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PALLADIUM - CATALYZED DIASTEREOSELECTIVE SYNTHESES OF (E)-1-TRIMETHYLSILYL-2-ALKENES, (E)-1-TRIMETHYLSILYL-1-ALKEN-3-YNES, (1E,5E)-1-TRIMETHYLSILYL-1,5-ALKADIEN-3-YNES, (1E,3Z)- AND (1E,3E)-1-TRIMETHYLSILYL-1,3-ALKADIENES[1]

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Abstract: On the basis of our observation that (E)-1-bromo-1-alkenes undergo preferentially stereospecific Pd-catalyzed cross-couplings with a variety of organometallics, in the presence of the corresponding (Z)-stereoisomers, efficient and convenient diastereoselective procedures have been developed to prepare nearly stereoisomerically pure (E)-1-trimethylsilyl-2-alkenes (*4*), (E)-1-trimethylsilyl-1-alken-3-ynes (*5*), (1E, 5E)-1-trimethylsilyl-1,5-alkadien-3-ynes (*6*), and (1E,3E)-1-trimethylsilyl-1,3-alkadienes (*8*) from stereoisomeric mixtures of alkenyl bromides. Compounds *5* have been stereoselectively converted into (1E,3Z)-1-trimethylsilyl-1,3-dienes (*7*) by selective hydrometallations, followed by hydrolysis. Some synthetic applications of compounds *5-8* have been also examined.

Organosilanes containing stereodefined mono- or polyunsaturated moieties are quite interesting reagents which are tolerant of a wide variety of organic functionality and undergo many synthetically useful transformations with a host of electrophiles[2]. Consequently, efficient synthetic methods for their preparation from easily accessible substances are desiderable.

During our previous studies on highly diastereoselective palladium-catalyzed cross-couplings between 1-alkynylzinc chlorides and stereoisomeric mixtures of 1,2-dibromoethene[3,4] or 1-alkenyl bromides[5], we have developed efficient procedures for the synthesis of (E)-1,6-bis(trimethylsilyl)-hexa-3-en-1,5-diyne (*1*)[3,4] and (E)-1-trimethylsilyl-3-alken-1-ynes (*2*)[5].

Interestingly, these last compounds can be easily converted into (1Z,3E)-1-trimethylsilyl-1,3-alkadienes (*3*) by hydroalumination in ether solution, followed by hydrolysis with ice-cold 3 N NaOH[6,7].

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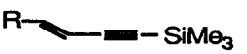

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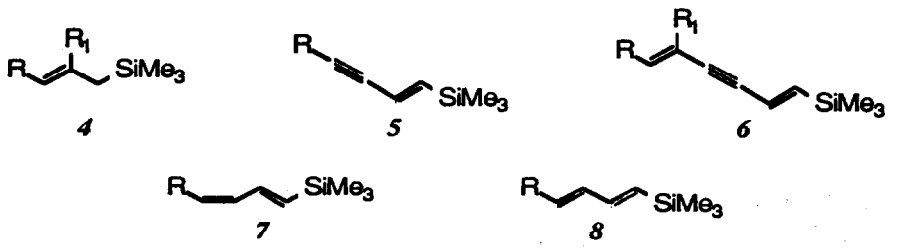
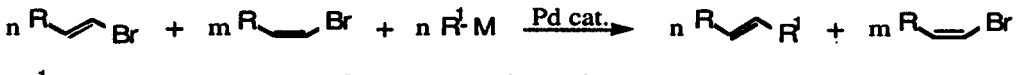
In continuation of the studies in the area of the highly diastereoselective palladium-cat-

alyzed carbon-carbon bond forming reactions involving the use of stereoisomeric mixtures of alkenyl bromides[8], we now wish to report simple and convenient procedures for the synthesis of (E)-1-trimethylsilyl-2-alkenes (***4***), (E)-1-trimethylsilyl-1-alken-3-ynes (***5***), (1E,5E)-1-trimethylsilyl-1,5-alkadien-3-ynes (***6***), (1E,3Z)-1-trimethylsilyl-1,3-alkadienes (***7***), and (1E,3E)-1-trimethylsilyl-1,3-alkadienes (***8***)[9].



These procedures stem from our observation that (E)-1-bromo-1-alkenes undergo preferentially stereospecific palladium-catalyzed cross-couplings with a variety of organometallics, in the presence of the corresponding (Z)-stereoisomers[3-5,7-10] (eq 1).



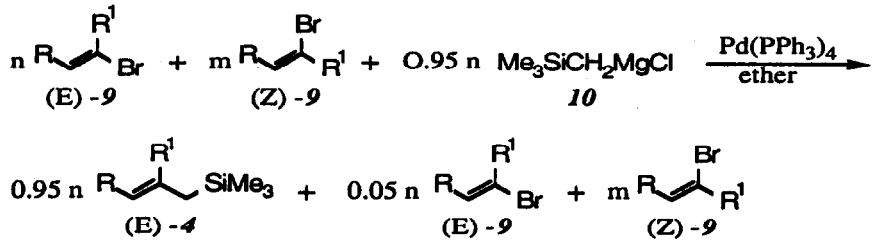
[R^1 = alkyl, aryl, 1-alkynyl, PhS; M = MgX, Cu, ZnCl, $SnBu_3$] [1]

Moreover, some synthetic applications of compounds ***5*** - ***8*** will be discussed.

RESULTS AND DISCUSSION

A) Synthesis of (E)-1-trimethylsilyl-2-alkenes (*4*)[11]

Compounds ***4*** were diastereoselectively synthesized from stereoisomeric mixtures of alkenyl bromides (***9***) and trimethylsilylmethylmagnesium chloride (***10***) (eq 2).



[2]

Two of the alkenyl bromides employed, i.e. (E)/(Z)-ß-bromostyrene (***9a***) (R = Ph, R^1 = H) and (E)/(Z)-2-bromo-2-butene (***9c***) (R = R^1 = CH_3), were commercially available. A stereoisomeric mixture of 1-bromo-1-octene (***9b***) (R = n-C_6H_{13}, R^1 = H) was prepared from 1-octene according to a previously reported general procedure for the synthesis of (E)/(Z)-1-bromo-1-alkenes[8a].

The following procedure was employed to prepare compounds (E)-***4***[11]. An ether solution of 0.95 equiv of ***10*** was added to an ether solution of a diastereoisomeric mixture of an alkenyl bromide (***9***), containing n equiv of the (E)-stereoisomer, and 4-7 mol % of $Pd(PPh_3)_4$. The reaction mixture was maintained at 0 °C for 0.5 h, then stirred at 25-35 °C for 15-17 h. GLC/MS of this mixture showed the presence of unreacted (Z)-***9*** and a new compound, ***4***, in addition to the expected small amount of unreacted (E)-***9***. Usual work up and purification by MPLC on a silica gel column, followed by fractional distillation, allowed to obtain the desired (E)-1-trimethylsilyl-2-alkene, having 97-99 % stereoisomeric purity, in good isolated yield (70-80 %). Since there was no coupling in the absence of the palladium catalyst, the reaction was catalytic in palladium.

Interestingly, either 1-bromo-1-alkenes such as ***9a*** (R = Ph, R^1 = H) and ***9b*** (R = n-C_6H_{13}, R^1 = H), or a 1,2-dialkyl substituted vinyl bromide, i.e. ***9c*** (R = R^1 = CH_3), underwent the highly diastereoselective cross-coupling with ***10*** (Table 1).

Compound ***4a*** (R = Ph, R^1 = H) had been previously reported[12,13]. Evidence for the stereochemistry of ***4b*** (R = n-C_6H_{13}, R^1 = H) was obtained from its ^1H NMR spectrum which exhibited a typical trans-olefinic coupling constant (J = 15.1 Hz). On the other hand, ^1H NMR analysis of compound ***4c*** (R = R^1 = CH_3), also using nuclear Overhauser enhancement (NOE) experiments, did not allow to confirm the (E)-configuration of its carbon-carbon double bond[14]. However, on the basis either of the stereochemical results obtained in the preparation of ***4a*** and ***4b***, or of the fact that the expected amount of (Z)-2-bromo-2-butene (***9c***) was present in the final reaction mixture derived from the diastereoselective cross-coupling between ***10*** and (E)/(Z)-***9c***, the (E)-configuration was attributed to compound ***4c***.

TABLE 1

Diastereoselective synthesis of (E)-1-trimethylsilyl-2-alkenes (***4***)[a]

Alkenyl bromide: ***9***				Reaction conditions	Product: (E)-***4***		
Compound	R	R^1	E/Z ratio	Temp (°C) / Time (h)	Compound	Isolated yield (%)	Stereoisom. purity (%)
9a	Ph	H	88.3/11.7	25/17 → 35/1	***4a***	80.1	>99
9b	n-C_6H_{13}	H	58.0/42.0	20/6.5	***4b***	77.0	97
9c	CH_3	CH_3	16.5/83.5	35/15	***4c***	70.5	>99

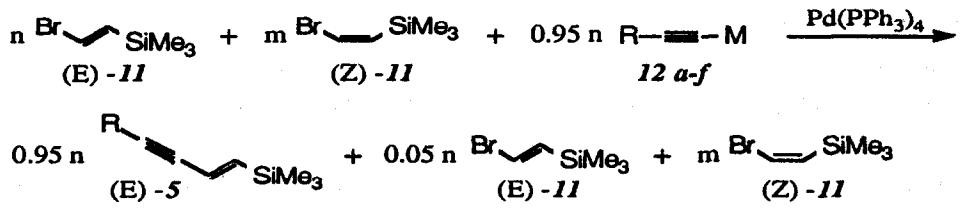
a) All reactions were carried out using 0.95 equiv of ***10*** and 4-7 mol % of $Pd(PPh_3)_4$

Owing to the high yields and stereoisomeric purities, as well as the simplicity and the possibility of large scale preparations, this diastereoselective procedure was more convenient than those based either on the stereospecific Ni- or Pd-catalyzed cross-coupling between ***10*** and (E)-alkenyl iodides[11b,c], or on the coupling between alkyllithium compounds and (E)-1-iodo-2-methyl-3-trimethylsilyl-1-propene[11b]. In fact, the usefulness of these stereospecific proce-

dures is limited by the fact they require the use of stereoisomerically pure alkenyl iodides, which are synthesized by several manipulations involving the use of expensive reagents[15].

B) Synthesis of (E)-1-trimethylsilyl-1-alken-3-ynes (*5*)[16] and (1E,5E)-1-trimethylsilyl-1,5-alkadien-3-ynes (*6*)[17]

The following typical procedure was developed to prepare (E)-1-trimethylsilyl-1-alken-3-ynes (*5*) from a commercially available diastereoisomeric mixture of 2-(bromovinyl)trimethylsilane (*11*). Treatment of a THF solution of (E)/(Z)-*11*, containing 1 equiv of the (E)-stereoisomer, with 3-4 mol % of $Pd(PPh_3)_4$ and 0.95 equiv of a THF solution of a 1-alkynylzinc chloride (*12a-d*) (R = n-C_5H_{11}, Ph, Me_3Si, 2-thienyl) at -20+0 °C for 2-15 h afforded the desired compound *5a-d* (R = n-C_5H_{11}, Ph, Me_3Si, 2-thienyl), having stereoisomeric purity higher than 99.5 %, in good isolated yield (77-88 %) (eq 3).



[3]

5 and *12*	R
a, *e*	n-C_5H_{11}
b	Ph
c	Me_3Si
d	2-thienyl

12	M
a - *d*	ZnCl
e	$SnMe_3$

Interestingly enough, the diastereoselective alkynylation of (E)/(Z)-*11* was also accomplished by treatment of a DMF solution of *11*, containing 1 equiv of (E)-*11*, with 0.95 equiv of a 1-alkynyltrimethylstannane, in the presence of $Pd(PPh_3)_4$. However, the isolated yield was low. Some typical results are reported in Table 2 (entries 1-5).

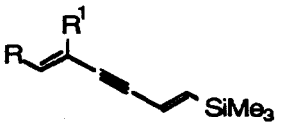
Of particular significance is that this same procedure, which is more convenient than that previously employed to prepare (E)-1-trimethylsilyl-1-alken-3-ynes such as *5b* (R = Ph)[16], when (E)-3-en-1-ynylzinc chlorides were used as alkynylating reagents, allowed to prepare difficult to obtain (1E,5E)-1-trimethylsilyl-1,5-alkadienes (*6*). Thus, (1E,5E)-1-trimethylsilyl-1,5-nonadien-3-yne (*6a*) (R = (E)-1-pentenyl; R^1 = H), having 99 % stereoisomeric purity, was prepared in 65 % isolated yield starting from (E)/(Z)-*11* and (E)-3-hepten-1-ynylzinc chloride (*12f*) (entry 6, Table 2). Analogously, (E)-1-trimethylsilyl-4-(1-cyclohexenyl)-1-buten-3-yne (*6b*) (R , R^1 = -$(CH_2)_4$-) was obtained in 81 % yield from (1-cyclohexenyl)ethynylzinc chloride (*12g*) (entry 7, Table 2).

TABLE 2

Diastereoselective synthesis of (E)-1-trimethylsilyl-1-en-3-ynes (*5*) and (1E,5E)-1-trimethylsilyl-1,5-dien-3-ynes (*6*)[a)]

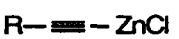
Entry	Organometallic Reagent			Solvent	Reaction time (h)/ Temp. (°C)	Product		
	12	R	M			*5* or *6*	Yield (%)	Stereoisom. purity (%)
1	*12a*	n-C_5H_{11}-	ZnCl	THF	2/0	*5a*	78	>99.5
2	*12b*	Ph-	ZnCl	THF	15/0	*5b*	88	>99.5
3	*12c*	Me_3Si-	ZnCl	THF	2/-20	*5c*	77	>99.5
4	*12d*		ZnCl	THF	15/0	*5d*	87	99.4
5	*12e*	n-C_4H_9	$SnMe_3$	DMF	1.5/80	*5e*	53	99.0
6	*12f*	n-C_3H_7- 	ZnCl	THF	20/0	*6a*	65	99.0
7	*12g*		ZnCl	THF	4/0	*6b*	81	99.0

a) All reactions were carried out in the presence of 3-4 mol % of $Pd(PPh_3)_4$

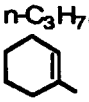


6a R = n-C_3H_7-  , R^1 = H

6b R, R^1 = -$(CH_2)_4$-

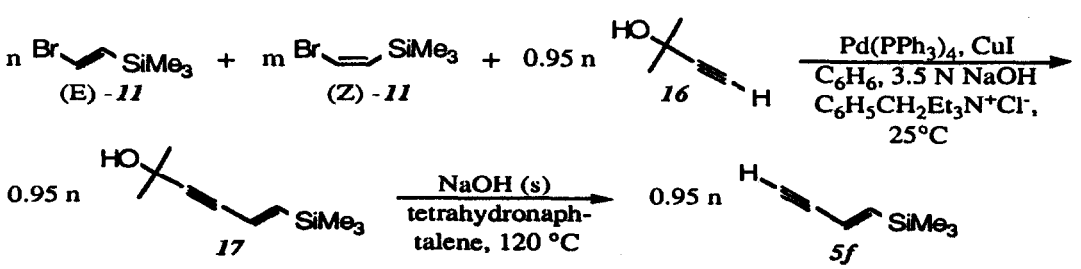


12f R = n-C_3H_7- 

12g R = 

However, this procedure did not appear suitable to prepare (E)-1-trimethylsilyl-1-buten-3-yne (*5f*) in good yield by reaction of (E)/(Z)-*11* with a THF solution of ethynylzinc chloride. In fact, the low boiling point of *5f* caused difficulties in isolation of this pure compound from the THF solution of the reaction mixture. Therefore, a different diastereoselective synthesis of *5f* was devised (Scheme 1).

SCHEME 1



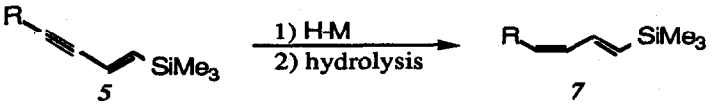
Thus, according to a previously reported diastereoselective method to prepare (E)-ω-

hydroxy-1,3-enynes[8a] having high stereoisomeric purity, a stereoisomeric mixture of ***11***, containing 1 equiv of (E)-***11***, was reacted at room temperature with 0.95 equiv of commercially available 2-methyl-3-butyn-2-ol (***16***), in the presence of catalytic amounts of $Pd(PPh_3)_4$ and CuI. The reaction, which was carried out under phase-transfer conditions, employing benzene as organic solvent, a large excess of 3.5 N NaOH as base, and benzyltriethylammonium chloride as phase-transfer agent, gave pure (E)-6-trimethylsilyl-2-methyl-5-hexen-3-yn-2-ol (***17***) in 84 % yield. Reaction of a tetrahydronaphtalene solution of ***17*** with an equimolar amount of solid NaOH at 125 °C for 1 h gave compound ***5f*** in 68 % isolated yield. Compound ***5f*** represents an interesting C_4 building block not yet reported in the literature.

Taking into account that the synthesis of ***5f*** did not require the use of costly reagents and it was accomplished in a satisfactory overall yield (57 %), the diastereoselective synthesis reported in Scheme 1 appears more convenient than that based on the preparation of ***5c*** (R = $SiMe_3$) and the subsequent selective desilylation of this compound by reaction with KOH or K_2CO_3 in methanol or with $KF{\cdot}2H_2O$ in DMF[18].

C) Synthesis of (1E,3Z)- and (1E,3E)-1-trimethylsilyl-1,3-alkadienes, (*7*)[19] and (*8*)[20], respectively

Although several methods have been reported for the synthesis of (1E,3Z)-1-trimethylsilyl-1,3-dienes (*7*)[19], many of these methods are either limited in scope or require precursors which are not readily available. Thus, taking into account that a variety of nearly stereoisomerically pure (E)-1-trimethylsilyl-1-en-3-ynes (*5*) could be easily synthesized in one step and high yields, we tested the possibility to reduce (Z)-stereoselectively these enynes using some procedures previously employed to prepare (Z)-1-alkenylsilanes via hydroalumination [21], hydromagnesiation[22], or hydroboration[23] of the corresponding 1-alkynylsilanes (eq 4).



5 *7* [4]

As shown in Table 3, different methods had to be employed to convert selectively alkyl or silyl and aryl substituted (E)-1-trimethylsilyl-1-en-3-ynes (*5*) into the corresponding (1E, 3Z)-dienes (*7*) in satisfactory yields.

Thus, (1E,3Z)-1-trimethylsilyl-1,3-nonadiene (***7a***) (R = $n\text{-}C_5H_{11}$) was obtained in 71 % yield and 99.3 % stereoisomeric purity by application of a hydroboration-protonolysis sequence (entry 3, Table 3). Other procedures based on the reaction of ***5a*** with diisobutylaluminium hydride in hexane, followed by treatment with cold 3 N NaOH (entry 1), or on the hydromagnesiation of ***5a*** with isobutylmagnesium bromide, in the presence of a catalytic amount of Cp_2TiCl_2, followed by hydrolysis of the resulting Grignard reagent (entry 2), were plagued with low yields as well as stereoisomeric purity lower than that obtained in entry 3.

TABLE 3

Synthesis of (1E,3Z)-1-trimethylsilyl-1,3-dienes (*7*) from (E)-1-trimethylsilyl-1-en-3-ynes (*5*)

Entry	Product : *7*		Procedure	Yield (%)	E/Z ratio [a]
	Compound	R			
1	*7a*	n-C_5H_{11}	i) i-Bu_2AlH, hexane, 4 h at 25 °C, 25 h at 45 °C; ii) 3 N NaOH, 0 °C	38[b,c]	94.2 / 5.8[f]
2	*7a*	n-C_5H_{11}	i) i-BuMgBr, Cp_2TiCl_2, ether, 20 h; ii) H_2O, 0 °C	33[b]	42.5 / 57.5[f]
3	*7a*	n-C_5H_{11}	i) Sia_2BH, THF, 3 h, 20 °C; ii) AcOH, 7 h, 60 °C; iii) H_2O_2, OH^-, 3.5 h, 40 °C	71[d]	95.2 / 4.8[f] (99.3 / 0.7)[g]
4	*7b*	C_6H_5	i) i-Bu_2AlH, hexane, 24 h, 50 °C; ii) 3 N NaOH, 0 °C	19[d,e]	84.3 / 16.7[f]
5	*7b*	C_6H_5	i) i-Bu_2AlH, ether, 30 h, 35 °C; ii) 3 N NaOH, 0 °C	38[d,c]	96.2 / 3.8[f]
6	*7b*	C_6H_5	i) Sia_2BH, THF, 3 h, 20 °C; ii) AcOH, 7 h, 70 °C; iii) H_2O_2, OH^-, 3.5 h, 40 °C	59[d]	(91.9 / 8.1)[g]
7	*7c*	Me_3Si	i) i-Bu_2AlH, ether, 35 °C, 7h; ii) 3 N NaOH, 0 °C	87[d]	99.4 / 0.6[f] (99.4 / 0.6)[g]

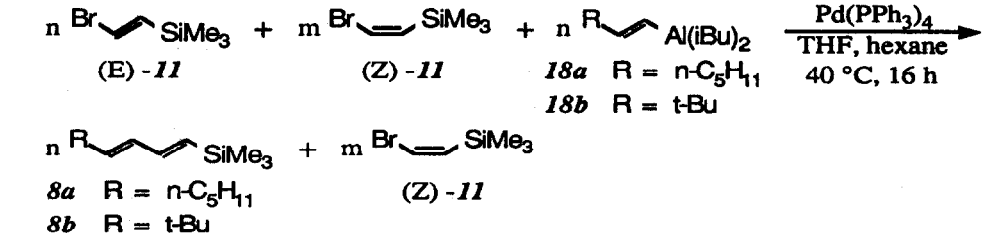
a) Evaluated by GLC/MS and ^1H NMR analyses; b) Evaluated by GLC analysis of the crude reaction mixture; c) The reaction mixture contained only the desired (1E,3Z)-silylated butadiene *7* and unreacted *5*; d) Isolated yield; e) This compound was contaminated by ca. 20 % of the corresponding (E)-monounsaturated silyl alkenes; f) E/Z ratio for the crude reaction mixture; g) E/Z ratio for the isolated product.

On the other hand, hydroalumination of compound *5c* (R = Me_3Si) in ether, followed by hydrolysis of the derived dienylalane with ice-cold 3 N NaOH, was used to prepare (1E,3Z)-1,4-bis(trimethylsilyl)-1,3-butadiene (*7c*) in 87 % yield and 99.4 % stereoisomeric purity (entry 7). This same method, in spite of the modest conversion, appeared suitable to prepare (1E,3Z)-1-trimethylsilyl-4-phenyl-1,3-butadiene (*7b*) having 96.2 % stereoisomeric purity (entry 5).

The synthetic method we developed to prepare 4-alkyl substituted (1E,3E)-1-trimethylsilyl-1,3-dienes (*8*)[20] was straightforward and easily amenable to large scale preparations. In fact, these compounds, having stereoisomeric purity higher than 99 %, were synthesized by cross-coupling between a stereoisomeric mixture of 2-(bromovinyl)trimethylsilane (*11*) and easily available (E)-1-alkenylalanes (*18*), in the presence of catalytic amounts of $Pd(PPh_3)_4$ (eq 5).

Thus, when a THF solution of a stereoisomeric mixture of *11*, containing 1 equiv of (E)-*11*, was allowed to react at 40 °C for 16 h with a hexane solution of (E)-1-heptenyl diisobutylalane (*18a*), in the presence of 3 mol % of $Pd(PPh_3)_4$, (1E,3E)-1-trimethylsilyl-1,3-nonadiene (*8a*) was obtained in 74.7 % yield. Analogously, (1E,3E)-1-trimethylsilyl-5,5-dimethyl-1,3-hexadiene (*8b*) was prepared in 84 % yield starting from (E)-3,3-dimethyl-

1-butenyl diisobutylalane (***18b***). Compounds ***18a*** and ***18b*** were prepared by reaction of a hexane solution of diisobutylalane with 1-heptyne and 3,3-dimethyl-1-propyne, respectively, at 50 °C for 6 h.

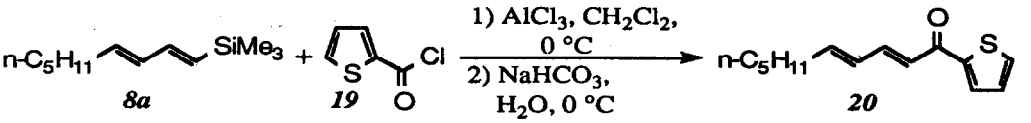


[5]

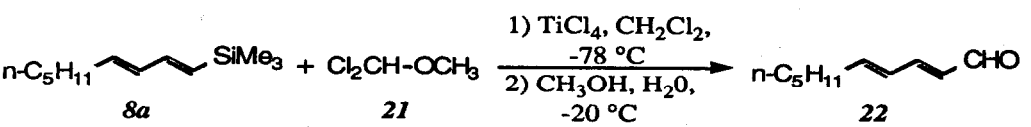
It must be noted that the usefulness of this simple and efficient diastereoselective procedure, which represents a new example of palladium-catalyzed highly diastereoselective cross-couplings involving the use of stereoisomeric mixtures of alkenyl bromides, is limited to the preparation of 4-alkyl substituted (1E,3E)-1-trimethylsilyl-1,3-dienes. In fact, while (E)-2-alkylethenyl diisobutylalanes such as ***18a*** and ***18b*** are easily and selectively prepared by hydroalumination of the corresponding 1-alkynes, hydroalumination of (hetero)arylacetylenes gives rise to mixtures of (E)-1-alkenyl and 1-alkynylalanes[24]. On this basis, no attempt was performed to use the above reported palladium-catalyzed alkenylation procedure for the synthesis of 4-(hetero)aryl substituted (1E,3E)-1-trimethylsilyl-1,3-dienes.

D) Utility of compounds *5 - 8* as synthetic intermediates

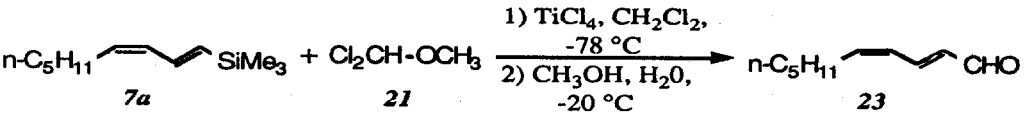
With efficient stereoselective methods for the preparation of polyunsaturated organosilanes available, we turned our attention to some their synthetic applications. First of all, some electrophilic substitution reactions were examined. Reaction of (1E,3E)-***8a*** with 2-thiophene carbonyl chloride (***19***), in the presence of $AlCl_3$, take place readily at 0 °C to give stereospecifically, upon hydrolysis, (1E,3E)-1-(2-thenoyl)-1,3-nonadiene (***20***) in 37 % yield (eq 6).



[6]



[7]



[8]

Interestingly enough, treatment of (1E,3E)-***8a*** with dichloromethyl methyl ether (***21***) at

–78 °C, in the presence of $TiCl_4$, upon hydrolysis at low temperature, gave pure (2E,4E)-2,4-decadienal (***22***) in 40 % yield (eq 7). Compound ***22*** is a flavouring chemical present in peanut, cottonseed and soybean oils[25]. Analogously, reaction of (1E,3Z)-***7a*** with ***21*** at –78 °C, in the presence of $TiCl_4$, produced stereospecifically (2E,4Z)-2,4-decadienal (***23***) in 45.1 % yield (eq 8). Compound ***23*** is one of the volatile constituents of black tea[26].

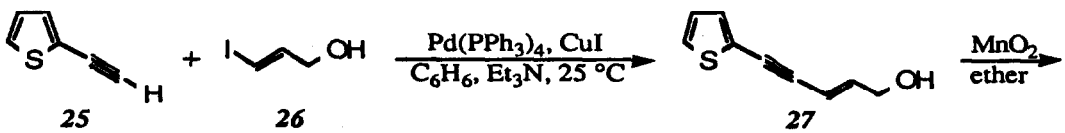
The 1-chloromethoxymethylation of (E)-1-trimethylsilyl-1-en-3-ynes (***5***), with replacement of the silyl group, appeared also interesting. In particular, the 1-chloromethoxymethylation of (E)-1-trimethylsilyl-4-(2-thienyl)-1-buten-3-yne (***5d***) could provide a convenient access to (E)-5-(2-thienyl)-2-penten-4-ynal (***24***), which is an acetylenic thiophene isolated from *Anthemis saguramica*[27].

5d

24

However, treatment of ***5d*** with ***21*** in dichloromethane at -78 °C, in the presence of $TiCl_4$, produced a relevant amount of a tarry material. GLC/MS analysis of the reaction mixture, after hydrolysis, using an authentic sample of ***24*** as standard, showed the absence of this aldehyde. The authentic sample of ***24***, which we also needed for biological studies, was prepared according to the reaction sequence reported in Scheme 2.

SCHEME 2

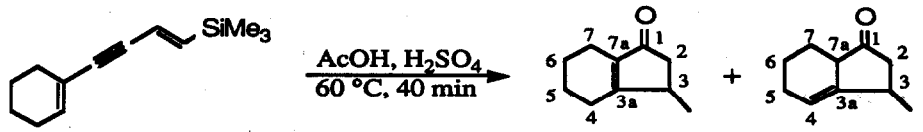


25 ***26*** ***27***

24

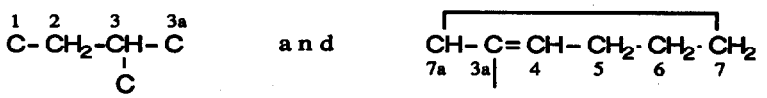
Thus, according to an improved Sonagashira procedure[28], 2-ethynylthiophene (***25***)[29] was coupled with (E)-3-iodo-2-propen-1-ol (***26***)[18c], in the presence of catalytic amounts of $Pd(PPh_3)_4$ and CuI. Compound ***27*** was obtained in 54.3 % yield. This pure alcohol was oxidized using manganese dioxide[30] to provide the desired aldehyde in 53.7 % yield.

Afterwards, a simple application of (1E,5E)-1-trimethylsilyl-1,5-dien-3-ynes (***6***) to the synthesis of 4-methylcyclopenten-2-ones was examined. The Nazarov cyclization[31] of (E)-1-trimethylsilyl-4-(1-cyclohexenyl)-1-buten-3-yne (***6b***) by reaction with a mixture of acetic acid and sulfuric acid at 60 °C for 40 min gave a mixture containing two regioisomeric ketones, ***28a*** and ***29***, which were separated by MPLC on a silica gel column (eq 9).



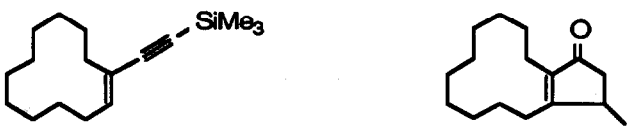
6b *28a* *29* [9]

Compound ***29***, which was recovered in 17.5 % yield from the first eluted fractions, exhibited a complex ^1H NMR spectrum. However, the structure of this ketone, which corresponded to 3-methyl-5,6,7,7a-tetrahydroindan-1-one, was elucidated using 2D NMR spectroscopy. In fact, a 2D ^1H NMR correlation (COSY)[32] spectrum helped to define two isolated spin systems in the molecule. These systems indicated the following moieties:



This structure determination was confirmed by single frequency decoupling experiments. The less easily eluted ketone, i.e. 3-methyl-4,5,6,7,-tetrahydroindan-1-one (***28a***), was obtained in 65 % yield. Its physical and spectroscopic properties were in agreement with those previously reported[33].

It must be noted that few years ago an analogous Nazarov cyclization of (E)-1-trimethylsilyl-4-[(E)-1-dodecenyl]-2-buten-3-yne (***6c***) allowed to prepare cyclopentenone ***28b*** in 64 % yield[17]. However, no mention on the formation of an isomeric cyclopentenone was reported in this communication[17].



6c *28b*

Finally, in order to evaluate the possibility to use polyunsaturated organosilanes as organometallic reagents in palladium-catalyzed carbon-carbon bond forming reactions, we examined the reactivity of compounds ***5a***, ***7a***, and ***8a*** with some (E)-1-iodo-1-alkenes and aryl iodides, in the presence of equimolar amounts of tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) and catalytic amounts of η^3-allylpalladium chloride. In fact, Hatanaka and Hiyama[34] have recently reported that vinyl-, ethynyl-, and allylsilanes react with aryl, vinyl and allyl halides, in the presence of TASF and η^3-allylpalladium chloride, to give stereospecifically the corresponding coupled products in synthetically useful yields (eq 10).

$$R^1X + R\text{-}SiMe_3 \xrightarrow[(\eta^3\text{-}C_3H_5PdCl)_2]{\text{TASF}} R\text{-}R^1 \qquad [10]$$

R^1 = aryl, alkenyl, allyl
R = vinyl, ethynyl, allyl

However, it was found that the trimethylsilyl substituted organosilanes ***5a***, ***7a***, and ***8a*** did not undergo the coupling reactions under the conditions reported in literature[34]. More recently, these unsuccessful results have been confirmed by Hatanaka and Hiyama[35] who found that the scope of the reactions reported in eq 10 is severely limited mainly due to low reactivity of trimethylsilyl substituted organosilanes compared with other organometallics.

Since introduction of a fluorine atom into the silicon substituent extremely accelerates the palladium-catalyzed reactions carried out in the presence of TASF or TBAB[35], we are now developing synthetically useful methods to prepare diastereoselectively mono- and polyunsaturated stereodefined dimethylfluorosilyl substituted organosilanes.

EXPERIMENTAL

All boiling and melting points are uncorrected. IR spectra were determined on a Perkin-Elmer 283B spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200, a Varian VXR 300, or a Brucker 360 spectrometer, using TMS as an internal standard. Mass spectra were recorded on a VG 70-70E mass spectrometer interfaced with a Dani 3800 gas-chromatograph. GLC analyses were performed on a Dani 6500 gas-chromatograph equipped with a Perkin Elmer LCI-100 integrator. Three types of capillary columns were used: a PEG-Permaphase bonded FSOT column (25 m x 0.23 mm i.d.), a SRL-300 bonded FSOT column (30 m x 0.25 mm i.d.), and a SRL-150 bonded FSOT column (30 m x 0.25 mm i.d.). Purifications by MPLC were performed on a Jobin-Yvon Chromatospac Prep 10 liquid chromatograph using a Knauer differential refractometer as detector. All reactions of air and water sensitive materials were performed in flame-dried glassware under an atmosphere of nitrogen or argon. All solvents were dried by conventional methods, freshly distilled and deareated. Air and water sensitive solutions were transferred with hypodermic syringes or double-ended needles.

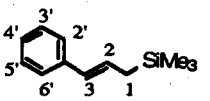
Starting materials - Tetrakis(triphenylphosphine)palladium was prepared according to the literature[36]. Titanocene dichloride, (E)/(Z)-ß-bromostyrene (***9a***), (E)/(Z)-2-bromo-2-butene (***9c***), (E)/(Z)-2-(bromovinyl)trimethylsilane (***11***), 2-methyl-3-butyn-2-ol (***16***), and 1-ethynylcyclohexene were commercially available. The following compounds were prepared according to literature procedures: (E)/(Z)-1-bromo-1-octene (***9b***)[8a], (E)-3-iodo-2-propen-1-ol (***26***)[18c], 2-ethynylthiophene (***25***)[29]. 1-Hexynyltrimethylstannane (***12e***) (b.p. 80.5 °C/12 torr) was prepared by reaction of an ether solution of 1-hexynyllithium with an equimolar amount of trimethyl chlorostannane at 0 °C[15].

General procedure for the synthesis of (E)-1-trimethylsilyl-2-alkenes (4) - In a typical procedure, to a suspension of $Pd(PPh_3)_4$ (6.0 g, 5.2 mmol) in THF (150 ml) was added a stereoisomeric mixture of an alkenyl bromide (***9***) (0.12 mol) containing 1 equiv of the (E)-stereoisomer. The resulting mixture, which was stirred at 20 °C, became homogeneous within 10 min.

A solution of trimethylsilylmethylmagnesium chloride (***10***) (0.1 mol) in THF (130 ml) was immediately added to this mixture maintained at 0 °C. The resulting reaction mixture, which was monitored by GLC until ca. 95 % of (E)-***9*** was consumed, was stirred at the temperature reported in Table 1. Ice-cold water was added and the mixture was extracted with ether. The extracts, which were analyzed by GLC, were filtered through Celite, dried and concentrated under reduced pressure. The residue was diluted with hexane

and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by MPLC on a silica gel column, using hexane as eluant, followed by fractional distillation on a Fisher column (Spaltrohr-system). Yields and stereoisomeric purities of (E)-1-trimethylsilyl-2-alkenes (*4*) so obtained are reported in Table 1. Some physical and spectroscopic properties of compounds *4* are reported below.

(E)-1-Trimethylsilyl-3-phenyl-2-propene (4a) - B.p. 122-3 °C/15 Torr. ^{1}H NMR (CCl_4): ∂ 7.35-6.90 (5H, m, H2' and H6'), 6.28-6.00 (2H, m, H2 and H3), 1.76-1.50 (2H, m, H1), 0.05 ppm (9H, s, CH_3)



IR (film): 3080, 3060, 3020, 2900, 2890, 2790, 1940, 1870, 1800, 1740, 1640, 1595, 1490, 1445, 1400, 1300, 1280, 1245, 1205, 1145, 1070, 1020, 1000, 970, 955, 900, 855, 840, 830, 780, 750, 735, and 685 cm^{-1}. These physical and spectroscopic properties matched with those previously reported[12,13].

(E)-1-Trimethylsilyl-2-nonene (4b) - B.p. 95-96 °C/11 Torr. ^{1}H NMR ($CDCl_3$): ∂ 5.38 (1H, dt, J = 15.1 and 7.4 Hz, H2), 5.23 (1H, dt, J = 15.1 and 6.0 Hz, H3), 1.97 (2H, br q, J = 6.0 Hz, H4), 1.40 (2H, d, H1), 1.45-1.16 (8H, br, H5, H6, H7, and H8), 0.88 (3H, t, J = 6.4 Hz, H9), -0.02 (9H, s, CH_3). IR (film): 3005, 2950, 2920, 2870, 2850, 1660, 1465, 1435, 1400, 1375, 1290, 1245, 1150, 1090, 1055, 1025, 955, 840, 740, 715, and 685 cm^{-1}. MS (m/e): 199 (M+1, 3), 198 (M, 15), 184 (3), 183 (13), 155 (3), 127(3), 97 (7), 75 (8), 74 (20), 73 (100), 69 (5), 67 (5), 59 (19), 55 (8), 54 (11), 45 (12), 43 (11). Found : C, 72.61; H, 13.08. Calc. for $C_{12}H_{26}Si$: C, 72.64; H, 13.21.

(E)-1-Trimethylsilyl-2-methyl-2-butene (4c) - B.p. 84-85 °C/150 Torr. ^{1}H NMR ($CDCl_3$): ∂ 5.01 (1H, br q, J = 6.0 Hz, H3), 1.68-1.42 (8H, br m, allylic protons), 0.02 ppm (9H, s, $Si(CH_3)_3$). IR (film): 3045, 3020, 2955, 2910, 2860, 1660, 1440, 1410, 1380, 1245, 1210, 1160, 1000, 850, 840, 745, 685, and 650 cm^{-1}. MS (m/e): 142 (M, 10), 127 (3), 99 (5), 85 (4), 75 (4), 74 (8), 73 (100), 59 (12), 45 (10), 43 (8). Found : C, 67.47; H, 12.68. Calc. for $C_8H_{18}Si$: C, 67.51; H, 12.75.

General procedure for the synthesis of (E)-1-trimethylsilyl-1-alken-3-ynes (5) and (1E,5E)-1-trimethylsilyl-1,5-alkadien-3-ynes (6) - In a typical experiment, a freshly distilled 1-alkyne (50 mmol) was slowly added to a solution of ethylmagnesium bromide (50 mmol) in THF (70 ml) maintained under stirring at 65 °C. After the addition was complete, heating was continued for 1 h. The THF solution was added to a solution of $ZnCl_2$ (6.81 g, 50 mmol) in THF (50 ml) cooled at -20 °C and the resulting mixture was stirred for 0.5 h. A solution of $Pd(PPh_3)_4$ (1.73 g, 1.5 mmol) and (E)/(Z)-2-(bromovinyl)trimethylsilane (*11*) (10.6g, 59 mmol) (E/Z = 89/11) in THF (45 ml), which was prepared immediately prior to use, was added and the resulting mixture was stirred at the temperature reported in Table 2. The reaction mixture, which was monitored by GLC until ca. 95 % of (E)-11 was consumed, was stirred for the required lenght of time (Table 2). Then, it was quenched by addition of a saturated NH_4Cl solution, diluted with water, and extracted with ether (4 x 60 ml). The combined extracts were washed with water, filtered through Celite, dried and concentrated *in vacuo*. The residue was diluted with hexane and filtered. The filtrate was concentrated *in vacuo* and purified by fractional distillation. Yields and stereoisomeric purities of (E)-1-trimethylsilyl-1-alken-3-ynes (*5*) and (1E,5E)-1-trimethylsilyl-1,5-alkadien-3-ynes (*6*) so prepared are reported in Table 2. Some physical and spectroscopic properties of compounds *5* and *6*, as well as the starting materials used in their preparation, are reported below.

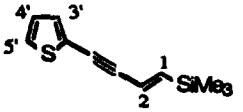
(E)-1-Trimethylsilyl-1-nonen-3-yne (5a) - This compound, which was prepared in 78 % yield from 1-heptynylzinc chloride (*12a*) and (E)/(Z)-*11*, had: b.p. 97 °C/3 Torr. ^{1}H NMR ($CDCl_3$) : ∂ 6.29 (1H,

d, J = 20.1 Hz, H1), 5.94 (1H, dt, J = 20.1 and 3.0 Hz, H2), 2.27 (2H, td, J = 6.2 and 2.2 Hz, H5), 1.56-1.44 (2H, br m, H6), 1.42-1.22 (4H, br m, H7 and H8), 0.87 (3H, t, H9), 0.07 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 194 (M, 9), 181 (18), 179 (100), 139 (10), 138 (46), 123 (54), 109 (16), 95 (18), 85 (14), 83 (24), 73 (58), 59 (94), 45 (16). IR (film): 3000, 2960, 2930, 2900, 2890, 2880, 2200, 1575, 1470, 1460, 1430, 1380, 1330, 1260, 1250, 1210, 1050, 980, 860, 845, 735, 720, and 685 cm^{-1}. Found : C, 73.92; H, 11.51. Calc. for $C_{12}H_{22}Si$: C, 74.14; H, 11.40.

(E)-1-Trimethylsilyl-4-phenyl-1-buten-3-yne (5b) - This compound, which was prepared in 88 % yield from phenylethynylzinc chloride (***12b***) and (E)/(Z)-***11***, had: b.p. 85-86 °C/0.2 Torr. Lit[16] b.p. 140 °C/15 Torr. ^1H NMR (CCl_4): ∂ 7.39-7.16 (5H, m, C_6H_5), 6.42 (1H, d, J = 19.2 Hz, H1), 6.07 (1H, d, J = 19.2 Hz, H2), 0.10 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 200 (M, 34), 185 (98), 181 (18), 160 (17), 159 (100), 145 (11), 129 (8.5), 73 (8), 59 (18), 43 (13). IR (film): 3090, 3070, 3040, 3000, 2960, 2200, 1600, 1575, 1490, 1445, 1265, 1250, 1210, 1070, 1030, 1005, 975, 910, 860, 840, 750, 730, 710, and 690 cm^{-1}.

(E)-1,4-Bis(trimethylsilyl)-1-buten-3-yne (5c) - This compound, which was prepared in 77 % yield from trimethylsilylethynylzinc chloride (***12c***) and (E)/(Z)-***11***, had: b.p. 88 °C/16 Torr. ^1H NMR ($CDCl_3$): ∂ 6.51 (1H, d, J = 19.5 Hz, H1), 5.97 (1H, d, J = 19.5 Hz, H2), 0.19 and 0.08 ppm (18H, 2s, $Si(CH_3)_3$). MS (m/e): 196 (M, 15), 182 (20), 181 (100), 155 (20), 123 (15), 119 (12), 97 (10), 83 (18), 72 (82), 70 (52), 45 (10). IR (film): 3000, 2960, 2900, 2150, 2080, 1570, 1410, 1250, 1050, 975, 840, 755, 740, 735, 690, and 635 cm^{-1}. Found : C, 61.55; H, 9.44. Calc. for $C_{10}H_{20}Si_2$: C, 61.14; H, 10.26.

(E)-1-Trimethylsilyl-4-(2-thienyl)-1-buten-3-yne (5d) - This compound, which was prepared in 87 % yield from 2-thienylethynylzinc chloride (***12d***) and (E)/(Z)-***11***, had: b.p. 82 °C/0.02 Torr. ^1H NMR ($CDCl_3$): ∂ 7.24 (1H, dd, H5'), 7.18 (1H, dd, H3'), 6.96 (1H, dd, H4'), 6.53 (1H, d, J = 19.3 Hz, H1 or H2), 6.15 (1H, d, J = 19.3 Hz, H2 or H1), 0.11 ppm (9H, s, $Si(CH_3)_3$).

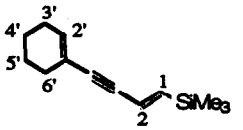


IR (film): 3015, 3075, 2990, 2955, 2890, 2180, 1570, 1420, 1400, 1295, 1260, 1250, 1205, 1195, 1075, 1040, 970, 860, 845, 835, 770, 730, 720, 690, 655, and 610 cm^{-1}. MS (m/e): 207 (M+1, 8), 206 (M, 45), 193 (7), 192 (14), 191 (84), 167 (9), 166 (15), 165 (100), 151 (7), 73 (18), 59 (13), 45 (7), 43 (10). Found : C, 64.02; H, 6.84. Calc. for $C_{11}H_{14}SSi$: C, 64.25; H, 7.00.

(1E,5E)-1-Trimethylsilyl-1,5-nonadien-3-yne (6a) - This compound was obtained in 65 % yield from (E)-3-hepten-1-ynylzinc chloride (***12f***) and (E)/(Z)-***11***. Compound ***12f*** was prepared from (E)-3-hepten-1-yne[18c], according to the procedure described for the preparation of ***12a-d***. Compound ***6a*** had: b.p. 95-96 °C/2 Torr. ^1H NMR ($CDCl_3$): ∂ 6.39 (1H, d, J = 19.2 Hz, H1), 6.15 (1H, dt, J = 15.9 and 7.2 Hz, H6), 6.04 (1H, dd, J = 19.2 and 1.8 Hz, H2), 5.60 (1H, br dd, J =15.9 and 1.8 Hz, H5), 2.10 (2H, dq, J = 7.2 and 1.3 Hz, H7), 1.43 (2H, m, J = 7.3 Hz, H8), 0.91 (3H, t, J = 7.3 Hz, H9), and 0.08 ppm (9H, s, $Si(CH_3)_3$). IR (film): 3020, 2990, 2950, 2920, 2890, 2865, 2830, 2175, 1565, 1455, 1430, 1375, 1335, 1330, 1245, 1205, 1180, 1005, 970, 855, 835, 755, 730, 720, and 680 cm^{-1}. MS (m/e): 193 (M+1, 7), 192 (M, 33), 183 (12), 178 (12), 177 (64), 163 (14), 152 (10), 151 (65), 137 (8), 135 (13), 133 (8), 123 (8), 111 (8), 110 (23), 109 (16), 95 (10), 83 (13), 74 (10), 73 (100), 59 (47), 45 (13), 43 (14). Found : C, 75.17; H, 11.07. Calc. for $C_{12}H_{20}Si$: C, 74.92; H, 10.48.

(E)-1-Trimethylsilyl-4-(1-cyclohexenyl)-1-buten-3-yne (6b) - This compound, which was obtained in 81 % yield from (1-cyclohexenyl)ethynylzinc chloride (***12g***) and (E)/(Z)-***11***, had: b.p. 77

°C/0.15 Torr. ^{1}H NMR ($CDCl_3$): ∂ 6.38 (1H, d, J = 19.2 Hz, H1 or H2), 6.15-6.08 (1H, m, H2'), 6.06 (1H, d, J = 19.2 Hz, H2 or H1), 2.20-2.16 (4H, br m, H3' and H6'), 1.72-1.50 (4H, br m, H4' and H5'), and 0.08 ppm (9H, s, $Si(CH_3)_3$).



MS (m/e) : 205 (M+1, 10), 204 (M, 15), 190 (13), 189 (71), 164 (16), 163 (100), 150 (10), 145 (12), 126 (9), 123 (23), 109 (8), 83 (12), 73 (23), 72 (8), 59 (28), 45 (8). Found : C, 76.32; H, 9.95. Calc. for $C_{13}H_{20}Si$: C, 76.39; H, 9.86.

Synthesis of (E)-1-trimethylsilyl-1-octen-3-yne (5e) from 1-hexynyltrimethylstannane (12e) and (E)/(Z)-11 - A solution of $Pd(PPh_3)_4$ (2.5 g, 2.2 mmol) and (E)/(Z)-2-(bromovinyl)-trimethylsilane (*11*) (7.5 ml, 49 mmol) (E/Z = 93.5/6.5) in DMF (100 ml) was cooled at 0 °C. 1-Hexynyl-trimethylstannane (*12e*) (10.7 g, 43.5 mmol) was added and the resulting mixture was stirred for 0.5 h at 0 °C, then maintained at 80 °C for 1.5 h. During this time ca. 95 % of (E)-*11* was consumed. The mixture was poured into ice-water and extracted with pentane (3 x 100 ml). The combined extracts were filtered, dried and concentrated *in vacuo*. The residue was purified by MPLC on a silica gel column, followed by fractional distillation. (E)-1-Trimethylsilyl-1-octen-3-yne (*5e*), having stereoisomeric purity higher than 99 %, was obtained in 53 % yield. B.p. 100-101 °C/25 Torr. ^{1}H NMR ($CDCl_3$): ∂ 6.18 (1H, d, J = 19.2 Hz, H1), 5.82 (1H, dt, J = 19.2 and 2.0 Hz, H2), 2.27 (2H, td, J = 6.6 and 2.0 Hz, H3 and H5), 1.61-1.31 (4H, br m, H6 and H7), 0.94 (3H, t, J = 7.1 Hz, H8), and 0.08 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 180 (M, 9), 165 (81), 139 (21), 138 (31), 123 (44), 109 (16), 97 (16), 96 (16), 95 (18), 85 (13), 83 (32), 73 (58), 60 (9), 59 (100), 45 (33), 43 (38). Found : C, 73.05; H, 11.12. Calc. for $C_{11}H_{20}Si$: C, 73.25; H, 11.14.

(E)-6-Trimethylsilyl-2-methyl-5-hexen-3-yn-2-ol (17) - Deareated 2-methyl-3-butyn-2-ol (*16*) (12.0 g, 143 mmol) and 2-(bromovinyl)trimethylsilane (*11*) (28.9 g, 161 mmol) (E/Z = 93.3/6.7) were added to a mixture of $BnEt_3N^+Cl^-$ (1.69 g, 5 mmol), CuI (1.63 g, 8.5 mmol), and $Pd(PPh_3)_4$ (4.96 g, 4.3 mmol) in benzene (128 ml). A deareated 10 % aqueous solution of NaOH (268 ml) was added and the resulting mixture was stirred at 20 °C for 4 h. After this time the mixture was treated with a large excess of a saturated NH_4Cl solution, and extracted with pentane (4 x 100 ml). The extracts were washed with a saturated NH_4Cl solution, and water until neutrality, filtered through Celite, dried and concentrated *in vacuo*. The residue was purified by MPLC on a silica gel column, using a mixture of hexane and ether (9/1 ratio) as eluant. The collected fractions were concentrated, diluted with pentane, and filtered through Celite. The filtrate was concentrated and fractionally distilled to give compound *17* (21.8 g, 83.8 % yield): b.p. 108-109 °C/13 Torr. ^{1}H NMR (CCl_4): ∂ 6.26 (1H, d, J = 19.3 Hz, H6), 5.88 (1H, d, J = 19.3 Hz, H5), 2.89 (1H, s, OH), 1.47 (6H, s, H1 and CH_3), 0.08 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 182 (M, 46), 181 (11), 167 (28), 101 (9), 91 (11), 76 (11), 75 (100), 73 (19), 59 (25), 43 (14). IR (film): 3350, 2980, 2960, 2900, 1575, 1460, 1440, 1405, 1375, 1365, 1330, 1310, 1250, 1210, 1165, 1140, 1070, 980, 950, 860, 840, 740, 725, 690, and 660 cm^{-1}. Found : C, 65.73, H, 9.86. Calc. for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95.

(E)-1-Trimethylsilyl-1-buten-3-yne (5f) - A solution of compound *17* (21.3 g, 115 mmol) in tetrahydronaphtalene (60 ml) was reacted under a nitrogen atmosphere with solid NaOH (4.69 g, 117 mmol). The mixture was stirred at 125 °C for 1 h, cooled and subsequently distilled at 13 Torr, while the temperature was gradually increased to 100 °C. The crude reaction product, which was collected in a trap maintained at –78 °C, was washed twice with a saturated NaCl and Na_2CO_3 solution, dried, and distilled to give compound *5f* (9.84 g, 67.7 % yield). GLC analysis showed that compound *5f* had 97 % chemical purity

and stereoisomeric purity higher than 99 %. B.p. 120 °C. ^{1}H NMR (CCl_4): ∂ 6.45 (1H, d, J = 19.3 Hz, H1), 5.85 (1H, dd, J = 19.3 and 2.1 Hz, H2), 2.80 (1H, d, J = 2.1 Hz, H4), 0.10 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 124 (M, 8), 111 (13), 109 (100), 83 (35), 73 (13), 67 (13), 59 (54), 53 (24), 45 (16), 43 (44). IR (film): 3300, 3000, 2980, 2900, 2100, 1300, 1260, 1250, 1210, 1050, 975, 865, 840, 770, 720, 690, and 610 cm^{-1}. Owing to its volatility, a satisfactory elemental analysis of ***5f*** could not be obtained.

(1E,3Z)-1-Trimethylsilyl-1,3-nonadiene ***(7a)*** - In a typical procedure (Table 3, entry 3), 2-methyl-2-butene (1.49 g, 21.3 mmol) was added during 20 min to a 10 M solution of borane-dimethylsulfide complex (1.03 ml, 10.3 mmol) in THF (11.7 ml), cooled at -20 °C. The resulting solution was stirred at 20 °C for 2h and, subsequently, added during 10 min to a solution of (E)-1-trimethylsilyl-1-nonen-3-yne (***5a***) (2.0 g, 10.3 mmol) in THF (2.1 ml), cooled at -10 °C. The mixture was stirred at 20 °C for 3 h and, then, concentrated at 20 Torr in order to eliminate dimethylsulfide. The resulting solution was diluted with THF (5 ml) and cooled at 0 °C. Acetic acid (6.4 g, 86 mmol) was added and the mixture was stirred at 60 °C for 7 h. After cooling at 0 °C, 3 N NaOH (38 ml) was slowly added. Finally, 35 % hydrogen peroxide (2.5 ml) was slowly added, while the temperature was maintained lower than 40 °C. The resulting reaction mixture was stirred at 40 °C for 3 h, then cooled to 20 °C, diluted with a saturated NaCl solution and extracted with hexane (4 x 50 ml). The combined extracts were washed with water, dried, concentrated *in vacuo*, and purified by MPLC on a silica gel column, using hexane as eluant. The collected chromatographic fractions were concentrated to give compound ***7a*** (1.43 g, 71 % yield). ^{1}H NMR ($CDCl_3$): ∂ 6.81 (1H, ddd, J = 18.2, 10.7, and 1.1 Hz, H2), 5.92 (1H, t, J = 10.8 Hz, H3), 5.82 (1H, d, J = 18.2 Hz, H1), 5.43 (1H, dt, J = 10.8 and 7.6 Hz, H4), 2.26-2.16 (2H, m, H5), 1.45-1.22 (6H, m, H6, H7 and H8), 0.93-0.83 (3H, m, H9), 0.08 ppm (9H, s, $Si(CH_3)_3$). Decoupling experiments showed that $J_{(H1-H2)}$ = 10.8 Hz, $J_{(H2-H3)}$ = 10.6 Hz, $J_{(H3-H4)}$ = 18.2 Hz. Ms (m/e): 196 (M, 5), 181 (17), 126 (5), 125 (11), 112 (6), 111 (17), 97 (6), 85 (6), 74 (8), 73 (100), 59 (67), 55 (48), 52 (45), 45 (11), 42 (10). IR (film): 3020, 2960, 2930, 2880, 2860, 1635, 1575, 1470, 1460, 1400, 1380, 1260, 1250, 1000, 960, 865, 840, 770, 730, 710, 690, and 615 cm^{-1}. Found : C, 73.66; H, 12.53. Calc. for $C_{12}H_{24}Si$: C, 73.88; H, 12.32. GLC analysis showed that compound ***7a*** had 99.3 % stereoisomeric purity.

Two other different procedures to prepare ***7a***, which were based on the hydroalumination or the hydromagnesiation of ***5a***, followed by protonolysis (Table 3, entries 1 and 2) gave unsatisfactory results.

(1E,3Z)-1-Trimethylsilyl-4-phenyl-1,3-butadiene ***(7b)*** - In a typical experiment (Table 3, entry 5), neat diisobutylaluminium hydride (0.88 g, 6.16 mmol) was added to a solution of (E)-1-trimethylsilyl-4-phenyl-1-buten-3-yne (***5b***) (1.12 g, 5.6 mmol) in ether (6 ml). The mixture was stirred at 35 °C for 30 h, then cooled to 20 °C, carefully poured into ice-cold 3 N NaOH (28 ml), and extracted with hexane (4 x 30 ml). The combined extracts were washed with a saturated NaCl solution, dried, and concentrated *in vacuo* to give compound ***7b*** (0.42 g, 38 % yield): ^{1}H NMR (CCl_4): ∂ 7.31-7.12 (5H, br m, C_6H_5), 7.00 (1H, dd, J = 18.3 and 11.1 Hz, H2), 6.37 (1H, d, J = 11.5 Hz, H4), 6.16 (1H, t, J = 11.1 Hz, H3), 5.95 (1H, dd, J = 18.3 and 0.9 Hz, H1), 0.08 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 202 (M, 8), 187 (14), 145 (9), 129 (13), 128 (47), 73 (46), 59 (100), 58 (11), 45 (11), 43 (29). Found : C, 77.41; H, 9.03. Calc. for $C_{13}H_{18}Si$: C, 77.15; H, 8.96. GLC analysis showed that compound ***7b*** had 96.2 % stereoisomeric purity.

The preparation of compound ***7b*** by hydroboration of ***5b***, according to the procedure followed to prepare compound ***7a***, afforded the desired dienylsilane in 59 % yield and 91.9 % stereoisomeric purity (Table 3, entry 6).

Poorer results were obtained by hydroalumination of ***5b*** in hexane solution at 50 °C (Table 3, entry 4).

(1E,3Z)-1,4-Bis(trimethylsilyl)-1,3-butadiene ***(7c)*** - Neat diisobutylaluminium hydride (5.06 g, 35.6 mmol) was added to a solution of 1,4-bis(trimethylsilyl)-1-buten-3-yne (***5c***) (6.35 g, 32.4 mmol) in

ether (33 ml), which was maintained at 20 °C. The mixture, which was monitored by GLC, was stirred at 35 °C for 7 h, then cooled to room temperature, carefully poured into ice-cold 3 N NaOH (162 ml), and extracted with pentane (4 x 50 ml). The combined extracts were washed with a saturated NaCl solution, dried, and fractionally distilled to give compound ***7c*** (5.6 g, 87 % yield): b.p. 80 °C/21 Torr. ^{1}H NMR (CCl_4): ∂ 6.78-6.63 (2H, br m, H2 and H3), 5.83 (1H, br d, J = 16.6 Hz, H1), 5.61 (1H, d, J = 11.2 Hz, H4), 0.16 and 0.09 ppm (18 H, 2s, $Si(CH_3)_3$). MS (m/e): 198 (M, 6), 183 (11), 181 (6), 131 (8), 110 (22), 75 (13), 73 (100), 69 (30). IR (film): 3050, 2960, 2900, 1545, 1410, 1260, 1250, 1175, 1045, 1000, 965, 870, 835, 760, 745, 730, 685, 670, and 615 cm^{-1}. Found: C, 59.99; H, 11.32. Calc for $C_{10}H_{22}Si$: C, 60.52; H, 11.17. GLC analysis showed that compound ***7c*** had 99.4 % stereoisomeric purity (Table 3, entry 7).

General procedure for the diastereoselective alkenylation of (E)/(Z)-2-(bromovinyl)trimethylsilane ***(11)*** - In a typical experiment, a 1 M hexane solution of diisobutylaluminium hydride (72.5 ml, 72.5 mmol), was slowly added to a freshly distilled 1-alkyne (72.5 mmol). The mixture was stirred for 6 h at 50 °C and, subsequently, added to a solution of (E)/(Z)-***11*** (13.8 g, 76.8 mmol) (E/Z = 94.4/5.6) and $Pd(PPh_3)_4$ (2.50 g, 2.2 mmol) in THF (100 ml), cooled at 0 °C. The mixture was stirred for 16 h at 42 °C, then poured into ice-water and extracted with ether (4 x 100 ml). The combined extracts were filtered, dried, and concentrated *in vacuo*. The residue was diluted with pentane, filtered through Celite, concentrated *in vacuo*, and purified by MPLC on a silica gel column, using hexane as eluant. Fractional distillation of the collected chromatographic fractions gave the desired (1E,3E)-1-trimethylsilyl-1,3-alkadiene (***8***) having stereoisomeric purity higher than 99 %.

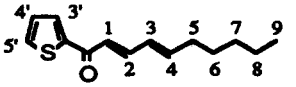
Some physical and spectroscopic properties of the (1E,3E)-1-trimethylsilyl-1,3-alkadienes prepared using this procedure, i.e ***8a*** and ***8b***, are reported below.

(1E,3E)-1-Trimethylsilyl-1,3-nonadiene ***(8a)*** - This compound, which was prepared in 74.7 % yield from 1-heptyne and (E)/(Z)-***11***, had: b.p. 79-80 °C/6 Torr. ^{1}H NMR (CCl_4): ∂ 6.37 (1H, dd, J = 18.6 and 10.1 Hz, H2), 5.95 (1H, br dd, J =14.1 and 10.1 Hz, H3), 5.70-5.53 (2H, m, H1 and H4), 2.12-2.00 (2H, m, H5), 1.46-1.22 (6H, br m, H6, H7, and H8), 0.89 (3H, br t, J = 6.6 Hz, H9), 0.05 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 196 (M, 16), 181 (54), 125 (18), 112 (13), 111 (29), 109 (10), 73 (54), 59 (100), 45 (15), 43 (15). IR (film): 3050, 2960, 2930, 2870, 1640, 1580, 1470, 1460, 1380, 1310, 1260, 1245, 1180, 1000, 950, 860, 830, 770, 720, 685, and 610 cm^{-1}. Found : C, 73.92; H, 11.51. Calc for $C_{12}H_{24}Si$: C, 74.14; H, 11.40.

(1E,3E)-1-Trimethylsilyl-5,5-dimethyl-1,3-hexadiene ***(8b)*** - This compound, which was prepared in 84 % yield from 3,3-dimethyl-1-propyne and (E)/(Z)-***11***, had: b.p. 96 °C/29 Torr. Lit[20a] b.p. 87-89 °C/136 Torr. ^{1}H NMR ($CDCl_3$): ∂ 6.37 (1H, dd, J = 18.3 and 9.5 Hz, H2), 5.90 (1H, dd, J = 15.4 and 9.5 Hz, H3), 5.67 (1H, d, J = 15.4 Hz, H4), 5.64 (1H, d, J = 18.3 Hz, H1), 1.04 (9H, s, $C(CH_3)_3$), and 0.06 ppm (9H, s, $Si(CH_3)_3$). MS (m/e): 182 (M, 8), 167 (11), 107 (6), 74 (8), 73 (100), 59 (32), 57 (14), 45 (8), 43 (8). Found : C, 72.62; H, 12.51. Calc. for $C_{11}H_{22}Si$: C, 72.44; H, 12.17.

(1E,3E)-1-(2-Thenoyl)-1,3-nonadiene ***(20)*** - A suspension of anydrous $AlCl_3$ (1.2 g, 8.9 mmol) in dichloromethane (45 ml) was stirred for 20 min at room temperature, then it was cooled to 0 °C. 2-Thenoyl chloride (***19***) (11.3 g, 8.9 mmol) was added and the mixture was stirred at 20 °C for 1 h, then cooled to 0 °C. (1E,3E)-1-Trimethylsilyl-1,3-nonadiene (***8a***) (1.75 g, 9.9 mmol) was added and the mixture was stirred at 0 °C for 1h and 45 min, and subsequently at 20 °C for 2 h. This mixture was poured into ice-cold water and $NaHCO_3$ and extracted with hexane (3 x 100 ml). The combined extracts, after usual work up, were concentrated and purified by MPLC on a silica gel column, using a mixture of hexane and ether (95/5) as eluant. The collected chromatographic fractions were concentrated *in vacuo* to give compound ***20*** (0.73 g,

37 % yield). ^{1}H NMR (CCl_4): ∂ 7.75 (1H, dd, J = 3.8 and 1.1 Hz, H3' or H5'), 7.63 (1H, dd, J = 4.9 and 1.2 Hz, H5' or H3'), 7.44 (1H, dd of m, J = 14.9 and 10.2 Hz, H2), 7.14 (1H, dd, J = 4.9 and 3.8 Hz, H4'), 6.79 (1H, d, J = 14.9 Hz, H1), 6.32-6.25 (2H, m, H3 and H4), 2.25-2.16 (2H, m, H5), 1.52-1.22 (6H, br m, H6, H7, and H8), 0.90 ppm (3H, br t, J = 6.9 Hz, H9).



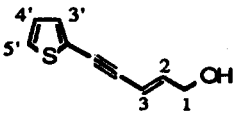
MS (m/e): 234 (M, 6), 164 (14), 163 (100), 135 (10), 111 (43), 91 (63), 83 (6), 67 (6), 41 (9), 39 (14). Found : C, 72.03; H 8.01. Calc. for $C_{14}H_{18}OSi$: C, 71.75; H, 7.74. GLC analysis showed that compound **20** had chemical and stereoisomeric purity higher than 98.5 %.

(2E,4E)-2,4-Decadienal (22) - A solution of $TiCl_4$ (0.86 ml, 7.8 mmol) in dichloromethane (15 ml) was added during 40 min to a solution of dichloromethyl methyl ether (0.92 g, 7.7 mmol) and (1E,3E)-1-trimethylsilyl-1,3-nonadiene (*8a*) (1.50 g, 7.6 mmol) in dichlorometane (15 ml) cooled at -78 °C. The resulting mixture was stirred at -78 °C for 1 h and 20 min, then hydrolyzed by addition of 50 % aqueous methanol at -20 °C. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 x 10 ml). The combined organic extracts were washed with 5 % aqueous $NaHCO_3$ solution, dried and concentrated. The residue was purified by MPLC on a silica gel column, using a mixture of hexane and ether (9/1) as eluant. The eluted chromatographic fractions were analyzed by GLC and concentrated *in vacuo* to give compound *22* (0.47 g, 40.4 % yield): ^{1}H NMR ($CDCl_3$): ∂ 9.54 (1H, d, J = 8.1 Hz, H1), 7.10 (1H, dd of m, J = 15.1 and 10.0 Hz, H3), 6.34-6.27 (2H, m, H4 and H5), 6.07 (1H, dd, J = 15.1 and 8.1 Hz, H2), 2.27-2.17 (2H, m, H6), 1.60-1.20 (6H, m, H7, H8, and H9), 1.00-0.85 ppm (3H, br t, H10). ^{1}H NMR ($CDCl_3$, in the presence of 0.5 mol % of Resolve-Al EuFOD): ∂ 11.20 (1H, d, J = 8.0 Hz, H1), 8.36 (1H, dd, J = 14.8 and 8.0 Hz, H2), 7.85 (1H, dd, J = 14.8 and 10.8 Hz, H3), 6.85 (1H, dd, J = 14.9 and 10.8 Hz, H4), 6.50 ppm (1H, dt, J = 14.9 and 6.9 Hz, H5). ^{13}C NMR ($CDCl_3$): ∂ 194.2, 153.0, 147.5, 130.2, 128.8, 32.8, 31.0, 27.9, 22.0, 13.5 ppm. MS (m/e): 152 (M, 56), 123 (37), 109 (37), 108 (16), 95 (8), 83 (11), 81 (100), 67 (18), 55 (13), 41 (39), 39 (30). IR (film): 3360, 3040, 2960, 2930, 2880, 2740, 1690, 1860, 1640, 1600, 1590, 1470, 1460, 1435, 1380, 1290, 1165, 1120, 1110, 1010 cm^{-1}. GLC analysis showed that compound *22* had 97.3 % stereoisomeric purity and chemical purity higher than 99 %. 2,4-Dinitrophenylhydrazone of *22* had: m.p. 141 °C (from ethanol). Lit.[37] m.p. 142-144 °C.

(2E,4Z)-2,4-Decadienal (23) - This compound was prepared in 45.1 % yield from (1E,3Z)-1-trimethylsilyl-1,3-nonadiene (*7a*) and dichloromethyl methyl ether (*21*), according to the same procedure employed to prepare compound *22*.

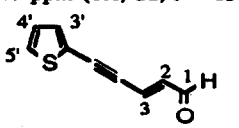
The spectroscopic properties of compound *23*, which had stereoisomeric purity higher than 98.6 %, matched those previously reported [38].

(E)-5-(2-Thienyl)-2-penten-4-yn-1-ol (27) - A deareated solution of 2-ethynylthiophene (*25*)[29] (6.5g, 60 mmol) and (E)-3-iodo-2-propen-1-ol (*26*)[18c] (11.0 g, 60 mmol) in benzene (75 ml) was added to a stirred mixture of $Pd(PPh_3)_4$ (2.6 g, 2.3 mmol), CuI (0.87 g, 4.6 mmol) and triethylamine (14 ml) in benzene (85 ml). The resulting mixture was stirred at room temperature for 2 h, then diluted with ether and washed repeatedly with a saturated NH_4Cl solution. The organic phase was washed with water, dried, and concentrated *in vacuo*. The residue was purified by MPLC on a silica gel column, using a mixture of hexane and benzene (2/1) as eluant. The collected chromatographic fractions were fractionally distilled to give compound *27* (5.3 g, 54.3 % yield): b.p. 115-116 °C/0.03 Torr. ^{1}H NMR ($CDCl_3$): ∂ 7.48-7.22 (2H, m, H3' and H5'), 7.08 (1H, dd, J = 5.0 and 3.6 Hz, H4'), 6.52 (1H, dt, J = 15.3 and 4.5 Hz, H2), 6.10 (1H, d, J = 15.3 Hz, H3), 4.41 (2H, br d, J= 4.5 Hz, H1), and 2.00 ppm (1H, br s, OH).



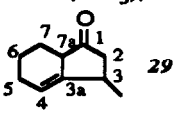
IR (film): 3940, 3820, 3340, 3100, 3030, 2910, 2860, 2700, 2190, 1990, 1940, 1900, 1800, 1755, 1725, 1660, 1630, 1600, 1530, 1445, 1425, 1370, 1290, 1270, 1240, 1195, 1135, 1090, 1040, 975, 945, 900, 845, 825, and 695 cm^{-1}. MS (m/e): 165 (M+1, 13), 164 (M, 100), 163 (28), 136 (20), 135 (87), 134 (20), 121 (27), 120 (16), 108 (40), 91 (51), 89 (13), 77 (13), 69 (14), 63 (15), 43 (20). Found : C, 66.00; H, 5.01. Calc. for C_9H_8OS : C, 65.82; H, 4.91. GLC analysis showed that compound ***27*** had chemical and stereoisomeric purity higher than 99 %.

(E)-5-(2-Thienyl)-2-penten-4-ynal (24) - A mixture of compound ***27*** (5.0 g, 30 mmol) and manganese dioxide[30] (100g, 1.15 mol) in ether (375 ml) was stirred for 2 h at room temperature. The mixture was filtered through Celite and the solid obtained was washed repeatedly with ether (4 x 50 ml). The collected organic phases were concentrated and the residue was crystallyzed from hexane to give compound ***24*** (2.6 g, 53.7 % yield): m.p. 40-41 °C. Lit[27] m.p. 41.5 °C. ^1H NMR (CCl_4): ∂ 9.56 (1H, d, J = 7.3 Hz, H1), 7.38 (1H, d, J = 5.0 Hz, H5'), 7.29 (1H, d, J = 3.6 Hz, H3'), 7.02 (1H, dd, J = 5.0 and 3.6 Hz, H4'), 6.74 (1H, d, J = 15.9 Hz, H3), and 6.47 ppm (1H, dd, J = 15.9 and 7.3 Hz, H2).



MS (m/e): 163 (M+1, 10), 162 (M, 82), 134 (93), 133 (15), 108 (100), 93 (10), 90 (19), 89 (38), 87 (10), 75 (15), 74 (18), 69 (24), 63 (28), 62 (14), 58 (14), 50 (13), 45 (23). IR (film): 3300, 3100, 3005, 2980, 2820, 2725, 2225, 2180, 1600, 1580, 1420, 1390, 1355, 1285, 1255, 1220, 1200, 1155, 1080, 1045, 950, 845, 830, and 700 cm^{-1}.

3-Methyl-4,5,6,7-tetrahydroindan-1-one (28a) and 3-methyl-5,6,7,7a-tetrahydroindan-1-one (29) - (E)-1-Trimethylsilyl-4-(1-cyclohexenyl)-1-buten-3-yne (***6b***) (6.4 g, 31.3 mmol) was added to a mixture of concentrated sulfuric acid (35.5 ml) and acetic acid (177 ml). The resulting solution was heated at 60 °C for 40 min, then cooled to room temperature, poured into ice-cold water, and extracted repeatedly with hexane (5 x 100 ml). The collected organic extracts were washed with water, saturated $NaHCO_3$ solution, and water, dried and concentrated. GLC/MS analysis of the residue showed the presence of two isomeric compounds in a ca. 22/78 ratio. This residue was purified by MPLC on a silica gel column, using a mixture of hexane and ether (8/2) as eluant. Fractional distillation of the first eluted fractions gave 3-methyl-5,6,7,7a-tetrahydroindan-1-one (***29***) (1.06 g, 17.5 % yield). The structure of this ketone was established on the basis of a 2D ^1H NMR correlation (COSY) spectrum. Compound 29 had: b.p. 105 °C/7.5 Torr. ^1H NMR ($CDCl_3$): ∂ 7.98-7.92 (1H, m, H4), 2.89 (1H, dd, J = 17.5 and 7.0 Hz, 1H2), 2.82-2.68 (1H, m, 1H5), 2.82-2.58 (3H, m, 1H5 and 1H6), 2.35-2.25 (2H, m, 1H2 and H7a), 2.10-1.92 (1H, m, H3), 1.92-1.75 (1H, m, 1H7), 1.42 (3H, d, J = 6.0 Hz, CH_3), 1.30-1.15 ppm (1H, m, 1H7).

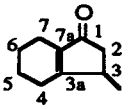


29

IR (film): 3430, 3030, 2960, 2930, 2870, 2820, 1720, 1660, 1450, 1430, 1380, 1340, 1330, 1300, 1270, 1250, 1225, 1210, 1120, 1070, 1055, 1005, 970, 940, 920, 900, 875, 855, 785, 745, 655, and 620 cm^{-1}. MS (m/e): 150 (M, 24), 135 (14), 108 (100), 107 (12), 93 (21), 91 (10), 80 (35), 79 (75), 77 (12), 52 (10),

41 (13), 39 (14). Found : C, 74.85; H, 9.51. Calc. for $C_{10}H_{14}O$: C, 74.96; H, 9.39.

Fractional distillation of the less easily eluted fractions gave 3-methyl-4,5,6,7-tetrahydroindan-1-one (*28a*) (3.9 g, 65 % yield): b.p. 109 °C/7.5 Torr. Lit[33] b.p. 83-85 °C/1 Torr. ^{1}H NMR ($CDCl_3$): ∂ 2.79-2.69 (1H, m, H3), 2.62 (1H, dd, J = 18.0 and 6.0 Hz, 1H2), 2.30 (1H, dt, J = 19.0 and 5.0 Hz, 1H4 or 1H7), 2.18 (1H, dt, J = 19.0 and 3.0 Hz, 1H4 or 1H7), 2.15-2,08 (2H, m, H7 or H4), 1.95 (1H, d, J = 18.0 Hz, 1H2), 1.83-1.54 (4H, m, H5 and H6), 1.15 ppm (3H, d, J = 6.0 Hz, CH_3)



28a

IR (film): 3380, 2930, 2870, 2820, 1700, 1650, 1440, 1420, 1395, 1375, 1350, 1295, 1280, 1250, 1235, 1125, 1095, 1060, 1045, 1010, 945, 810, 800, 775, 745, and 720 cm^{-1}. MS (m/e): 151 (M+1, 10), 150 (M, 84), 149 (15), 135 (100), 122 (26), 108 (18), 107 (51), 94 (19), 93 (24), 91 (18), 80 (12), 79 (57), 77 (20), 53 (10), 41 (14), 39 (15).

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