The Ring Opening of Unsymmetrical Allylic, Benzylic, Propargylic, and Si-Substituted Epoxides by Titanium Acetylides: A Convenient Access to Certain 2-Substituted 3-Butyn-1-ols

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Recveived March 7, 1988

Epoxides bearing aryl, alkenyl, alkynyl, and trimethylsilyl substituents react with titanium acetylides at the higher substituted carbon atom exclusively; the 2-substituted 3-butyn-1-ols thus formed are isolated in 33–79% yield. The dependence of the yield on the solvent, the ratio of the reactands, and their structure is discussed and a reaction mechanism is proposed.

Die Ringöffnung unsymmetrischer allylischer, benzylischer, propargylischer und silylsubstituierter Epoxide durch Titanacetylide: Ein bequemer Zugang zu 2-substituierten 3-Butin-1-olen

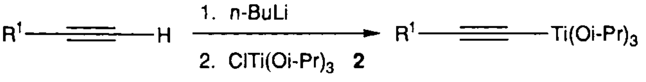
Epoxide mit Aryl-, Alkenyl-, Alkinyl- und Trimethylsilyl-Substituenten reagieren mit Titanacetyliden ausschließlich am höher substituierten Kohlenstoffatom; die so gebildeten 2-substituierten 3-Butin-1-ole werden in 33–79% Ausbeute isoliert. Die Abhängigkeit der Ausbeute vom Lösungsmittel, dem Verhältnis der Reaktanden und ihrer Struktur wird diskutiert und ein Reaktionsmechanismus wird vorgeschlagen.

A) Introduction

In a previous paper2) we reported the preparation of titanium acetylides and their reactions with various electrophiles, the most intriguing result being the ring opening of styrene oxide with exclusive attack of the acetylide at the higher substituted carbon atom of the oxirane ring. Whereas the regioselectivity of the reaction of unsymmetrical epoxides with nucleophiles depends strongly on the nature of the epoxide and the nucleophile3), the ring opening by lithium, magnesium, and aluminium acetylides usually occurs at the less substituted carbon atom4). Two remarkable exceptions are the reaction of alkenyl- and alkynyl-substituted oxiranes with organometallic compounds, which usually yields appreciable amounts of 1,5-adducts with allylic/propargylic rearrangement3a,f,m,s,u), and the ring opening of styrene oxide by alkynyl boranes, which provides mixtures of the two possible regioisomers5). The surprising regioselectivity of the ring opening by titanium acetylides prompted us to examine this reaction in detail, in particular the dependence on the structure of the reactands; furthermore, an investigation of the stereochemical course of the reaction should lead to conclusions about its mechanism.

B) Preparative Results

We first applied the reaction conditions which led to 2,4-diphenyl-3-butyn-1-ol (**5a**) in 70% yield (mixing of equimolar amounts of the titanium acetylide and the epoxide at −50°C in a 3:2 THF/hexane mixture, warming up to room temperature and stirring for 3 days2)) to the reaction of styrene oxide (**4a**) with 1-octyn-1-yltriisopropoxy titanium (**3b**). After 1 day at room temperature the acetylide was consumed completely; however, the product 2-phenyl-3-decyn-1-ol (**5b**) was obtained in a disappointing 26% yield.



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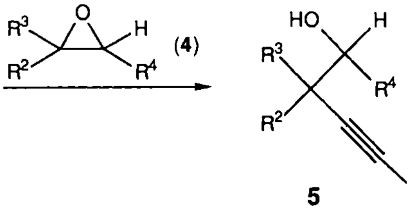

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(see formulae in scheme 1)

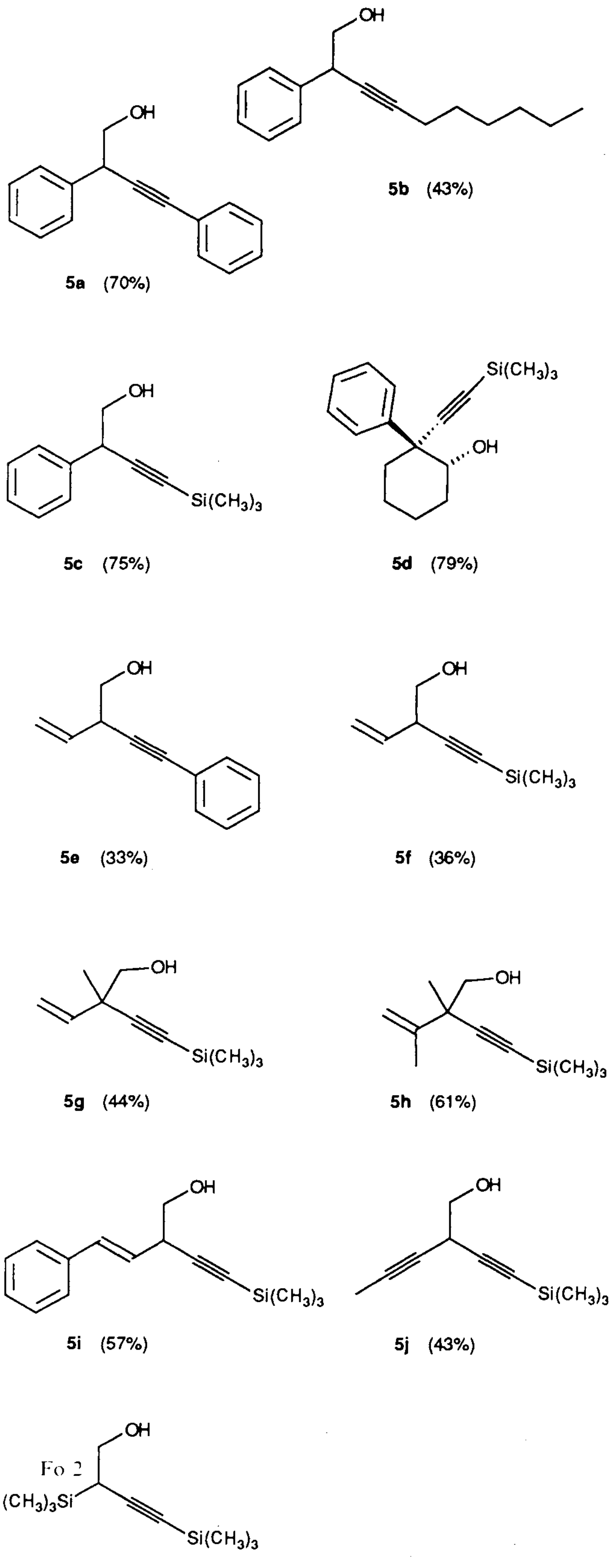
1a, 3a ($R^1 = C_6H_5$)
1b, 3b ($R^1 = C_6H_{13}$)
1c, 3c ($R^1 = Si(CH_3)_3$)

4a ($R^2 = C_6H_5$, $R^3 = R^4 = H$)
4b (R^2-$R^4 = (CH_2)_4$, $R^3 = C_6H_5$)
4c ($R^2 = CH{=}CH_2$, $R^3 = R^4 = H$)
4d ($R^2 = CH{=}CH_2$, $R^3 = CH_3$, $R^4 = H$)
4e ($R^2 = C(CH_3){=}CH_2$, $R^3 = CH_3$, $R^4 = H$)
4f ($R^2 = CH{=}CHC_6H_5$, $R^3 = R^4 = H$)
4g ($R^2 = C{\equiv}C\text{-}CH_3$, $R^3 = R^4 = H$)
4h ($R^2 = Si(CH_3)_3$, $R^3 = R^4 = H$)

Attempts to improve these results by variation of the ligands attached to the titanium failed6). However, the solvent has a remarkable effect on the yield, the optimum of 43% **5b** being obtained in pure THF7). In spite of this, the yield of **5a** was hardly affected by the change from THF/hexane (3:2) to pure THF; however, the stereoselectivity of (*S*)-**5a** formation starting form (*R*)-**4a** was improved (from 18% ee2) to 33% ee) by this change. As the removal of hexane had in no case a negative effect on the outcome of the re-

Chem. Ber. **121**, 1315–1320 (1988) © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1988 0009–2940/88/0707–1315 $ 02.50/0

Scheme 1. Products of ring opening of unsymmetrical epoxides by titanium acetylides



action, the following procedure was used throughout this paper: The acetylene in THF was treated with *n*-BuLi in hexane at 0°C, the solution was warmed up to room temperature, and the solvent was removed in vacuo; after cooling to −50°C, the lithium acetylide was dissolved in THF, chlorotriisopropoxy titanium in THF and the epoxide in THF were added, the mixture was warmed up to room temperature, stirred for 1 − 3 days and worked up as usual. This procedure proved successful also in the reaction of styrene oxide (**4a**) with (trimethylsilylethynyl)triisopropoxy titanium (**3c**), which led to the expected adduct **5c** in 55% yield.

The ratio of the reactands turned out to strongly influence the yield. Whereas an excess of the epoxide slows the reaction down considerably – probably by stabilisation of the titanium acetylide by coordination[8] – an excess of the titanium acetylide leads to different results. In the cases of R^1 = phenyl and R^1 = *n*-hexyl the yield drops from 70% to 13% **5a** and 43% to 26% **5b**, respectively; in the case of R^1 = trimethylsilyl, however, the yield of **5c** rises from 55% to 75% (all values for 100% excess of **3**). The reason for this behavior is unclear; it was also confirmed for the reaction of **3a** with vinyl oxirane (see below). As a consequence of this, a ratio **3**:**4** of 1:1 (in the case of **3a** and **3b**) and of 2:1 (in the case of **3c**) was used throughout this work. The results obtained under these conditions with various epoxides and titanium acetylides are summarized in Scheme 1.

As can be seen from Scheme 1, the reaction takes place with aryl-, alkenyl-, alkynyl- and trimethylsilyl-substituted epoxides in moderate to good yields; further substitution at the epoxide ring (**5d**, **5g**, **5h**) or at the alkenyl group (**5h**, **5i**) increases the yield. Alkyl-substituted epoxides produce less than 10% of the expected adducts, whereas 3-phenylglycidic acid methyl ester reacts exclusively under transesterification to give the isopropyl ester. The reactivity of the titanium acetylide decreases in the order R^1 = TMS > phenyl > *n*-hexyl. For 2-(phenylethynyl)-3-buten-1-ol (**5e**), the mentioned dependence of the yield on the ratio of the reactands was observed again: with a 100% excess of the titanium acetylide, the yield drops from 33% to 15%, whereas with a 100% excess of the epoxide, the reaction is slowed down so much, that it takes seven days at room temperature to reach a 30% yield of **5e**. In each case only the adduct resulting from attack of the acetylide at the higher substituted carbon atom of the epoxide ring is formed; even in the case of alkenyl-oxiranes, especially **4f**[3f] which are notoriously reacting with double bond shift, no other regioisomers were detected. Therefore, this reaction is useful even if only moderate yields are obtained. The purification of the products by kugelrohr distillation poses no problem (some of the silyl-substituted products did not give correct elemental analyses, although all other properties were fully compatible with the structures **5** shown).

C) Mechanistic Studies

The structural assignment of the products **5** deserves some comment. Of the three possible structures, the S_N1-type products (in the case of alkenyl- and alkynyl-oxiranes) would have been readily identified from the multiplicities of the signals in the ^{1}H-NMR spectra; however, the decision between the two possible products of direct ring opening, which exhibit identical multiplicities, had to be based on the chemical shifts of the former epoxide protons and the change of the chemical shifts by derivatisation of the products. For example, the CH- and CH_2 protons of 2,4-diphenyl-3-butyn-1-ol (**5a**) exhibit chemical shifts of δ = 4.08 and 3.85, respectively, whereas the values for the regioisomer 1,4-diphenyl-3-butyn-1-ol are δ = 5.10 and 3.00[9)], respectively. Usually the signals of the former epoxide protons are found between δ = 3 and 4, values which are also in agreement with calculations using increment systems[10)]. The only major exception is compound **5k** formed from trimethylsilyloxirane; due to the electron-releasing effect of the 2-TMS group, the signal of the CH proton is observed at δ = 2.08, whereas the signal of the CH_2 protons is found in the normal range (δ = 3.68). The structural assignment is confirmed by the ^{1}H-NMR spectrum of the 3,5-dinitrobenzoate of **5k**: the CH proton is shifted slightly from δ = 2.08 to 2.39, whereas the shift of the CH_2 protons is considerably (from δ = 3.68 to 4.47/4.58); for the regioisomer 1,4-bis(trimethylsilyl)-3-butyn-1-ol, the opposite behavior would have been expected. Finally, the configuration of **5d** was established to be *u* as follows: the coupling constants $J_{1,6}$ = 4.1 Hz and 10.8 Hz prove the axial position of 1-H[10)]; the considerably larger sterical requirements of the phenyl compared with the alkynyl moiety makes the *u* configuration[11)] probable. Final proof is obtained from a NOE experiment: irradiation of the signal of 1-H causes an intensity enhancement for the *ortho* protons of the phenyl ring, whereas no enhancement is observed by irradiations with the frequency of the TMS group.

A proposal for a mechanism of the reaction of epoxides with titanium acetylides must be compatible with the following observations:

– An electron-releasing substituent is necessary[12)] at the epoxide, and is favorable at the titanium acetylide.

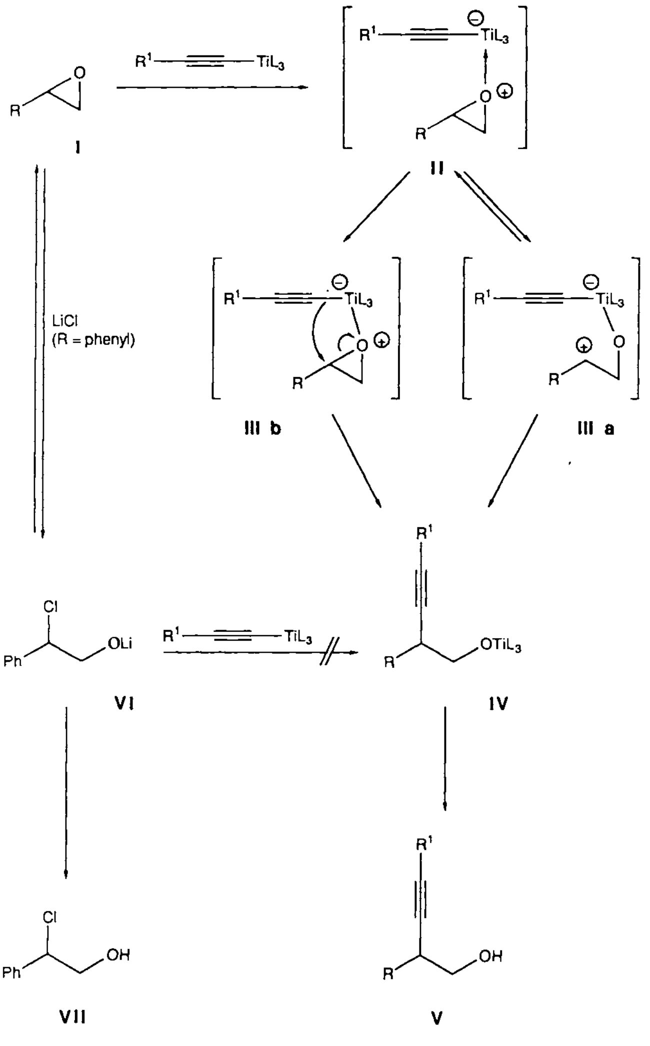
– The ring opening takes place with partial (**5a**)[2)] or complete (**5d**) retention of the configuration.

The second observation is especially remarkable, although not unprecedented for reactions at the higher substituted carbon atom of unsymmetrical epoxides: the acid-catalyzed methanolysis of 1-phenylcyclohexene epoxide[3c,v)] and the palladium-catalyzed reaction of alkenyl-oxiranes with *p*-tosyl isocyanate[3p)] also take place with retention of configuration. In contrast, the ring-opening of epoxides at the higher substituted carbon by hydrogen chloride[3b)], tin halides[3r)] and methanol/Hg(II)[3u)] occurs with inversion of configuration the result expected for an S_N2-type reaction.

The reaction commences with the coordination of the epoxide oxygen to the titanium atom (see Scheme 2). The next step on the reaction pathway may be the formation of an intermediate **IIIa**, the positive charge in which being stabilized by conjugation with the π system of the substitutend R. Depending on the stability of **IIIa** it may collaps faster than rotation occurs (retention, cf. the reaction of alcohols with thionyl chloride). A direct retentive substitution in the ligand sphere of titanium is of course also conceivable, see **IIIb**.

Using (*R*)-styrene oxide, it was shown that unreacted epoxide isolated from the reaction mixture had not lost optical activity (which would have taken place in an equilibrium between **I** and **II**/**IIIa**). The mechanism in Scheme 2 is analogous to that proposed for the gas-phase acid-induced ring opening of 1-phenylcyclohexene oxide[3v)].

Scheme 2. On the mechanism of the reaction of epoxides with titanium acetylides



In the case of styrene oxide, the reaction mixture always contains appreciable amounts (up to 40%) of 2-chloro-2-phenylethanol (**VII**); this is formed via **VI** by reaction of the epoxide with lithium chloride[13)] (which in turn is produced from the reaction of the lithium acetylide with chlorotriisopropoxy titanium). It is conceivable that the ring-opening product **IV** could also be formed by nucleophilic substitution of the chloride in **VI** by the titanium acetylide; this would also be compatible with the stereochemical course of the reaction since double inversion (**I** → **VI** → **IV**) would result in overall retention of the configuration. However, for the following reasons a participation of **VI** in the formation of **V** appears to be unlikely:

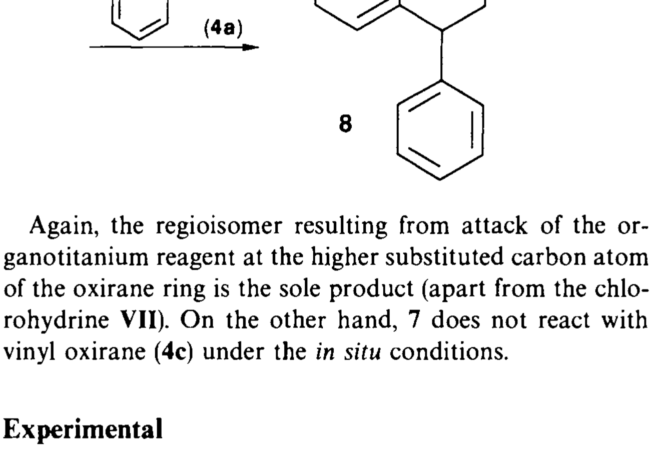
– Organotitanium reagents are not alkylated by alkylhalides[14]; this is also true for titanium acetylides[15].

– When the reaction is started with **VI** (from **VII** and *n*-BuLi), the formation of **V** is much slower than if it is started from **I**; after 1 day at room temperature, only 10% of **V** (R = R′ = phenyl) is obtained.

– The formation of **V** from **I** is also slowed down by saturation of the reaction mixture with lithium chloride (10 equiv.); after 3 days at room temperature, the yield of **V** (R = R′ = phenyl) is 26%, and apart from **V** the reaction mixture contains only the chlorohydrine **VII**.

– With none of the other epoxides used in this paper the corresponding chlorohydrine was found.

Another intriguing feature of the ring opening of epoxides by organotitanium compounds is the dependence of the reactivity on the nature of the organotitanium reagent. Whereas allyl-[3] and alkynyl-titanium derivatives react with epoxides, no reaction takes place with methyltriisopropoxy titanium and styrene oxide[14a]; even heating at reflux and adding lithium chloride does not promote the ring opening. This is also true for styrene oxide and phenyltriisopropoxy titanium, the latter being prepared independently[16] and dissolved in THF prior to use. However, when the titanium reagent **7** is formed from bromobenzene (**6**) and *n*-BuLi/chlorotriisopropoxy titanium (**2**)[17] and (without isolation) is treated with styrene oxide (**4a**) for 1 day at room temperature and 1 day at 40°C, the adduct 2,2-diphenylethanol (**8**) is produced in 48% yield. Thus, the presence of LiCl/LiBr has a dramatic effect on the reactivity of **7**!



Again, the regioisomer resulting from attack of the organotitanium reagent at the higher substituted carbon atom of the oxirane ring is the sole product (apart from the chlorohydrine **VII**). On the other hand, **7** does not react with vinyl oxirane (**4c**) under the *in situ* conditions.

Experimental

Melting points: (not corrected) Tottoli apparatus, Büchi. – Kugelrohr distillation: GKR-50, Büchi. – Specific rotations: Perkin-Elmer polarimeter 241. – IR spectra: Perkin-Elmer IR spectrometers 297 and 983 (abbreviations: s = strong, m = medium, w = weak). – ^{1}H-NMR spectra: Bruker WM-300 (300 MHz) in CDCl$_3$ with (CH$_3$)$_4$Si as internal standard. – Mass spectra: Hitachi-Perkin-Elmer RMU-6M (EI, 70 eV).

All reactions were carried out in a carefully dried apparatus under argon. THF was distilled under argon from potassium/benzophenone. Chlorotriisopropoxy titanium (**2**) was prepared from titanium tetrachloride and tetraisopropoxy titanium[14a] and stored as a solution in THF.

General Procedure for the Reaction of Epoxides with Titanium Acetylides: A solution of 10 mmol of the terminal acetylene **1** in 10 ml of THF was treated at 0°C with 10 mmol (6.7 ml) of *n*-BuLi (1.5 M solution in hexane). The mixture was warmed up to room temperature and the solvent was removed in vacuo. After cooling to –50°C, the lithium acetylide was dissolved in 20 ml of THF and treated with 10 mmol (6.3 ml) of chlorotriisopropoxy titanium (**2**, 1.59 M solution in THF). To the resulting solution of the titanium acetylide was added at –50°C a 1 M solution of the epoxide **4** in THF (10 mmol in the case of **3a** and **3b**, 5 mmol in the case of **3c**); the mixture was gradually warmed up to room temperature within 2 h and stirred for 1 day (in the case of **3b** and **3c**) or for 3 days (in the case of **3a**). Hydrolysis with 10 ml of 1 N hydrochloric acid was followed by extraction with diethyl ether, washing of the combined organic layers with brine and drying with MgSO$_4$. The solvent was removed in vacuo, and the crude product was purified by kugelrohr distillation.

2,4-Diphenyl-3-butyn-1-ol **5a**): From 1.02 g (10 mmol) of phenylacetylene (**1a**) and 1.20 g (10 mmol) of styrene oxide (**4a**). Purification by kugelrohr distillation (175°C/0.01 Torr); yield 1.55 g (70%, colorless oil, which crystallized upon standing). – M.p. 51°C. – IR (neat): ν = 3600–3200 cm^{-1} (s, OH), 3060 (m), 3025 (m), 2935 (m), 2880 (m), 2220 (w, C≡C), 1600 (m), 1490 (s), 1450 (s), 1440 (m), 1060 (s), 910 (m), 755 (s), 695 (s). – ^{1}H NMR: δ = 1.96 (s, 1H, OH); 3.85 (d, *J* = 6.7 Hz, 2H, 1-H); 4.08 (t, *J* = 6.7 Hz, 1H, 2-H); 7.28–7.48 (m, 10H, aromatic-H). – MS: *m/z* (%) = 222 (7, M$^+$), 204 (3), 191 (100), 189 (16), 165 (7), 152 (1), 122 (2), 115 (3), 105 (6), 91 (2), 89 (2), 77 (4).

C$_{16}$H$_{14}$O (222.3) Calcd. C 86.45 H 6.35
Found C 86.29 H 6.39

2-Phenyl-3-decyn-1-ol (**5b**): From 0.55 g (5 mmol) of 1-octyne (**1b**) and 0.60 g (5 mmol) of styrene oxide (**4a**). Purification by kugelrohr distillation (180°C/0.005 Torr); yield 0.50 g (43%, colorless oil). – IR (neat): ν = 3600–3200 cm^{-1} (m, OH), 3060 (w), 3030 (w), 2930 (s), 2860 (s), 2220 (w, C≡C), 1600 (w), 1490 (m), 1450 (m), 1050 (s), 750 (m), 700 (s). – ^{1}H NMR: δ = 0.89 (t, *J* = 6.9 Hz, 3H, 10-H); 1.25–1.59 (m, 8H, 6-H-7-H, 8-H, 9-H); 1.86 (s, 1H, OH), 2.26 (dt, *J* = 2.2/7.0 Hz, 2H, 5-H); 3.70 (pseudo-t, *J* = 7 Hz, 2H, 1-H); 3.84 (m, 1H, 2-H); 7.23–7.40 (m, 5H, aromatic H). – MS: *m/z* (%) = 230 (1, M$^+$), 215 (1), 200 (30), 171 (8), 157 (12), 143 (22), 130 (100), 117 (33), 115 (39), 105 (16), 102 (12), 95 (25), 91 (77), 77 (17), 69 (13), 55 (22).

C$_{16}$H$_{22}$O (230.4) Calcd. C 83.43 H 9.63
Found C 83.46 H 9.81

2-Phenyl-4-trimethylsilyl-3-butyn-1-ol (**5c**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.60 g (5 mmol) of styrene oxide (**4a**). Purification by kugelrohr distillation (130°C/0.005 Torr); yield 0.82 g (75% bright yellow oil which crystallized upon standing). – M.p. 40–41°C. – IR (KBr): ν = 3600–3200 cm^{-1} (m, OH), 3060 (w), 3030 (w), 2960 (m), 2900 (w), 2175 (m, C≡C), 1600 (w), 1490 (m), 1450 (m), 1250 (s), 1040 (s), 840 (s), 755 (s), 700 (s). – ^{1}H-NMR: δ = 0.20 [s, 9H, Si(CH$_3$)$_3$]; 1.83 (s, 1H, OH); 3.73 (m, 2H, 1-H); 3.91 (m, 1H, 2-H); 7.25–7.40 (m, 5H, aromatic H). –

MS: *m/z* (%) = 218 (1, M^+), 203 (1), 188 (47), 173 (11), 159 (29), 145 (9), 128 (12), 107 (6), 91 (6), 83 (10), 75 (39), 73 (100).

$C_{13}H_{18}OSi$ (218.4) Calcd. C 71.50 H 8.31
Found C 71.19 H 8.66

2-Phenyl-2-(trimethylsilylethynyl)cyclohexanol (**5d**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.87 g (5 mmol) of 1-phenylcyclohexene oxide (**4b**)[18]. Purification by kugelrohr distillation (170°C/0.03 Torr); yield 1.07 g (79%, yellow oil). – IR (neat): ν = 3600–3300 cm^{-1} (w, OH), 2940 (s), 2860 (m), 2165 (m, C≡C), 1490 (w), 1450 (m), 1250 (s), 995 (m), 840 (s), 760 (s), 700 (s). – ^1H NMR: δ = 0.24 [s, 9H, $Si(CH_3)_3$]; 1.35–2.01 (m, 9H, 3-H, 4-H, 5-H, 6-H, OH); 3.78 (dd, *J* = 4.1/10.8 Hz, 1H, 1-H); 7.21–7.27 (m, 1H, *para*-aromat. H); 7.32–7.38 (m, 2H, *meta*-aromat. H); 7.60–7.63 (m, 2H, *ortho*-aromat. H). – MS: *m/z* (%) = 272 (29, M^+), 257 (1), 243 (2), 229 (2), 185 (6), 181 (6), 169 (6), 167 (9), 154 (14), 141 (8), 129 (7), 115 (5), 105 (4), 103 (5), 97 (4), 91 (6), 83 (4), 75 (24), 73 (100), 59 (6).

$C_{17}H_{24}OSi$ (272.5) Calcd. C 74.94 H 8.88
Found C 73.84 H 8.91

2-(Phenylethynyl)-3-buten-1-ol (**5e**): From 0.51 g (5 mmol) of phenylacetylene (**1a**) and 0.35 g (5 mmol) of vinyloxirane (**4c**). Purification by kugelrohr distillation (120°C/0.005 Torr); yield 0.28 g (33%, colorless oil). – IR (neat): 3600–3200 cm^{-1} (s, OH), 3080 (m), 3055 (m), 2940 (m), 2880 (m), 2230 (w, C≡C), 1640 (m), 1600 (m), 1570 (w), 1490 (s), 1440 (m), 1050 (s), 990 (s), 920 (s), 755 (s), 690 (s). – ^1H NMR: δ = 1.67 (s, 1H, OH); 3.53 (m, 1H, 2-H); 3.73 (m, 2H, 1-H); 5.28 (dt, *J* = 10.0/1.4 Hz, 1H, 4a-H); 5.48 (dt, *J* = 17.0/1.4 Hz, 1H, 4b-H); 5.86 (ddd, *J* = 6.2/10.0/17.0 Hz, 1H, 3-H); 7.28–7.31 (m, 3H, aromatic H); 7.40–7.45 (m, 2H, aromatic H). – MS: *m/z* (%) = 172 (12, M^+), 154 (3), 141 (100), 139 (12), 128 (4), 115 (61), 102 (4), 91 (6), 89 (7), 77 (4), 63 (11), 51 (5).

$C_{12}H_{12}O$ (172.2) Calcd. C 83.69 H 7.02
Found C 83.32 H 7.23

2-(Trimethylsilylethynyl)-3-buten-1-ol (**5f**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.35 g (5 mmol) of vinyloxirane (**4c**). Purification by kugelrohr distillation (100°C/2 Torr); yield 0.30 g (36%, bright yellow liquid). – IR: ν = 3600–3200 cm^{-1} (s, OH), 3090 (w), 3020 (w), 2960 (s), 2900 (m), 2180 (s, C≡C), 1640 (w), 1410 (w), 1250 (s), 1050 (s), 990 (m), 925 (s), 885 (s), 845 (s), 760 (s), 700 (m). – ^1H NMR: δ = 0.18 [s, 9H, $Si(CH_3)_3$]; 1.71 (s, 1H, OH); 3.32 (tq, *J* = 1.4/6.2 Hz, 1H, 2-H); 3.62 (dd, *J* = 5.4/6.2 Hz, 2H, 1-H); 5.23 (dt, *J* = 10.0/1.4 Hz, 1H, 4a-H); 5.40 (dt, *J* = 17.0/1.4 Hz, 1H, 4b-H); 5.76 (ddd, *J* = 6.2/10.0/17.0 Hz, 1H, 3-H). – MS: *m/z* (%) = 138 (31) [M^+ – 30], 123 (15), 109 (4), 107 (5), 103 (5), 99 (7), 83 (7), 78 (25), 75 (45), 73 (100), 59 (9).

3,5-Dinitrobenzoate: Colorless crystals, m.p. 54–55°C.

$C_{16}H_{18}N_2O_6Si$ (362.4) Calcd. C 53.03 H 5.01 N 7.73
Found C 51.41 H 4.97 N 8.45

2-Methyl-2-(trimethylsilylethynyl)-3-buten-1-ol (**5g**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.42 g (5 mmol) of 1,2-epoxy-2-methyl-3-butene (**4d**)[19]. Purification by kugelrohr distillation (100°C/1.5 Torr); yield 0.40 g (44%, bright yellow liquid). – IR (neat): ν = 3600–3200 cm^{-1} (s, OH), 3090 (w), 2960 (s), 2900 (m), 2880 (m), 2170 (s, C≡C), 1640 (w), 1410 (w), 1250 (s), 1050 (s), 935 (m), 900 (m), 845 (s), 760 (s), 700 (m). – ^1H NMR: δ = 0.18 [s, 9H, $Si(CH_3)_3$]; 1.28 (s, 3H, 2-CH_3); 1.76 (s, 1H, OH); 3.44 (pseudo-s, 2H, 1-H); 5.18 (dd, *J* = 1.4/10.1 Hz, 1H, 4a-H); 5.43 (dd, *J* = 1.4/17.0 Hz, 1H, 4b-H); 5.71 (dd, *J* = 10.1/17.0 Hz, 1H, 3-H). – MS: *m/z* (%) = 182 (1, M^+), 164 (4), 152 (32), 149 (10), 137 (15), 123 (4), 121 (4), 109 (8), 107 (4), 97 (16), 92 (16), 83 (9), 75 (44), 73 (100), 59 (18).

3,5-Dinitrobenzoate: Colorless crystals, m.p. 77°C.

$C_{17}H_{20}N_2O_6Si$ (376.4) Calcd. C 54.24 H 5.36 N 7.44
Found C 53.16 H 5.20 N 7.66

2,3-Dimethyl-2-(trimethylsilylethynyl)-3-buten-1-ol (**5h**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.49 g (5 mmol) of 1,2-epoxy-2,3-dimethyl-3-butene (**4e**)[20]. Purification by kugelrohr distillation (100–110°C/1.5 Torr); yield 0.60 g (61%, bright yellow liquid). – IR (neat): ν = 3600–3200 cm^{-1} (s, OH), 3090 (w), 2960 (s), 2900 (s), 2170 (s, C≡C), 1640 (s), 1450 (s), 1375 (s), 1250 (s), 1050 (s), 870 (s), 840 (s), 760 (s), 700 (s). – ^1H NMR: δ = 0.17 [s, 9H, $Si(CH_3)_3$], 1.33 (s, 3H, 2-CH_3); 1.67 (s, 1H, OH); 1.81 (d, *J* = 0.6 Hz, 3H, 3-CH_3); 3.50 (d, *J* = 10.5 Hz, 1H, 1a-H); 3.55 (d, *J* = 10.5 Hz, 1H, 1b-H); 4.96 (t, *J* = 0.6 Hz, 1H, 4a-H); 5.15 (s, 1H, 4b-H). – MS: *m/z* (%) = 196 (1, M^+), 166 (44), 151 (26), 135 (5), 123 (6), 109 (4), 106 (9), 97 (20), 91 (9), 83 (10), 75 (30), 73 (100), 59 (27).

$C_{11}H_{20}OSi$ (196.4) Calcd. C 67.28 H 10.27
Found C 66.35 H 10.48

3,5-Dinitrobenzoate: Colorless crystals, m.p. 92–93°C.

4-Phenyl-2-(trimethylsilylethynyl)-3-buten-1-ol (**5i**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.73 g (5 mmol) of 1,2-epoxy-4-phenyl-3-butene (**4f**)[21]. Purification by kugelrohr distillation (170°C/0.02 Torr); yield 0.70 g (57%, yellow oil). – IR (neat): ν = 3600–3200 cm^{-1} (w, OH), 3030 (w), 2960 (m), 2800 (w), 2170 (m, C≡C), 1490 (w), 1450 (w), 1250 (s), 965 (m), 840 (s), 760 (s), 750 (s), 695 (s). – ^1H NMR: δ = 0.20 [s, 9H, $Si(CH_3)_3$], 1.86 (s, 1H, OH); 3.48 (m, 1H, 2-H); 3.69 (m, 2H, 1-H); 6.11 (dd, *J* = 6.6/15.8 Hz, 1H, 3-H); 6.70 (dd, *J* = 1.1/15.8 Hz, 1H, 4-H); 7.20–7.39 (m, 5H, arom. H). – MS: *m/z* (%) = 244 (2, M^+), 213 (30), 199 (6), 197 (4), 183 (7), 173 (5), 154 (14), 145 (7), 141 (7), 115 (7), 103 (12), 97 (20), 91 (4), 83 (5), 75 (22), 73 (100), 59 (10).

3,5-Dinitrobenzoate: Colorless crystals, m.p. 118–119°C.

$C_{22}H_{22}N_2O_6Si$ (438.5) Calcd. C 60.26 H 5.06 N 6.39
Found C 59.78 H 5.20 N 6.29

2-(Trimethylsilylethynyl)-3-pentyn-1-ol (**5j**): From 0.98 g (10 mmol) of trimethylsiylacetylene (**1c**) and 0.41 g (5 mmol) of 1,2-epoxy-3-pentyne (**4g**)[22]. Purification by kugelrohr distillation (100–110°C/0.4 Torr); yield 0.39 g (43%, yellow oil, which turns rapidly dark on contact with air). – IR (neat): ν = 3600–3200 cm^{-1} (s, OH), 2970 (s), 2930 (m), 2910 (m), 2180 (s, C≡C), 1310 (m), 1255 (s), 1060 (s), 1045 (s), 900 (s), 850 (s), 765 (s), 705 (m), 650 (m). – ^1H NMR: δ = 0.17 [s, 9H, $Si(CH_3)_3$], 1.80 (s, 1H, OH); 1.83 (d, *J* = 2.4 Hz, 3H, 5-H); 3.55 (m, 1H, 2-H); 3.68 (d, *J* = 6.8 Hz, 2H, 1-H). – MS: *m/z* (%) = 180 (2, M^+), 150 (53), 135 (27), 121 (22), 107 (8), 99 (10), 90 (25), 83 (7), 75 (40), 73 (100), 67 (10).

The hydrogenation of **5j** with palladium on charcoal as catalyst furnished *2-(2-trimethylsilylethyl)-1-pentanol.*

$C_{10}H_{24}OSi$ (188.4) Calcd. C 63.76 H 12.84
Found C 63.44 H 12.34

2,4-Bis(trimethylsilyl)-3-butyn-1-ol (**5k**): From 0.98 g (10 mmol) of trimethylsilylacetylene (**1c**) and 0.58 g (5 mmol) of trimethylsilyloxirane (**4h**)[3d]. Purification by kugelrohr distillation (90–100°C/0.6 Torr); yield 0.40 g (37%, bright yellow liquid). – ^1H NMR: δ = 0.11 [s, 9H, 2-$Si(CH_3)_3$]; 0.15 [s, 9H, 4-$Si(CH_3)_3$]; 1.73 (s, 1H, OH); 2.08 (dd, *J* = 5.5/8.7 Hz, 1H, 2-H); 3.68 (m, 2H, 1-H).

3,5-Dinitrobenzoate: Colorless crystals, m.p. 99–100°C. – IR (KBr): ν = 3110 cm^{-1} (m), 2960 (m), 2900 (w), 2150 (m, C≡C), 1730 (s, C=O), 1630 (m), 1555 (s, NO_2), 1545 (s), 1460 (m), 1350 (s, NO_2), 1295 (s), 1250 (s), 1175 (m), 845 (s), 710 (s). – ^1H NMR: δ = 0.12 [s, 9H, 2-$Si(CH_3)_3$], 0.21 [s, 9H, 4-$Si(CH_3)_3$], 2.39 (dd, *J* = 5.0/

10.4 hz, 1 H, 2-H); 4.47 (t, J = 10.4 Hz, 1 H, 1a-H); 4.58 (dd, J = 5.0/10.6 Hz, 1 H, 1b-H); 9.18 (m, 2 H, arom. H); 9.22 (m, 1 H, arom. H). – MS: m/z (%) = 408 (1, M^+), 393 (1), 319 (2), 305 (4), 269 (20), 253 (2), 240 (5), 223 (4), 195 (4), 177 (4), 155 (3), 149 (5), 124 (34), 109 (64), 73 (100).

$C_{17}H_{24}N_2O_6Si_2$ (408.6) Calcd. C 49.98 H 5.92 N 6.86
Found C 49.13 H 5.87 N 6.88

2,2-Diphenylethanol (**8**): A solution of 1.57 g (10 mmol) of bromobenzene (**6**) in 50 ml of THF was treated at −100°C with 6.7 ml (10 mmol) of *n*-BuLi (1.5 M solution in hexane); stirring for 10 min followed by additon of 6.3 ml (10 mmol) of chlorotriisopropoxy titanium (**2**, 1.59 M solution in THF) at −100°C. The mixture was warmed up to room temperature, and a solution of 1.20 g (10 mmol) of styrene oxide (**4a**) in 10 ml THF was added. After stirring for 1 day at room temperature and for 1 day at 40°C, workup was carried out as described in the general procedure. The crude product was purified by kugelrohr distillation (160°C/0.005 Torr); yield 0.96 g (48%).

CAS Registry Numbers

1a: 536-74-3 / **1b**: 629-05-0 / **1c**: 1066-54-2 / **2**: 20717-86-6 / **4a**: 96-09-3 / **4b**: 4829-01-0 / **4c**: 930-22-3 / **4d**: 1838-94-4 / **4e**: 34485-82-0 / **4f**: 50901-75-2 / **4g**: 6924-82-9 / **4h**: 16722-09-1 / **5a**: 86100-15-4 / **5b**: 114274-97-4 / **5c**: 114299-63-7 / **5d**: 114274-98-5 / **5e**: 99806-32-3 / **5f**: 114274-99-6 / **5f**-3,5-dinitrobenzoate deriv.: 114275-05-7 / **5g**: 114275-00-2 / **5g**-3,5-dinitrobenzoate deriv.: 114275-06-8 / **5h**: 114275-01-3 / **5h**-3,5-dinitrobenzoate deriv.: 114275-07-9 / **5i**: 114275-02-4 / **5i**-3,5-dinitrobenzoate deriv.: 114275-08-0 / **5j**: 114275-03-5 / **5k**: 114275-04-6 / **5k**-3,5-dinitrobenzoate deriv.: 114275-09-1 / **6**: 108-86-1 / **8**: 1883-32-5 / 2-(2-trimethylsilylethyl)-1-pentanol: 114275-10-4

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[1] Postdoctoral fellow at the ETH Zürich, 1986–1987. We gratefully acknowledge a grant from the *Deutsche Forschungsgemeinschaft*.

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[7] Dependence of the yield of **5b** on the solvent: THF/hexane (3:2): 26%, THF/hexane (4:1): 40%, THF (0.25 M of **3b** and **4a**): 43%, THF (0.125 M of **3b** and **4a**): 39%, diethyl ether: 33%, dimethoxyethane: 14%, THF/DMPU (2:1): 0%.

[8] Whereas with 1:1 to 3:1 ratios of isobutylene oxide and (phenylethynyl)triisopropoxy titanium the expected adduct 2,2-dimethyl-4-phenyl-3-butyn-1-ol is formed in 5–10% yield, with a 10:1 ratio no reaction takes place anymore; even the polymerization of the titanium acetylide is suppressed, so that the mixture remains colorless and unchanged for several days at room temperature!

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[53/88]