), 75 (44), 73 (93), 69 (60), 61 (17), 59 (14).

$C_9H_{16}OSi$ (168.34) Calc. C 64.23 H 9.58% Found C 64.03 H 9.43%

(E)*-4-Methyl-1-trimethylsilyl-1,4-pentadien-3-one* (**3f**). Yield 76%, b.p. 100°/12 Torr, R_f 0.30 (pentane/Et_2O 25:1). IR: 2920*s*, 1655*s* (C=O), 1625*s*, 1445*m*, 1370*m*, 1330*s*, 1290*m*, 1245*s*, 1130*m*, 1085*s*, 995*s*, 935*s*, 910*s*. ^{1}H-NMR (90 MHz, CCl_4 $(CH_2Cl)_2$): 6.77 (*s*, 2 H, H–C(1) and H–C(2)); 5.68 (br.*s*, 1 H, H–C(5)); 5.55 (br.*s*, 1 H, H–C(5)); 1.72 (*s*, 3 H, CH_3–C(4)); 0.03 (*s*, 9 H, $(CH_3)_3Si$); Addition of 15 mol-% Eu(fod)$_3$ [33] resolves signal at 6.77 into two *d*, *J* = 18.5. MS (70 eV): 168 (3, M^+), 153 (69), 75 (28), *73* (100), 69 (30), 64 (14), 59 (10).

$C_8H_{16}OSi$ (168.34) Calc. C 64.23 H 9.58% Found C 64.35 H 9.44%

(*1*E,*4*E)*-4-Methyl-1-trimethylsilyl-1,4-hexadien-3-one* (**3g**). Yield 92%, b.p. 123°/13 Torr. IR: 3050*m*, 1645*s* (C=O), 1585*m*, 1435*w*, 1380*m*, 1355*w*, 1255*s*, 1200*w*, 1065*m*, 1055*m*, 995*m*, 850*s*. ^{1}H-NMR (360 MHz): 7.05 (*d*, *J* = 19.0, 1 H, H–C(2)); 6.98 (*d*, *J* = 19.0, 1 H, H–C(1)); 6.77 (*q*, *J* = 6.8, 1 H, H–C(5)); 1.87 (*d*, *J* = 6.8, 3 H, 3 H–C(6)); 1.84 (*s*, 3 H, CH_3–C(4)); 0.14 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 182 (12, M^+), 167 (55), 83 (46), 75 (47), *73* (100), 55 (39).

$C_{10}H_{18}OSi$ (182.37) Calc. C 65.87 H 9.95% Found C 65.82 H 9.73%

(*1*E,*4*E)*-5-Phenyl-1-trimethylsilyl-1,4-pentadien-3-one* (**3h**). Yield 91%, b.p. 135°/0.07 Torr. IR: 3005*m*, 2900*m*, 1665*s* (C=O), 1640*s*, 1605*s*, 1555*s*, 1425*m*, 1310*s*, 1240*s*, 1170*s*, 1140*s*, 1105*m*, 1080*s*, 990*s*, 970*m*, 915*m*, 860*s*. ^{1}H-NMR (220 MHz, CH_2Cl_2): 7.71 (*d*, *J* = 16.1, 1 H, H–C(5)); 7.65–7.61 (*m*, 2 H, arom. H); 7.44–7.41 (*m*, 3 H, arom. H); 7.27 (*d*, *J* = 19.0, 1 H, H–C(2)); 7.12 (*d*, *J* = 16.1, 1 H, H–C(4)); 6.84 (*d*, *J* = 19.0, 1 H, H–C(1)); 0.22 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 230 (41, M^+), 229 (19), 215 (38), 131 (68), 103 (29), 77 (23), 76 (15), *73* (100), 59 (13).

$C_{14}H_{18}OSi$ (230.41) Calc. C 72.99 H 7.87% Found C 72.68 H 7.83%

(E)*-1-(4-*tert*-Butyl-1-cyclohexenyl)-3-trimethylsilyl-2-propen-1-one* (**3i**). Yield 100%, m.p. 82–83°. IR: 3025*m*, 3015*m*, 2960*s*, 1640*s* (C=O), 1582*w*, 1480*w*, 1470*w*, 1435*w*, 1425*w*, 1385*w*, 1368*w*, 1312*w*, 1250*s*, 1225*s*, 1215*s*, 1207*s*, 1168*w*, 1080*w*, 1020*w*, 992*w*, 938*w*, 870*s*, 845*s*. ^{1}H-NMR (220 MHz): 7.08 (*s*, 2 H, H–C(1) and H–C(2)); 6.99–6.97 (*m*, 1 H, H–C(2′)); 2.66–1.89 (br. *m*, 4 H, 2 H–C(3′) and 2 H–C(6′)); 1.37–0.96 (*m*, 3 H, H–C(4′) and 2 H–C(5′)); 0.90 (*s*, 9 H, $(CH_3)_3C$–C(4′)); 0.15 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV); 264 (12, M^+), 249 (10), 207 (24), 191 (16), 179 (16), 174 (12), 165 (25), 135 (10), 118 (21), 117 (23), 81 (16), 75 (38), *73* (100), 59 (10), 57 (79), 43 (12).

$C_{16}H_{28}OSi$ (264.53) Calc. C 72.66 H 10.67% Found C 72.49 H 10.78%

(E)*-1-(1-Cyclododecenyl)-3-trimethylsilyl-2-propen-1-one* (**3j**). Yield 78%, b.p. 145°/0.03 Torr, m.p. 51–53°. IR: 3020*s*, 2930*s*, 2860*m*, 1643*s* (C=O), 1583*w*, 1470*m*, 1398*w*, 1250*s*, 1210*s*, 1138*w*, 1092*w*, 1050*w*, 993*m*, 870*s*, 851*s*. ^{1}H-NMR (220 MHz): 7.07 (*d*, *J* = 18.5, 1 H, H–C(2)); 6.97 (*d*, *J* = 18.5, 1 H, H–C(1)); 6.58 (*t*, *J* = 7.9, 1 H, H–C(2′)); 2.43 (*t*, *J* = 6.7, 2 H, 2 H–C(3′)); 2.31 (*q*, *J* = 7.4, 2 H, 2-H–C(12′)); 1.65–1.44 (br. *m*, 16 H); 0.16 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 292 (9, M^+), 181 (13), 180 (13), 179 (52), 168 (14), 167 (12), 164 (14), 153 (14), 109 (15), 107 (13), 105 (16), 95 (10), 91 (15), 82 (17), 81 (25), 79 (13), 75 (40), *73* (100), 69 (14), 67 (19), 59 (11), 58 (73), 57 (11), 55 (36).

$C_{18}H_{32}OSi$ (292.59) Calc. C 73.90 H 11.30% Found C 73.58 H 11.33%

(E)*-1-(1-Naphthyl)-3-trimethylsilyl-2-propen-1-one* (**3k**). Yield 90%, b.p. 150°/0.3 Torr, R_f 0.35 (hexane/EtOAc 10:1). IR: 2900*m*, 1645*s* (C=O), 1530*m*, 1460*w*, 1340*w*, 1290*s*, 1225*s*, 1130*s*, 1100*s*, 1000*s*, 985*m*, 965*m*, 850*s*. ^{1}H-NMR (220 MHz): 8.30 (*d*, *J* = 7.0, 1 H, H–C(8′)); 7.99 (*d*, *J* = 8.1, 1 H, H–C(2′)); 7.93–7.89 (*m*, 1 H, arom. H); 7.71 (*d*, *J* = 7.3, 1 H, arom. H); 7.58–7.50 (*m*, 3 H, arom. H); 7.18 (*d*, *J* = 19.1, 1 H, H–C(2)); 7.06 (*d*, *J* = 19.1, 1 H, H–C(1)); 0.19 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 254 (23, M^+), 253 (27), 239 (23), 165 (11), 156 (11), *155* (100), 128 (11), 127 (85), 126 (13), 77 (14), 75 (12), 73 (84), 59 (11), 58 (10).

$C_{16}H_{18}OSi$ (254.43) Calc. C 75.54 H 7.13% Found C 75.35 H 7.21%

(E)*-1-(6-Methyl-1-cyclohexenyl)-3-trimethylsilyl-2-propen-1-one* (**3l**). Yield 85%, b.p. 140°/0.08 Torr, R_f 0.30 (hexane/EtOAc 15:1). IR: 3020*m*, 2965*m*, 2945*m*, 2875*w*, 1645*s* (C=O), 1630*m*, 1585*w*, 1425*w*, 1385*w*, 1368*w*, 1251*s*, 1232*s*, 1225*s*, 1210*m*, 995*m*, 970*m*, 930*w*, 875*s*, 855*s*, 840*s*. ^{1}H-NMR (220 MHz): 7.08 (*d*, *J* = 18.7, 1 H, H–C(2)); 6.96 (*d*, *J* = 18.7, 1 H, H–C(3)); 6.83 (*t*, *J* = 3.7, 1 H, H–C(2′)); 2.89 (*m*, 1 H, H–C(6′)); 2.25–2.18 (*m*, 2 H, 2 H–C(3′)); 1.82–1.44 (br. *m*, 4 H, 2 H–C(4′) and 2 H–C(5′)); 1.01 (*d*, *J* = 6.9, 3 H, CH_3–C(6′)); 0.50 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 222 (5, M^+), 207 (17), 180 (11), 149 (39), 148 (10), 132 (24), 131 (12), 123 (40), 117 (34), 113 (10), 104 (13), 95 (55), 91 (10), 75 (36), *73* (100), 67 (25), 59 (12), 55 (15), 53 (10).

$C_{13}H_{22}OSi$ (222.44) Calc. C 70.21 H 9.97% Found C 69.97 H 9.80%

*(*E*)-4-Ethyl-1-trimethylsilyl-1,4-pentadien-3-one* (**3n**). Yield 87%, b.p. 120°/28 Torr, R_f 0.27 (hexane/EtOAc 40:1). IR: 3015*m*, 2960*m*, 1655*s* (C=O), 1622*w*, 1587*w*, 1463*w*, 1438*w*, 1345*w*, 1328*w*, 1250*s*, 1220*m*, 1210*m*, 1140*w*, 1100*w*, 1088*w*, 1030*w*, 992*m*, 935*w*, 867*s*, 842*s*. ^{1}H-NMR (220 MHz): 7.04 (*d*, J = 18.8, 1 H, H–C(2)); 6.09 (*d*, J = 18.8, 1 H, H–C(1)); 2.36 (*q*, J = 7.5, 2 H, CH_3CH_2); 1.06 (*t*, J = 7.5, 3 H, CH_3CH_2); 0.15 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 182 (2, M^+), 167 (53), 83 (21), 75 (39), *73* (100), 55 (22).

$C_{10}H_{18}OSi$ (182.37) Calc. C 65.87 H 9.95% Found C 65.67 H 9.94%

*(1*E*,4*E*)-4-Ethyl-1-trimethylsilyl-1,4-hexadien-3-one* (**3o**). Yield 93%, b.p. 140°/20 Torr. IR: 3015*m*, 2970*w*, 1653*s* (C=O), 1585*w*, 1465*w*, 1455*w*, 1390*m*, 1285*m*, 1250*s*, 1210*m*, 1103*m*, 995*m*, 915*w*, 870*s*, 845*s*. ^{1}H-NMR (220 MHz): 7.04 (*s*, 2 H, H–C(1) and H–C(2)); 6.72 (*q*, J = 6.8, 1 H, H–C(5)); 2.37 (*q*, J = 7.4, 2 H, CH_3CH_2); 1.90 (*d*, J = 6.8, 3 H, 3 H–C(6)); 0.96 (*t*, J = 7.4, 3 H, CH_3CH_2); 0.14 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 196 (1, M^+), 181 (37), 167 (12), 123 (12), 97 (42), 91 (21), 75 (40), *73* (100), 69 (47).

$C_{11}H_{20}OSi$ (196.40) Calc. C 67.29 H 10.27% Found C 67.44 H 10.43%

*(*E*)-4-*tert*-Butyl-1-trimethylsilyl-1,4-pentadien-3-one* (**3p**). Yield 84%, b.p. 110°/40 Torr, R_f 0.28 (hexane/Et_2O 20:1). IR: 3020*s*, 2960*m*, 1653*m* (C=O), 1608*w*, 1585*w*, 1482*w*, 1465*w*, 1425*w*, 1388*w*, 1363*w*, 1318*w*, 1250*s*, 1212*s*, 1095*w*, 1048*m*, 1012*w*, 1000*m*, 930*w*, 870*m*, 840*m*. ^{1}H-NMR (220 MHz): 7.02 (*d*, J = 18.8, 1 H, H–C(2)); 6.86 (*d*, J = 18.8, 1 H, H–C(1)); 5.61 (*s*, 1 H, H–C(5)); 5.41 (*s*, 1 H, H–C(5)); 1.17 (*s*, 9 H, $(CH_3)_3C$–C(4)); 0.14 (*s*, 9 H, $(CH_3)_3Si$). MS (70 eV): 195 (42, $M^+ - 15$), 179 (11), 127 (11), 105 (11), 83 (11), 75 (18), *73* (100), 57 (11), 55 (15).

$C_{12}H_{22}OSi$ (210.43) Calc. C 68.51 H 10.54% Found C 69.08 H 10.54%

1-(1-Cyclohexenyl)-2-propen-1-one (**9**) [6b]. Yield 41%, b.p. 50-52°/0.1 Torr. IR: 3030*w*, 3018*w*, 2940*m*, 2865*w*, 1655*s* (C=O), 1635*m*, 1605*m*, 1410*m*, 1225*w*, 980*w*. ^{1}H-NMR (220 MHz, TMS): 7.00-6.87 (br. *m*, 2 H, 2 H–C(3)); 6.29-6.20 (*dd*, J = 17.0, 2.0, 1 H, H–C(2)); 5.72-5.67 (*dd*, J = 10.4, 2.0, 1 H, H–C(2')); 2.39-2.28 (*m*, 4 H, 2 H–C(3') and 2 H–C(6')); 1.66-1.64 (*m*, 4 H, 2 H–C(4') and 2 H–C(5')). MS (70 eV): 136 (41, M^+), 81 (87), 79 (65), 55 (79), 41 (74), *27* (100).

6. Preparation of 2-Cyclopentenones (4). – *General Procedure.* To a cold (0°), magnetically-stirred solution of the divinyl ketone (**3**) in the indicated solvent (see *Table 4*) (0.08 M), was added rapidly, in one portion, 1.05 equiv. of anh. $FeCl_3$. The progress of the reaction was monitored by TLC. Upon consumption of the educt an equal volume of H_2O was added. The mixture was diluted with Et_2O (50 ml/g ketone), the aq. phase separated and then extracted with Et_2O (2 × 50 ml/g ketone). The individual org. extracts were washed with H_2O (35 ml/g ketone) and brine (3 × 35 ml/g ketone). The combined org. layers were dried (K_2CO_3) and evaporated to afford a yellow oil which was purified by chromatography and distillation.

6.1. Hydrogenation of 2-Cyclopentenones (**4**). – *General Procedure.* The enone, **4**, (30-100 mg) was placed in 5 ml of distilled EtOAc with 0.01 equiv. of 5% Pd/C in a round bottomed flask. The flask was purged with H_2 (4 ×) and then stirred at r.t. until H_2 uptake ceased (*ca.* 2.5 h). The mixture was filtered through *Celite*, the catalyst washed with EtOAc (5 ml) and the filtrate concentrated *in vacuo*.

6.2.1. Base-catalyzed Epimerization of Ketones. – *General Procedure.* The saturated ketone (10 mg) was placed in 1 ml of freshly distilled MeOH. MeONa (0.05 equiv. of a 0.45 M solution in MeOH) was added and the solution was stirred at r.t. The equilibration was monitored by capillary GC until the ratios were constant (2-12 h).

6.2.2. Alumina-catalyzed Epimerization. – *General Procedure.* The unsaturated ketone (2 mg) is placed in 0.5 ml of CH_2Cl_2. Basic alumina (activity I, 10 mg) was added and the mixture was stirred at r.t. until the product ratios were constant as judged by GC analysis.

cis-*1,3,4,5,6,6a-Hexahydropentalen-1-one* (**4a**). Yield 55%, b.p. 145°/0.01 Torr. IR: 2970*s*, 2940*s*, 2850*s*, 1710*s* (C=O), 1680*s* (C=C), 1480*w*, 1450*w*, 1375*w*, 1355*m*, 1300*w*, 1190*m*, 1140*w*, 1130*s*, 1110*m*, 1080*m*, 1030*w*, 960*w*, 935*m*, 920*m*, 850*m*, 825*m*, 760*m*. ^{1}H-NMR (360 MHz): 7.52 (*dd*, $J = 5.5$, 2.6, 1 H, H–C(3)); 6.13 (*dd*, $J = 5.5$, 1.0, 1 H, H–C(2)); 3.35 (*m*, 1 H, H–C(3a)); 2.68 (*dd*, $J = 9.6$, 5.7, 1 H, H–C(6a)); 1.92–1.56 (br. *m*, 5 H, 2 H–C(4), H–C(5) and 2 H–C(6)); 1.27–1.19 (*m*, 1 H, H_{endo}–C(5)). MS (70 eV): 122 (53, M^+), 121 (12), *94* (100), 93 (16), 91 (10), 81 (17), 79 (50), 77 (17), 67 (13), 66 (36), 65 (14), 53 (21), 51 (10). 2,4-Dinitrophenylhydrazone of **4a**, m.p. 193–194° ([34]: 192–194°).

cis-*3a,4,5,6,7,7a-Hexahydro-1*H*-inden-1-one* (**4b**). Yield 84%, b.p. 100°/0.08 Torr, R_f 0.30 (hexane/EtOAc 3:1). GC analysis: column B (10 m, 70° isothermal) t_R 4.9 min. IR: 3010*m*, 2940*s*, 2860*m*, 1705*s* (C=O), 1585*m* (C=C), 1450*m*, 1350*m*, 1185*m*, 1165*w*, 880*s*. ^{1}H-NMR (360 MHz): 7.64 (*dd*, $J = 5.7$, 2.8, 1 H, H–C(3)); 6.14 (*dd*, $J = 5.7$, 1.1, 1 H, H–C(2)); 3.00–2.94 (*m*, 1 H, H–C(3a)); 2.40 (*q*, $J = 6.2$, 1 H, H–C(7a)); 2.00–1.00 (br. *m*, 8 H, 4 CH_2). MS (70 eV): 136 (87, M^+), 135 (21), 118 (10), 108 (40), *107* (100), 95 (54), 94 (22), 93 (38), 91 (17), 81 (28), 80 (37), 79 (87), 77 (34), 67 (32), 53 (36).

$C_9H_{12}O$ (136.21) Calc. C 79.37 H 8.88% Found C 79.23 H 8.80%

Ketone **4b** was hydrogenated according to the general procedure (yield 83%) from which an oxime was prepared, m.p. 92.5–94.5° ([35]: 88–89°).

cis,trans-*1,3,4,5,6,7,8,8a-Octahydrazulene-1-one* (**4c**). Yield 74%, b.p. 110°/0.01 Torr, R_f 0.30 (hexane/EtOAc 3:1). GC analysis: column B (10 m, 70°, isothermal) two components: t_R 12.25 min (15%) and 13.00 min (85%). IR: 3120*w*, 3010*m*, 3000*s*, 2925*s*, 2875*m*, 1700*s* (C=O), 1580*m* (C=C), 1430*m*, 1390*m*, 1325*w*, 1260*s*, 1250*s*. ^{1}H-NMR (90 MHz, TMS): 7.85 (*dd*, $J = 5.0$, 2.0, 1 H, H–C(3)); 6.40 (*dd*, $J = 5.0$, 1.5, 1 H, H–C(2)); 3.55–3.25 (*m*, 1 H, H–C(3a)); 2.92–2.62 (*m*, 1 H, H–C(8a)); 2.48–1.38 (br. *m*, 10 H, 5 CH_2). MS (70 eV): 150 (68, M^+), 135 (28), 122 (15), 121 (20), 108 (65), 107 (78), 96 (16), *95* (100), 94 (30), 93 (32), 91 (24), 83 (35), 81 (28), 80 (26), 79 (71), 77 (36), 68 (32), 67 (40), 66 (32), 65 (21), 55 (27), 53 (42).

$C_{10}H_{14}O$ (150.24) Calc. C 79.96 H 9.39% Found C 79.85 H 9.50%

Ketone **4c** was hydrogenated as described (yield 93%) and a 2,4-DNP was prepared m.p. 170–171° ([36a]: 189–190° (*cis*); [36b]: 229° (*trans*)).

$C_{16}H_{20}N_4O_4$ (332.39) Calc. C 57.82 H 6.07 N 16.85% Found C 57.44 H 5.94 N 16.49%

The saturated ketone was subjected to base-catalyzed epimerization. GC analysis; column B (10 m, 70° isothermal): before base addition, two components t_R 5.3 (24%) and 5.5 (76%) min, after base addition, t_R 5.3 (74%) and 5.5 (26%) min.

cis,trans-*Bicyclo[10.3.0]pentadec-14-en-13-one* (**4j**). Yield 78%, b.p. 145°/0.03 Torr, R_f 0.44 (hexane/EtOAc 4:1). GC analysis: column A (150° (3 min), 10°/min, 200° (10 min)), two components t_R (*trans*) 7.0 min (54%) and t_R (*cis*) 7.4 min (46%). IR: 3020*m*, 2938*s*, 2855*m*, 1699*s* (C=O), 1588*m*, 1578*m*, 1471*m*, 1448*m*, 1345*w*, 1222*s*, 1210*s*, 1045*w*, 930*w*, 882*w*. ^{1}H-NMR (360 MHz): 7.65 (*dd*, $J = 5.8$, 2.9, 1 H, H–C(13) *cis*); 7.58 (*dd*, $J = 5.7$, 2.8, 1 H, H–C(13) *trans*); 6.10 (*dd*, $J = 5.8$, 1.8, 1 H, H–C(14) *cis*); 6.04 (*dd*, $J = 5.7$, 1.6, 1 H, H–C(14) *trans*); 2.93–2.89 (*m*, 1 H, H–C(12) *cis*); 2.77–2.74 (*m*, 1 H, H–C(12) *trans*); 2.33–2.25 (*m*, 1 H, H–C(1) *cis*); 2.20–2.13 (*m*, 1 H, H–C(1) *trans*); 1.90–1.20 (*m*, 20 H, 10 CH_2). MS (70 eV): 220 (12, M^+), 149 (16), 96 (10), 55 (95), 82 (19), 79 (10), 67 (11), 55 (13), 53 (10). *28* (100).

$C_{15}H_{24}O$ (220.39) Calc. C 81.76 H 10.98% Found C 81.92 H 11.12%

GC analysis of **4j** after alumina equilibration showed complete conversion to *trans* (t_R 7.0 min).

4-Methyl-2-cyclopenten-1-one (**4e**). Yield 49%, b.p. 111°/19 Torr. R_f 0.30 (pentane/Et_2O 4:1). IR: 2950*m*, 1708*s* (C=O), 1590*m* (C=C), 1450*w*, 1405*m*, 1380*m*, 1340*m*, 1290*w*, 1235*w*, 1180*m*, 1125*m*, 1095*m*, 1080*w*, 1065*w*, 950*w*, 895*m*, 840*m*. ^{1}H-NMR (90 MHz, Me_4Si): 7.53 (*dd*, $J = 5.3$, 2.5, 1 H, H–C(3)); 6.08 (*dd*, $J = 5.3$, 1.9, 1 H, H–C(2)); 3.17–2.77 (br. *m*, 1 H, H–C(4)); 2.59 (*dd*, $J = 16.0$, 6.5, 1 H, H–C(5)); 1.86 (*dd*, $J = 16.0$, 2.0, 1 H, H–C(5)); 1.25 (*d*, $J = 7.0$, 3 H, CH_3–C(4)). MS (70 eV): 96 (20, M^+), 85 (23), 67 (11), 53 (18), *28* (100). HR-MS: C_6H_8O, calc. 96.0575, obs. 96.0575. 2,4-Dinitrophenylhydrazone of **4e**, m.p. 168.5–169.5° ([37]: 170–172°).

*5-Methyl-5-(*E*)-(2-methyl-3-oxo-5-trimethylsilyl-4-pentenyl)-2-cyclopenten-1-one* (**4f**). Yield 42%, b.p. 185°/13 Torr, R_f 0.30 (pentane/Et_2O 2:1). GC analysis: column A (60°, 20°/min, 200° (8 min)). t_R 11.85 min. IR: 2950*s*, 1730*m*, 1690*s*, 1665 sh, 1585*m*, 1450*m*, 1425*m*, 1370*m*, 1340*m*, 1305*w*, 1250*s*, 1205*s*, 1120*m*, 1080*m*, 1050*m*, 995*s*. ^{1}H-NMR (360 MHz): 7.60 (*dt*, $J = 5.8$, 2.4, 1 H, H–C(3)); 7.07

(*d*, J = 19.0, 1 H, H–C(5′)); 6.49 (*d*, J = 19.0, 1 H, H–C(4′)); 6.15 (*dt*, J = 5.8, 2.4, 1 H, H–C(2)); 2.84-2.80 (*m*, 1 H, H–C(2′)); 2.58 (*dt*, J = 19.5, 2.4, 1 H, H–C(4)); 2.41 (*dt*, J = 19.5, 2.4, 1 H, H–C(4)); 2.19 (*dd*, J = 14.2, 7.8, 1 H, H–C(1′)); 1.53 (*dd*, J = 14.1, 3.3, 1 H, H–C(1′)); 1.09 (*s*, 3 H, CH_3–C(5)); 1.05 (*d*, J = 7.1, 3 H, CH_3–C(2′)); 0.17 and 0.15 (2 *s*, 9 H, $(CH_3)_3Si$). MS (10 eV): 264 (1, M^+), 222 (29), 128 (11), *127* (100), 99 (14), 91 (20), 73 (28).

cis,trans-*4,5-Dimethyl-2-cyclopentenone* (**4g**) [38]. Yield 95%, b.p. 95°/13 Torr. GC analysis: column A (60°, 20°/min, 200° (20 min)). t_R (*trans*) 4.37 min (45%) and t_R (*cis*) 4.78 min (55%). IR: 2970*s*, 2925*m*, 2570*m*, 1720*s* (C=O), 1590*m*, 1465*m*, 1455*m*, 1380*m*, 1350*m*, 1185*w*, 830*w*. ^{1}H-NMR (360 MHz): 7.57 (*dd*, J = 5.5, 2.5, 1 H, H–C(3) *cis*); 7.49 (*dd*, J = 5.5, 2.1, 1 H, H–C(3) *trans*); 6.10 (*m*, 2 H, H–C(2) *cis* and *trans*); 3.08-3.05 (*m*, 1 H, H–C(4) *cis*); 2.55-2.40 (*m*, 2 H, H–C(5) *cis* and H–C(4) *trans*); 1.89-1.82 (*m*, 1 H, H–C(5) *trans*); 1.20 (*d*, J = 7.2, 3 H, CH_3); 1.18 (*d*, J = 7.4, 3 H, CH_3); 1.06 (*d*, J = 3.8, 3 H, CH_3); 1.04 (*d*, J = 3.6, 3 H, CH_3). MS (70 eV): 110 (51, M^+), 95 (99), 82 (11), 81 (11), 68 (25), *67* (100), 65 (12), 53 (17). HR-MS: $C_7H_{10}O$, calc. 110.0731, obs. 110.0728. GC analysis of **4g** after alumina equilibration (18 h) showed a 90:10 *trans/cis* ratio.

4-Phenyl-2-cyclopenten-1-one (**4h**). Yield 27%, b.p. 90°/0.01 Torr, R_f 0.30 (hexane/EtOAc 3:1). IR: 3000*w*, 1705*s* (C=O), 1575*m* (C=C), 1505*w*, 1490*w*, 1430*w*, 1335*w*, 1070*w*, 950*m*. ^{1}H-NMR (90 MHz, TMS): 7.65 (*dm*, J = 7.5, 1 H, H–C(3)); 7.37-7.03 (*m*, 5 H, arom. H); 6.25 (*dd*, J = 7.5, 1.5, 1 H, H–C(2)); 4.22-4.05 (*m*, 1 H, H–C(4)); 2.89 (*dd*, J = 18.5, 7.0, 1 H, H–C(5)); 2.33 (*dd*, J = 18.5, 3.0, 1 H, H–C(5)). MS (70 eV): 158 (44, M^+), 157 (13), 130 (58), 129 (57), 128 (18), 115 (33), 105 (11), 103 (15), 91 (19), 78 (19), 77 (18), 75 (56), 73 (55), 67 (13), 64 (12), 51 (18), *28* (100).

$C_{11}H_{10}O$ (158.21) Calc. C 83.52 H 6.37% Found C 83.30 H 6.26%

5-Ethyl-2-cyclopenten-1-one (**4n**) [39]. Yield[13]) 51%, b.p. 110°/30 Torr, R_f 0.30 (pentane/Et_2O 3:1). IR: 3010*w*, 2965*w*, 2930*w*, 2878*w*, 1699*s* (C=O), 1590*w*, 1463*w*, 1430*w*, 1382*w*, 1345*w*, 1230*w*, 1210*w*, 1190*w*, 1095*w*, 938*w*, 910*w*. ^{1}H-NMR (220 MHz): 7.69 (*m*, 1 H, H–C(3)); 6.17 (*m*, 1 H, H–C(2)); 2.85 (*m*, 1 H, H–C(4)); 2.35 (*m*, 1 H, H–C(4)); 1.88-1.33 (br. *m*, 3 H, CH_3CH_2 and H–C(5)); 0.94 (*t*, J = 7.3, 3 H, CH_3CH_2). MS (70 eV): 110 (19, M^+), *82* (100), 81 (55), 68 (22), 67 (15), 53 (31).

cis,trans-*5-Ethyl-4-methyl-2-cyclopenten-1-one* (**4o**). Yield 70%, b.p. 105°/20 Torr, R_f 0.30 (pentane/Et_2O 4:1). GC analysis: column A (70° (3 min), 20°/min, 200° (5 min)), t_R (*trans*) 7.4 min (57%) and t_R (*cis*) 7.8 min (43%). IR: 3015*m*, 2965*m*, 2935*w*, 2878*w*, 1698*s* (C=O), 1588*w* (C=C), 1455*w*, 1380*w*, 1348*w*, 1215*m*, 1208*m*. ^{1}H-NMR (220 MHz, TMS): 7.59 (*dd*, J = 5.7, 2.8, 1 H, H–C(3) *cis*); 7.51 (*dd*, J = 4.5, 2.3, 1 H, H–C(3) *trans*); 6.09 (*m*, 2 H, H–C(2) *cis* and *trans*); 3.14-3.07 (*m*, 1 H, *H–C(5) cis*); 2.70-2.63 (*m*, 1 H, H–C(4) *trans*); 2.28-2.19 (*m*, 1 H, H–C(4) *cis*); 1.88-1.69 (*m*, 4 H, CH_3CH_2 *cis* and *trans*); 1.60-1.29 (*m*, 1 H, H–C(5) *trans*); 1.22 (*d*, J = 7.3, 3 H, CH_3–C(4) *trans*); 1.08 (*d*, J = 7.3, 3 H, CH_3–C(4) *cis*); 1.05 (*t*, J = 7.4, CH_3CH_2 *cis*); 0.97 (*t*, J = 7, 3 H, CH_3CH_2 *trans*). MS (70 eV): 124 (22, M^+), 109 (19), 97 (9), *96* (100), 95 (57), 82 (12), 81 (25), 79 (10), 67 (54), 55 (11), 54 (11), 53 (18).

$C_8H_{12}O$ (124.20) Calc. C 77.38 H 9.74% Found C 77.16 H 9.71%

GC analysis of **4o** after alumina equilibration (12 h) showed a 94:6 *trans/cis* ratio.

5-tert-*Butyl-2-cyclopenten-1-one* (**4p**). Yield 97%, b.p. 150°/40 Torr, R_f 0.30 (pentane/Et_2O 4:1). IR: 3018*s*, 2960*m*, 2870*w*, 1695*s* (C=O), 1595*w* (C=C), 1475*w*, 1468*w*, 1428*w*, 1367*m*, 1345*m*, 1210*s*, 908*s*. ^{1}H-NMR (220 MHz, TMS): 7.64 (*dt*, J = 5.7, 2.8, 1 H, H–C(3)); 6.12 (*dt*, J = 5.7, 2.1, 1 H, H–C(2)); 2.72 (*dddd*, J = 19.5, 6.5, 2.8, 2.1, 1 H, H–C(4)); 2.19 (*dddd*, J = 19.5, 2.8, 2.6, 2.1, 1 H, H–C(4)); 2.12 (*dd*, J = 6.5, 2.6, 1 H, H–C(5)); 0.99 (*s*, 9 H, $(CH_3)_3C$–C(5)). MS (70 eV): 138 (4, M^+), 95 (11), *82* (100), 57 (16), 55 (11), 41 (19), 39 (11), 27 (13), 26 (11).

$C_9H_{14}O$ (138.23) Calc. C 78.20 H 10.23% Found C 78.16 H 10.40%

*1*H-*2,3-Dihydrobenz[*e*]inden-1-one* (**4k**). Yield 60%, R_f 0.37 (hexane/EtOAc 6:1). IR: 3018*m*, 1698*s* (C=O), 1692*s*, 1628*w*, 1590*w*, 1572*w*, 1520*m*, 1512*m*, 1492*m*, 1380*w*, 1305*w*, 1205*m*, 1170*m*, 1103*m*, 1040*w*, 930*w*, 840*m*. ^{1}H-NMR (360 MHz): 9.19 (*d*, J = 8.3, 1 H, H–C(9)); 8.07 (*d*, J = 8.4, 1 H, H–C(5)); 7.92 (*d*, J = 8.1, 1 H, H–C(6)); 7.70 (*dd*, J = 8.1, 8.1, 1 H, H–C(7)); 7.59 (*t*, J = 8.0, 1 H, H–C(8)); 7.55 (*d*, J = 8.5, 1 H, H–C(4)); 3.26 (*t*, J = 5.2, 2 H, 2 H–C(3)); 2.84 (*m*, 2 H, 2 H–C(2)).

---

[13]) Reaction performed at high dilution (0.004 M).

MS (70 eV): 183 (14, $M^+ + 1$), *182* (100, M^+), 181 (11), 154 (45), 153 (39), 152 (23), 126 (11), 76 (25), 63 (10).

*3-Trimethylsilyl-1*H*-2,3-dihydrobenz[e]inden-1-one*[14]) (**4k'**). Yield 70% (based on 84% conversion), R_f 0.64 (hexane/EtOAc 6:1). IR: 3025*m*, 3015*m*, 2945*w*, 1690*s* (C=O), 1678*s*, 1625*w*, 1585*w*, 1568*w*, 1510*m*, 1438*w*, 1412*w*, 1372*w*, 1252*m*, 1222*m*, 1215*m*, 1208*m*, 1198*m*, 1172*w*, 1145*w*, 1109*w*, 1090*w*, 1015*w*, 935*w*, 848*s*, 840*s*. ^{1}H-NMR (360 MHz, CH_2Cl_2): 9.18 (*d*, $J = 8.3$, 1 H, H–C(9)); 8.02 (*d*, $J = 8.4$, 1 H, H–C(5)); 7.90 (*d*, $J = 8.0$, 1 H, H–C(6)); 7.68 (*dd*, $J = 8.0$, 8.3, 1 H, H–C(8)); 7.54 (*t*, $J = 8.0$, 1 H, H–C(7)); 7.46 (*d*, $J = 8.4$, 1 H, H–C(4)); 3.03 (*dd*, $J = 19.2$, 7.9, 1 H, H–C(2)); 2.79 (*dd*, $J = 7.9$, 1.1, 1 H, H–C(3)); 2.72 (*dd*, $J = 19.2$, 1.1, 1 H, H–C(2)); 0.12 (*s*, 9 H, $(H_3C)_3Si$). MS (70 eV): 255 (14, $M^+ + 1$), 254 (62, M^+), 253 (43), 165 (17), 152 (11), *73* (100).

*2,3,4,5,6,7-Hexahydro-1*H*-inden-1-one* (**10a**) [6d] *and 2,3,3a,4,5,6-Hexahydro-1*H*-inden-1-one* (**10b**). Yield 75%. GC analysis: column A (100° (4 min), 20°/min, 200° (10 min)), t_R (**10b**) 9.06 min (78%) and t_R (**10a**) 10.00 min (22%). Separated by CC on silica gel. R_f (hexane/EtOAc 4:1): **10a**, 0.33; **10b**, 0.15. *Data for* **10a**: b.p. 90-93°/0.3 Torr. IR: 3012*w*, 3005*m*, 2915*m*, 2880*w*, 1688*s* (C=O), 1642*s* (C=C), 1395*w*, 1220*m*, 1210*m*, 760*w*. ^{1}H-NMR (360 MHz): 2.48-1.61 (br. *m*, 12 H). MS (70 eV): 136 (47, M^+), 94 (47), 79 (70), *28* (100).

$C_9H_{12}O$ (136.21) Calc. C 79.37 H 8.88% Found C 79.61 H 9.07%

2,4-Dinitrophenylhydrazone of **10a**, m.p. 231-232°.

Data for **10b**: b.p. 135°/0.06 Torr. IR: 3015*w*, 3008*w*, 2940*m*, 2880*w*, 1715*s* (C=O), 1650*s* (C=C), 1210*m*, 1175*w*, 785*w*, 760*w*, 725*w*. ^{1}H-NMR (360 MHz): 6.68 (*t*, $J = 3.2$, 1 H, H–C(7)); 2.57-1.07 (br. *m*, 11 H). MS (70 eV): 136 (35, M^+), 94 (65), *79* (100), 77 (28).

$C_9H_{12}O$ (136.21) Calc. C 79.37 H 8.88% Found C 79.11 H 8.86%

REFERENCES

[1] a) *E. Colvin*, 'Silicon in Organic Synthesis', Butterworths, London, 1981; b) *W.P. Weber*, 'Silicon Reagents for Organic Synthesis', Springer Verlag, Berlin, 1983; c) *I. Fleming*, in 'Comprehensive Organic Chemistry', eds. D.H.R. Barton and W.D. Ollis, Vol. 3, Pergamon Press, Oxford, 1979, p. 608; d) *P. Magnus, T. Sarkar & S. Djuric*, in 'Comprehensive Organometallic Chemistry', eds. G.W. Wilkinson, F.G.A. Stone and E.W. Abel, Vol. 7, Pergamon Press, Oxford, 1982, p. 515.

[2] a) *A.W.P. Jarvie*, Organomet. Chem. Rev., Sect. A *6*, 153 (1970); b) *M.A. Cook, C. Eaborn & D.R.M. Walton*, J. Organomet. Chem. *24*, 301 (1970); c) *A.J. Bourne & A.W.P. Jarvie*, ibid. *24*, 335 (1970); d) *T.G. Traylor, H.J. Berwin, J. Jerkunika & M.L. Hall*, Pure Appl. Chem. *30*, 599 (1972).

[3] a) *T.H. Chan & I. Fleming*, Synthesis *1979*, 761; b) *S.D. Burke, C.W. Murtiashaw, M.S. Dike, S.M.S. Strickland & J.O. Saunders*, J. Org. Chem. *46*, 2400 (1981); c) *B.M. Trost & E. Maruyama*, J. Am. Chem. Soc. *103*, 6529 (1981); d) *L.E. Overman & L.K. Bell*, ibid. *103*, 1851 (1981); e) *H. Nishiyama & K. Itoh*, J. Org. Chem. *47*, 2496 (1982); f) *E. Fujita, M. Ochiai & K. Sumi*, Chem. Lett. *1982*, 79; g) *K. Mikami, K. Kishi & T. Nakai*, Tetrahedron Lett. *1983*, 795; h) *H. Hiemstra & W.N. Speckamp*, ibid. *1983*, 1407.

[4] *T.S. Sorenson & A. Rauk*, in 'Pericyclic Reactions', eds. A.P. Marchand and R.E. Lehr, Vol. 2, Academic Press, New York, 1978, p. 1.

[5] a) *I.N. Nazarov & I.I. Zaretskoya*, J. Gen. Chem. USSR (Engl. Transl.) *27*, 693 (1957) and refs. cited therein; b) *C.W. Shoppee & J.A. Cooke*, J. Chem. Soc., Perkin Trans. 1 *1973*, 1026 and refs. cited therein.

[6] a) *S. Dev*, J. Indian Chem. Soc. *34*, 169 (1957); b) *E.A. Braude & J.A. Coles*, J. Chem. Soc. *1952*, 1430; c) *S. Hirano, S. Takagi, T. Hiyama & H. Nozaki*, Bull. Chem. Soc. Jpn. *53*, 169 (1980); d) *F. Cooke, R. Moerck, J. Schwindeman & P. Magnus*, J. Org. Chem. *45*, 1046 (1980); e) *L.A. Paquette, D.S. Dime, W.E. Fristad & T.R. Bailey*, ibid. *45*, 3017 (1980).

---

[14]) Two equiv. of $FeCl_3$ were used.

[7] *R. B. Woodward & R. Hoffmann*, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1971.

[8] *T. S. Sorensen*, J. Am. Chem. Soc. *89*, 3782 (1967).

[9] a) *J.-M. Conia & M.-L. Leriverend*, Bull. Soc. Chim. Fr. *1970*, 2981; b) *G. Ohloff, K. H. Schulte-Elte & E. Demole*, Helv. Chim. Acta *54*, 2913 (1971).

[10] a) *P. Magnus, D. A. Quagliato & J. C. Huffmann*, Organometallics *1*, 1240 (1982); b) *P. Magnus & D. A. Quagliato*, ibid. *1*, 1243 (1982).

[11] *M. Ono*, J. Syn. Org. Chem. Jpn. *39*, 872 (1981).

[12] *C. H. Heathcock, E. G. DelMar & S. L. Graham*, J. Am. Chem. Soc. *104*, 1907 (1982); see however: *C. H. Heathcock, C. M. Tice & T. C. Gemroth*, ibid. *104*, 6081 (1982).

[13] *S. E. Denmark & T. K. Jones*, J. Am. Chem. Soc. *104*, 2642 (1982).

[14] *V. F. Mironov, A. D. Petrov & N. D. Maskimova*, Bull. Acad. Sci. USSR Ser. Chem. Sci. (Engl. Transl.) *1959*, 1864.

[15] *M. J. Jorgensen*, in 'Organic Reactions', ed. W. G. Dauben, Vol. 18, Wiley, New York, 1970, p. 1.

[16] *D. A. Shirley*, in 'Organic Reactions', ed. R. Adams, Vol. 8, Wiley, New York, 1954, p. 28.

[17] *J.-P. Pillot, J. Dunogues & R. Calas*, Bull. Soc. Chim. Fr. *1975*, 2143.

[18] *R. H. Shapiro*, in 'Organic Reactions', ed. W. G. Dauben, Vol. 23, Wiley, New York, 1976, p. 405.

[19] *A. R. Chamberlain, J. E. Stemke & F. T. Bond*, J. Org. Chem. *43*, 147 (1978).

[20] *S. E. Denmark & T. K. Jones*, J. Org. Chem. *47*, 4595 (1982).

[21] *H. O. House & B. M. Trost*, J. Org. Chem. *30*, 1341 (1965).

[22] *J. K. Stille*, 183rd American Chemical Society Meeting, Las Vegas, March 1982, ORGN 71.

[23] *T. S. Sorensen & R. Bladek*, Can. J. Chem. *50*, 2806 (1972).

[24] a) *A. C. Hopkinson & M. H. Lien*, J. Org. Chem. *46*, 998 (1981); b) *F. K. Cartledge & J. P. Jones*, Tetrahedron Lett. *1971*, 2193; c) *M. A. Cook, C. Eaborn & D. R. M. Walton*, J. Organomet. Chem. *29*, 389 (1971); d) *Y. Apeloig, P. V. R. Schleyer & J. A. Pople*, J. Am. Chem. Soc. *99*, 1291 (1977); e) *G. A. Olah, A. L. Berrier, L. D. Field & G. K. S. Prakash*, ibid. *104*, 1349 (1982).

[25] *W. C. Still, M. Kahn & A. Mitra*, J. Org. Chem. *43*, 2923 (1978).

[26] *D. F. Taber*, J. Org. Chem. *47*, 1351 (1982).

[27] *K. Nakagawa, R. Konaka & R. Nakata*, J. Org. Chem. *27*, 1597 (1962).

[28] *J. B. Brown, H. B. Henbest & E. R. H. Jones*, J. Chem. Soc. *1950*, 3634.

[29] a) *L. A. Paquette, B. A. Johnson & F. M. Hinga*, in 'Organic Syntheses', ed. H. E. Baumgarten, Coll. Vol. 5, Wiley, New York, 1973, p. 215; b) *C. H. Heathcock & R. D. Clark*, J. Org. Chem. *38*, 3658 (1973).

[30] *N. J. Cusack, C. B. Reese, A. C. Risius & B. Roozpeikar*, Tetrahedron *32*, 2157 (1976).

[31] *L. Ruzicka, C. F. Seidel, H. Schinz & M. Pfeiffer*, Helv. Chim. Acta *31*, 422 (1948).

[32] *E. A. Braude & J. A. Coles*, J. Chem. Soc. *1950*, 2014.

[33] *A. F. Cockerill, G. L. O. Davies, R. C. Harden & D. M. Rackham*, Chem. Rev. *73*, 553 (1973).

[34] *W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl & R. M. Dodson*, J. Am. Chem. Soc. *57*, 321 (1965).

[35] *G. A. Tolstikov, U. M. Dzemiler & S. S. Shavanov*, Bull. Acad. Sci. USSR Ser. Chem. Sci. (Engl. Transl.) *1975*, 1754.

[36] a) *H. C. Brown & E. Negishi*, Chem. Commun. *1968*, 549; b) *C. D. Gutsche, I. C. Y. Tao & J. Kozma*, J. Org. Chem. *32*, 1782 (1967).

[37] *G. W. K. Cavill, B. S. Goodrich & D. G. Laing*, Aust. J. Chem. *23*, 83 (1970).

[38] *D. Strike & H. Smith*, Ann. N. Y. Acad. Sci. *91*, 180 (1971).

[39] *W. C. Agosta & A. B. Smith*, J. Am. Chem. Soc. *93*, 5513 (1971).

[40] *C. Santelli-Rouvier & M. Santelli*, Synthesis *1983*, 429.