rahedron Vol. 39, No. 19, pp. 3073 to 3081, 1983
ıted in Great Britain.

0040-4020/83 $3.00 + .00
Pergamon Press Ltd.

LITHIATED 2-ALKYNYL-1,3-DIOXANES AS FULLY OXYGENATED ACYL-ANION EQUIVALENTS: SYNTHESIS OF 1-ALKYNYL KETONES

KLAAS J. H. KRUITHOF, ROBERT F. SCHMITZ, GERHARD W. KLUMPP *

Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083,
1081 HV Amsterdam, The Netherlands

(*Received in UK* 10 *June* 1983)

Abstract- 2-Lithio-2-(trimethylsilylethynyl)-1,3-dioxane **3** is prepared from 2-(trimethylsilylethynyl)-1,3-dioxane with *n*-BuLi. Alkylation of **3** produces propargylic ketals **2** exclusively. Reaction with group IV-B chlorotrimethylmetalanes gives both propargylic products **2** and allenes **6** depending on the solvent used.
Desilylation of **2** as well as hydrolysis to the alkynyl ketones **1** can be carried out under mild conditions. The first 1-alkynyl stannyl ketone has been prepared in this way. Formation of 2-lithio-2-(3,3-dimethyl-1-butynyl)-1,3-dioxane **10** requires *t*-BuLi. With various electrophiles **10** yields propargylic products and/or allenes in ratios depending on the solvent used.

troduction

agents exhibiting reversed polarity ("umpo-ng") have become important tools of modern nthetic organic chemistry[1,2].

sked acyl-anions are frequently used in the ıthesis of aldehydes and ketones[3,4].

ong the many known synthons of that kind ters of α,α-dialkoxyacetic acids[5] and ostituted 2-arylacetals[6], are the ly representatives of the fully oxyge-ed type.

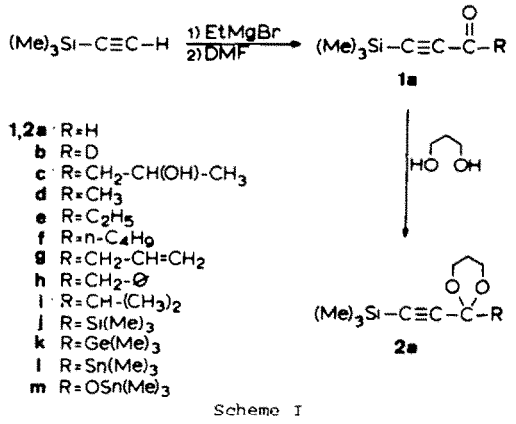
now report that 2-alkynyl-2-lithio-1,3-oxanes are useful fully oxygenated acyl-anion ıthons, easily accesible by deprotonation of corresponding 2-alkynyl-1,3-dioxanes.

ng these synthons we were able to synthesize ariety of 1-alkynyl ketones, including sub-ates containing a group IV-B ligand as the ond carbonyl substituent.

the latter case, we took advantage of the y hydrolysis of 1,3-dioxanes.

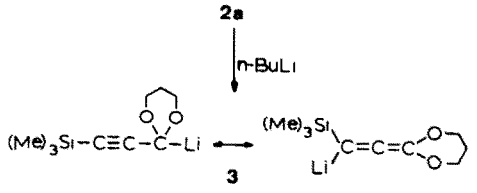
thesis and lithiation of 2-(trimethylsilyl ynyl)-1,3-dioxane 2a

title compound, **2a** was synthesized accor-g to Scheme I, starting from trimethylsilyl-yne[7].



Scheme I

Lithiation of **2a** is preferably carried out by reaction with *n*-butyllithium at -65°C though *t*-butyllithium leads to similar results.

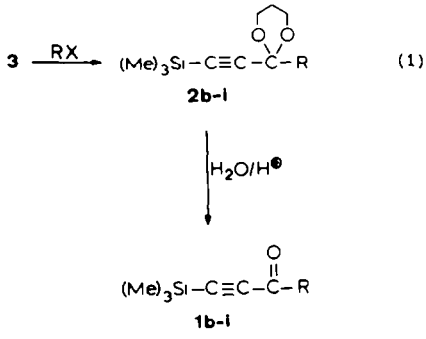


Both diethyl ether (DEE) and tetrahydrofuran (THF) can be used as solvent: in the latter case it is necessary to add **2a** to the solution of the organolithium reagent, otherwise attack

of initially formed **3** on the alkynyltrimethylsilyl group of **2a** leads to **2j**. Under the conditions of inverse addition the contribution of this reaction, not observed in DEE, amounts 5% or less.

Reaction of **3** with deuterium oxide, 1,2-epoxypropane and alkyl halides

Unlike many other lithium compounds derived from propargylic starting materials, which upon reaction with electrophiles yield mixtures of acetylenic and allenic products[8,9], **3** reacted with D_2O, 1,2-epoxypropane and primary and secondary alkyl halides to give propargylic derivatives exclusively (eqn. (1), Table 1):



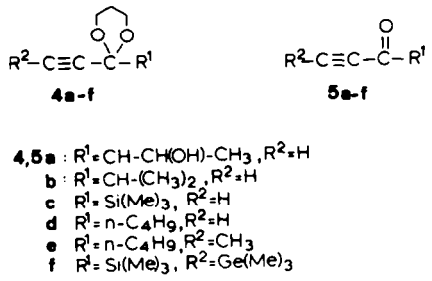
(1)

With the epoxide attack on the primary carbon led to the formation of **2c**. Since the ring opening proceeds rather slowly[10] extensive desilylation of the product formed, **2c**, leads to **2j** and **4a**.

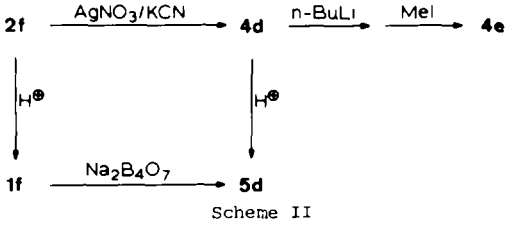
Hydrolysis of ketals **2** was performed with 0.2 M H_2SO_4 in acetone/water (4:1), leading to the corresponding 1-alkynyl ketones **1** (eqn. 1), which are useful reagents for further synthetic elaboration. It is pointed out that a dithiane derivative closely related to **2** is reported to require delicate control of reaction conditions in order to obtain the corresponding ketone[11].

Desilylation of 1-trimethylsilylalkynes is easily effected by several reagents, including hydroxide ion[12], fluoride ion[13] and silver(I) ion followed by cyanide ion[14]. The latter combination was applied successfully to **2f** (see Scheme II).

Removal of the silicon moiety from the conjugated alkynyl ketones **1** is still easier. In the case tested, **1f**, even methanolic borax[15] was sufficient. In order to demonstrate the possibility of further modification **4d** was deprotonated with *n*-BuLi. Subsequent methylation with iodomethane gave **4e** (Scheme II).



4,5a : R^1=CH-CH(OH)-CH_3, R^2=H
b : R^1=CH-$(CH_3)_2$, R^2=H
c R^1=Si(Me)$_3$, R^2=H
d R^1=n-C_4H_9, R^2=H
e R^1=n-C_4H_9, R^2=CH_3
f R^1=Si(Me)$_3$, R^2=Ge(Me)$_3$



Scheme II

Table 1. Reaction of **3** with electrophiles[a]; hydrolysis to ketones

E	Dioxane Yield[c] (%)		Ketone Yield (%)	
D_2O	**2b**	95,88[b]	**1b**	-[d]
CH_3-CH(O)-CH_2	**2c**	12	-	-[d]
CH_3I	**2d**	78	**1d**	63
C_2H_5I	**2e**	81	**1e**	84
n-C_4H_9Br	**2f**	74	**1f**	86
CH_2=CH-CH_2Cl	**2g**	73	**1g**	89
Ø-CH_2Cl	**2h**	83	**1h**	67
$(CH_3)_2CHBr$	**2i**	25	**1i**	-[d,e]
$(CH_3)_3CBr$	-[f]	-	-	-

[a] Solvent THF; [b] Solvent DEE; [c] Isolated yield after distillation; [d] Not determined; [e] Isolated by prep. GCL; [f] No reaction.

Reaction of **3** with group IV-B chlorotrimethylmetalanes[16]

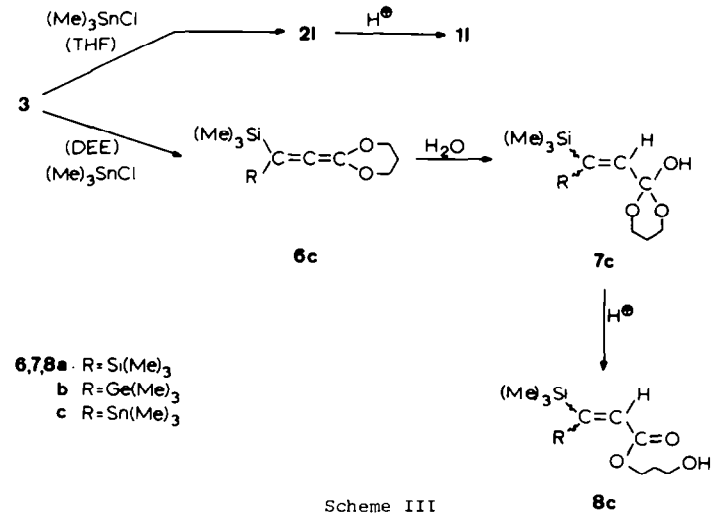
Reaction of **3** with chlorotrimethylstannane in THF led to propargylic substitution product **2i** exclusively (Scheme III, Tables 2 and 3).

By contrast reaction in DEE gave the allenic isomer **6c**, as the only reaction product isolated by basic work-up (Scheme III, Tables 2 and 3).

All allenes **6** reacted rapidly with water yielding a mixture of E and Z-**7** which was detectable by NMR, but could not be isolated.

Traces of acid isomerize **7** to the esters **8**, whose (E-Z)-isomers could be separated by preparative GLC.

Reaction of **3** with chlorotrimethylsilane yielded a mixture of propargylic and allenylic products in a ratio that was solvent dependent (Tables 2 and 3).



Scheme III

and **7a** could be detected by NMR but could be isolated. Addition of water gave **8a** immediately.

ng THF/HMPT (9:1) as solvent **2j** could be lated as the only detectable product (Tables nd 3).

ilar results were obtained in the germanium e. Using THF/HMPT as solvent exchange of methylmetal groups led to a mixture of **2j**, and **4f** (Tables 2 and 3).

le 2. Propargylic vs. allenylic products (**2**/**6**) upon reaction of **3** with Me_3MCl

THF	DEE	THF/HMPT (9:1)
60/40	35/65	100/0
50/50	20/80	100/0[a]
100/0	0/100	- [b]

See text; [b] Not determined.

:olysis of **2j** yielded **1j** (Table 3). 1-Alky--silyl ketones, hardly known up to now, are aising starting materials for the synthesis enol, dienol and allenol silyl ethers[17]. .larly, the 1-alkynyl germyl and 1-alkynyl inyl ketones, **1k** and **1l**, were obtained from ind **2l** (Table 3). To our knowlegde **1k** and **1l** novel compounds.

tin case is of particular interest, since .ier attempts to hydrolyse stannyl-1,3-ianes failed[18], thereby excluding the ver-.le dithiane-method[19] as an approach to inyl ketones.

'as rapidly oxidised[20] by atmospheric oxygen he stannyl ester **2m**, which upon chromato-hy decomposed to trimethylsilyltrimethyl-nylethyne and CO_2.

Table 3. Reaction of **3** with Me_3MCl; hydrolysis to ketones

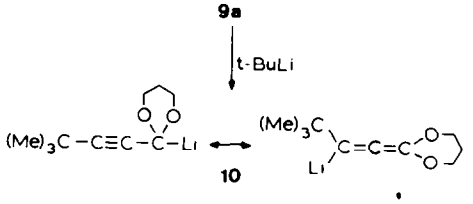
M	Solvent	Dioxane	Yield[a] (%)	Ketone	Yield(%)
Si	THF/HMPT[c]	**2j**	70	**1j**[b]	84
Si	THF	**2j**	48	-	-
Ge	THF	**2k**	25	**1k**[b]	68
Sn	THF	**2l**	76	**1l**[a]	70
Sn	DEE	**6c**	59	- [d]	-

[a] Yield after distillation; [b] Yield after column chromatography; [c] THF/HMPT (9:1); [d] **8c** was formed in this case.

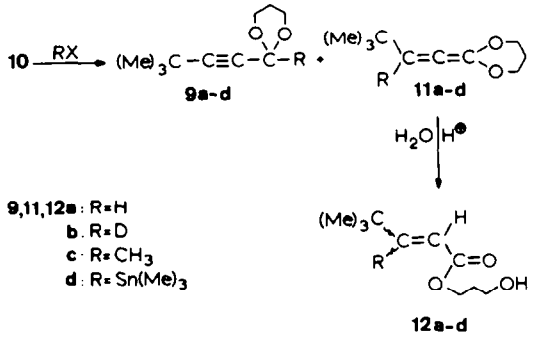
2-(3,3-Dimethyl-1-butynyl)-1,3-dioxane **9a**; synthesis, lithiation and reaction with electrophiles

In order to investigate the influence of the trimethylsilyl group of **2a**, the title compound **9a** was synthesized from 3,3-dimethyl-1-butyne[7] following a route analoguous to that leading to **2a**.

Under similar conditions, deprotonation of **9a** with *n*-BuLi was much slower than that of **2a**. In order to achieve lithiation within a reasonable time use of *t*-BuLi was necessary.



Reaction of **10** in THF with H_2O or D_2O gave a mixture of propargylic (**9a,b**) and allenylic (**11a,b**) products (Table 4), the latter undergoing hydrolysis to **12a,b** during aqueous work-up; only the *E*-isomer could be detected (Scheme IV).



Scheme IV

Reaction of **10** with iodomethane yielded, both in THF or DEE, the propargylic product **9c** only (Table 4).

The reaction of **10** with chlorotrimethylstannane was strongly solvent dependent (Table 4). In contrast with the behaviour of **3** the ratio of propargylic to allenylic isomers increased with decreasing solvent polarity.

Table 4. Reaction of **10** with electrophiles

E	Solvent	Product(s)	(**9**/**12**)
H_2O/D_2O	THF	**9a,b**,**12a,b**	80/20
H_2O/D_2O	DEE	**9a,b**	100/0
CH_3I	THF	**9c**	100/0
CH_3I	DEE	**9c**	100/0
Me_3SnCl	THF/HMPT(9:1)	**9d**,**12d**	25/75
Me_3SnCl	THF	**9d**,**12d**	70/30
Me_3SnCl	DEE	**9d**	100/0

Discussion

Although the acidity of acetals is less than that of the corresponding sulfur compounds, due to the lesser polarizability of oxygen compared to sulfur[21], the proton abstraction from **2a** proceeds very smoothly.

This is in line with the recent findings of Meyers, Eliel and coworkers[22] that aryl acetals undergo proton abstraction by *n*-BuLi or LDA at -45°C in THF, if H(α) can assume the equatorial or an "equatorial-like" position.

Clearly, fulfillment of this condition (rooted in stereoelectronics) is facilitated by the low conformational energy of the 1-alkynyl group ($-\Delta G^{\circ}_{-C\equiv CH}$=0.18 kcal/mole)[23].

In addition, carbanion stabilization by silicon[24] plays a role, since **9a** is less reactive towards base than **2a**.

No products resulting from fragmentation and/or rearrangement of the α,α-dialkoxy carbanions were detected[25].

Steric effects have been invoked to explain the predominant formation of propargylic products from 3-lithio-1-trimethylsilylpropyne[26]. The difference in regioselectivity towards water and chlorotrimethylstannane displayed by **3** and **10**, respectively, shows that acetylene/allene ratios are governed by factors more complicated. Besides solvent polarity the nature of the metal has been shown to influence the regioselectivity of electrophile attack upon $Me_3Si-C\equiv C-CH_2^{\ominus}$ derived anionoïds[27a,b].

Closely related systems, lacking the trimethylsilylgroup, are reported to react with electrophiles in the allenic form exclusively[28,29].

Experimental

IR-spectra were recorded of 10% solutions in CCl_4 on a Perkin-Elmer 580B spectrophotometer. Only absorptions used for structure elucidation are given (cm^{-1}) with a precision of 5 cm^{-1}. UV-spectra were recorded (λ_{max}(nm)(ε)) from solutions in cyclohexane on a Cary 118 spectrophotometer.

Mass spectra were obtained from a Varian Mat CH_5-DF mass-spectrometer (70 eV) or a Finnigan 4000 mass-spectrometer (70 eV) coupled with a gaschromatograph fitted with a capillary C_p^{sil} 5 (fused silica; 0.2 mm x 25 m) column for GCMS analysis. Peak heights of the most relevant fragments (m/z) are given in brackets relative to the base-peak (100%). Data given for compounds containing germanium or tin refer to the most abundant isotope, ^{74}Ge and ^{120}Sn, respectively. NMR-spectra were recorded on a Bruker WH-90 (^1H) or WH-250 (^{13}C) in $CDCl_3$ with $CHCl_3$ or $CDCl_3$ as internal standard. Chemical shifts (δ_{TMS}) are given in ppm with a precision of 0.01 ppm (^1H) or 0.1 ppm (^{13}C); coupling constants (Hz) have an accuracy of 0.4 Hz (^1H) or 1.5 Hz (^{13}C).

Gaschromatographic analyses (GLC) were performed on a Intersmat GC 120, equipped with a katharometer detector, using H_2 as carrier-gas. Columns used: A 10% SE-30 on Chromosorb WAW-DMCS, 60-80 mesh (glass, 0.4 x 180 cm); B 10% SE-30 on Chromosorb P-AW, 80-100 mesh, (stainless steel, 0.2 x 100 cm); C 10% Carbowax 20M on Chromosorb W-AW, 80-100 mesh (glass, 0.4 x 180 cm). The column temperature was linearly raised by 6°C/min starting at the temperature given. Column chromatography (glass, 1 x 30 cm) was performed on Kieselgel 60, 70-230 mesh ASTM. Some of the reaction products were purified by short-path evaporative distillation (MDA); temperatures given are heating bath temperatures. Chromatograms were integrated using a Pye Unicam DP 101. All compounds were colourless liquids, unless stated otherwise. Solvents were distilled shortly before use: THF and DEE from $LiAlH_4$, then stored under N_2 over sodium-wire; hexamethylphosphoric triamide (HMPT) from CaH_2, then stored over molecular sieves (3Å). All reactions using organometallics were carried out in dried glassware under an inert atmosphere (Ar).

Abbreviations used: b = broad, d = doublet, m = multiplet, p = perturbed, q = quadruplet, qi = quintuplet, s = singulet, t = triplet, rrt = relative retention time.

Trimethylsilylpropynal, **1a** [30]. To a magnetically stirred solution of 0.13 mol EtMgBr[7] (1.5 M in THF, 87 ml) was added 10.5 g trimethylsilylethyne (0.11 mol) dissolved in 75 ml THF. The temperature was kept at 10-15 °C by an ice-water bath. After stirring at room temperature for 1 hour the mixture was transferred into a dropping funnel and added to an efficiently stirred mixture of 28 g dimethylformamide (DMF) and 50 ml DEE at -25 °C over a period of 45 minutes. The white suspension was allowed to reach room temperature, stirred for 1 hour, heated at 30 °C for 15 minutes and poured into 200 ml 5% H_2SO_4 at 0 °C. After two extractions with DEE the water layer was stirred overnight, under N_2, with a fresh portion of DEE to which was added a trace of hydroquinone[31]. The organic layer was separated and the water layer was extracted four times with DEE. The combined organic layers were washed with a saturated NH_4Cl solution, dried ($MgSO_4$) and carefully concentrated in vacuo. Distillation (trace of hydroquinone added, bp. 44-45 °C/20 mm) yielded 9.59 g **1a** (69%), which should be collected in an ice-cooled receiver and stored in the cold.
IR[32]: 2160, 1670; ^{1}H-NMR: 9.16 (s, 1H, CHO), 0.27 (s, 9H, $Si(CH_3)_3$); MS: 125(1), 111(100), 97(62), 83(28); calculated for C_6H_9OSi: 125.0423, found: 125.0420.

2-Trimethylsilylethyne-1,3-dioxane, **2a**. 3.80 g **1a** (30 mmol) was dissolved in 125 ml benzene; 15 ml 1,3-propanediol and 700 mg *p*-toluenesulfonic acid were added and the mixture was refluxed overnight using a water separator. After cooling the mixture was poured into 150 ml brine, the organic layer was separated and the water layer was extracted three times with DEE. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Distillation (bp. 75-76 °C/3 mm) yielded 4.48 g (81%) **2a**.
IR: 2170; ^{1}H-NMR: 5.34 (s, 1H, O_2C-H), 4.4-4.1 (m, 2H, OCH_2), 4.0-3.7 (m, 2H, OCH_2), 2.2-1,4 (m, 2H, CH_2), 0.21 (s, 9H, $Si(CH_3)_3$); MS: 183(28), 169(5), 111(88), 75(100), 73(44); calculated for $C_9H_{15}O_2Si$: 183.0841; found: 183.0835.

Lithiation of **2a**. A. 15 ml THF, magnetically stirred, was cooled to -65 °C and 5.4 ml *n*-BuLi (1.6 M in hexane, 8.6 mmol) was slowly added with a syringe. 1.38 g **2a** (7.5 mmol) was slowly added and the mixture was stirred at low temperature for 30 minutes. The clear, yellow solution of **3** formed was used for further reactions. B. 5.4 ml *n*-BuLi (8.6 mmol) was slowly added to a magnetically stirred solution of 1.38 g **2a** (7.5 mmol) dissolved in 15 ml DEE and cooled to -65 °C. After 30 minutes a white suspension of **3** had formed, which was used for further reactions.

2-Deutero-2-(trimethylsilylethynyl)-1,3-dioxane, **2b**. To a solution of **3** in THF or a suspension in DEE, obtained as described from 230 mg **2a** (1.25 mmol), was added with vigorous stirring 1 ml D_2O. After warming to room temperature the mixture was poured into a saturated $NaHCO_3$ solution, the organic layer was separated and the water layer was extracted twice with DEE. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo, yielding 220 mg **2b** (95%; d_1 > 95%) when the reaction was performed in DEE and 200 mg **2b** (88%; d_1 > 95%) contaminated with 5% **2j** when the reaction was run in THF.
2b: MS: 183(11), 170(8), 144(25), 140(37), 112(98). 99(28), 75(100), 73(38); calculated for $C_8H_{12}DO_2Si$: 170.0747; found: 170.0749.

2-(Trimethylsilylethynyl)-2-(2-hydroxypropyl)-1,3-dioxane, **2c**. To a solution of **3** in THF obtained as described from 460 mg **2a** (2.5 mmol) was added 200 mg freshly distilled 1,2-epoxypropane (3.5 mmol). The mixture was stirred overnight, during which time the temperature rose to room temperature. After aqueous work-up the product was distilled (MDA, 120 °C/2 mm) yielding 300 mg of an oil containing (GLC; B; 120 °C) **2j** (rrt = 0.62; 40%), **2c** (rrt = 1.00; 24%) and **4a** (rrt = 0.51; 36%). **2c** was purified by preparative GLC (A; 120 °C): IR: 2160; ^{1}H-NMR: 4.5-4.1 (m, 3H, HC(OH), OCH_2), 4.0-3.8 (m, 2H, OCH_2), 3.41 (bs, 1H, OH) 2.4-1.8 (m, 3H, CH_2, H_2C-CHOH), 1.5-1.3 (m, 1H, CH_2), 1.19 (d, 3H, J = 6.3, CH_3), 0.23 (s, 9H, $Si(CH_3)_3$); MS: 227(2), 183(78), 141(28), 127(25), 125(55), 97(26), 75(62), 73(100). **4a**: ^{1}H-NMR: 2.71 (s, 1H, ≡CH); MS: 169(4), 155(6), 111(100), 69(40), 68(55).

Reaction of **3** with alkyl halides; general procedure. To a solution of **3** in THF, or a suspension in DEE, (for the synthesis of **2c**) obtained as described above from 460 mg **2a** (2.5 mmol) was added 25 mmol alkyl halide. The mixture was stirred overnight, during which time the temperature slowly reached room temperature. After aqueous work-up the residue was distilled and analysed.

2-Methyl-2-(trimethylsilylethynyl)-1,3-dioxane, **2d**. (MDA, 90 °C/2 mm) 390 mg (78%); IR: 2170; ^{1}H-NMR: 4.4-4.1 (m, 2H, OCH_2), 4.0-3.7 (m, 2H, OCH_2), 2.3-1.8 (m, 1H, CH_2), 1.59 (s, 3H, CH_3), 1.5-1.2 (m, 1H, CH_2), 0.21 (s, 9H, $Si(CH_3)_3$); MS: 183(34), 153(40), 141(31), 125(99), 97(35), 85(100), 75(79), 73(63); calculated for $C_9H_{15}O_2Si$: 183.0841; found: 183.0851.

2-Ethyl-2-(trimethylsilylethynyl)-1,3-dioxane, **2e**. Use of an equimolar amount of **2a** and *n*-BuLi is necessary to prevent formation of **2f** due to bromine-metal exchange between *n*-BuLi and bromoethane. (MDA, 100 °C/2 mm) 430 g (81%); IR: 2160; ^{1}H-NMR: 4.4-4.1 (m, 2H, OCH_2), 4.0-3.8 (m, 2H, OCH_2), 2.3-1.2 (m, 4H, CH_2), 1.02 (t, 3H, J = 7.2, CH_3), 0.22 (s, 9H, $Si(CH_3)_3$; MS: 197(3), 183(82), 139(23), 125(73), 109(66), 99(25), 97(38), 83(45), 75(74), 73(100); calculated for $C_9H_{15}O_2Si$: 183.0841; found: 183.0855.

2-Butyl-2-(trimethylsilylethynyl)-1,3-dioxane, **2f**. (MDA, 120 °C/2 mm) 450 mg (74%); IR: 2160; ^{1}H-NMR: 4.4-4.1 (m, 2H, OCH_2), 4.0-3.8 (m, 2H, OCH_2), 2.3-1.2 (m, 8H, CH_2), 0.95 (t, 3H, CH_3), 0.25 (s, 9H, $Si(CH_3)_3$); MS: 225(0.1), 183(74), 167(7), 125(53), 97(27), 83(27), 75(56), 73(100); calculated for $C_{13}H_{24}O_2Si$: 239.1467; found: 239.1461.

2-(2-Propenyl)-2-(trimethylsilylethynyl)-1,3-dioxane, **2g**. (MDA, 120 °C/2 mm), 410 mg (73%); IR: 2170; ^{1}H-NMR: 5.95 (m, 1H, =CH-), 5.16 (m, 1H, $=CH_2$), 5.14 (m, 1H, $=CH_2$), 4.5-4.1 (m, 2H, OCH_2), 4.0-3.8 (m, 2H, OCH_2), 2.59 (d, 2H, J = 7.2, CH_2-C=), 2.4-1.8 (m, 1H, CH_2), 1.5-1.2 (m, 1H, CH_2), 0.24 (s, 9H, $Si(CH_3)_3$); MS: 209(3), 183(78), 151(7), 125(87), 97(50), 75(26), 73(100); calculated for $C_{11}H_{17}O_2Si$: 209.0998; found: 209.1007.

2-(Phenylmethyl)-2-(trimethylsilylethynyl)-1,3-dioxane, **2h**. (Bulb-to-bulb distillation, 130 °C/10^{-3} mm) 570 mg (83%); IR: 2170; ^{1}H-NMR: 7.6-7.0 (m, 5H, arom.), 4.5-4.1 (m, 2H, OCH_2), 4.1-3.8 (m, 2H, OCH_2), 3.15 (s, 2H, $CH_2\phi$), 2.4-1.9 (m, 1H, CH_2), 1.6-1.3 (m, 1H, CH_2), 0.24 (s, 9H, $Si(CH_3)_3$); MS: 274(0.1), 201(1), 183(100), 125(45), 73(27); calculated for $C_{16}H_{22}O_2Si$: 274.1388; found: 274.1369.

2-(1-Methylethyl)-2-(trimethylsilylethynyl)-1,3-dioxane, **2i**. (MDA, 110 °C/2 mm) 310 mg oil containing (GLC; B; 120 °C) **2i** (rrt = 0.92; 46%), **2j** (rrt = 1.00; 37%), **4b** (rrt = 0.30; 10%) and **4c** (rrt = 0.36; 7%). **2i**: IR: 2160; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 4.0-3.8 (m, 2H, OCH_2), 2.3-1.8 (m, 3H, CH_2, CH), 1.5-1.3 (m, 1H, CH_2), 1.05 (d, 6H, J = 7.2, CH_3), 0.25 (s, 9H, $Si(CH_3)_3$); MS: 211(2), 183(91), 153(10), 125(89), 123(44), 97(47), 83(29), 75(37), 73(100). **4b**: ^{1}H-NMR: 2.64 (s, 1H, ≡CH); MS: 139(5), 111(100). **4c**: ^{1}H-NMR: 2.80 (s, 1H, ≡CH); MS: 143(8), 83(62), 75(52), 73(100). Attempted reaction of **3** with *t*-butyl bromide (THF) gave a brownish reaction product (420 mg) shown by GLC to be a mixture of **2j**(49%) and **4c** (51%).

Desilylation of **2f**. To a magnetically stirred solution of 240 mg **2f** (1 mmol) in 2 ml EtOH was added a solution of 500 mg $AgNO_3$ in 4 ml EtOH/H_2O (3:1). After stirring at room temperature for 30 minutes a solution of 850 mg NaCN in 2 ml H_2O was added. The resulting orange-yellow solution was poured into a saturated NH_4Cl solution and the water layer was extracted twice with DEE. The combined organic layers were washed with brine, dried ($MgSO_4$), concentrated in vacuo and distilled.
2-Butyl-2-ethynyl-1,3-dioxane, **4d**. (MDA, 100 °C/2 mm) 90 mg (54%); IR: 3310, 2110; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 4.0-3.8 (m, 2H, OCH_2), 2.65 (s, 1H, ≡CH), 2.4-1.2 (m, 8H, CH_2), 0.93 (bt, 3H, CH_3). MS: 167(0.3), 153(0.2), 139(2), 111(100), 96(17); calculated for $C_{10}H_{15}O_2$: 167.1072; found: 167.1066.

Desilylation of **1f**. $Na_2B_4O_7$ (0.6 ml, 0.01 M) was added to a magnetically stirred solution of 130 mg **1f** (0.7 mmol) in 5 ml MeOH. After stirring for 30 minutes the mixture was poured into 0.1 M HCl. The water layer was saturated with NaCl and extracted five times with DEE. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. 1-Heptyn-3-one **5d**[33] was isolated by preparative GLC (A; 70 °C): 60 mg (78%); IR: 3310, 2090, 1685; ^{1}H-NMR: 3.22 (s, 1H, ≡CH), 2.61 (t, 2H, J = 7.2, CH_2CO), 1.9-1.2 (m, 4H, CH_2), 0.95 (pt, 3H, CH_3); MS: 110(0.4), 109(8), 95(8), 81(16), 68(100); calculated for C_7H_9O: 109.0653; found: 109.0650.

Lithiation and alkylation of **4d**. To a magnetically stirred solution of 80 mg **4d** (0.4 mmol) in 3 ml THF, cooled to -65 °C 0.5 ml *n*-BuLi (1.6 M, 0.8 mmol) was slowly added. After 15 minutes 500 µl MeI was injected and the reaction mixture was slowly warmed to room temperature. After aqueous work-up the product was distilled.
2-Butyl-2-(1-propynyl)-1,3-dioxane, **4e**: (MDA, 100 °C/2 mm) 80 mg (85%); IR: 2240; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 4.0-3.7 (m, 2H, OCH_2), 2.4-1.2 (m, 8H, CH_2), 1.95 (s, 3H, ≡C-CH_3), 0.93 (bt, 3H, CH_3); MS: 181(0.5), 167(3), 125(54), 67(100).

Formation of 1-alkynyl ketones, general procedure. The dioxane derivative was dissolved in acidified (H_2SO_4, 0.2 M) acetone/H_2O (4:1) and refluxed for about 5 hours. After cooling a saturated $NaHCO_3$ solution was carefully added, the water layer was extracted three times with DEE, the combined organic layers were washed with brine, dried ($MgSO_4$), concentrated in vacuo and distilled. For yields see Table 1.
4-Trimethylsilyl-3-butyn-2-one, **1d**[34]. (MDA, 80 °C/70 mm); IR: 2150, 1680; ^{1}H-NMR: 2.33 (s, 3H, CH_3), 0.22 (s, 9H, $Si(CH_3)_3$); MS: 140(3), 125(100), 97(26), 83(42), 73(5); calculated for $C_7H_{12}OSi$: 140.0657; found: 140.0651.
1-Trimethylsilyl-1-pentyn-3-one, **1e**. (MDA, 90 °C/20 mm). IR: 2150, 1680; ^{1}H-NMR: 2.58 (q, 2H, J = 7.2, CH_2), 1.13 (t, 3H, J = 7.2, CH_3), 0.22 (s, 9H, $Si(CH_3)_3$). MS: 154 (3), 139 (24), 126(17), 125(100), 83(29), 73(13); calculated for $C_8H_{14}OSi$: 154.0814; found: 154.0815.
1-Trimethylsilyl-1-heptyn-3-one, **1f**[35]. (MDA, 100 °C/20 mm). IR: 2150, 1680; ^{1}H-NMR: 2.58 (bt, 2H, J = 7.2, CH_2CO), 1.9-1.2 (m, 4H, CH_2), 0.95 (pt, 3H, J = 7.2, CH_3), 0.27 (s, 9H, $Si(CH_3)_3$; MS: 167(14), 140(40), 125(100), 97(24), 83(28), 75(43), 73(23); calculated for $C_9H_{15}OSi$: 167.0892; found: 167.0892.
1-Trimethylsilylhex-5-en-1-yn-3-one, **1g**. (MDA, 130 °C/50 mm). IR: 2155, 1640, 1630; ^{1}H-NMR: 7.4-7.0 (m, 1H, -CH=), 6.2-6.0 (m, 2H, $=CH_2$), 2.00 (dd, 2H, CH_2), 0.26 (s, 9H, $Si(CH_3)_3$); MS: 166(12), 151(100), 123(30), 83(34), 73(12); calculated for $C_9H_{14}OSi$: 166.0814; found: 166.0819.
4-Phenyl-1-trimethylsilyl-1-butyn-3-one, **1h**. (MDA, 100 °C/2 mm). IR: 2155, 1680; ^{1}H-NMR: 7.5-7.2 (m, 5H, arom.), 3.84 (s, 2H, ϕ-CH_2), 0.19 (s, 9H, $Si(CH_3)_3$). MS: 216 (7), 188(9). 173(25), 125(100), 97(43), 73(53); calculated for $C_{13}H_{16}OSi$: 216.0970; found: 216.0975.
4-Methyl-1-trimethylsilyl-1-pentyn-3-one, **1i**[36]. (MDA, 90 °C/40 mm). IR: 2150, 1680; ^{1}H-NMR: 2.64 (heptet, 1H, J = 7.0, >CH). 1.20 (d, 6H, J = 7.0, CH_3), 0.24 (s, 9H, $Si(CH_3)_3$; MS: 168 (1), 153(9), 140(9), 125(100), 73(15); calculated for $C_9H_{16}OSi$: 168.0970; found: 168.0972.

Reaction of **3** with Me_3SnCl. To a solution of **3** in THF obtained from 460 mg **2a** (2.5 mmol) was added 642 mg Me_3SnCl (3.2 mmol) dissolved in 1 ml THF. After stirring for 3 hours the cooling bath was removed. After warming to room temperature (1 hour) the mixture was poured into a saturated $NaHCO_3$ solution and worked-up as usual.
2-(Trimethylsilylethynyl)-2-trimethylstannyl-1,3-dioxane, **2l**. (MDA, 85 °C/10^{-2} mm) 660 mg (76%); IR: 2150; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 3.9-3.6 (m, 2H, OCH_2), 2.5-1.9 (m, 1H, CH_2), 1.6-1.2 (m, 1H, CH_2), 0.28 (s, 9H, $Sn(CH_3)_3$), 0.24 (s, 9H, $Si(CH_3)_3$), MS: 333(1), 183(100), 125(51); calculated for $C_{11}H_{21}O_2SiSn$:333.0332; found: 333.0333.
To a suspension of **3** in DEE obtained from 1.00 g **2a** (5.4 mmol) was added 1.2 g Me_3SnCl (6 mmol) in 1 ml DEE. After stirring for 2 hours at low temperature the mixture was allowed to reach room temperature in 1 hour. 250 µl Triethylamine (TEA) was added and the mixture was poured into brine to which a little TEA had been added. Separation of the organic layer, three extractions of the water layer with DEE, washing of the combined organic layers with brine, drying ($MgSO_4$) and concentration in vacuo yielded 2-(trimethylsilyltrimethylstannylethenylidene)-1,3-dioxane (**6c**), which could be distilled but decomposed upon GLC.

6c: (MDA, 100 °C/5.10^{-2} mm) 410 mg (59%) light yellow oil; IR: 2070, 1330, 1110, 1060; ^{1}H-NMR: 4.15 (t, 4H, J = 5.6, OCH_2), 2.00 (qi, 2H, J = 5.6, CH_2), 0.25 (s, 9H, $Sn(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$; ^{13}C-NMR: 201.2 (=C=), 145.3 (C-O,O), 117.8 (C-Si, Sn), 69.9 (C-O), 26.5 (-C-), -0.4 (Si-C), -7.9 (Sn-C); calculated for $C_{12}H_{24}O_2SiSn$: 348.0567; found 348.0581.
Work-up without addition of TEA resulted in the formation of considerable amounts of **8c** while the NMR spectrum also showed both isomers of **7c**. Treatment of **6c** with dilute acid (acetone/H_2O (4:1); 0.2 M H_2SO_4) yielded, after aqueous work-up, a mixture of the *E*- and *Z*-isomer of **8c** directly, which was separated by preparative GLC (A; 120 °C; isomer 1, rrt = 0.95: isomer 2, rrt = 1.00 = 3:2); no efforts were directed at an *E*-*Z* assignment of these isomers.
7c: isomer 1: ^{1}H-NMR: 6.53 (s, 1H, =CH-); isomer 2: ^{1}H-NMR: 6.35 (s, 1H, =CH-).
8c: isomer 1: IR: 3640, 3440, 1710, 1695, 1195; ^{1}H-NMR: 6.91 (s, 1H, =CH-), 4.35 (t, 2H, J = 6.1, CH_2OCO), 3.72 (bt, 2H, J = 6.1, $C\underline{H}_2OH$), 2.1-1.8 (m, 2H, CH_2), 1.60 (bs, 1H, OH), 0.20 (s, 9H, $Sn(CH_3)_3$), 0.18 (s, 9H, $Si(CH_3)_3$); MS: 351(92), 293(65), 165(100), 127(30); calculated for $C_{11}H_{23}O_3SiSn$: 347.0437; found: 347.0433
8c: isomer 2: IR: 3640, 3480, 1720, 1705, 1180; ^{1}H-NMR: 6.78 (s, 1H, =CH-), 4.33 (t, 2H, J = 6.1, CH_2OCO), 3.73 (bt, 2H, J = 6.1, $C\underline{H}_2OH$), 2.1-1.8 (m, 2H, CH_2), 1.58 (bs, 1H, OH), 0.22 (s, 9H, $Sn(CH_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$); MS: 351(29), 293(35), 165(100), 143(40), 127(25).

Reaction of **3** with Me_3GeCl. Solvent THF: The procedure given for Me_3SnCl was followed, using 490 mg Me_3GeCl (3.2 mmol) and work-up with TEA. The crude product was distilled (MDA, 90 °C/2 mm) giving 380 mg of distillate containing (NMR) **2k** (50%) and **6b** (50%). **2k** was isolated by preparative GLC, (A; 120 °C); **6b** decomposed upon GLC.
2-(Trimethylsilylethynyl)-2-trimethylgermyl--1,3-dioxane, **2k**. IR: 2160; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 3.9-3.7 (m, 2H, OCH_2), 2.4-1.8 (m, 1H, CH_2), 1.5-1.2 (m, 1H, CH_2), 0.29 (s, 9H, $Ge(CH_3)_3$), 0.22 (s, 9H, $Si(CH_3)_3$); MS: 287(0.4), 229(2), 183(100), 125(77), 119(27), 97(29), 73(48); calculated for $C_{12}H_{24}O_2GeSi$: 302.0757; found: 302.0756.
2-(Trimethylgermyltrimethylsilylethenylidene)--1,3-dioxane, **6b**. IR: 1335, 1110, 1065; ^{1}H-NMR: 4.15 (t, 4H, J = 5.6, OCH_2), 2.01 (qi, 2H, J = 5.6, CH_2), 0.31 (s, 9H, $Ge(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$).
Treatment of reaction mixture containing **2k** and **6b**, and often small amounts of **7b**, with dilute acid yielded, besides **1k**, a (*E*-*Z*)-mixture (1:1) of the esters **8b** which only could be separated by GCMS.
7b (*E*-*Z* mixture): ^{1}H-NMR: 6.41 (s, 1H, =CH-), 6.33 (s, 1H, =CH-).
8b (*E*-*Z* mixture): IR: 3640, 3440, 1725, 1710, 1190; ^{1}H-NMR: 6.78 (s, 1H, =CH-), 6.70 (s, 1H, =CH-), 4.31 (t, 4H, J = 6.1), CH_2OCO), 3.72 (t, 4H, J = 6.1, $C\underline{H}_2$-OH), 2.02 (s, 2H, OH), 1.93, (qi, 4H, J = 6.1, CH_2), 0.36 (s, 9H, $Ge(CH_3)_3$), 0.33 (s, 9H, $Ge(CH_3)_3$), 0.23 (s, 9H, $Si(CH_3)_3$), 0.19 (s, 9H, $Si(CH_3)_3$); MS (isomer 1): 305(9), 247 (20), 119(100), 75(29), 73(86); (isomer 2): 305 (5), 247(15), 143(41), 119(100), 75(40), 73(58).
Solvent DEE: The procedure given for THF was followed: (MDA, 85 °C/2 mm) 400 mg oil containing (NMR) **3k** (20%) and **6b** (80%).
Solvent THF/HMPT: The procedure given for THF was used, however before adding Me_3GeCl HMPT (500 µl) was added. The crude reaction product was (GLC, NMR) a mixture of **2j** (23%), **2k** (13%) and **4f** (64%). **4f**: ^{1}H-NMR: 0,40 (s, 9H, $Ge(CH_3)_3$), 0.15 (s, 9H, $Si(CH_3)_3$).

Reaction of **3** with Me_3SiCl. Solvent THF: The procudure given for Me_3SnCl was followed, using 350 mg Me_3SiCl (3.3 mmol). The crude reaction product contained (NMR) **2j** (60%) and **6a** (40%). **2j** was isolated by column chromatography (pentane/DEE, 95:5): 310 mg.
2-(Trimethylsilylethynyl)-2-trimethylsilyl--1,3-dioxane, **2j** (48%): IR: 2150; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 3.9-3.7 (m, 2H, OCH_2), 2,4-1.8 (m, 1H, CH_2), 1.5-1.2 (m, 1H, CH_2), 0.23 (s, 9H, $\equiv C\text{-}Si(CH_3)_3$); 0.16 (s, 9H, $Si(CH_3)_3$); MS: 256(1), 241(2), 183(31), 155 (30), 125(42), 97(25), 73(100); calculated for $C_{12}H_{24}O_2Si_2$: 256.1315; found: 256.1313.
2-(Bistrimethylsilylethenylidene)-1,3-dioxane, **6a** could not be chromatographed and data given were obtained from a mixture containing **2j**.
IR: 1330, 1065; ^{1}H-NMR: 4.41 (t, 4H, J = 5.6, OCH_2), 2.01 (qi, 2H, J = 5.6, CH_2), 0.18 (s, 18H, $Si(CH_3)_3$). Despite all precautions a small amount of **7a** was formed during work-up. Treatment of the reaction mixture with dilute acid converted **6a** and **7a** into **8a**.
7a: ^{1}H-NMR: 6.42 (s, 1H, =CH-).
8a: IR: 3640, 3440, 1725, 1710, 1190; ^{1}H-NMR: 6.76 (s, 1H, =CH-), 4.33 (t, 2H, J = 6.1, CH_2OCO), 3.74 (bt, 2H, J = 6.1, $C\underline{H}_2OH$), 1.94 (qi, 2H, J = 6.1, CH_2), 0.25 (s, 9H, $Si(CH_3)_3$), 0.21 (s, 9H, $Si(CH_3)_3$); MS: 259(6), 201(33), 75(28), 73(100).
Solvent DEE: Following the same procedure as described for the reaction in THF 470 mg of an oil (MDA, 80 °C/2 mm) was obtained containing (NMR) **2j** (35%) and **6a** (65%).
Solvent THF/HMPT: The procedure given for Me_3GeCl was followed, using 340 mg Me_3SiCl (3.2 mmol).
Distillation (MDA, 80 °C/2 mm) afforded 450 mg **2j** (70%) uncontaminated (NMR, GLC) by allenic products or derivatives thereof.

Silyl, germyl and stannyl ketones. 300 mg **2j** (1.17 mmol) was stirred overnight in 10 ml acidified (H_2SO_4, 0.2 M) acetone/H_2O (4:1) at room temperature. Saturated $NaHCO_3$ solution was carefully added and the water layer was extracted three times with DEE. The combined organic layers were washed twice with brine, dried ($MgSO_4$) and concentrated in vacuo. Trimethylsilylethynyl trimethylsilyl ketone, **1j** was isolated as a bright yellow liquid by column chromatography (pentane/DEE: 95:5): 194 mg (84%): IR: 2135, 1600; UV: 224(8529); ^{1}H-NMR: 0.29 (s, 18H, $Si(CH_3)_3$; ^{13}C-NMR: 227.1 (CO), 107.3 (≡C), 104.7 (≡C), -0.7 (≡C-Si$\underline{C}$), -3.7 (OC-Si$\underline{C}$): MS: 198(0.1), 183(0.1), 170(5), 155 (90), 73(100); calculated for $C_9H_{18}OSi_2$: 198.0896; found: 198.0884. Anal. calculated for $C_9H_{18}OSi_2$: C, 54.48; H, 9.14; found: C, 52.65; H, 8.47. In the same way, starting with 200 mg **2k** (0.66 mmol) trimethylsilylethynyl trimethylgermyl ketone **1k** was obtained: 110 mg (68%) yellow liquid: IR: 2130, 1610; UV: 222(11086); ^{1}H-NMR: 0.44 (s, 9H, $Ge(CH_3)_3$), 0.29 (s, 9H, $Si(CH_3)_3$); ^{13}C-NMR: 227.5 (CO), 108.9 (≡C), 103.6 (≡C), -0.7 (Si-C), -3.2 (Ge-C); MS: 244 (0.1), 216(0.2), 201(40), 119(100), 97(52), 73(71); calculated for $C_9H_{18}OGeSi$: 244.0338; found: 244.0331. Anal. calculated for $C_9H_{18}OGeSi$: C, 44.50; H, 7.47; found: C, 44.15, H, 7.69. 430 mg **2l** (1.24 mmol) was stirred at room temperature under an argon atmosphere in 15 ml acidified (H_2SO_4, 0.2 M) acetone/H_2O (4:1) for 30 minutes.

Saturated $NaHCO_3$ was added and the usual work-up was conducted under a nitrogen atmosphere: 250 mg trimethylsilylethynyl trimethylstannyl ketone, **1l** (70%) was isolated as an orange-yellow liquid by distillation (MDA, 120 °C/2 mm). Upon contact with air a solution of **1l** in $CDCl_3$ rapidly decolourised giving **1m**.
1l: IR: 2120, 1600, UV: 225(8549); ^{1}H-NMR: 0.37 (s, 9H, $Sn(CH_3)_3$); 0.29 (s, 9H, $Si(CH_3)_3$); ^{13}C-NMR: 236.8 (CO), 112.3 (C≡), 104.7 (≡C), -0.7 (Si-C), -8.8 (Sn-C); MS: 290(3), 247(57), 165 (100), 97(28), 73(23); calculated for $C_7H_{15}SiSn$: 246.9964; found: 246.9972.
1m: IR: 2160, 1580, 1550, 1375; UV: 206(8374); ^{1}H-NMR: 0.67 (s, 9H, $Sn(CH_3)_3$), 0.25 (s, 9H, $Si(CH_3)_3$).

4,4-Dimethyl-2-pentynal. The same procedure as given for the synthesis of **1a** was followed, using 0.20 mol EtMgBr (1.3 M in THF, 154 ml) and 15.2 g 3,3-dimethyl-1-butyne (0.19 mol). The alkynylic grignard reagent was added to 51 g DMF in 90 ml DEE.
Distillation (bp 39-41 °C/20 mm) yielded 18.3 g (90%): IR: 2210, 1670; ^{1}H-NMR: 9.13 (s, 1H, CHO), 1.29 (s, 9H, $C(CH_3)_3$).

2-(3,3-Dimethyl-1-butynyl)-1,3-dioxane, **9a**. 18.3 g 4,4-dimethyl-2-pentynal (0.17 mol) was dissolved in 500 ml benzene; 80 ml 1,3-propanediol and 1 g pyridinium *p*-toluenesulfonate (PPTS) were added and the mixture was refluxed overnight using a water separator. After aqueous work-up (as described for **2a**) the product was distilled: (bp 58-61 °C/1 mm) 14.5 g (52%): IR: 2270, 2255, 2235; ^{1}H-NMR: 5.33 (s, 1H, $HC(O)_2$), 4.4-4.1 (m, 2H, OCH_2), 4.0-3.7 (m, 2H, CH_2), 2.3-1.4 (m, 2H, CH_2), 1.29 (s, 9H, $C(CH_3)_3$); MS: 167(17), 153(30), 110(35), 109(29), 95(90), 81(55), 79(28), 67(100).

Lithiation of **9a** and reaction with D_2O (H_2O) and MeI. Solvent THF: to a magnetically stirred solution of 200 mg **9a** (1.2 mmol) in 4 ml THF, cooled to -65 °C, was added by syringe 0.8 *t*-BuLi (1.7 M in pentane, 1,4 mmol). After 0.5 hours a bright yellow solution of **10** was obtained and 1 ml D_2O (H_2O) was injected. After 15 minutes the cooling bath was removed and after reaching room temperature the mixture was worked-up in the usual way, using TEA. The crude product was a mixture (NMR) of **9b** (80%; d_1 > 95%) and **12b** (20%; d_1,d_2 > 95%), (**9a** and **12a** (80/20)).
9b: MS: 167(12), 154(30), 111(40), 96(100), 81(43), 67(28), 68(95).
12b: MS: 173(10), 131(48), 115(38), 113(85), 112(34), 111(62), 97(53), 96(62), 85(100), 84 (30).
12a: IR: 3640, 3470, 1720, 1705, 1650, 985; ^{1}H-NMR: 6.99 (d, 1H, J = 15.8, =CH-), 5.74 (d, 1H, J = 15.8, =CH-), 4.32 (t, 2H, J = 6.0, H_2COCO), 3.72 (bt, 2H, J = 6.0, H_2COH), 1.92 (qi, 2H, J = 6.0, CH_2), 1.58 (bs, 1H, OH), 1.10 (s, 9H, $C(CH_3)_3$); MS: 171(9), 129(46), 113(38), 111(67), 110(100), 95(88), 83(90), 67(42).
Reaction in DEE (in which **10** formed a white suspension) was carried out as above, as were the reactions with iodomethane (10 mmol, in THF or DEE) which yielded **9c** (180 mg, 83%).
2-(3,3-dimethyl-1-butynyl-2-methyl-1,3-dioxane, **9c**: IR: 2250, 2220; ^{1}H-NMR: 4.4-4.1 (m, 2H, OCH_2), 4.0-3.7 (m, 2H, OCH_2), 2.4-1.2 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.29 (s, 9H, $C(CH_3)_3$); MS: 181(4), 167(84), 137(61), 109(100), 85(52), 81(80), 79(34), 67(36).

Reaction of **10** with Me_3SnCl. Solvent DEE. To a stirred suspension of **10** in DEE prepared from 420 mg **9a** (2.5 mmol) at - 65 °C, was added 642 mg Me_3SnCl (3.2 mmol) and the mixture was stirred at low temperature for 15 minutes. After warming to room temperature the work-up procedure described before (using TEA) was employed, yielding (MDA, 130 °C/2 mm) 540 mg of an oil, which contained (NMR) **9d** as the only detectable product. Reactions in THF and THF/HMPT (9:1) were performed under the same conditions.
2-(3,3-dimethyl-1-butynyl)-2-(trimethylstannyl)-1,3-dioxane, **9d**: IR: 2220; ^{1}H-NMR: 4.5-4.1 (m, 2H, OCH_2), 3.8-3.6 (m, 2H, OCH_2), 2.4-1.9 (m, 1H, CH_2), 1.5-2.1 (m, 1H, CH_2), 1.27 (s, 9H, $C(CH_3)_3$), 0.22 (s, 9H, $Sn(CH_3)_3$); MS: 317(0.4), 167(100), 109(38), 81(25).
2-(3,3-dimethyl-2-trimethylstannyl-1-butenylidene)-1,3-dioxane, **11d**: ^{1}H-NMR: 4.12 (t, 4H, J = 5.4, OCH_2), 1.97 (septet, 2H, J = 5.4, CH_2), 1.08 (s, 9H, $C(CH_3)_3$), 0.19 (s, 9H, $Sn(CH_3)_3$); MS: 332(0.4), 317(0.2), 167(100), 109(40), 81(25). Treatment of **11d** with dilute acid (acetone/H_2O (4:1), 0.2 M H_2SO_4; 1 hour, room temperature) yielded **12d**; only one isomer was formed.
12d: IR: 3640, 3420, 1705, 1695, 1585; ^{1}H-NMR: 6.36 (s, 1H, =CH-), 4.30 (t, 2H, J = 6.3, H_2COCO), 3.71 (bq, 2H, CH_2OH), 1.97 (heptet, 2H, J = 6.3, CH_2), 1.16 (s, 9H, $C(CH_3)_3$), 0.23 (s, 9H, $Sn(CH_3)_3$); MS: 335(100), 277(88), 165 (79), 135(42), 67(27).

References and notes

1) Seebach, D., Angew. Chem., 91, 259 (1979).
2) Gröbel, B.T., Seebach, D., Synthesis, 357 (1977).
3) Hase, T.A., Koskimies, J.K., Aldrichimica Acta, 15, 35 (1982) and references cited.
4) Lever Jr., O.W., Tetrahedron, 32, 1943 (1976).
5) Huet, F., Pellet, M., Conia, J.M., Synthesis, 33 (1979).
6) Meyers, A.I., Campbell, A.L., Tetrahedron Lett., 4155 (1979).
7) Brandsma, L., Verkruijsse, H.D., "Synthesis of acetylenes, allenes and cumulenes", Elsevier Scientific Publishing Co., Amsterdam, 1981.
8) Klein, J. (a); Théron, F., Verny, M., Vessière, R. (b) in "The chemistry of the carbon-carbon triple bond", S. Patai (Ed.), J. Wiley & Sons, Chichester, 1978.
9) Moreau, J.L., "The chemistry of ketenes, allenes and related compounds", S. Patai, (Ed.), J. Wiley & Sons, Chichester, 1980.
10) 2-Lithiated dithianes are reported to react very slowly with oxiranes: Seebach, D., Corey, E.J., J. Org. Chem., 40, 231 (1975).
11) Johnson, W.S., Frei, B., Gopalan, A.S., J. Org. Chem., 46, 1513 (1981).
12) Eaborn, C., Walton, D.R.M., J. Organometal. Chem., 4, 217 (1965).
13) Corey, E.J., Ruden, R.A., Tetrahedron Lett., 1495 (1973).
14) Schmidt, H.M., Arens, J.F., Recl. Trav. Chim. Pays-Bas, 86, 1138 (1967).
15) Walton, D.R.M., Waugh, F., J. Organometal. Chem., 37, 45 (1972).
16) Kruithof, K.J.H., Schmitz, R.F., Klumpp, G.W., J. Chem. Soc., Chem. Commun., 239 (1983).
17) Reich, H.J., Kelly, M.J., J. Amer. Chem. Soc., 104, 1119 (1982).
18) Brook, A.G., Duff, J.M., Jones, P.F., Davis, N.R., J. Amer. Chem. Soc., 89, 431 (1967).

19) Seebach, D., Synthesis, 17 (1969).
20) This rapid oxidation is also reported for the scarcely known trialkylstannylketones: Kazankova, M.A., Zverkova, T.I., Lutsenko, A.I., Lutsenko, I.F., J. Gen. Chem. U.S.S.R., 44, 225 (1974).
21) Streitwieser Jr., A., Williams Jr., J.E., J. Amer. Chem. Soc., 97, 191 (1975).
22) Meyers, A.I., Campbell, A.L., Abatjoglou, A.G., Eliel, E.L., Tetrahedron Lett., 4159 (1979).
23) Hirsch, J.A., "Topics in stereochemistry", Part 1, N.L. Allinger and E.L. Eliel (Ed.), Interscience Publishers, New York, 1967, 199.
24) Colvin, E., "Silicon in organic synthesis", Butterworths, London, 1981.
25) Hines, J.N., Peagram, M.J., Thomas, E.J., Witham, G.H., J. Chem. Soc., Perkin I, 2332 (1973).
26) Corey, E.J., Kirst, H.A., Tetrahedron Lett., 5041 (1968).
27) (a) Daniels, R.G., Paquette, L.A., Tetrahedron Lett., 1579 (1981), (b) Ishiguro, M., Ikeda, N., Yamamoto, H., J. Org. Chem., 47, 2225 (1982).
28) Leroux, Y., Jacquelin, C., Synth. Commun., 6, 597 (1976).
29) Carlson, R.M., Isidor, J.L., Tetrahedron Lett., 4819 (1973).
30) Komarov, N.V., Yarosh, O.G., Astaf'eva, L.N., Zh. Obshch. Khim., 36, 907 (1966), cited in C.A., 65, 10607c (1966).
31) Hauptmann, H., Mader, M., Synthesis, 307 (1978).
32) Voronkov, M.G., Golovanova, N.I., Pukhnarevich, V.B., Shergina, N.I., Yarosh, O.G., Dokl. Akad. Nauk. S.S.S.R., Phys. Chem., 238, 127 (1978).
33) Joss, U., Schaltegger, H., Helv. Chim. Acta, 52, 2465 (1969).
34) Logue, M.W., Moore, G.L., J. Org. Chem., 40, 131 (1975).
35) Bourelle-Wargnier, F., Vincent, M., Chuche, J., J. Org. Chem., 45, 428 (1980).
36) Birkhofer, L., Richtzenhain, K., Chem. Ber., 112, 2829 (1979).