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CHEMISTRY OF ORGANOSILICON COMPOUNDS—165

2-TRIMETHYLSILYL-METHYL-1, 3-BUTADIENE—A VERSATILE BUILDING BLOCK FOR TERPENE SYNTHESIS

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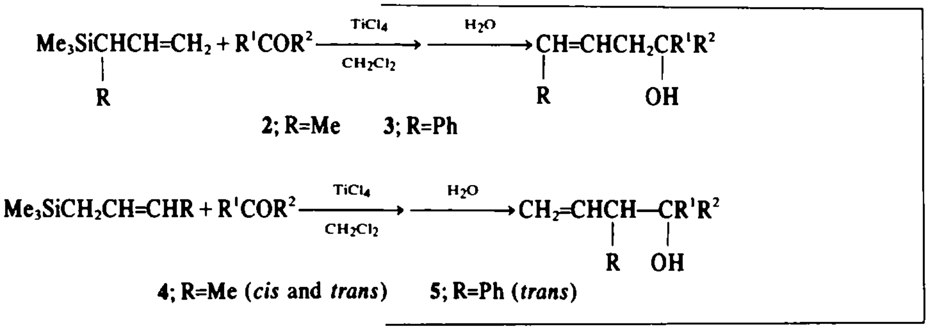
Abstract—Two types of synthetically useful reactions of 2-trimethylsilylmethyl-1,3-butadiene (7) are discussed. Reactions of 7 with acid chlorides, aldehydes, ketones and acetals activated by a Lewis acid give isoprenylated compounds, while 7 undergoes the Diels-Alder reaction with dienophiles. High regiospecificity of the reaction qualifies 7 for a versatile building block of terpene synthesis.

Recently, the use of organosilicon compounds as reagents and as intermediates in organic synthesis has become a field of considerable importance.[1] Especially the chemistry of allylsilanes has proved that the reagents are particularly useful as applied to synthesis, because the reagents can provide synthetic strategies which may not be achieved with other reagents. We have been engaged in exploring the chemistry of allylsilanes as a synthetic tool for several years, the results being reviewed recently.[2]

Sommer *et al.* reported for the first time, the cleavage of the silicon–allyl bond of allyltrimethylsilane with proton and some heteroatom electrophilic reagents,[3] and the first C–C bond forming reaction of allyltrimethylsilane has been reported for the reaction with bromotrichloromethane.[4] In 1976, the regiospecific γ substitution of allylsilanes with carbon electrophiles, one of the most remarkable and useful features in the reaction of allylsilanes, has been definitively demonstrated.[5] Thus the reaction of 1 with carbonyl compounds proceeds very rapidly to give γ, δ-unsaturated alcohols in the presence of a Lewis acid. Following examples indicate the regiospecificity of the reaction.



$$Me_3SiCH(R)CH{=}CH_2 + R^1COR^2 \xrightarrow[CH_2Cl_2]{TiCl_4} \xrightarrow{H_2O} CH(R){=}CHCH_2CR^1R^2(OH)$$

2; R=Me **3**; R=Ph

$$Me_3SiCH_2CH{=}CHR + R^1COR^2 \xrightarrow[CH_2Cl_2]{TiCl_4} \xrightarrow{H_2O} CH_2{=}CHCH(R){-}CR^1R^2(OH)$$

4; R=Me (*cis* and *trans*) **5**; R=Ph (*trans*)

The second important feature of the reaction of allylsilanes is its regiospecific conjugate addition to α, β-enones.[6]

$$Me_3SiCH_2CH{=}CR_2 + R^1R^2C{=}CHCOR \xrightarrow[CH_2Cl_2]{TiCl_4} \xrightarrow{H_2O} CH_2{=}CHCR_2CR^1R^2CH_2COR^3$$

1; R=H **6**; R=Me.

Thus, allylsilane gives δ, ε-enones exclusively in the reaction with α, β-enones. The regiospecific transposition in the allylic part was also observed.

These reactions are quite selective to give a desired product generally in high yield and the allyl group can be converted to a variety of functional groups. Therefore, numerous applications are possible by extending these reactions.[2]

Allylsilanes such as 1–6 are quite stable towards oxygen and moisture and no reaction occurs with carbonyl compounds by simple mixing. Activation is required. Principally, there are two ways of activation, electrophilic and nucleophilic catalysis (or activation).

Lewis acids such as $TiCl_4$, $AlCl_3$, $SnCl_4$ and $BF_3 \cdot OEt_2$ can be used conveniently to activate ketones, aldehydes, acid chlorides, enones, quinones, and acetals to increase electrophilicity of the reacting carbon site.

Trimethylsilyl cation equivalents (Me_3Si–X) such as trimethylsilyl trifluoromethanesulfonate, and trimethylsilyl iodide can also be used as electrophilic catalysts for the reaction of allylsilanes with acetals,[7,8] and chloromethyl ethers. Since Me_3SiX is regenerated, the reactions proceed catalytically.

Fluoride ion displays strong nucleophilic affinity specifically to a Si atom, and we have found that this can be applied in the allylsilane chemistry as nucleophilic catalysis.[9] The allyl-Si bond of allyltrimethylsilane is readily cleaved with tetra-*n*-butylammonium fluoride (TBAF) to give a new allylic anion species which undergoes addition to aldehydes and ketones. The reaction is also catalytic in fluoride ion.

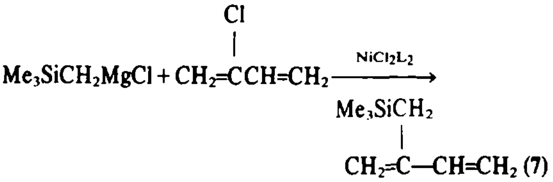
Among a number of substituted allylsilanes so far reported,[1,2] an interesting derivative is 2-trimethylsilylmethyl-1, 3-butadiene (isoprenyltrimethylsilane, 7) which may be used for introduction of an isoprenyl unit by substitution and cycloaddition reactions as discussed in this paper.

As a reagent for one-step isoprenylation, 2-bromomethyl-1, 3-butadiene has been used extensively.[10] The reagent can be used in the reaction with carbanionic species. An organozinc reagent derived from the compound has also been used for nucleophilic isoprenylation.[11] However, these reactions are rather limited in application because of poor availability and thermal instability of the reagent.

RESULTS AND DISCUSSION

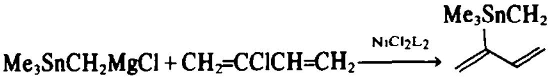
Preparation of isoprenyltrimethylsilane (7)

The coupling reaction of trimethylsilylmethylmagnesium chloride with 2-chloro-1, 3-butadiene (chloroprene) is the most straightforward method of preparing 7. The coupling reaction of a Grignard reagent with vinylic halides in the presence of a Ni complex has been studied extensively by Kumada *et al.*[12] We have found that the yield of 7 depends on the Ni complex used.[13] Ni complex used and % yield were: $\mathrm{Ni(Ph_2P)CH_2)_3PPH_2)Cl_2}$, 91; $\mathrm{Ni(PPh_2(CH_2)_2PPh_2)Cl_2}$, 35; $\mathrm{Ni(PPh_3)_2Cl_2}$, 3.4.



$$\mathrm{Me_3SiCH_2MgCl + CH_2{=}\overset{\overset{\textstyle Cl}{|}}{C}CH{=}CH_2 \xrightarrow{NiCl_2L_2} CH_2{=}\overset{\overset{\textstyle Me_3SiCH_2}{|}}{C}{-}CH{=}CH_2\ (7)}$$

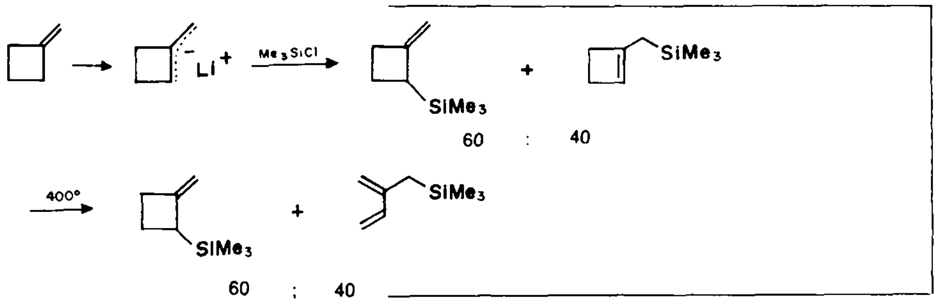
The reaction can be extended to the preparation of 2-trimethylstannylmethyl-1, 3-butadiene (8).[14]



8

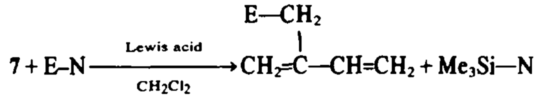
$\mathrm{L = Ph_2P(CH_2)_3PPh_2}$

A less attractive route to 7 has also been reported.[15]



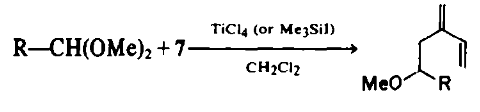
Reaction of isoprenylsilane (7) *as an allylsilane*

Like other allylsilanes,[2,5] the isoprenylsilane 7 can react with various electrophilic species such as acetals, acid chlorides, and carbonyl compounds with the aid of a Lewis acid to give the corresponding isoprenylated products.



$$7 + \mathrm{E{-}N} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{Lewis acid}} \mathrm{CH_2{=}\overset{\overset{\textstyle E{-}CH_2}{|}}{C}{-}CH{=}CH_2 + Me_3Si{-}N}$$

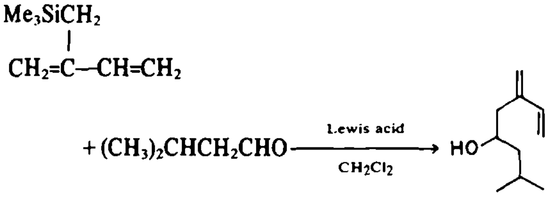
Titanium tetrachloride is the most effective activator for the reaction among various Lewis acids. Acid chlorides gave the corresponding ketones generally in high yields. Results with acetals are even better and in this case, iodotrimethylsilane can be used as a catalyst.



However, reactions of 7 with aldehydes activated by $\mathrm{TiCl_4}$ or $\mathrm{AlCl_3}$ are less satisfactory in respect of yields, although the reaction is convenient as a single-step reaction to isoprenylated alcohols. Results are listed in Table 1.

A new route to ipsenol (**9**) and ipsdienol (**10**), principal components of the aggregation pheromones of bark beetles such as *Ips paraconfusus* and *Ips typographusus*,[16] is a unique synthetic application of the isoprenylation.

The reaction of 7 with isovaleraldehyde in the presence of aluminum chloride or titanium tetrachloride directly afforded (±)-ipsenol (**9**), 2-methyl-6-methylene-oct-7-en-4-ol, although the yield was rather low.



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However, **9** was obtained in 62% yield by the reduction with diisobutylaluminum hydride (DIBAL) of a ketone **11**, which was prepared by the reaction of 7 with isovaleryl chloride in the presence of $\mathrm{TiCl_4}$. Similarly, (±)-ipsdienol (**10**), 2-methyl-6-methylene-octa-2, 7-diene-4-ol, was obtained by reduction of myrcenone (**12**), prepared from 7 and 3, 3-dimethylacryloyl chloride, in 75% yield.

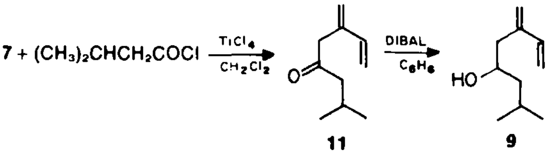
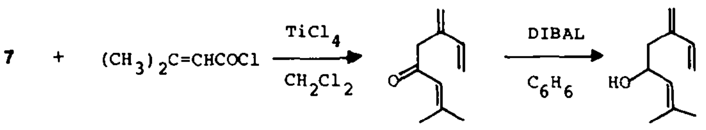


Table 1. Reactions of 2-trimethylsilylmethyl-1, 3-butadiene (7) with electrophilic chemical species in the presence of a Lewis acid^a or iodotrimethylsilane

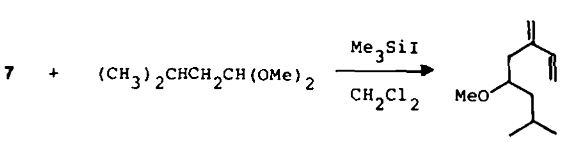
Electrophiles	Activator	Reaction Time	Product (% Yield)^{b,c}		
$(CH_3)_2CHCH_2COCl$	$TiCl_4$	1 min.	**11**		(77)
$(CH_3)_2C{=}CHCOCl$	$TiCl_4$	10 min.	**12**		(71)
$CH_3(CH_2)_4COCl$	$TiCl_4$	1 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2CO(CH_2)_4CH_3{}^d$	(**13**)	(66)
$CH_3COCO_2CH_3$	$TiCl_4$	5 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OH}{\mid}}{C}(CH_3)CO_2CH_3$	(**14**)	(51)
$(CH_3)_2CHCH_2CH(OMe)_2$	$TiCl_4$	10 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OMe}{\mid}}{CH}CH_2CH(CH_3)_2$	(**15**)	(88)
$PhCH_2CH_2CH(OMe)_2$	$TiCl_4$	5 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OMe}{\mid}}{CH}CH_2CH_2Ph$	(**16**)	(81)
$PhCH_2CH_2CH(OEt)_2$	$TiCl_4$	7 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OEt}{\mid}}{CH}CH_2CH_2Ph$	(**17**)	(63)
$(CH_3)_2CHCH_2CH(OMe)_2$	Me_3SiI	40 min.	**15**		(90)
$(CH_3)_2CHCH_2CHO$	$AlCl_3$	2 min.	**9**		(30)^e
	$TiCl_4$	5 sec.			(22)
$PhCH_2CH_2CHO$	$AlCl_3$	2 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OH}{\mid}}{CH}CH_2CH_2Ph$	(**18**)	(43)^e
	$TiCl_4$	1 sec.			(37)
$CH_3(CH_2)_3CHO$	$AlCl_3$	2 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OH}{\mid}}{CH}(CH_2)_3CH_3$	(**19**)	(25)^e
$CH_3CH_2CH(CH_3)CHO$	$AlCl_3$	2 min.	$CH_2{=}CH\underset{\underset{CH_2}{\|}}{C}CH_2\underset{\underset{OH}{\mid}}{CH}CH(CH_3)CH_2CH_3$		(44)^e
	$TiCl_4$	1 sec.		(**20**)	(15)

a. All reactions were carried out in dichloromethane at −78°C. b. Yields after isolation by tlc. C. Yields are not always optimized. d. The trimethylene dithioketal of this product is known as a precursor of PGE_1, PGA_1, $PGF_{1\beta}$. See ref. 10c. e. Yields after hydrolysis with MeOH-HCl.



12 **10**

The methyl ether of ipsenol (**15**) may be prepared in excellent yield from isovaleraldehyde dimethylacetal by the reaction of **7** with iodotrimethylsilane catalysis.[7]



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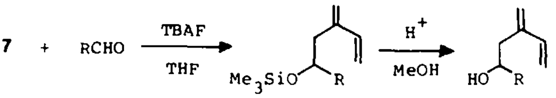
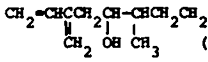
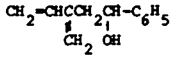
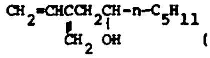
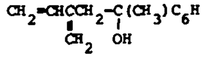
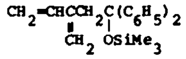
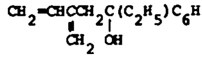
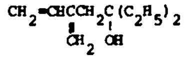
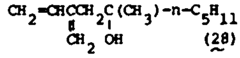
Isoprenylation of carbonyl compounds can also be carried out satisfactorily by the fluoride-ion catalysis. This reaction constituted the most effective and relatively non-basic route to the 2-vinylallylanion (or its equivalent) which reacts with aliphatic, aromatic and α, β-unsaturated aldehydes to give the isprenylated alcohols in good yields under a mild reaction condition in the presence of a ctalytic amount of tetrabutyl ammonium fluoride (TBAF). Free alcohols are obtained after protononlysis.



Ketones also gave the corresponding tertiary alcohols in high yields. However, some straight-chain aldehydes and ketones, which can undergo a facile aldol condensation, gave the product in low yield. Table 2 lists the results. In the case of the reaction with benzophenone, trimethylsilyl ether (**25**) instead of free alcohol was obtained. Because of rather severe steric hindrance, **25** is not converted to the corresponding alcohol by protonolysis under a mild condition.

The expected allyl anion species in the reaction is symmetric, so that is is not necessary to worry about the regiospecificity of the reaction. However, it should be noted that the mechanism of the fluoride-catalyzed reac-

Table 2. Isoprenylation with 7 catalyzed by tetrabutylammonium fluoride

Electrophiles	Reaction Condition	Products (% Yield)[a]	
$(CH_3)_2CHCH_2CHO$	rt, 30 min.	9	(74)
$CH_3CH_2CH(CH_3)CHO$	45°, 1.5 h.	20	(75)
$CH_3CH_2CH_2CH(CH_3)CHO$	45°, 35 min.	 $CH_2{=}CHC({=}CH_2)CH_2CH(OH){-}CH(CH_3)CH_2CH_2CH_3$ (21)	(81)
$(CH_3)_2C{=}CHCHO$	35°, 2 h.	10	(70)
C_6H_5CHO	40°, 1 h.	 $CH_2{=}CHC({=}CH_2)CH_2CH(OH){-}C_6H_5$ (22)	(90)
$CH_3(CH_2)_4CHO$	45°, 4 h.	 $CH_2{=}CHC({=}CH_2)CH_2CH(OH){-}n{-}C_5H_{11}$ (23)	(38)
$C_6H_5COCH_3$	rt, 2.5 h.	 $CH_2{=}CHC({=}CH_2)CH_2{-}C(OH)(CH_3)C_6H_5$ (24)	(87)
$C_6H_5COC_6H_5$	50°, 2.5 h	 $CH_2{=}CHC({=}CH_2)CH_2C(OSiMe_3)(C_6H_5)_2$ (25)	(100)
$C_6H_5COCH_2CH_3$	rt, 3 h.	 $CH_2{=}CHC({=}CH_2)CH_2C(OH)(C_2H_5)C_6H_5$ (26)	(89)
$CH_3CH_2COCH_2CH_3$	rt, 4 h.	 $CH_2{=}CHC({=}CH_2)CH_2C(OH)(C_2H_5)_2$ (27)	(61)
$CH_3CO{-}n{-}C_5H_{11}$	45°, 3.5 h	 $CH_2{=}CHC({=}CH_2)CH_2C(OH)(CH_3){-}n{-}C_5H_{11}$ (28)	(33)

a. Yields after isolation with TLC.

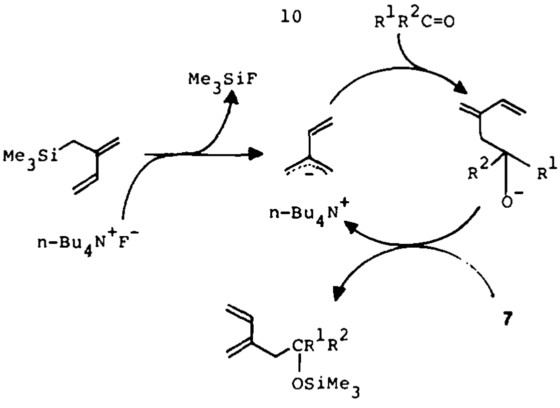
tion is still unclear. As suggested earlier,[9] a mechanism involving fluorotrimethyl-silane as an intermediate is possible. However, another mechanism involving only the alkoxide ion (Scheme 1) seems more plausible since the reaction of 7 with benzophenone gave the isoprenylated compound quantitatively even with heating at 50° for 2.5 hr. Note that the b.p. of fluorotrimethylsilane is 16.4° under atmospheric pressure. These two mechanisms indicate the generation of allyl anions. However, a hypervalent allylic silicon intermediate such as $[CH_2{=}CHCH_2{-}SiMe_3F]^-$ instead of allyl anions is also a possible intervening species and it is still premature to discuss the mechanism fully. Studies on the mechanism of the fluoride ion catalyzed reactions are important and interesting.

The fluoride ion-catalyzed reaction of 7 affords the best route to both ipsenol (74% yield) and ipsdienol (70% yield) as shown in Table 2. Since isoprenylsilane 7 can be prepared inexpensively from commercially available chemicals in large quantity, the present reaction will be valuable as a practical route to the pheromones.[17]

The reaction of isoprenylsilane (7) as a diene

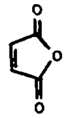
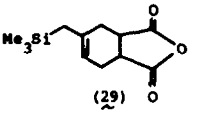
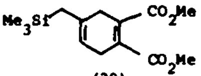
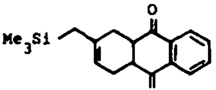
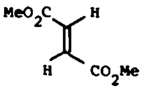
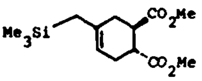
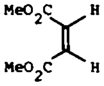
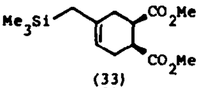
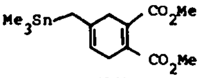
Isoprenylsilane 7 and stannane 8 are substituted dienes, so that these can enter the Diels-Alder reaction with various dienophiles.[14,15] The thermal reaction of 7 and 8 with symmetrical dienophiles proceeds smoothly with a stereospecific mode to afford cycloadducts.

The stereospecificity of the reaction can be demonstrated by the stereochemical outcomes in the reaction



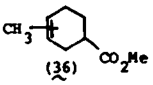
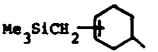
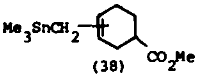
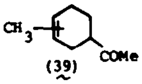
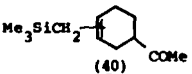
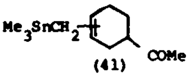
Scheme 1.

Table 3. Diels-Alder reactions of trimethylsilylmethyl and trimethylstannylmethyl-substituted dienes with symmetrical dienophiles

1,3-Diene	Dienophile	Condition	Adduct (% Yield)[a]	
7		Et_2O rt, 20 h	 (29)	(100)
7	$MeO_2CC\equiv CCO_2Me$	CH_2Cl_2 reflux, 16.5 h	 (30)	(96)
7		Benzene reflux, 17 h	 (31)	(88)
7		Benzene reflux, 108.5 h	 (32)	(79)
7		Xylene 180°, 64.5 h	 (33)	(79)
8	$MeO_2CC\equiv CCO_2Me$	CH_2Cl_2 reflux, 15 h	 (34)	(94)

a. Yields after isolation by TLC or GLC.

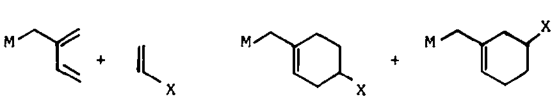
Table 4. Regioselectivity in the Diels-Alder reaction of 1, 3-dienes with unsymmetrical dienophiles

1,3-Diene	Dienophile	Reaction Condition[a] Time/h	(Temp/°C)	Product (% Yield)[b]		Ratio of Para : meta
		46	(80)		(11)	
35	$CH_2{=}CHCO_2Me$	6	(120)[d,e]	 (36)	(83)	70 : 30
7	$CH_2{=}CHCO_2Me$	46	(80)	 (37)	(58)	84 : 16
8	$CH_2{=}CHCO_2Me$	39	(80)	 (38)	(73)	91 : 9
35	$CH_2{=}CHCOMe$	15	(120)[d,e]	 (39)		71 : 29
7	$CH_2{=}CHCOMe$	36	(80)	 (40)	(83)	83 : 17
8	$CH_2{=}CHCOMe$	69	(80)	 (41)	(94)	92 : 8

a. Reactions were carried out in benzene, unless otherwise stated. b. Yield after isolation by TLC. c. Determined by GLC. d. ref. 8. e. in toluene.

of 7 with dimethyl maleate and with dimethyl fumarate, in which only one respective stereoisomer was obtained from each isomeric ester. The results are summarized in Table 3.

Interestingly, 7 and 8 undergo the Diels-Alder reaction with unsymmetrical dienophiles in more regioselective fashion than isoprene (Table 4).



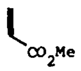
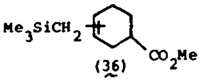
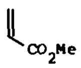
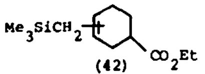
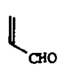
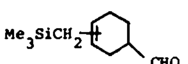
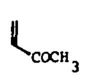
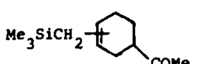
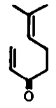
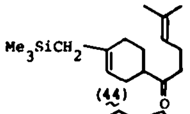
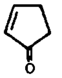
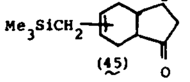
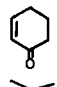
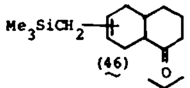
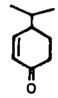
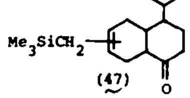
para meta

M=H (isoprene, 35), Me₃Si (7), Me₃Sn (8)

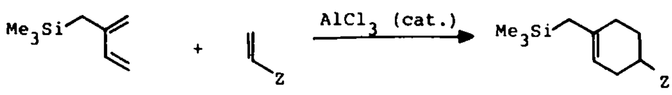
The Diels-Alder reaction of isoprene (35) with an unsymmetrical dienophile with an electron-withdrawing group gave predominantly a *para*-isomer, the *para*/meta ratio being around 70/30 at 120°.[18] Since it has been found that the ratio does not change in the temperature range from 25° to 200°,[18] we can compare the data with those of 7 and 8. With methyl acrylate, the ratio increases to 84/16 for 7 and to 91/9 for 8. The same trend can be observed for methyl vinyl ketone. Based on the HOMO-LUMO interaction in the Diels-Alder reaction,[19] the result can be explained in terms of the extensive $\sigma(M\text{-}C)\text{-}\pi$ conjugation for 7 and 8 that raises the HOMO of the dienes with increasing coefficients of atomic orbitals at the 1-position of the HOMO. Higher *para*/*meta* ratio of 8 is thus reasonable because of the stronger $\sigma\text{-}\pi$ conjugation effect exerted by the Sn–C than by the Si–C bond[20] (Fig. 1).

The regioselectivity in the Diels-Alder reaction of 7 can be improved dramatically by adding a small amount of aluminum trichloride.[18a] Aluminum trichloride can complex with dienophiles such as acrolein and methyl vinyl ketone and thus can lower the LUMO level of the dienophile. Table 5 lists the results of Lewis acid-catalyzed reactions of acrolein and acyclic and cyclic α,β-unsaturated ketones and esters together with those of uncatalyzed reactions.[21] It is important to note that Lewis acid-catalyzed reactions proceed not only faster but also more regioselectively than uncatalyzed reactions. Especially, acrolein and methyl vinyl ketone give pure "*para*" products in good yield.

Table 5. Diels-Alder reactions of isoprenylsilane (7) with various dienophiles catalyzed by aluminum chloride

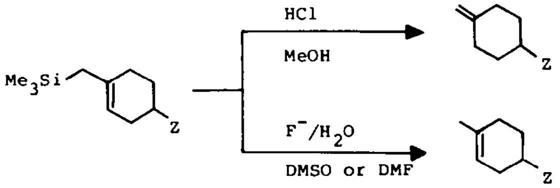
Dienophile	Reaction Conditions[a] Temp/°C, Time/h	Products (% Yield)		Ratio of Para : meta[c,d]
	50–60, 2 (80, 46)[d]	 (36)	75 (58)	99.5: 0.5 (84 : 16)
	50–60, 2 (80, 46)	 (42)	72 (63)	99 : 1 (82 : 18)
	15–20, 3.5 0, 6[e] (80, 34)	 (43)	69 61 (69)	100 : 0 100 : 0 (97 : 3)
	15–20, 3.5 0, 6[e] (80, 36)	 (40)	64 55 (83)	100 : 0 100 : 0 (83 : 17)
	30, 6[e]	 (44)	85	100 : 0
	80, 2 (130, 15)	 (45)	57 (43)	93 : 7) (89 : 11)
	80, 2 (135, 20)	 (46)	70 (17)	99 : 1 (84 : 16)
	60, 13	 (47)	56	95 : 5

a. All reactions were carried out in the presence of 0.08–0.1 equiv. of $AlCl_3$ in benzene unless otherwise noted. b. Yieldsaafter isolation by TLC. c. Determined by GLC. d. Ratios as well as yields of uncatalyzed reactions are shown in parentheses. e. Reactions were carried out in dichloromethane.

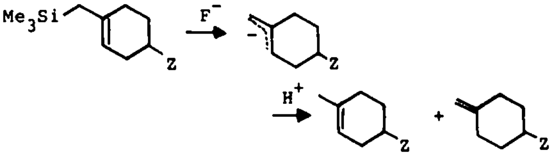


Z=CHO **(43)**
$COCH_3$ **(40)**

The "*para*" adducts can be readily protodesilylated regio-selectively by a Brønsted acid in methanol and caesium or potassium fluoride in aqueous dimethyl sulfoxide (DMSO) or dimethylformaldehyde (DMF) to give *exo*-methylenecyclohexanes and cyclohexenes, respectively.



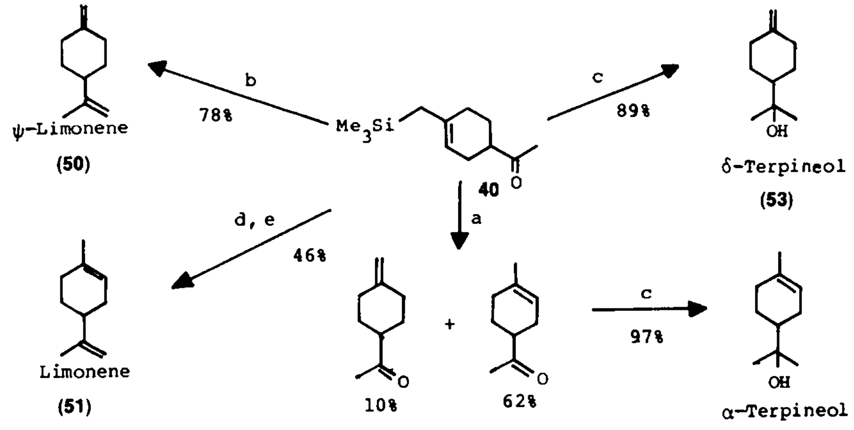
The regioselectivity in the protodesilylation is high for a double bond shift, giving the *exo*-methylene compound almost exclusively as found in another case.[22] However, the mechanism of fluoride-catalyzed desilylation involves the formation of allyl anions or equivalents, so that the regioselectivity is largely controlled by thermodynamic factors.



48 **49**

As can be seen in Table 6, the ratio of **48** to **49** is almost constant regardless of reaction conditions.

The Diels–Alder adduct (**40**) was obtained in 100% regiospecificity, and can be used for terpene synthesis. For example,



[a]KF/DMSO, 120°, 12 h. [b]1)Me_3SiCH_2MgCl/Et_2O, 35°, 2 h. 2) MeCOCl–MeOH, 0°, 15 min. [c]1) $MeMgBr/Et_2O$, 35°, 2H. 2) HCl–MeOH, rt, 20 min. [d]Me_3SiCH_2MgCl/Et_2O, 35°, 2 h. [e]CsF/DMSO, 130°, 3h.

Table 6. Fluoride ion-catalyzed clearage of silicon–carbon bonds

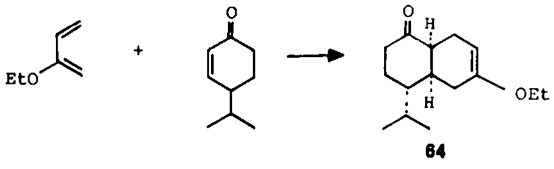
Compound[a]	Fluoride	Solvent	Temp (°C) Time (h)	Yield[b]	Ratio of 48 / 49 [c]
40	KF	DMSO	120 (12)	60 (72)	86 / 14
	KF	DMF	120 (25)	(48)	86 / 14
	CsF	DMSO	140 (0.2)	55	85 / 15
	CsF	DMSO	100 (0.5)	51	86 / 14
	CsF	DMSO	70 (23)	(55)	83 / 17
44	CsF	DMSO	100 (1)	94	84 / 16
47	CsF	DMSO	100 (1)	60	87 / 13[d]

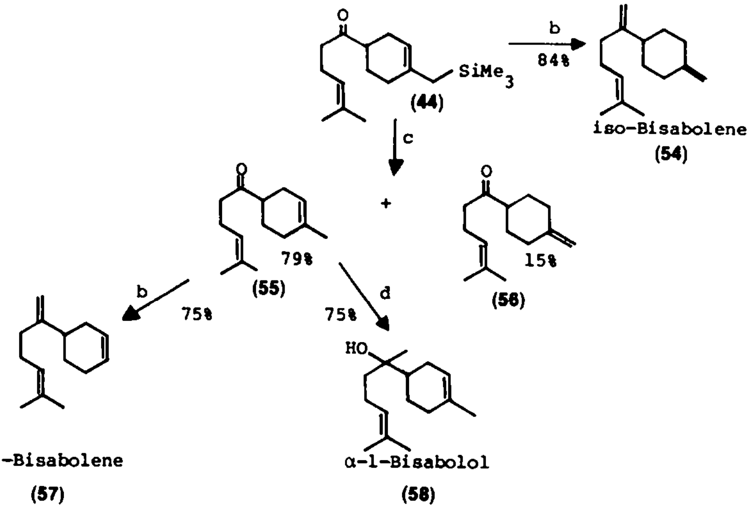
a. Pure "para" isomers were used. b. Yields after isolation with TLC (Yields by GLC determination). c. Determined by GLC unless otherwise noted. d. Determined by NMR.

Methylenation[23] of the ketone (**40**) followed by regioselective protodesilylation with hydrochloric acid in methanol or caesium fluoride in DMSO leads to ψ-limonene (**50**) and limonene (**51**), respectively. Desilylation followed by methylation with methylmagnesium bromide gave α- and δ-terpineol (**52** and **53**), respectively. Preparation of terpineol involving an *exo*-methylene group is rather tedious,[24] but the present method provides a convenient route to the *exo*-methylene compounds.

The adduct (**44**) of **7** with 7-methyl-1, 6-octadiene-3-one was formed also in 100% regiospecificity and can be used for bisabolane sesquiterpenes as follows.

Soffer *et al.*[28] reported the Diels–Alder reaction of 2-ethoxy-1, 3-butadiene with cryptone to give the adduct **64**. The stereochemistry of **64** has been established to be *anti-cis*.





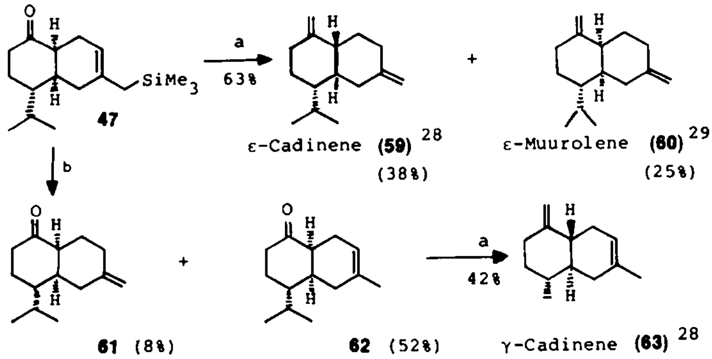
[a] $AlCl_3$(0.1 equiv.)/CH_2Cl_2, 30°, 16 h. [b] 1) Me_3SiCH_2MgCl/Et_2O, 35°, 3 h. 2) HCl-MeOH, 65°, 3 H. [c] CsF/DMSO, 100°, 1 h. [d] $MeMgBr/Et_2O$, 35°, 3 h.

Syntheses of isobisabolene,[25] β-bisabolene,[26] and α-1-bisabolol[27] have been reported previously, but the present method affords the shortest way to these compounds.

Similarly, some derivatives of cadinanes have been prepared from the adducts (**47**) with cryptone, the results being shown in the following scheme.

We assumed that our adduct **47** has also the same stereochemistry, since steric hindrance of a large isopropyl group can control the stereochemistry.

This work demonstrates that **7** can be viewed as one of the isoprene synthon. The synthetic utility of the reaction was displayed by very high—almost perfect—regioselectivity of the Diels–Alder reaction.

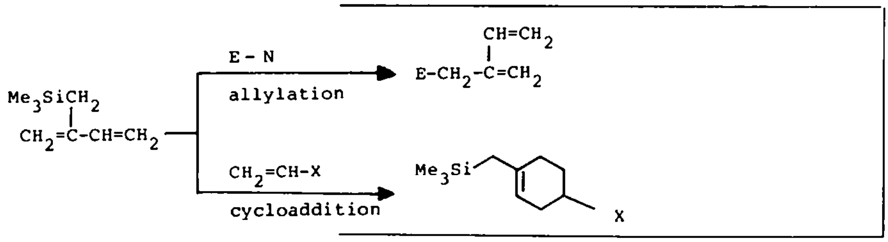


[a] 1) Me_3SiCH_2MgCl/Et_2O, reflux, 11h; 2) HCl/MeOH, rt, 15h

[b] CsF/DMSO, 100°, 1h

CONCLUSION

Two types of reactions of isoprenylsilane have been presented.



Each reaction provides useful method of introducing an isoprene unit in acyclic and cyclic forms. Some applications to the synthesis of naturally occurring compounds are presented.

EXPERIMENTAL

Gas chromatographic analyses were performed with Hitachi 063 and 163 instruments using 1m × 3mm and 1.5m × 3mm columns of 15% SE-30 on celite (60–80). Preparative gas chromatography was carried out with a Varian 90P instrument. IR spectra were recorded on a Hitachi EPI-G2 Grating spectrometer, and are for neat liquids unless otherwise specified. NMR spectra were recorded on Varian T-60, Varian EM-390, Varian XL-200 and JEOL FX-90Q spectrometers for solns in CCl_4, with TMS (2%) as internal standard, unless stated otherwise. Mass spectral data were obtained using a Double Focussing JEOL JMS-D-300 mass spectrometer. All b. and m.ps are uncorrected. Solvents were dried and purified by standard techniques prior to use. Chloromethyltrimethylsilane was prepared by methylation of (chloromethyl)dimethylchlorosilane[30] with MeMgBr. Dichloronickel complexes with 1, 3-bis(diphenylphosphino)propane,[31] 1, 2-bis(diphenylphosphino)ethane,[31] and triphenylphosphine[32] as ligands were prepared according to references. Chloroprene was supplied by Denkikagaku Kogyo Co., Ltd., and was used after distillation (b.p. 59°/760 mmHg). Other chemicals were purchased or prepared by standard methods.

2-*Trimethylsilylmethyl*-1, 3-*butadiene* (*isoprenylsilane*)7. Trimethylsilylmethylmagnesium chloride was prepared from chloromethyltrimethylsilane (18.67 g, 0.15 mol) and Mg (4.29 g, 0.18 mol) in ether (100 ml) and transferred to a dropping funnel which was fitted to a 500 ml 3-necked flask. Chloroprene (16.57 g, 0.19 mol), dichloro-1, 3-bis(diphenylphosphino)propane-nickel (0.47 g, 0.86 mmol), and ether (100 ml) were placed in the flask. The Grignard reagent was added dropwise to the soln at 0° with stirring. A moderate exothermic reaction was observed. After heat evolution ceased, stirring was continued with heating to reflux for 6 hr. Hydrolysis, extraction, evaporation of solvents and fractional distillation gave **7** (19.3 g, 0.14 mol) as a colorless oil (90.8%), b.p. 69–70°/80 mmHg. NMR δ 0.03 (9H, s), 1.71 (2H, d J = 1.1 Hz), 4.78 (1H, m), 4.88 (1H, m), 5.03 (1H, m), 5.09 (1H, m), 6.36 (1H, dd J = 10.5, 17.4 Hz). IR 3090, 1635, 1595, 995, 905 cm^{-1}. UV (hexane) 231.0 nm (1.17×10^4). (Found: C, 68.62; H, 11.53%. Calc. for $C_8H_{16}Si$: C, 68.49; H, 11.50).

5-*Methoxy*-7-*methyl*-3-*methylene*-1-*octene* **15**. $TiCl_4$ (0.11 ml, 1.0 mmol) and CH_2Cl_2 (20 ml) were placed in a 2-necked flask under N_2 and the soln was cooled to −78°. A mixture of **7** (0.168 g, 1.2 mmol) and isovaleraldehyde dimethylacetal (1.132 g, 1.0 mmol) was added dropwise to the soln. After 10 min, the mixture was hydrolyzed with a sat $NaHCO_3$ aq. An organic layer was separated and dried ($CaCl_2$). The residue after evaporation of the solvent was treated with tlc on silica gel eluting with ether/hexane (1:8) (R_f = 0.6) to give pure **15** (0.148 g, 88%). NMR δ 0.91 (3H, d J = 6.0 Hz), 0.92 (3H, d J = 6.0 Hz), 3.33 (3H, s), *ca* 3.9 (1H, m), 4.90–5.38 (4H, m), 6.37 (1H, dd J = 11.0, 18.0 Hz). (Found: C, 78.80; H, 12.05. Calc. for $C_{11}H_{20}O$: C, 78.51; H, 11.98%. MS Calc. for $C_{11}H_{20}O$: 168.1512, Found: 168.1494).

5-*Methoxy*-3-*methylene*-7-*phenyl*-1-*heptene* **16**. β-Phenylpropion-aldehyde dimethylacetal (0.180 g, 1.0 mmol) was reacted with **7** (0.168 g, 1.2 mmol) at −78°, for 5 min. Work-up as for **15** gave **16** (0.176 g, 81%). NMR δ 1.76 (2H, m), 2.20 (1H, ddd J = 14.0, 7.0, 1.0 Hz), 2.52 (1H, ddd J = 14.0, 5.5, 1.0 Hz), 2.60 (2H, m), 3.29 (3H, s), 3.3 (1H, m), 5.01 (1H, ddd J = 11.0, 1.0, 0.5 Hz) 5.02 (2H, m), 5.18 (1H, ddd J = 17.9, 1.0, 0.5 Hz), 6.31 (1H, dd, J = 17.9, 11.0 Hz), 6.60 (5H, m). (Found: C, 83.29; H, 9.52. Calc. for $C_{15}H_{20}O$: C, 83.29; H, 9.32).

5-*Ethoxy*-3-*methylene*-7-*phenyl*-1-*heptene* **17**. β-Phenylpropionaldehyde diethylacetal (0.208 g, 1.0 mmol) was reacted with **7** (0.168 g, 1.2 mmol) at −78°, for 7 min. Work-up as for **15** gave **17** (0.145 g, 63%). NMR δ 1.15 (3H, dd J = 7.0 Hz), 1.76 (2H, m), 2.22 (1H, ddd J = 14.0, 7.0, 1.0 Hz), 2.52 (1H, ddd J = 14.0, 6.5, 1.0 Hz), 2.70 (2H, m), 3.35 (1H, m), 3.36 (1H, d quart J = 9.0, 7.0 Hz), 3.51 (1H, d quart J = 9.0, 7.0 Hz), 5.00 (1H, ddd J = 11.0, 1.0, 0.5 Hz), 5.1 (2H, m), 5.18 (1H, ddd J = 17.0, 1.0, 0.5 Hz), 6.33 (1H, ddt J = 17.0, 11.0, 1.0 Hz), 7.15 (5H, m). (Found: C, 83.59; H, 9.60. Calc. for $C_{16}H_{22}O$: C, 83.43; H, 9.63).

5-*Methylene*-1-*phenyl*-6-*heptene*-3-*ol* **18**. The reaction of **7** (0.168 g, 1.2 mmol) and β-phenylpropionaldehyde (0.134 g, 1.0 mmol) at −78° for 10 sec and work-up as for **15** gave **18** (0.075 g, 37%). NMR δ 1.73 (2H, dt J = 6.0, 7.0 Hz), 2.19 (1H, dd J = 14.5, 8.6 Hz), 2.42 (1H, dd J = 14.5, 4.5 Hz), 2.64 (1H, bt J = 7.0), 2.79 (1H, bt J = 7.0 Hz), 3.65 (1H, m), 5.03 (1H, d J = 10.9 Hz), 5.07 (2H, m), 5.15 (1H, d J = 17.5 Hz), 6.27 (1H, dd J = 10.9, 17.5 Hz), 7.09 (5H, s). Found: C, 82.78; H, 9.16. Calc. for $C_{14}H_{18}O$: C, 83.12; H, 8.97).

2-*Methyl*-6-*methylene*-7-*octene*-4-*one* **11**.[10b] The reaction of **7** (0.168 g, 1.2 mmol) and isovaleryl chloride (0.121 g, 1.0 mmol) at −78°, for 1 min and work-up as for **15** gave **11** (0.117 g, 77%).

2-*Methyl*-6-*methylene*-2, 7-*octadiene*-4-*one* **12**.[10b] β, β-Dimethylacryl chloride (0.166 g, 1.4 mmol) was reacted with **7** (0.168 g, 1.2 mmol) at −78°, for 10 min. Work-up as for **15** gave **12** (0.128 g, 71%).

3-*Methylene*-1-*decene*-5-*one* **13**. The reaction of **7** (0.168 g, 1.2 mmol) and caproyl chloride (0.135 g, 1.0 mmol) at −78°, for 1 min gave, after work-up as for **15**, **13** (0.11 g, 66%). NMR δ 0.6–2.0 (9H, m), 2.31 (2H, m), 3.14 (2H, s), 4.85–5.35 (4H, m), 6.39 (1H, dd J = 18.0, 10.8 Hz). (Found: C, 79.72; H, 10.89. Calc. for $C_{11}H_{18}O$: C, 79.47; H, 10.91%).

By the same procedure, *ipsenol* **9** (22%) and 3-*methyl*-6-*methylene*-7-*octene*-4-*ol* **20** (15%) were prepared.

3-*Methylene*-1-*nonene*-5-*ol* **19**. CH_2Cl_2 (20 ml) and $AlCl_3$ (0.133 g, 1.0 mmol) were placed in a 50-ml 2-necked flask. Pentanal (0.172 g, 2.0 mmol) was added and the mixture was cooled to −78°. To the homogeneous mixture, **7** (0.140 g, 1.0 mmol) was added dropwise during the period of 2 min. After usual work-up and tlc purification gave **19** (0.038 g, 25%) as a colorless oil. NMR δ 0.50–1.70 (9H, m), 1.70–2.60 (3H, m), 3.60 (1H, m), 4.80–5.40 (4H, m), 6.34 (1H, dd J = 18.0, 10.8 Hz). (Found: C, 77.91; H, 11.84. Calc. for $C_{10}H_{18}O$: C, 77.87; H, 11.76).

By the same procedure, *ipsenol* **9** (30%) 5-*methylene*-1-*phenyl*-6-*heptene* **18** (43%), and 3-*Methyl*-6-*methylene*-7-*octene*-4-*ol* **20** (44%) were prepared.

Iodotrimethylsilane-catalyzed reaction of 7 *with isovaleraldehyde dimethylacetal*. Iodotrimethylsilane (0.025 g, 0.1 mmol), freshly prepared from hexamethyldisilane and I_2,[33] was added by means of a syringe to a CH_2Cl_2 soln (2 ml) of **7** (0.28 g, 2.0 mmol) and isovaleraldehyde dimethylacetal (0.132 g, 1.0 mmol) at −78°. The mixture was kept at −78° for 40 min and then at −40° for 3 hr. After usual work-up, **15** (0.151 g, 90%) was obtained.

Experimental details and spectral data for compounds listed in Table 2 will be published elsewhere.[34]

1-*Trimethylsilylmethyl*-1-*cyclohexene*-4, 5-*dicarboxylic anhydride* **29**

The Diels–Alder reaction of **7** *with maleic anhydride.* Ether (10 ml), **7** (0.168 g, 1.2 mmol), and maleic anhydride (0.0981 g, 1.0 mmol) were placed in a 50-ml 2-necked flask under N_2 and the mixture was stirred for 20 hr at room temp. After evaporation of volatile materials and recrystallization from ether gave **29**, m.p. 104° (0.239 g, 100%). NMR δ 0.02 (9H, s), 1.60 (2H, s), 2.40 (4H, m), 3.25 (2H, m), 5.40 (1H, m). IR (KBr) 3050, 1835, 1770, 1635, 1260, 940 cm^{-1}. (Found: C, 60.51; H, 7.83%. Calc. for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61.

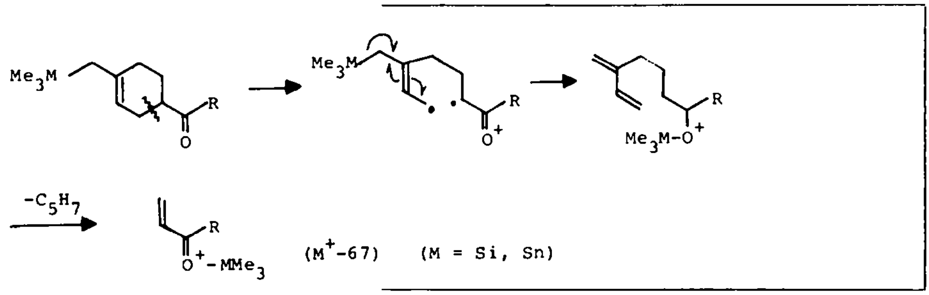
1, 2-*Dimethoxycarbonyl*-4-*trimethylsilylmethyl*-1, 4-*cyclohexadiene* **30**. The reaction of **7** (0.168 g, 1.2 mmol) and dimethyl acetylenedicarboxylate (0.142 g, 1.0 mmol) in CH_2Cl_2 (10 ml) under reflux for 16.5 hr gave **30** (0.272 g, 96%) after purification with tlc on silica gel (ether/hexane, 1/2, $R_f = 0.6$) as an oil. NMR δ 0.01 (9H, s), 1.45 (2H, m), 2.85 (4H, m), 3.70 (6H, s), 5.20 (1H, m). (Found: C, 59.43; H, 7.86. Calc. for $C_{14}H_{22}O_4Si$: C, 59.54; H, 7.85).

2 - *Trimethylsilylmethyl* - 1, 4 - *dihydroanthraquinone* **31**. The reaction of **7** (0.084 g, 0.6 mmol) and naphthoquinone (0.079 g, 0.5 mmol) in benzene at reflux for 17 hr gave **31** (0.131 g, 88%) after work-up as for **30** ($R_f = 0.8$) as an oil. NMR δ 0.08 (9H, s), 1.50 (2H, m), 2.38 (4H, m), 3.30 (2H, m), 5.26 (1H, m), 7.90 (4H, m). (Found: C, 72.67; H, 7.62. Calc. for $C_{18}H_{22}O_2Si$: C, 72.44; H, 7.43).

Trans - 4, 5 - *Dimethoxycarbonyl* - 1 - *trimethylsilylmethyl* - 1 - *cyclohexene* **32**. The reaction of **7** (0.084 g, 0.6 mmol) and dimethylfumarate (0.072 g, 0.5 mmol) in benzene at reflux for 108.5 hr gave **32** (0.112 g, 79%) after work-up as for **30** as an oil. NMR δ −0.02 (9H, s), 1.38 (2H, m), 2.12 (4H, m), 2.70 (2H, m), 3.59 (3H, s), 5.10 (1H, m). IR 1745, 1250, 850 cm^{-1}. (Found: C, 59.39; H, 8.67. Calc. for $C_{14}H_{24}O_4Si$: C, 59.12; H, 8.51).

cis - 4, 5 - *Dimethoxycarbonyl* - 1 - *trimethylsilylmethyl* - 1 - *cyclo hexene* **33**. In a glass ampule, **7** (0.168 g, 1.2 mmol), dimethyl maleate (0.144 g, 1.0 mmol), and *p*-xylene (5 ml) were placed. Under argon the ampule was sealed and kept at 180° for 64.5 hr. Work-up as for **30** gave **33** (0.226 g, 79%) as an oil. NMR δ −0.07 (9H, s), 1.36 (2H, m), 2.32 (4H, m), 2.84 (2H, m), 3.54 (3H, s), 3.56 (3H, s), 5.02 (1H, m). IR 3040, 3020, 3000, 1740, 860 cm^{-1}. (Found: C, 59.38; H, 8.70. Calc. for $C_{14}H_{24}O_4Si$: C, 59.12; H, 8.51).

Diels–Alder reactions of **7** *and* **8** *with unsymmetrical dienophiles.* The reactions of **7** and **8** with unsymmetrical dienophiles were carried out as for the reaction with symmetrical dienophiles. Two isomers in each case were not separated but the ratios were determined by glc. The "*para*" and "*meta*" isomers are easily distinguishable by MS. The M^+-67 fragment appears strongly for "*para*" isomers, while the corresponding fragment is very small for "*meta*" isomers. The M^+-67 peak may be generated by the following fragmentation.



NMR spectra and elemental analyses were taken for the mixture unless otherwise stated. Since the "*meta*" isomers are minor compounds, only $(CH_3)_3Si$ signals are recorded.

4 - *and* 5 - *Methoxycarbonyl* - 1 - *trimethylsilylmethyl* - 1 - *cyclohexene p*-**37** *and m*-**37**. NMR δ −0.05 (9H, s), (another Me_3Si signal at −0.04), 1.33 (2H, bs), 1.50–2.50 (7H, m), 3.56 (3H, s), 5.10 (1H, m). (Found: 63.52; H, 9.81. Calc. for $C_{12}H_{22}O_2Si$; C, 63.67; H, 9.79). MS *m/e* 159 (M^+ − 67; *p*-**37**, 33%; *m*-**37**, 2%).

4- *and* 5-*Methoxycarbonyl*-1-*trimethylstannylmethyl*-1-*cyclohexene p*-**38** *and m*-**38**. NMR δ 0.01 (9H, s) 1.70 (2H, m), 175–2.50 (7H, m), 3.67 (3H, s), 5.20 (1H, m). Found: C, 45.63; H, 7.25. Calc. for $C_{12}H_{22}O_2Sn$: C, 45.47; H, 7.00). MS *m/e* 251 (M^+ − 67: *p*-**38**, 3%; *m*-**38**, 0%).

4- *and* 5-*Acetyl*-1-*trimethylsilylmethyl*-1-*cyclohexene p*-**40** *and m*-**40**. NMR δ −0.05 (9H, s) (another Me_3Si signal at −0.04), 1.33 (2H, m), 1.65–2.30 (7H, m), 2.03 (3H, s), 5.10 (1H, m). (Found: C, 68.74; H, 10.47. Calc. for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54). MS *m/e* 143 (M^+-67: *p*-**40**, 94%; *m*-**40**, 4%).

4- 5-*Acetyl*-1-*trimethylstannylmethyl*-1-*cyclohexene p*-**41** *and m*-**41**. NMR δ 0.08 (9H, s), 1.65 (2H, m), 1.50–2.60 (7H, m), 2.08 (1H, s), 5.17 (1H, m). (Found: C, 47.69; H, 7.43. Calc. for $C_{12}H_{22}OSn$: C, 47.89; H, 7.37%). MS *m/e* 235 (M^+-67: *p*-**41**, 14%; *m*-**41**, 0%).

4- *and* 5-*Ethoxycarbonyl*-1-*trimethylsilylmethyl*-1-*cyclohexene p*-**42** *and m*-**42**. NMR δ −0.06 (9H, s) (another Me_3Si signal at −0.05), 1.18 (3H, t J = 7.0 Hz), 1.35 (2H, bs), 1.50–2.50 (7H, m), 4.03 (2H, q J = 7.0 Hz), 5.10 (1H, m). MS *m/e* 173 (M^+-67: *p*-**42**, 59%; *m*-**42**, 2%).

4- *and* 5-*Formyl*-1-*trimethylsilylmethyl*-1-*cyclohexene p*-**43** *and m*-**43**. NMR δ 0.00 (9H, s), (another Me_3Si signal at 0.02), 1.43 (2H, m), 1.55–2.40 (7H, m), 5.20 (1H, m), 9.63 (1H, m). (Found: C, 67.50; H, 10.43. Calc. for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27).

Diels–Alder reaction of **7** *with methyl vinyl ketone in the presence of aluminum chloride.* To a mixture of methyl vinyl ketone (7.2 g, 102 mmol), $AlCl_3$ (0.59 g, 4.4 mmol) and CH_2Cl_2 (2 ml) placed in a flask, **7** (7.75 g, 55 mmol) in CH_2Cl_2 (20 ml) was added at 0°. After stirring for 2.5 hr a sat $NaHCO_3$ aq was added to the mixture which was worked up as usual. Pure **40** was obtained (6.23 g, 55%), b.p. 135–140°/16 mmHg.

5-*Trimethylsilylmethyl*-2, 3, 3*a*, 4, 7, 7*a*-*hexahydroindene*-1-*one* **45**. The reaction of **7** (0.140 g, 1.0 mmol) and 2-cyclopentenone (0.165 g, 2.0 mmol) in benzene (1.5 ml) in the presence of $AlCl_3$ (0.013 g, 0.1 mmol) at 80°, for 2 hr and work-up as for **40** gave **45** (0.24 g, 57%, *para*/*meta* = 93/7). Similar reaction of **7** (0.150 g, 1.1 mmol) and 2-cyclopentenone (0.170 g, 2.1 mmol) at 130°, for 15 hr gave **45** (0.112 g, 43%, *para*/*meta* = 89/11). NMR δ −0.30 (9H, s), 1.0–2.2 (12H, m), 4.9–5.1 (1H, m). Pure **45** was separated by glc. MS calc. for $C_{13}H_{22}OSi$: 222.1440; Found: 222.1431.

Diels–Alder reactions of **7** *with* 2-*cyclohexenone and cryptone in the presence of aluminum chloride.* Similar reactions of **7** with 2-cyclohexenone and cryptone gave **46** (70%, *para*/*meta* = 99/1) and **47** (56%, *para*/*meta* = 95/5), respectively. Pure samples of "*para*" isomers were obtained by glc separation. **46** NMR δ −0.07 (9H, s), 1.30 (2H, bs), 1.5–2.4 (12H, m), 4.9–5.1 (1H, m). MS calc. for $C_{14}H_{24}OSi$: 236.1596; Found: 236.1591. **47** NMR δ 0.02 (9H, s), 0.78 (3H, d J = 7.0 Hz), 1.00 (3H, d J = 7.0 Hz), 1.20–2.50 (14H, m), 5.22 (1H, m). MS calc. for $C_{17}H_{30}OSi$: 278.2066; Found: 278.2069.

Fluoride ion-catalyzed cleavage of the silicon-carbon bond of **40**. A mixture of **40** (0.210 g, 1.0 mmol), KF (0.180 g, 3.1 mmol) and DMSO (1.0 ml) was stirred at 120°, for 12 hr. Water was added to the mixture. The organic layer and extracts with ether were combined, dried and evaporated. Glc (Apiezon L 20% on celite 545, 1 m × 4 mm) analysis gave the **48**/**49** ratio to be 86/14. Glc yield was 72%. Tlc (silica gel, hexane/ether = 5/1) gave 0.073 g (60%) of a mixture of isomers ($R_f = 0.55$).

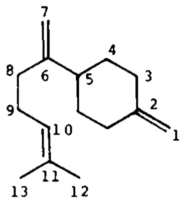
4-*Acetyl*-1-*methylcyclohexene.* NMR δ 1.60 (3H, bs), 2.05 (3H, s) 1.1–2.2 7H, m), 5.3 (1H, m). IR 2960, 2920, 2620, 1708, 1435, 1375, 1365 cm^{-1}. MS calc. for $C_9H_{14}O$: 138.1045; Found: 138.1053.

4-Acetyl-1-methylenecyclohexane. NMR δ 1.6–2.6 (9H, m), 1.95 (3H, s), 4.48–4.60 (2H, bs). IR 2940, 2850, 1719, 1690, 1655, 1355, 1240, 1010, 975 cm^{-1}. MS calc. for $C_9H_{14}O$: 138.1045; Found: 138.1055.

α-Terpineol **52**. 4-Acetyl-1-methylcyclohexene was treated with excess MeMgBr followed by hydrolysis (5% HCl) and work-up to give **52** (97%). Tlc (hexane/ether = 1/1, R_f 0.40). NMR δ 1.11 (6H, s), 1.55 (3H, bs), 1.00–1.95 (8H, m), 5.26–5.40 (1H, m). IR 3350, 2970, 2910, 1430, 1370, 1360, 1150, 1125, 915, 905, 825, 780 cm^{-1}. MS *m/e* (%) 138 (M$^+$-18, 35), 121 (31), 95 (12), 93 (47), 81 (30), 59 (100). (Found: C, 77.59; H, 11.80. Calc. for $C_{10}H_{18}O$: C, 77.87; H, 11.70).

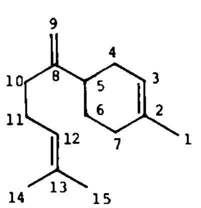
Some physical data of other terpenes prepared by the Diels–Alder route **51**

NMR δ 1.26 (3H, bs), 1.30 (3H, bs), 0.8–1.8 (7H, m), 4.50–4.70 (3H, m), IR 1640, 1625, 1380, 1125, 890, 875 cm^{-1}. MS *m/e* (%) 136 (M$^+$, 63), 121 (37), 107 (29), 93 (100), 79 (29), 68 (37), 67 (32). Calc. for $C_{10}H_{16}$: 136.1252; found 136.1254.



Compound **54**: NMR δ 1.20 (6H, bs), 1.56–2.30 (3H, m), 4.53 (2H, m), 4.65 (2H, m), 4.80–5.13 (1H, m). CMR (CDCl$_3$) δ 153.92 (s, C2), 149.22 (s, C6), 131.40 (s, C11), 124.29 (d, C10), 107.25 (t, C7), 106.92 (t, C1), 43.93 (d, C5), 35.05 (t, C3), 33.55 (t, C8), 29.27 (t, C9), 26.89 (t, C4), 25.65 (q, C12), 17.69 (q, C12). IR 2905, 2840, 1635, 1441, 1370, 879 cm^{-1}. MS *m/e* (%) 204 (M$^+$, 12), 161 (20), 109 (27), 93 (26), 79 (15), 69 (100). Calc. for $C_{15}H_{24}$: 204.1876; Found: 204.1870.

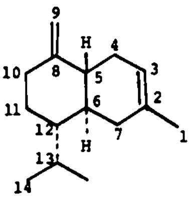
Compound **55**: NMR δ 1.60–1.66 (9H, m), 1.2–2.4 (1H, m), 4.88–5.15 (1H, m), 5.20–5.32 (1H, m). IR 2970, 2920, 2870, 1720, 1440, 1375, 780, 760 cm^{-1}. MS *m/e* (%) 206 (M$^+$, 75), 123 (53), 111 (31), 95 (90), 69 (100). Calc. for $C_{14}H_{22}O$: 206.1674; Found 206.1684. **56** MS *m/e* (%) 206 (M$^+$, 54), 139 (26), 111 (42), 95 (72), 69 (100). Calc. for $C_{14}H_{22}$: 206.1671; Found: 206.1681.



Compound **57**: NMR δ 1.26 (3H, s), 1.62 (3H, s), 168 (3H, s), 0.73–2.33 (11H, m), 4.71 (2H, m), 4.95–5.23 (1H, m), 5.25–5.42 (1H, m). CMR (CDCl$_3$) δ 154.19 (s, C2), 133.62 (s, C8), 131.40 (s, C13), 124.29 (d, C12), 120.76 (d, C3), 107.06 (t, C9), 39.82 (d, C5), 34.92 (t, C7), 33.55 (t, C10), 29.70 (t, C11), 28.33 (t, C4), 26.89 (t, C6), 25.55 (q, C15), 23.37 (q, C1), 17.69 (q, C14). IR 2930, 1640, 1442, 1380, 897 cm^{-1}. MS *m/e* (%) 204 (M$^+$, 77), 161 (34), 119 (35), 109 (44), 93 (100), 79 (34), 69 (96). Calc. for $C_{15}H_{24}$: 204.1879; Found: 204.1879.

Compound **58**: NMR δ 1.02 (3H, s), 1.60 (6H, bs), 0.8–2.2 (15H, m), 4.83–5.38 (2H, m). IR 2980, 2940, 1730, 1450, 1387, 1300, 1260, 1130, 955, 930, 872, 815, 800 cm^{-1}. MS *m/e* (%) 204 (M$^+$-18, 58), 121 (31), 119 (89), 109 (100), 95 (33), 93 (40), 69 (89). Calc. for $C_{15}H_{24}$ (M$^+$-H_2O) 204.1877; Found: 204.1882.

A mixture of **59** *and* **60**. NMR δ 0.71 (60) and 0.72 (59) (3H, d J = 7.0 Hz), 0.92 (60) and 0.93 (59) (3H, d J = 7.0 Hz), 1.05–2.63 (14H, m), 4.54 (4H, m). Calc for $C_{15}H_{24}$ (59): 204.1878; Found: 204.1879.



Compound **63**: NMR δ 0.71 (3H, d J = 7.0 Hz), 0.95 (3H, d J = 7.0 Hz), 1.62 (3H, bs), 1.5–2.6 (12H, m), 4.40–4.67 (2H, m), 5.20–5.46 (1H, m). CMR (CDCl$_3$) δ 152.62 (s, C2), 132.71 (s, C8), 120.11 (d, C3), 104.64 (t, C9), 49.22 (d, C5), 41.58 (d, C6), 36.56, 36.36 (t, C7, C4), 29.70 (t, C10), 28.92 (d, C12), 26.18 (d, C13), 25.78 (t, C11), 21.80 (q, C1), 15.14 (q, C7). IR 3060, 2950, 2920, 1650, 1380, 880, 795 cm^{-1}. MS calc. for $C_{15}H_{24}$ 204.1879; Found: 204.1879.

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