Synthesis and Intramolecular Aldol Reactions of 1,6- and 1,7-Bis(acylsilanes)

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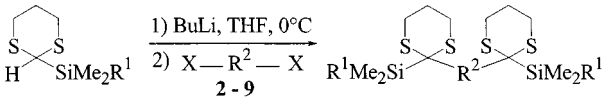
A series of 1,6- and 1,7-bis(acylsilanes) have been prepared using a strategy of substitution of dihalo derivatives with a synthetic equivalent of the trialkylsilylcarbonyl anion. These bis(acylsilanes) could easily be converted, under Lewis acid activation, into *cis*-β-hydroxyacylsilanes or the corresponding α,β-unsaturated derivatives, by means of a completely stereoselective intramolecular aldol reaction.

Since their discovery by Brook in 1957,[1] acylsilanes have been widely studied and employed in organic synthesis,[2] including in organofluorine[3] and carbohydrate[4] chemistry. In contrast, the chemistry of bis(acylsilanes) has been much less well investigated, despite the high potential of transformations one can expect from compounds of this type as a result of a combination of the usual properties of dicarbonyl compounds with the specific properties of acylsilanes. Only a few syntheses have been reported to date[5,6,7] and accounts of their further transformations are even more scarce.[5c,6,7] We have recently undertaken a program of syntheses and applications of various functionalized bis(acylsilanes). First papers dealt with the preparation of β-hydroxy- or β-oxo-bis(acylsilanes)[7a] and some interesting cyclization reactions.[3h,7b] We now report on the synthesis of various bis(acylsilanes) with the two carbonyl groups in a 1,6- or 1,7-relative orientation, as well as on intramolecular aldol reactions leading to five- or six-membered organosilicon carbocycles.

Synthesis of the Starting Bis(acylsilanes)

The previous syntheses of bis(acylsilanes) were based on coupling reactions between two acylsilanes, or on established methods for acylsilanes that were adapted to difunctional precursors. Michael addition of a 2-chloroacetyltrialkylsilane to an α,β-unsaturated acylsilane[5a] gave the corresponding 1,2-bis(trialkylsilyl)carbonylcyclopropane. Pd^{II}-catalyzed coupling between β-iodo- and β-tributylstannyl-α,β-unsaturated acylsilanes[5b] gave the conjugated 1,6-bis(acylsilane). Another Pd^{II}-catalyzed method involved Suzuki-type coupling between a 1,ω-alkanediyl-bis(boronic ester) and *p*-bromobenzoylsilane.[5c] Phthaloyldisilane and adipoyldisilane have been prepared by coupling of the corresponding diacyl dichlorides with lithium bis(trimethylsilyl)cuprate.[5d] Heptanedioylsilane has successfully been obtained by a sequence of alkylation of methoxy(phenylthio)trimethylsilylmethane and oxidation with $NaIO_4$.[5e] One of the more convenient sources of acylsilanes is the corresponding aldehyde, following the reaction sequence dithioketalization−silylation−dethioketalization, proposed simultaneously by Brook and Corey.[8] A variant of this methodology involves the metallation and treatment of 2-trimethylsilyl-1,3-dithiane **1a** with an electrophile. This sequence, previously mentioned by Brook,[8a] can be considered as an S_N reaction with an equivalent of the trimethylsilylcarbonyl anion, and has been widely used in this laboratory for the synthesis of functionalized acylsilanes[4] and bis(acylsilanes).[7] It has also been used by Tsai in the preparation of functionalized acylsilanes and bis(acylsilanes) from mono- and dihalogenated compounds.[6]

The bis(acylsilanes) reported here were prepared according to this method, via the corresponding bis(dithiane) derivatives **10**−**14**, **16**, **19**, **20**, **23**, and **24**. The nucleophilic displacement of a halide by 2-lithio-2-trialkylsilyl-1,3-dithiane **1a** or **1b** (Scheme 1, Table 1) gave excellent yields with the simple bis-primary alkyl halides **2**−**4**, **7**−**9** (entries 1−4, 7−10). Some competing elimination (entries 5, 6) occurred when one (dibromide **5**) or two (dibromide **6**) halogens were attached to secondary carbon atoms. Some substitution leading to compounds **21** and **22** was also observed (entry 8).



Scheme 1

The conversion of the bis(dithioketals) into the corresponding acylsilanes (Scheme 2, Table 2) proved to be more problematic. Many methods[9] have been described for such a transformation, because an efficient general one does not exist. Several procedures were attempted with varying degrees of success. Chloramine-T, a cheap and convenient reagent,[10] gave moderate yields of the saturated compounds **25** and **27** (entries 1, 4). Using mercuric reagents,[11] the aliphatic bis(acylsilanes) **26**, **27**, **28**, **29**, and **30** were obtained efficiently (entries 3, 5−8). Finally, a good method for obtaining **25** was found to be dethioketalization with

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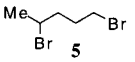
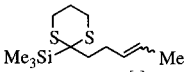
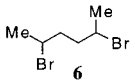
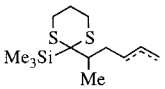
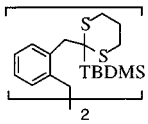
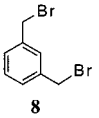
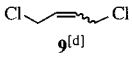
Table 1. Preparation of 2-bis(trialkylsilyl)-1,3-dithianes

Entry	Halides **2-9**	R^1	Dithianes (% yield)	By-products (% yield)
1	I-$(CH_2)_4$-I : **2**	Me	**10** (89)	
2	**2**	t-Bu	**11** (85)	
3	Br-$(CH_2)_5$-Br : **3**	Me	**12** (97)	
4	Br-$(CH_2)_6$-Br : **4**	Me	**13** (92)	
5	 **5**	Me	**14** (31)	 **15** (44)[a]
6	 **6**	Me	**16** (20)	 **17** + **18** (25)[b]
7	 **7**	Me	**19** (85)	
8	**7**	t-Bu	**20** (30)	 **21** (32)[c]
9	 **8**	Me	**23** (88)	
10	 **9**[d]	Me	**24** (89)[d]	

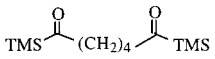
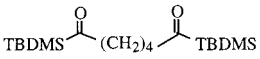
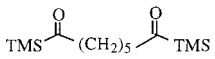
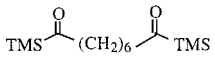
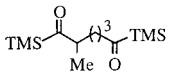
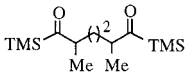
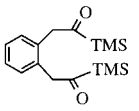
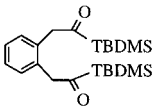
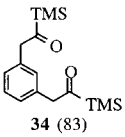
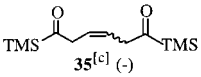
[a] Mixture of stereoisomers (86:14). – [b] Mixture of isomers **17** and **18**. – [c] Compound **22** (yield 8%), derived from a substitution reaction with *n*BuLi, was additionally isolated. – [d] Mixture of *cis*/*trans* stereoisomers (93:7).

methyl iodide,[12] which gave a high yield of the desired compound (entry 2) without the drawback of using heavy metal salts. In some cases, minor amounts of by-products (yield <10%), generally deriving from partial dethioketalization or side reactions, were detected in the crude product mixtures.

Scheme 2

Attempts to prepare aromatic derivatives **31**, **33**, and **34** using chloramine-T or methyl iodide were unsuccessful. Whereas iodine[13] gave a poor yield of aliphatic bis(acylsilane) **25**, it gave the best results in the aromatic series (entries 9–12). After filtration through silica gel, the aromatic derivative **31** was found to be contaminated by a small amount of the corresponding cycloaldol **32** (vide infra), even though NMR analysis of the crude reaction product showed the acylsilane to be the sole product. The unsaturated bis(acylsilane) **35** was also prepared according to the same method (entry 12), but quickly decomposed at room temperature to give a small amount of aldol **36**. On the basis of ^{13}C-NMR and IR data (vide infra), its stereochemistry could be assigned as having a *cis* relationship between the hydroxyl and carbonyl groups.

Table 2. Preparation of bis(acylsilanes)

Entry	Dithianes	Hydrolysis Method[a]	Conv. (%)	Bis(acylsilanes) (% yield)
1	**10**	i	100	 **25** (65)
2	**10**	iii	100	**25** (86)
3	**11**	ii	100	 **26** (84)
4	**12**	i	100	 **27** (60)
5	**12**	ii	98	**27** (77)
6	**13**	ii	100	 **28** (83)
7	**14**	ii	98	 **29** (77)
8	**16**	ii	100	 **30** (75)
9	**19**	iv	100	 **31**[b] (50)
10	**20**	iv	100	 **33** (15)
11	**23**	iv	100	 **34** (83)
12	**24**	iv	100	 **35**[c] (-)

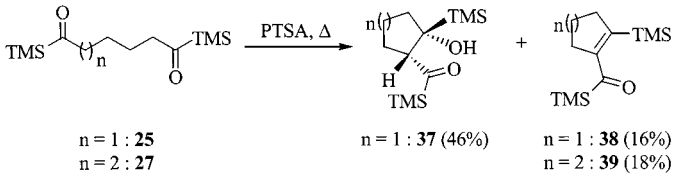
[a] Method i: chloramine-T, MeCOMe/MeOH/H_2O (1:4:1), room temp., 0.5 h. Method ii: $Hg(ClO_4)_2 \cdot x\,H_2O$, $CaCO_3$, THF/H_2O (4:1), room temp., 2–5 h. Method iii: MeI, $CaCO_3$, MeCN/H_2O (1:1), 55°C, 8–15 h. Method iv: I_2, $CaCO_3$, THF/H_2O (4:1), room temp., 3–7 h. – [b] Mixture of bis(acylsilane) **31**/aldol **32** (9:1). – [c] This compound was characterized in the crude mixture but quickly decomposed into a small amount of its aldol **36** (15%).

Acid-Induced Aldol Cyclizations

As mentioned above, some spontaneous cyclization occurred during purification of acylsilane **31** on silica gel. This observation prompted us to further investigate the generality of this transformation, which might lead to interesting multifunctional cycloacylsilanes. In view of the acidic character of silica gel and the sensitivity of the acylsilane function to basic conditions,[14] this cyclization was mainly investigated under acidic activation. Thus, the enol form of an acylsilane function underwent addition to the activated carbonyl of the second group.

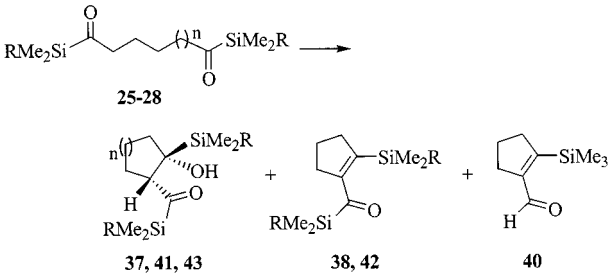
Only one example of a cycloketol of this type has been mentioned by Tsai, namely compound **37**, which was obtained as a by-product in the reaction of bis(acylsilane) **25** with samarium diiodide.[6] On the other hand, intramolecular aldol reactions of 1,6- and 1,7-dialdehydes and -diketones have been described in many reports,[15] most of these being base-promoted and leading directly to the enone. The most comparable situation to that described here is that of dialdehydes or diketones that are non-enolizable at the external α- and α′-carbon atoms under conditions where an enamine (i.e. piperidine, AcOH)[16] or an enoxysilane (Mukaiyama aldol reaction)[17] is involved.

The saturated aliphatic bis(acylsilane) **25** underwent spontaneous yet very slow cyclization to the aldol **37**; a 45% conversion was measured after storage for six months in a refrigerator. At the same time, a minor amount (12%) of the corresponding condensation product **38** was produced. When a solution of **25** in petroleum ether/AcOEt was treated with a suspension of silica gel, less than 15% of the aldol **37** was obtained after stirring for 24 h. Thus, more vigorous conditions were clearly required to efficiently induce the cyclization of such simple aliphatic bis(acylsilanes). Both Brønsted and Lewis acid activation were then investigated. Addition of a catalytic amount (10%) of *p*-toluenesulfonic acid to **25** and distillation in a kugelrohr apparatus gave a mixture of the aldol **37** (46%), the condensation product **38** (16%), and the starting material (7%) (Scheme 3). The same conditions gave only a poor yield of the corresponding cyclohexene derivative **39** (18%).



Scheme 3

More interesting results were obtained using Lewis acid catalysts (Scheme 4, Table 3). Titanium tetrachloride,[17][18] trimethylsilyl trifluoromethanesulfonate,[19] and boron trifluoride etherate[20] proved to be effective, furnishing high yields of **37** (entries 1−4). When the reaction with TMSOTf was performed at higher temperatures (entry 2), no aldol **37** was detected but rather the α,β-unsaturated acylsilane **38** and aldehyde **40** were obtained in moderate yields. The TBDMS analogue **26** and the higher homologue **27** were similarly cyclized under Lewis acid activation, although in these cases titanium tetrachloride was found to be the only effective catalyst, giving the cycloaldols **41** and **43** in 73% and 77% yield, respectively (entries 6, 10). Boron trifluoride or TMSOTf gave only poor yields of aldols **41** and **43**, along with small amounts of the dehydrated product **42** (entries 5, 7−9, 11).



Scheme 4

Only one diastereomer was observed in these cyclizations leading to five- or six-membered adducts. We were unable to detect any trace of the other, even by careful NMR analyses of the crude reaction products. The stereochemistries of **37**[6] and **43** were determined by NOE experiments. Irradiation of the Me_3Si group (at $\delta = -0.01$ in **37**; at $\delta = -0.04$ in **43**) induced an 18% NOE on the α-proton in **37** and a 10% NOE on the α-proton in **43**, indicating a *cis* relationship between the hydroxyl and silylcarbonyl groups (Scheme 5). This relative stereochemistry was confirmed by an internal hydrogen bond between these groups. This hydrogen bond induced a shift of 7−10 ppm (downfield) and 20−25 cm^{-1} (lower frequency) for the carbonyl group in the ^{13}C-NMR and IR spectra, respectively.[21] Moreover, the fact that the positions of the hydroxyl and the carbonyl bands were found to be independent of the concentration corroborated this intramolecular association. It is worth noting that the hydroxyl group of **43** appeared as a doublet ($J = 2.3$ Hz) at $\delta = 3.87$ in the ^1H-NMR spectrum. This splitting could be attributed to the intramolecular hydrogen bond, which imposes a rigid W-geometry that leads to long-range coupling between H_a and H_c (Scheme 5).[22]

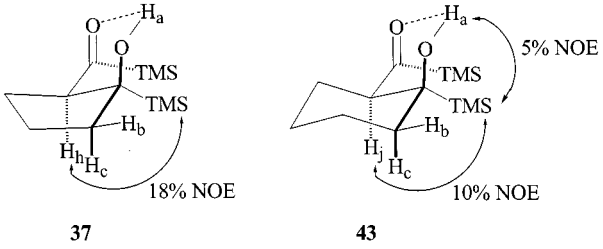
The optimized aldol conditions ($TiCl_4$, −25°C) were then applied to the α-methyl-substituted bis(acylsilane) **29**, giving a good yield of the aldol product **44** (Scheme 6). Interestingly, the high stereoselectivity of the cyclization was illustrated by the formation of only two diastereomers, despite the presence of a third asymmetric carbon. The spectral observations mentioned above (shift of the carbonyl group in the ^{13}C-NMR and IR spectra) applied here too, indicating that in the two diastereomers, obtained in a 4:1 ratio, the hydroxyl and silylcarbonyl groups have a mutual *cis* relationship.

These electrophilic activated aldol additions involved an enol intermediate. As the diastereoselectivity was independent of the nature of the catalyst, irrespective of its chelating ($TiCl_4$) or non-chelating (APTS, TMSOTf, or $BF_3 \cdot OEt_2$) character, the diastereoselectivity was most probably controlled by steric interactions and hydrogen-

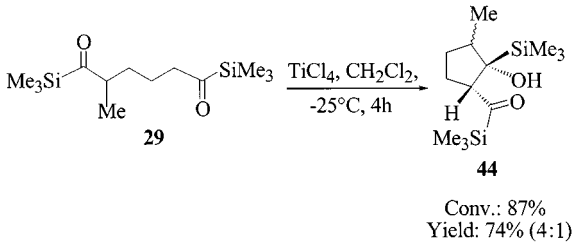
Table 3. Reactions of bis(acylsilanes) **25**−**28** with Lewis acids

Entry	Bis(acylsilanes)	*n*	R	Method[a]	*T* [°C]	React. time [h]	Conv. (%)	Aldols[b] (% yield)	Unsaturated acylsilanes (% yield)	Aldehyde (% yield)
1	**25**	1	Me	i	−50	4	93	**37** (78)	**38** (10)	–
2					0	1	100	–	**38** (13)	**40** (26)
3				ii	−25	2	89	**37** (63)	**38** (9)	–
4				iii	−25	6	93	**37** (77)	**38** (5)	–
5	**26**	1	*t*Bu	i	−25	7	57	**41** (5)	**42** (8)	–
6				ii	−25	5	88	**41** (73)	–	–
7				iii	[c]	[c]	60	**41** (10)	–	–
8	**27**	2	Me	i	−25	4	100	**43** (25)	–	–
9					0	3	95	–	–	–
10				ii	−25	8	92	**43** (77)	–	–
11				iii	−25	22	13	**43** (5)	–	–
12	**28**	3	Me	ii	−25	8	0	–	–	–
13					[d]	[d]	90	–	–	–

[a] All reactions were performed in dry CH_2Cl_2. Method i: TMSOTf (1.0−5.0 equiv.). Method ii: $TiCl_4$ (1.5−2.0 equiv.). Method iii: $BF_3 \cdot OEt_2$ (1.5−3.0 equiv.). − [b] Only one diastereomer was detected in the crude product mixture. − [c] 8 h at −25°C then 24 h at room temp. − [d] 2 h at 0°C then 18 h at room temp.

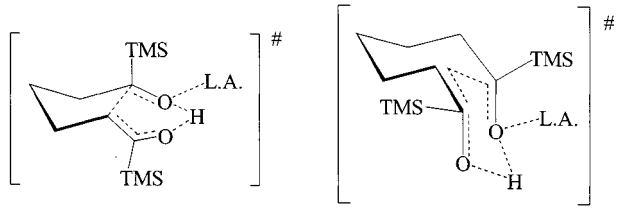


Scheme 5



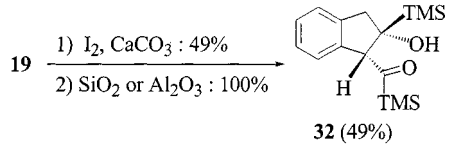
Scheme 6

bonding in chair-like cyclic transition states. Tentatively favored transition states are depicted in Scheme 7.



Scheme 7

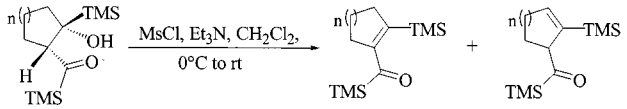
Initially observed during the silica gel purification of acylsilane **31**, aldol cyclization of the aromatic bis(acylsilane) proceeded smoothly under the adapted conditions. Compound **31** was converted directly into the corresponding aldol **32** after dethioketalization by contact with silica gel or neutral alumina for several hours in a petroleum ether/AcOEt mixture (Scheme 8). Such spontaneous intramolecular aldol reaction during silica gel[23] or alumina purification[24] has previously been mentioned in the literature for 1,6- and 1,7-dialdehydes and -diketones. In the case of the aliphatic compounds **25**, **26**, and **27**, the cyclization was completely diastereoselective, giving the same relative configurations. The stereochemistry of **32** was also determined by NOE experiments. Irradiation of the Me_3Si group at $\delta = 0.01$ induced an 8% NOE on the α-proton, confirming the *cis* relationship between the hydroxyl and silylcarbonyl groups.



Scheme 8

In view of the small amounts of unsaturated compounds **38**, **39**, and **42** sometimes observed as by-products in the aldol reactions [especially those performed with *p*-toluenesulfonic acid (Scheme 3) and with TMSOTf (Table 3, entries 1−3, 7)], we investigated the reaction conditions with regard to optimizing this dehydration. α-Hydroxy-γ-oxoalkyltrimethylsilanes were generally dehydrated under acidic or basic conditions to produce stereoselectively the (*Z*)- and (*E*)-γ-oxovinyltrimethylsilanes.[25] The cyclopentane derivative **37** was effectively dehydrated upon mesylation and treatment with base, giving the expected product **38** along with a minor amount of the deconjugated isomer **45** (Scheme 9). The same conditions gave only poor yields of the corresponding cyclohexene compounds **39** and **46**. The unusual dehydration of **37** and **43** to give β,γ-unsaturated ketones could be rationalized in terms of steric effects. Similar observations have previously been mentioned in the literature for β-keto-cyclopentanol[26] and -cyclohexanol.[22]

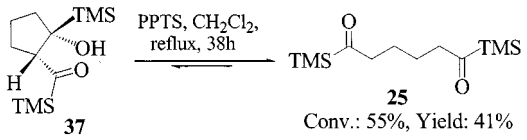
Under weakly acidic conditions, aldol **37** was slowly converted with a high selectivity back to the parent bis(acylsilane) **25**, through an acid-catalyzed retro-aldol reaction (Scheme 10). This behavior is in contrast to that of the α-



n = 1 : **37** Conv.: 94%, Yield: 77% n = 1 : **38** (88/12) n = 1 : **45**
n = 2 : **43** Conv.: 57%, Yield: 15% n = 2 : **39** (70/30) n = 2 : **46**

Scheme 9

hydroxy-γ-oxotrimethylsilane analogues, which gave excellent yields of dehydrated products using camphorsulfonic acid or pyridinium *p*-toluenesulfonate.[25b,25c]



37 **25** Conv.: 55%, Yield: 41%

Scheme 10

Conclusion

A series of aliphatic and aromatic 1,6- and 1,7-bis(acylsilanes) have been prepared and characterized. These bis(acylsilanes) could easily be converted, under Lewis acid activation, into *cis* β-hydroxyacylsilanes or the corresponding α,β-unsaturated derivatives through a completely stereoselective intramolecular aldol reaction. This cyclization led to the generation of new functionalized organosilicon compounds with various potential synthetic applications.

Experimental Section

Melting points are uncorrected. − FT-IR spectra were recorded on a MIDAS Corporation apparatus. − ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC-250 spectrometer. Tetramethylsilane (δ = 0.00) or $CHCl_3$ (δ = 7.27) were used as internal standards, and $CDCl_3$ was used as the solvent. − MS data were generally obtained on a JEOL D 300 apparatus at 70 eV in the electron impact mode. − Elemental analyses were performed with a Perkin-Elmer CHN 2400 apparatus. − All reactions were monitored by TLC (Merck silica gel F 254). Merck silica gel 9385 (40−63 μm) was used for flash chromatography. − All anhydrous reactions were performed under a blanket of dry argon. THF and CH_2Cl_2 were distilled under argon from sodium benzophenone ketyl and calcium hydride, respectively. Dihalogenated compounds **2**−**9** and 2-trimethylsilyl-1,3-dithiane **1a** were obtained from commercial sources and were distilled prior to use.

General Procedure for the Alkylation of 2-Trimethylsilyl-1,3-dithiane (1a) or 2-(*tert*-Butyldimethylsilyl)-1,3-dithiane (1b) with Dihalogenated Compounds 2−9: To a solution of the 2-trimethylsilyl-1,3-dithiane **1a** or 2-(*tert*-butyldimethylsilyl)-1,3-dithiane **1b** (2.4 mmol, 2.4 equiv.) in 7 mL of THF cooled in an ice-water bath, a solution of *n*-butyllithium in hexane (2.4 mmol, 2.4 equiv.) was added dropwise over a period of 5 min. After stirring for 2 h at 0 °C, a solution of the dihalogenated compound (1.0 mmol, 1.0 equiv.) in 3 mL of THF was added over a period of 5 min. The mixture was stirred for a further 2 h at 0 °C, and then the reaction was quenched by the addition of water (10 mL). After stirring for 10 min, the crude mixture was poured into diethyl ether (30 mL) and extracted four times with further ether (4 × 30 mL). The combined organic phases were washed with brine (20 mL), dried with $MgSO_4$, and concentrated in vacuo. The excess 1,3-dithiane **1a** or **1b** was generally distilled off in a kugelrohr apparatus (70−100 °C/2·10^{-2} mbar) and then the residue was either recrystallized (petroleum ether or petroleum ether/ethyl acetate) or chromatographed on silica gel using petroleum ether/ethyl acetate as eluent.

Reaction of 1,4-Diiodobutane (2) − 1,4-Bis[2-(trimethylsilyl)[1,3]-dithian-2-yl]butane (10): Yield 89%. Recrystallization from petroleum ether. White solid; m.p. 137−139 °C. − TLC (petroleum ether/AcOEt, 99:1): R_f = 0.52. − ^{1}H NMR: δ = 0.22 (s, 18 H), 1.57 (quint, *J* = 3.9 Hz, 4 H), 1.8−2.1 (m, 4 H), 2.23 (m, 4 H), 2.48 (ddd, *J* = 13.7, 3.8, 3.7 Hz, 4 H), 3.05 (ddd, *J* = 13.4, 13.0, 3.1 Hz, 4 H). − ^{13}C NMR: δ = −2.6 ($SiMe_3$), 23.3 (SCH_2), 24.9 (CH_2), 28.1 (CH_2), 37.3 (CH_2), 38.4 (C_4). − IR (KBr): $\tilde{\nu}$ = 2950, 2930, 2863, 1424, 1404, 1271, 1244, 1113 cm^{-1}. − MS: *m*/*z* = 438 [M$^+$], 365, 292, 259, 227, 191, 153, 111. − $C_{18}H_{38}S_4Si_2$: calcd. C 49.26, H 8.73; found C 48.95, H 8.78.

1,4-Bis[2-(*tert*-butyldimethylsilyl)[1,3]dithian-2-yl]butane (11): Yield 85%. Recrystallization from petroleum ether. White solid; m.p. 118−119 °C. − TLC (petroleum ether/AcOEt, 99:1): R_f = 0.35. − ^{1}H NMR: δ = 0.23 (s, 12 H), 1.05 (s, 18 H), 1.5−1.6 (m, 4 H), 1.8−2.1 (m, 4 H), 2.3−2.4 (m, 4 H), 2.43 (ddd, *J* = 14.1, 3.8, 3.4 Hz, 4 H), 3.07 (ddd, *J* = 14.5, 11.8, 2.7 Hz, 4 H). − ^{13}C NMR: δ = −5.2 ($SiMe_2$), 19.7 (C_4), 23.4 (SCH_2), 25.0 (CH_2), 28.2 (CH_3), 28.6 (CH_2), 37.9 (CH_2), 40.9 (C_4). − IR (KBr): $\tilde{\nu}$ = 2928, 2899, 2856, 1474, 1462, 1429, 1364, 1271, 822 cm^{-1}. − MS: *m*/*z* = 522 [M$^+$], 507, 465, 407, 259, 233, 221, 185, 149, 115. − $C_{24}H_{50}S_4Si_2$: calcd. C 55.11, H 9.63; found C 55.01, H 10.03.

Reaction of 1,5-Dibromopentane (3) − 1,5-Bis[2-(trimethylsilyl)-[1,3]dithian-2-yl]pentane (12): Yield 97%. The excess 2-trimethylsilyl-1,3-dithiane **1a** was distilled off in a kugelrohr apparatus. White solid; m.p. 81−83 °C. − TLC (petroleum ether): R_f = 0.35. − ^{1}H NMR: δ = 0.21 (s, 18 H), 1.3−1.5 (m, 2 H), 1.5−1.7 (m, 4 H), 1.8−2.1 (m, 4 H), 2.2−2.3 (m, 4 H), 2.47 (ddd, *J* = 14.1, 3.8, 3.7 Hz, 4 H), 3.05 (ddd, *J* = 14.5, 11.8, 2.7 Hz, 4 H). − ^{13}C NMR: δ = −2.5 ($SiMe_3$), 23.5 (SCH_2), 25.1 (CH_2), 27.7 (CH_2), 30.8 (CH_2), 37.5 (CH_2), 38.7 (C_4). − IR (KBr): $\tilde{\nu}$ = 2926, 2858, 1420, 1410, 1271, 1244, 909, 841 cm^{-1}. − MS: *m*/*z* = 452 [M$^+$], 437, 379, 347, 273, 241, 191, 145. − $C_{19}H_{40}S_4Si_2$: calcd. C 50.38, H 8.90; found C 50.55, H 9.14.

Reaction of 1,6-Dibromohexane (4) − 1,6-Bis[2-(trimethylsilyl)[1,3]-dithian-2-yl]hexane (13):[6] Yield 92%.

Reaction of 1,4-Dibromopentane (5) − 1,4-Bis[2-(trimethylsilyl)-[1,3]dithian-2-yl]pentane (14): Yield 31%. Recrystallization from petroleum ether. White solid; m.p. 104−106 °C. − TLC (petroleum ether): R_f = 0.16. − ^{1}H NMR: δ = 0.22 (s, 9 H), 0.25 (s, 9 H), 1.25 (d, *J* = 6.9 Hz, 3 H), 1.4−1.5 (m, 1 H), 1.6−1.8 (m, 1 H), 1.8−2.3 (m, 6 H), 2.4−2.5 (m, 6 H), 2.9−3.1 (m, 5 H). − ^{13}C NMR: δ = −2.5 ($SiMe_3$), −0.2 ($SiMe_3$), 18.0 (CH_3), 23.5 (SCH_2), 23.6 (SCH_2), 23.8 (SCH_2), 24.7 (CH_2), 25.1 (CH_2), 27.5 (CH_2), 35.3 (CH_2), 37.5 (CH_2), 38.7 (C_4), 39.9 (CH), 44.8 (C_4). − IR (KBr): $\tilde{\nu}$ = 2980, 2908, 1461, 1418, 1375, 1021, 838 cm^{-1}. − MS: *m*/*z* = 452 [M$^+$], 437, 379, 347, 273, 199, 191, 145, 125. − $C_{19}H_{40}S_4Si_2$: calcd. C 50.38, H 8.90; found C 50.28, H 8.51.

(2-Pent-3-enyl[1,3]dithian-2-yl)trimethylsilane (15): Yield 44%; oil; mixture of stereoisomers (86:14). Chromatography: petroleum ether. TLC (petroleum ether): R_f = 0.29. − IR (film): $\tilde{\nu}$ = 3015, 2930, 2855, 1455, 1424, 1250, 843 cm^{-1}. − MS: *m*/*z* = 260 [M$^+$], 245, 205, 191, 187, 155, 133.

Major Stereoisomer: ^{1}H NMR (500 MHz): δ = 0.21 (s, 9 H), 1.67 (d, *J* = 6.5 Hz, 3 H), 1.85−1.95 (m, 1 H), 2.01−2.08 (m, 1 H), 2.13−2.20 (m, 2 H), 2.20−2.26 (m, 2 H), 2.45 (ddd, *J* = 13.6, 4.4, 3.5 Hz, 2 H), 3.04 (ddd, *J* = 14.6, 12.6, 2.9 Hz, 2 H), 5.4−5.5 (m, 2 H). − ^{13}C NMR: δ = −2.5 ($SiMe_3$), 17.9 (CH_3), 23.4 (SCH_2), 25.1 (CH_2), 30.9 (CH_2), 37.3 (CH_2), 38.5 (C_4), 125.2 (CH), 130.9 (CH).

Minor Stereoisomer: Selected NMR data: ^{1}H NMR (500 MHz): δ = 0.23 (s, 9 H), 1.65 (d, *J* = 6.0 Hz, 3 H). − ^{13}C NMR: δ = 25.5 (CH_2), 29.7 (CH_2), 37.0 (CH_2), 124.2 (CH), 129.9 (CH).

Reaction of 2,5-Dibromohexane (6) − 2,5-Bis[2-(trimethylsilyl)[1,3]-dithian-2-yl]hexane (16): Yield 20%. Chromatography: petroleum ether. Recrystallization from petroleum ether/AcOEt. White solid; m.p. 154−156°C. − TLC (petroleum ether): R_f = 0.43. − ^{1}H NMR: δ = 0.25 (s, 18 H), 1.26 (d, *J* = 6.9 Hz, 6 H), 1.8−2.1 (m, 4 H), 2.3−2.4 (m, 4 H), 2.45 (d, *J* = 14.1 Hz, 4 H), 2.98 (ddd, *J* = 14.1, 11.8, 2.7 Hz, 4 H), 3.0−3.1 (m, 2 H). − ^{13}C NMR: δ = −0.1 ($SiMe_3$), 18.3 (CH_3), 23.7 (CH_2), 23.9 (CH_2), 24.7 (CH_2), 35.2 (CH_2), 40.9 (CH), 45.0 (C_4). − IR (KBr): $\tilde{\nu}$ = 2949, 2907, 2872, 1460, 1421, 1378, 1246, 843 cm^{-1}. − MS: *m*/*z* = 466 [M$^+$], 451, 393, 298, 287, 219, 191, 179, 159, 149, 119. − $C_{20}H_{42}S_4Si_2$: calcd. C 51.44, H 9.07; found C 51.56, H 9.20.

Mixture of Compounds 17 and 18: Yield 25%; oil. Chromatography: petroleum ether. TLC (petroleum ether): R_f = 0.39. − IR (film): $\tilde{\nu}$ = 2953, 2930, 2856, 1559, 1540, 1507, 1424, 1372, 1248, 843 cm^{-1}. − MS: *m*/*z* = 274 [M$^+$], 259, 219, 201, 191, 179, 169, 147, 119.

[2-(1-Methylpent-3-enyl)[1,3]dithian-2-yl]trimethylsilane (17). − Major Stereoisomer: ^{1}H NMR: δ = 0.24 (s, 9 H), 1.21 (d, *J* = 6.9 Hz, 3 H), 1.69 (d, *J* = 6.5 Hz, 3 H), 1.8−2.1 (m, 3 H), 2.4−2.5 (m, 2 H), 2.8−3.1 (m, 4 H), 5.4−5.6 (m, 2 H). − ^{13}C NMR: δ = −0.2 ($SiMe_3$), 17.4 (CH_3), 17.5 (CH_3), 23.7 (SCH_2), 24.7 (CH_2), 32.3 (CH_2), 40.9 (CH), 44.7 (C_4), 124.6 (CH), 130.5 (CH).

Minor Stereoisomer: Selected NMR data: ^{1}H NMR: δ = 1.20 (d, *J* = 7.3 Hz, 3 H), 1.66 (d, *J* = 6.3 Hz, 3 H). − ^{13}C NMR: δ = 38.0 (CH_2), 40.6 (CH), 45.4 (C_4), 126.0 (CH), 131.3 (CH).

[2-(1-Methylpent-4-enyl)[1,3]dithian-2-yl]trimethylsilane (18): ^{1}H NMR: δ = 0.27 (s, 9 H), 1.26 (d, *J* = 6.1 Hz, 3 H), 1.8−2.1 (m, 7 H), 2.4−2.5 (m, 2 H), 2.8−3.1 (m, 2 H), 4.9−5.1 (m, 2 H), 5.4−5.6 (m, 1 H). − ^{13}C NMR: δ = −0.2 ($SiMe_3$), 17.9 (CH_3), 23.7 (SCH_2), 24.7 (CH_2), 29.7 (CH_2), 33.8 (CH_2), 38.9 (CH), 46.5 (C_4), 114.7 (CH_2), 138.8 (CH).

Reaction of α,α′-Dibromo-*o*-xylene (7) − α,α′-Bis-[2-(trimethylsilyl)[1,3]dithian-2-yl]-*o*-xylene (19): Yield 85%. Recrystallization from petroleum ether/AcOEt. White solid; m.p. 167−168°C. − TLC (petroleum ether): R_f = 0.41. − ^{1}H NMR: δ = 0.28 (s, 18 H), 1.5−1.7 (m, 4 H), 2.02 (ddd, *J* = 13.4, 11.8, 3.1 Hz, 4 H), 2.15 (ddd, *J* = 13.4, 3.8, 3.7 Hz, 4 H), 3.82 (s, 4 H), 7.22 (dd, *J* = 5.7, 3.4 Hz, 2 H), 7.75 (dd, *J* = 5.7, 3.4 Hz, 2 H). − ^{13}C NMR: δ = −3.5 ($SiMe_3$), 23.3 (CH_2), 25.1 (SCH_2), 36.2 (C_4), 44.4 (CH_2), 126.5 (CH), 132.6 (CH), 139.4 (C_4). − IR (KBr): $\tilde{\nu}$ = 2951, 2913, 2899, 1493, 1435, 1420, 1271, 1248, 847 cm^{-1}. − MS: *m*/*z* = 486 [M$^+$], 471, 413, 295, 191, 149, 115. − $C_{22}H_{38}S_4Si_2$: calcd. C 54.26, H 7.87; found C 54.11, H 8.02.

α,α′-Bis-[2-(*tert*-butyldimethylsilyl)[1,3]dithian-2-yl]-*o*-xylene (20): Yield 30%. Chromatography: petroleum ether/AcOEt, 99:1. Recrystallization from petroleum ether/AcOEt. White solid; m.p. 155−157°C. − TLC (petroleum ether): R_f = 0.47. − ^{1}H NMR: δ = 0.32 (s, 12 H), 1.12 (s, 18 H), 1.5−1.7 (m, 4 H), 1.89 (ddd, *J* = 14.5, 11.1, 3.4 Hz, 4 H), 2.08 (ddd, *J* = 13.4, 3.8, 3.4 Hz, 4 H), 4.04 (s, 4 H), 7.22 (dd, *J* = 5.7, 3.4 Hz, 2 H), 7.75 (dd, *J* = 5.7, 3.8 Hz, 2 H). − ^{13}C NMR: δ = −6.4 ($SiMe_2$), 20.2 (C_4), 23.1 (CH_2), 25.6 (SCH_2), 28.7 (CH_3), 38.8 (C_4), 45.9 (CH_2), 126.4 (CH), 133.2 (CH), 139.5 (C_4). − IR (KBr): $\tilde{\nu}$ = 3063, 2961, 2930, 2917, 1491, 1464, 1424, 1248, 914 cm^{-1}. − MS: *m*/*z* = 571 [M$^+$], 570, 555, 513, 455, 357, 337, 233, 149, 115. − $C_{28}H_{50}S_4Si_2$: calcd. C 58.89, H 8.82; found C 58.72, H 8.74.

Dimer of *tert*-Butyldimethyl-[2-(2-methylenebenzyl)[1,3]dithian-2-yl]silane (21): Yield 32%. Chromatography: petroleum ether/AcOEt, 99:1. Recrystallization from petroleum ether/AcOEt. White solid; m.p. 219−221°C. − TLC (petroleum ether): R_f = 0.40. − ^{1}H NMR: δ = 0.27 (s, 12 H), 1.09 (s, 18 H), 1.5−1.7 (m, 4 H), 1.9−2.1 (m, 8 H), 3.29 (s, 4 H), 3.36 (s, 4 H), 7.1−7.2 (m, 6 H), 7.70 (d, *J* = 7.2 Hz, 2 H). − ^{13}C NMR: δ = −6.5 ($SiMe_2$), 20.1 (C_4), 23.1 (CH_2), 25.6 (CH_2), 28.9 (CH_3), 35.5 (CH_2), 38.6 (C_4), 44.6 (CH_2), 125.6 (CH), 127.0 (CH), 129.8 (CH), 132.7 (CH), 137.5 (C_4), 141.7 (C_4). − IR (KBr): $\tilde{\nu}$ = 3058, 3019, 2959, 2928, 2911, 2857, 1489, 1472, 1464, 1422, 1364, 1273, 1246, 916, 829 cm^{-1}. − MS: *m*/*z* = 674 [M$^+$], 659, 617, 559, 411, 368, 341, 233, 115. − $C_{36}H_{58}S_4Si_2$: calcd. C 64.03, H 8.66; found C 64.03, H 8.50.

***tert*-Butyldimethyl-[2-(2-pentylbenzyl)[1,3]dithian-2-yl]silane (22):** Yield 8%. Chromatography: petroleum ether/AcOEt, 99:1. Yellow oil. TLC (petroleum ether): R_f = 0.57. − ^{1}H NMR: δ = 0.31 (s, 6 H), 0.91 (t, *J* = 6.1 Hz, 3 H), 1.12 (s, 9 H), 1.3−1.4 (m, 4 H), 1.5−1.7 (m, 4 H), 2.0−2.2 (m, 4 H), 3.08 (dd, *J* = 8.0, 7.6 Hz, 2 H), 3.52 (s, 2 H), 7.1−7.2 (m, 3 H), 7.77 (d, *J* = 7.3 Hz, 1 H). − ^{13}C NMR: δ = −6.5 ($SiMe_2$), 14.0 (CH_3), 20.2 (C_4), 22.6 (CH_2), 23.2 (CH_2), 25.6 (CH_2), 28.8 (CH_3), 31.4 (CH_2), 32.0 (CH_2), 33.7 (CH_2), 38.7 (C_4), 44.8 (CH_2), 125.3 (CH), 126.9 (CH), 129.4 (CH), 132.7 (CH), 137.3 (C_4), 143.0 (C_4). − IR (film): $\tilde{\nu}$ = 3019, 2957, 2928, 2857, 1489, 1464, 1426, 1273, 1248 cm^{-1}. − MS: *m*/*z* = 394 [M$^+$], 379, 365, 337, 279, 233, 149, 115.

Reaction of α,α′-Dibromo-*m*-xylene (8). − α,α′-Bis-[2-(trimethylsilyl)[1,3]dithian-2-yl]-*m*-xylene (23): Yield 88%. Recrystallization from petroleum ether/AcOEt. White solid; m.p. 135−136°C. − TLC (petroleum ether): R_f = 0.15. − ^{1}H NMR: δ = 0.11 (s, 18 H), 1.7−2.0 (m, 4 H), 2.41 (ddd, *J* = 13.4, 4.2, 3.4 Hz, 4 H), 2.82 (ddd, *J* = 14.1, 12.2, 3.1 Hz, 4 H), 3.45 (s, 4 H), 7.21 (dd, *J* = 7.6, 7.3 Hz, 1 H), 7.41 (dd, *J* = 7.6, 1.5 Hz, 2 H), 7.59 (dd, *J* = 1.2, 1.0 Hz, 1 H). − ^{13}C NMR: δ = −3.1 ($SiMe_3$), 24.0 (SCH_2), 24.3 (CH_2), 38.2 (C_4), 44.1 (CH_2), 127.1 (CH), 129.3 (CH), 134.1 (CH), 138.3 (C_4). − IR (KBr): $\tilde{\nu}$ = 2952, 2923, 2898, 1483, 1424, 1414, 1249, 847 cm^{-1}. − MS: *m*/*z* = 486 [M$^+$], 471, 413, 339, 307, 191. − HRMS: calcd. for $C_{22}H_{38}S_4Si_2$ *m*/*z* = 486.1395; found 486.1409.

Reaction of *cis*-1,4-Dichlorobut-2-ene (9) (Mixture of Stereoisomers, 93:7). − 1,4-Bis[2-(trimethylsilyl)[1,3]dithian-2-yl]but-2-ene (24): Yield 89%. Mixture of stereomers (93:7). Chromatography: petroleum ether/AcOEt, 98:2. White solid.

Major Stereoisomer (24a): Recrystallization from petroleum ether/AcOEt; m.p. 137−139°C. − TLC (petroleum ether/AcOEt, 99:1): R_f = 0.14. − ^{1}H NMR: δ = 0.21 (s, 18 H), 1.8−2.1 (m, 4 H), 2.50 (dt, *J* = 14.1, 3.8 Hz, 4 H), 3.07 (m, 8 H), 5.74 (t, *J* = 4.2 Hz, 2 H). − ^{13}C NMR: δ = −2.9 ($SiMe_3$), 23.4 (SCH_2), 24.9 (CH_2), 35.3 (CH_2), 38.0 (C_4), 128.4 (CH). − IR (KBr): $\tilde{\nu}$ = 2951, 2905, 1441, 1424, 1244, 1022 cm^{-1}. − MS: *m*/*z* = 436 [M$^+$], 421, 363, 230, 191, 179, 171, 149, 117. − $C_{18}H_{36}S_4Si_2$: calcd. C 49.49, H 8.31; found C 49.25, H 8.54.

Minor Stereoisomer (24b): Selected ^{13}C-NMR data: δ = −3.3 ($SiMe_3$), 23.2 (SCH_2), 37.8 (C_4), 129.6 (CH).

General Procedure for the Dethioketalization of Bis(1,3-dithianes). − Dethioketalization with Chloramine-T (*N*-Chloro-*p*-toluenesulfon-

amide, Sodium Salt). − Method i: A solution of bis(1,3-dithiane) (5.0 mmol, 1.0 equiv.) in acetone (20 mL) was treated with a solution of chloramine-T trihydrate (40.0 mmol, 8.0 equiv.) in 4:1 MeOH/H_2O (40 mL) at room temperature. After stirring for 30 min, the crude mixture was diluted with 9:1 petroleum ether/diethyl ether (50 mL), filtered through Celite, and extracted with 9:1 petroleum ether/diethyl ether (6 × 25 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with petroleum ether/AcOEt as eluent.

Dethioketalization with Mercury(II) Perchlorate. − Method ii: To a solution of bis(1,3-dithiane) (1.0 mmol, 1.0 equiv.) in 4:1 THF/H_2O (5 mL) was added calcium carbonate (6.1 mmol, 6.1 equiv.) followed by mercury(II) perchlorate trihydrate (6.0 mmol, 6.0 equiv.). The mixture was stirred at room temperature until total conversion (2−5 h), then partitioned between 30 mL of CH_2Cl_2 and 20 mL of brine. After filtration through Celite, the filtrate was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether/AcOEt as eluent.

Dethioketalization with Methyl Iodide. − Method iii: Methyl iodide (28.89 mmol, 20.4 equiv.) was added to a stirred suspension of the bis(1,3-dithiane) (1.42 mmol, 1.0 equiv.) and calcium carbonate (31.14 mmol, 22.0 equiv.) in 1:1 MeCN/H_2O (50 mL). The mixture was heated to reflux (oil-bath temperature 55°C) for 8−15 h. After complete conversion (TLC control), the crude mixture was diluted with AcOEt (30 mL), filtered through Celite, and extracted with AcOEt (5 × 25 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether/AcOEt as eluent.

Dethioketalization with Iodine. − Method iv: To a solution of the bis(1,3-dithiane) (3.87 mmol, 1.0 equiv.) in 4:1 THF/H_2O (20 mL) at room temperature were added calcium carbonate (60.37 mmol, 15.6 equiv.) and iodine (46.44 mmol, 12.0 equiv.). The mixture was stirred at the same temperature until total conversion (3−7 h), and then partitioned between 50 mL of diethyl ether and 30 mL of saturated aqueous $Na_2S_2O_3$ solution. After stirring for 10 min, the crude mixture was filtered through Celite and extracted with diethyl ether (5 × 30 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was either recrystallized (petroleum ether/AcOEt) or chromatographed on silica gel with petroleum ether/ethyl acetate as eluent.

Dethioketalization of 10. − Method iii. − 1,6-Bis(trimethylsilyl)-1,6-hexanedione (25):[6] Yield 86%.

Dethioketalization of 11. − Method ii. − 1,6-Bis(*tert*-butyldimethylsilyl)-1,6-hexanedione (26): Yield 84%; oil. Chromatography: petroleum ether/AcOEt, 97:3. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.38. − ^{1}H NMR: δ = 0.17 (s, 12 H), 0.92 (s, 18 H), 1.46 (quint, J = 3.4 Hz, 4 H), 2.59 (t, J = 5.3 Hz, 4 H). − ^{13}C NMR: δ = −7.1 ($SiMe_2$), 16.4 (C4), 21.4 (CH_2), 26.3 (CH_3), 50.1 (CH_2), 247.0 (CO). − IR (film): $\tilde{\nu}$ = 2930, 2859, 1642, 1464, 1364, 1250, 837 cm^{-1}. − MS: m/z = 342 [M$^+$], 301, 285, 257, 233, 199, 171, 147, 133, 115. − HRMS: calcd. for $C_{18}H_{38}O_2Si_2$ m/z = 342.2410; found 342.2416.

Dethioketalization of 12. − Method ii. − 1,7-Bis(trimethylsilyl)-1,7-heptanedione (27): Yield 77%; oil. Chromatography: petroleum ether/AcOEt, 96:4. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.27. − ^{1}H NMR: δ = 0.20 (s, 18 H), 1.2−1.3 (m, 2 H), 1.52 (m, 4 H), 2.59 (t, J = 7.3 Hz, 4 H). − ^{13}C NMR: δ = −3.2 ($SiMe_3$), 21.8 (CH_2), 28.9 (CH_2), 48.1 (CH_2), 248.2 (CO). − IR (film): $\tilde{\nu}$ = 2940, 2862, 1642, 1403, 1249, 846 cm^{-1}. − MS: m/z = 272 [M$^+$], 257, 217, 171, 147, 133, 129. − $C_{13}H_{28}O_2Si_2$: calcd. C 57.29, H 10.36; found C 57.02, H 10.55.

Dethioketalization of 13. − Method ii. − 1,8-Bis(trimethylsilyl)-1,8-octanedione (28):[6] Yield 83%.

Dethioketalization of 14. − Method ii. − 2-Methyl-1,6-bis(trimethylsilyl)-1,6-hexanedione (29): Yield 77%; oil. Chromatography: petroleum ether/AcOEt, 96:4. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.35. − ^{1}H NMR: δ = 0.20 (s, 9 H), 0.21 (s, 9 H), 0.97 (d, J = 7.3 Hz, 3 H), 1.1−1.2 (m, 1 H), 1.4−1.7 (m, 3 H), 2.59 (dd, J = 6.9, 6.7 Hz, 2 H), 2.86 (m, 1 H). − ^{13}C NMR: δ = −3.4 ($SiMe_3$), −2.8 ($SiMe_3$), 14.3 (CH_3), 19.8 (CH_2), 30.5 (CH_2), 48.2 (CH_2), 50.1 (CH), 247.4 (CO), 250.1 (CO). − IR (film): $\tilde{\nu}$ = 2961, 2903, 2874, 1642, 1456, 1250, 843 cm^{-1}. − MS: m/z = 272 [M$^+$], 267, 257, 231, 199, 171, 147, 135. − $C_{13}H_{28}O_2Si_2$: calcd. C 57.29, H 10.36; found C 57.51, H 10.71.

Dethioketalization of 16. − Method ii. − 2,5-Dimethyl-1,6-bis(trimethylsilyl)-1,6-hexanedione (30): Yield 75%; oil. Chromatography: petroleum ether/AcOEt, 97:3. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.35. − ^{1}H NMR: δ = 0.21 (s, 18 H), 0.97 (d, J = 6.9 Hz, 6 H), 1.0−1.1 (m, 2 H), 1.5−1.7 (m, 2 H), 2.8−2.9 (m, 2 H). − ^{13}C NMR: δ = −2.7 ($SiMe_3$), 14.6 (CH_3), 29.7 (CH_2), 50.5 (CH), 250.5 (CO). − IR (film): $\tilde{\nu}$ = 2963, 2930, 2857, 1642, 1460, 1250, 843 cm^{-1}. − MS: m/z = 286 [M$^+$], 271, 239, 231, 185, 169, 147. − HRMS: calcd. for $C_{14}H_{30}O_2Si_2$ m/z = 286.1784; found 286.1802.

Dethioketalization of 19. − Method iv. − α,α′-Bis-[1-(trimethylsilyl)-2-oxo]-*o*-xylene (31): Yield 50%. Mixture of bis(acylsilane) **31** and aldol **32** (9:1). Chromatography: petroleum ether/AcOEt, 97:3. Recrystallization from petroleum ether/AcOEt. Yellow solid; m.p. 55−57°C. − TLC (petroleum ether/AcOEt, 98:2): R_f = 0.16. − ^{1}H NMR: δ = 0.17 (s, 18 H), 3.81 (s, 4 H), 7.16 (dd, J = 5.5, 3.7 Hz, 2 H), 7.29 (dd, J = 5.5, 3.1 Hz, 2 H). − ^{13}C NMR: δ = −3.0 ($SiMe_3$), 53.7 (CH_2), 127.1 (CH), 131.2 (CH), 133.0 (C_4), 243.7 (CO). − IR (KBr): $\tilde{\nu}$ = 3020, 2957, 2903, 2889, 1642, 1399, 1313, 1250, 845 cm^{-1}. − MS: m/z = 307 [M$^+$ + 1], 306 [M$^+$], 250, 217, 205, 188, 147, 116. − HRMS: calcd. for $C_{16}H_{26}O_2Si_2$ m/z = 306.1471; found 306.1459.

Dethioketalization of 20. − Method iv. − α,α′-Bis-[1-(*tert*-butyldimethylsilyl)-2-oxo]-*o*-xylene (33): Yield 15%; yellow oil. Chromatography: petroleum ether/AcOEt, 97:3. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.15. − ^{1}H NMR: δ = 0.20 (s, 12 H), 0.94 (s, 18 H), 3.85 (s, 4 H), 7.03 (dd, J = 5.3, 3.4 Hz, 2 H), 7.21 (dd, J = 5.3, 3.4 Hz, 2 H). − ^{13}C NMR: δ = −6.7 ($SiMe_2$), 16.7 (C_4), 26.4 (CH_3), 55.5 (CH_2), 127.0 (CH), 131.1 (CH), 133.2 (C_4), 243.2 (CO). − IR (film): $\tilde{\nu}$ = 2926, 2897, 2855, 1640, 1462, 1402, 1316, 1260 cm^{-1}. − MS: m/z = 390 [M$^+$], 333, 307, 247, 189, 147, 133, 115. − HRMS: calcd. for $C_{22}H_{38}O_2Si_2$ m/z = 390.2410; found 390.2395.

Dethioketalization of 23. − Method iv. − α,α′-Bis-[1-(trimethylsilyl)-2-oxo]-*m*-xylene (34): Yield 83%; oil. Chromatography: petroleum ether/AcOEt, 94:6. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.17. − ^{1}H NMR: δ = 0.14 (s, 18 H), 3.84 (s, 4 H), 6.90 (s, 1 H), 7.01 (d, J = 7.6 Hz, 2 H), 7.27 (dd, J = 8.0, 6.9 Hz, 1 H). − ^{13}C NMR: δ = −3.0 ($SiMe_3$), 55.0 (CH_2), 128.2 (CH), 128.5 (CH), 131.3 (CH), 133.4 (C_4), 243.4 (CO). − IR (film): $\tilde{\nu}$ = 2959, 2900, 1650, 1633, 1603, 1413, 1249, 846 cm^{-1}. − MS: m/z = 306 [M$^+$], 278, 263, 222, 205, 190, 175, 162, 147, 118. − HRMS: calcd. for $C_{16}H_{26}O_2Si_2$ m/z = 306.1471; found 306.1460.

Dethioketalization of 24. − Method iv. − 1,6-Bis(trimethylsilyl)-hex-3-ene-1,6-dione (35): This compound was characterized in the crude product mixture, but quickly decomposed into a small amount of

aldol **36**. Yellow oil. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.35. − ^{1}H NMR: δ = 0.22 (s, 18 H), 3.33 (d, J = 5.4 Hz, 4 H), 5.78 (t, J = 4.6 Hz, 2 H). − ^{13}C NMR: δ = −3.2 ($SiMe_3$), 47.3 (CH_2), 124.0 (CH), 244.1 (CO). − Selected IR data (film): $\tilde{\nu}$ = 1642 cm^{-1}.

2-(2-Hydroxy-2-trimethylsilylcyclopent-4-enyl)-1-formyltrimethylsilane (36): Yield 15%; oil. Chromatography: petroleum ether/AcOEt, 95:5. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.41. − ^{1}H NMR: δ = 0.04 (s, 9 H), 0.24 (s, 9 H), 2.53 (ddd, J = 17.4, 2.3, 1.9 Hz, 2 H), 3.44 (s, OH), 3.91 (m, 1 H), 5.69 (dd, J = 5.7, 2.3 Hz, 1 H), 5.96 (dd, J = 5.7, 2.7 Hz, 1 H). − ^{13}C NMR: δ = −4.1 ($SiMe_3$), −2.9 ($SiMe_3$), 44.8 (CH_2), 66.2 (CH), 77.3 (C4), 126.2 (CH), 133.4 (CH), 252.9 (CO). − IR (film): $\tilde{\nu}$ = 3461, 2957, 2900, 1626, 1250, 844 cm^{-1}. − MS: m/z = 256 [M$^+$], 255, 241, 239, 183, 155, 149, 138, 123.

Aldolization of Bis(acylsilanes) 25 and 27 with *p*-Toluenesulfonic Acid (PTSA): A mixture of bis(acylsilane) **25** or **27** (0.26 mmol, 1.0 equiv.) and PTSA (0.03 mmol, 0.1 equiv.) was heated in a kugelrohr apparatus (60−80°C/2·10^{-2} mbar) for 10 min. After cooling to room temperature, the crude mixture was chromatographed on silica gel using petroleum ether/AcOEt (99:1 to 96:4) as eluent, to give the aldol **37** (46%) along with compounds **38** or **39** (16% or 18%, respectively).

General Procedure for the Aldolization of Bis(acylsilanes) 25−27 and 29 with Lewis Acids: To a cooled solution of the bis(acylsilane) **25−27** or **29** (0.75 mmol, 1.0 equiv.) in 20 mL of dry CH_2Cl_2 (generally at −50°C or −25°C), was added a solution of the Lewis acid (TMSOTf, $TiCl_4$, or $BF_3{\cdot}OEt_2$) (1.0−2.0 equiv.). The mixture was stirred at the same temperature for 3−8 h, then diluted with CH_2Cl_2 (20 mL), hydrolysed with brine (15 mL), and allowed to warm to 0°C (15 min). The crude mixture was extracted with CH_2Cl_2 (5 × 25 mL) and the combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with petroleum ether/AcOEt as eluent.

Aldolization of 25 with Trimethylsilyl Trifluoromethanesulfonate

At −50°C: (2-Hydroxy-2-trimethylsilylcyclopentyl)formyltrimethylsilane (37):[6] Yield 78%. **(2-Trimethylsilylcyclopent-1-enyl)formyltrimethylsilane (38):** Yield 10%; yellow oil. Chromatography: petroleum ether/AcOEt, 99:1. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.44. − ^{1}H NMR: δ = 0.09 (s, 9 H), 0.23 (s, 9 H), 1.90 (tt, J = 7.6, 7.3 Hz, 2 H), 2.4−2.6 (m, 2 H), 2.7−2.9 (m, 2 H). − ^{13}C NMR: δ = −2.5 ($SiMe_3$), −0.9 ($SiMe_3$), 24.3 (CH_2), 35.3 (CH_2), 38.5 (CH_2), 151.2 (C_4), 157.9 (C_4), 240.0 (CO). − IR (film): $\tilde{\nu}$ = 2955, 2901, 2847, 1605, 1539, 1408, 1248, 1076, 841 cm^{-1}. − MS: m/z = 240 [M$^+$], 225, 197, 167, 147, 133. − HRMS: calcd. for $C_{12}H_{24}OSi_2$ m/z = 240.1366; found 240.1360.

At 0°C: Yield of **38:** 13%. **− (2-Trimethylsilylcyclopent-1-enyl)carbaldehyde (40):** Yield 26%; oil. Chromatography: petroleum ether/AcOEt, 98:2. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.39. − ^{1}H NMR: δ = 0.27 (s, 9 H), 1.86 (tt, J = 7.6, 7.3 Hz, 2 H), 2.6−2.8 (m, 4 H), 10.02 (s, 1 H). − ^{13}C NMR: δ = −0.04 ($SiMe_3$), 23.0 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 169.2 (C_4), 179.5 (C_4), 190.3 (CH). − IR (film): $\tilde{\nu}$ = 2924, 2853, 1667, 1466, 1252, 837 cm^{-1}. − MS: m/z = 169 [M$^+$ + 1], 149, 121, 105.

Aldolization of 26 with Trimethylsilyl Trifluoromethanesulfonate: Yield of **41**: 5%. **[2-(*tert*-Butyldimethylsilyl)cyclopent-1-enyl]formyl-(*tert*-butyldimethyl)silane (42):** Yield 8%; yellow oil. Chromatography: petroleum ether/AcOEt, 99:1. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.67. − ^{1}H NMR: δ = −0.01 (s, 6 H), 0.20 (s, 6 H), 0.92 (s, 9 H), 0.95 (s, 9 H), 1.84 (tt, J = 7.6, 7.3 Hz, 2 H), 2.50 (tdd, J = 7.3, 2.3, 1.9 Hz, 2 H), 2.70 (ddt, J = 7.6, 7.3, 1.9 Hz, 2 H). − IR (film): $\tilde{\nu}$ = 2955, 2928, 2857, 1603, 1464, 1260, 1020 cm^{-1}. − MS: m/z = 324 [M$^+$], 267, 233, 209, 149, 133, 115, 111.

Aldolization of 26 with Titanium(IV) Chloride − [2-Hydroxy-2-(*tert*-butyldimethylsilyl)cyclopentyl]formyl(*tert*-butyldimethyl)silane (41): Yield 73%; oil. Chromatography: petroleum ether/AcOEt, 98:2. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.33. − ^{1}H NMR: δ = −0.053 (s, 3 H), −0.047 (s, 3 H), 0.19 (s, 3 H), 0.25 (s, 3 H), 0.95 (s, 18 H), 1.6−1.8 (m, 3 H), 1.8−2.1 (m, 3 H), 3.22 (dd, J = 10.3, 8.8 Hz, 1 H), 4.40 (s, OH). − ^{13}C NMR: δ = −6.6 ($SiMe_3$), −6.3 ($SiMe_3$), −6.0 ($SiMe_3$), 16.9 (C_4), 17.8 (C_4), 23.0 (CH_2), 26.5 (CH_3), 27.7 (CH_3), 29.7 (CH_2), 38.9 (CH_2), 61.8 (CH), 78.7 (C4), 257.3 (CO). − IR (film): $\tilde{\nu}$ = 3455, 2955, 2930, 2859, 1618, 1464, 1364, 1250, 833 cm^{-1}. − MS: m/z = 342 [M$^+$], 325, 317, 301, 285, 227, 199, 154, 147, 125, 115. − HRMS: calcd. for $C_{18}H_{38}O_2Si_2$ m/z = 342.2410; found 342.2417.

Aldolization of 27 with Titanium(IV) Chloride − (2-Hydroxy-2-trimethylsilylcyclohexyl)formyltrimethylsilane (43): Yield 77%; oil. Chromatography: petroleum ether/AcOEt, 97:3. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.39. − ^{1}H NMR: δ = −0.04 (s, 9 H), 0.23 (s, 9 H), 1.2−1.3 (m, 2 H), 1.4−1.6 (m, 2 H), 1.7−1.9 (m, 4 H), 3.04 (dd, J = 11.5, 3.8 Hz, 1 H), 3.87 (d, J = 2.3 Hz, OH). − ^{13}C NMR: δ = −2.8 ($SiMe_3$), −2.7 ($SiMe_3$), 19.4 (CH_2), 22.5 (CH_2), 25.9 (CH_2), 33.0 (CH_2), 56.2 (CH), 66.2 (C_4), 255.8 (CO). − IR (film): $\tilde{\nu}$ = 3480, 2934, 2855, 1622, 1447, 1314, 1250, 845 cm^{-1}. − MS: m/z = 272 [M$^+$], 271, 243, 239, 199, 182, 171, 167, 147, 139, 105. − HRMS: calcd. for $C_{13}H_{28}O_2Si_2$ m/z = 272.1628; found 272.1629.

Aldolization of 29 with Titanium(IV) Chloride − (2-Hydroxy-3-methyl-2-trimethylsilylcyclopentyl)formyltrimethylsilane (44): Yield 74%. Mixture of diastereomers (4:1).

Major Diastereomer: Chromatography: petroleum ether/AcOEt, 98:2. Oil. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.33. − ^{1}H NMR: δ = −0.01 (s, 9 H), 0.21 (s, 9 H), 1.00 (d, J = 6.1 Hz, 3 H), 1.6−2.0 (m, 5 H), 3.33 (dd, J = 9.2, 9.0 Hz, 1 H), 4.36 (s, OH). − ^{13}C NMR: δ = −3.0 ($SiMe_3$), −2.4 ($SiMe_3$), 13.5 (CH_3), 27.2 (CH_2), 32.2 (CH_2), 43.3 (CH), 60.5 (CH), 78.3 (C_4), 257.0 (CO). − IR (film): $\tilde{\nu}$ = 3453, 2959, 2903, 2878, 1620, 1373, 1360, 1250, 845 cm^{-1}. − MS: m/z = 272 [M$^+$], 271, 257, 243, 199, 182, 171, 167, 147, 139. − HRMS: calcd. for $C_{13}H_{28}O_2Si_2$ m/z = 272.1628; found 272.1626.

Minor Diastereomer: Chromatography: petroleum ether/AcOEt, 97:3. Oil. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.25. − ^{1}H NMR: δ = 0.05 (s, 9 H), 0.23 (s, 9 H), 0.91 (d, J = 7.3 Hz, 3 H), 1.6−1.8 (m, 3 H), 2.0−2.2 (m, 2 H), 3.49 (dd, J = 9.5, 9.2 Hz, 1 H), 4.27 (s, OH). − Selected ^{13}C-NMR data: δ = −3.2 ($SiMe_3$), −1.9 ($SiMe_3$), 18.6 (CH_3), 26.8 (CH_2), 31.7 (CH_2), 46.3 (CH), 56.9 (CH), 80.9 (C_4). − IR (film): $\tilde{\nu}$ = 3455, 2959, 2874, 1620, 1462, 1250, 843 cm^{-1}.

Aldolization of Acylsilane 31 with Silica Gel or Alumina: To a solution of the acylsilane **31** (0.75 mmol, 1.0 equiv.) in 20 mL of petroleum ether/AcOEt, 98:2, was added 2.0 g of either silica gel or alumina. The suspension was stirred overnight (15−19 h) at room temperature. The solid was then removed by filtration and washed with AcOEt (2 × 10 mL). After concentration of the combined filtrates in vacuo, the residue was recrystallized from petroleum ether/AcOEt to give quantitatively the aldol **32**. **(2-Hydroxy-2-trimethylsilylindan-1-yl)formyltrimethylsilane (32):** Yellow solid; m.p. 102−104°C. − TLC (petroleum ether/AcOEt, 98:2): R_f = 0.11. − ^{1}H NMR: δ = 0.01 (s, 9 H), 0.18 (s, 9 H), 2.63 (s, OH), 3.17 (d, J = 5.7 Hz, 2 H), 4.50 (s, 1 H), 7.04 (d, J = 6.9 Hz, 1 H), 7.1−7.3

(m, 3 H). – ^{13}C NMR: δ = −4.3 ($SiMe_3$), −2.7 ($SiMe_3$), 44.8 (CH_2), 65.9 (CH), 77.5 (C_4), 124.7 (CH), 125.2 (CH), 126.6 (CH), 127.5 (CH), 140.2 (C_4), 143.1 (C_4), 252.6 (CO). – IR (KBr): $\tilde{\nu}$ = 3496, 2956, 2899, 2872, 1618, 1478, 1298, 1254, 1241, 844 cm^{-1}. – MS: *m/z* = 306 [M^+], 278, 229, 205, 188, 173, 147, 132, 115. – $C_{16}H_{26}O_2Si_2$: calcd. C 62.69, H 8.55; found C 62.62, H 8.22.

General Procedure for Dehydration of Aldols 37 and 43 with Methanesulfonyl Chloride: To a solution of the aldol **37** or **43** (0.30 mmol, 1.0 equiv.) in dry CH_2Cl_2 (4 mL) at 0°C were added Et_3N (3.78 mmol, 12.6 equiv.) and MsCl (1.80 mmol, 6.0 equiv.). The mixture was stirred for 40 min at 0°C, and then was allowed to warm to 25°C (45 min). After dilution with CH_2Cl_2 (20 mL) and hydrolysis with brine (15 mL), the aqueous phase was extracted with CH_2Cl_2 (5 × 20 mL). The combined extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with petroleum ether/AcOEt as eluent.

Dehydration of Aldol 37: Mixture of stereoisomers **38** and **45** (88:12). Yield 77%. Conversion 94%. Chromatography: petroleum ether/AcOEt, 99:1. Oil. TLC (petroleum ether/AcOEt, 96:4): R_f = 0.51.

(2-Trimethylsilylcyclopent-2-enyl)formyltrimethylsilane (45): ^{1}H NMR: δ = 0.04 (s, 9 H), 0.23 (s, 9 H), 1.7−1.9 (m, 1 H), 2.0−2.2 (m, 1 H), 2.43 (m, 2 H), 4.0−4.1 (m, 1 H), 6.23 (dd, *J* = 1.9, 1.7 Hz, 1 H). – ^{13}C NMR: δ = −2.4 ($SiMe_3$), 1.0 ($SiMe_3$), 26.6 (CH_2), 34.3 (CH_2), 66.6 (CH), 142.9 (C_4), 144.8 (CH), 247.9 (CO). – Selected IR data (film): $\tilde{\nu}$ = 1640, 1539 cm^{-1}.

Dehydration of Aldol 43: Mixture of stereoisomers **39** and **46** (70:30). Yield 15%. Conversion 57%. Chromatography: petroleum ether/AcOEt, 98:2. Oil. TLC (petroleum ether/AcOEt, 98:2): R_f = 0.35. – IR (film): $\tilde{\nu}$ = 2959, 2928, 2857, 1642, 1615, 1539, 1449, 1410, 1262, 841 cm^{-1}. – MS: *m/z* = 254 [M^+], 239, 181, 147, 138, 133, 123, 109. – HRMS: calcd. for $C_{13}H_{26}OSi_2$ *m/z* = 254.1522; found 254.1515.

(2-Trimethylsilylcyclohex-1-enyl)formyltrimethylsilane (39): ^{1}H NMR: δ = 0.08 (s, 9 H), 0.24 (s, 9 H), 1.5−1.8 (m, 4 H), 2.2−2.3 (m, 2 H), 2.3−2.4 (m, 2 H).

(2-Trimethylsilylcyclohex-2-enyl)formyltrimethylsilane (46): ^{1}H NMR: δ = 0.05 (s, 9 H), 0.24 (s, 9 H), 1.5−1.8 (m, 4 H), 2.0−2.1 (m, 2 H), 3.7−3.8 (m, 1 H), 6.26 (dd, *J* = 3.4, 3.2 Hz, 1 H).

Retro-Aldol Reaction of 37 with Pyridinium *p*-Toluenesulfonate (PPTS): A mixture of aldol **37** (0.16 mmol, 1.0 equiv.) and PPTS (0.04 mmol, 0.3 equiv.) in dry CH_2Cl_2 (4 mL) was refluxed for 38 h. After cooling to room temperature, the crude mixture was extracted with AcOEt (5 × 10 mL). The combined extracts were washed with brine (20 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel with petroleum ether/AcOEt (97:3) as eluent, to give the bis(acylsilane) **25** (yield 41%) and the starting material **37** (conversion 55%).

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[1] A. G. Brook, R. J. Mauris, *J. Am. Chem. Soc*. **1957**, *79*, 971.
[2] [2a] A. Ricci, A. Degl′Innocenti, *Synthesis* **1989**, 647. – [2b] P. C. B. Page, S. S. Klair, S. Rosenthal, *Chem. Soc. Rev.* **1990**, *19*, 147. – [2c] P. F. Cirillo, J. S. Panek, *Org. Prep. Proc. Int*. **1992**, *24*, 555. – [2d] C. Nájera, M. Yus, *Org. Prep. Proc. Int*. **1995**, *27*, 385.
[3] [3a] B. Dondy, C. Portella, *J. Org. Chem*. **1993**, *58*, 6671. – [3b] P. Doussot, C. Portella, *J. Org. Chem*. **1993**, *58*, 6675. – [3c] T. Brigaud, P. Doussot, C. Portella, *J. Chem. Soc*., *Chem. Commun*. **1994**, 2117. – [3d] F. Jin, B. Jiang, Y. Xu, *Tetrahedron Lett*. **1992**, *33*, 1221. – [3e] F. Jin, Y. Xu, W. Huang, *J. Chem. Soc., Perkin Trans. 1* **1993**, 795. – [3f] F. Jin, Y. Xu, W. Huang, *J. Chem. Soc., Chem. Commun.* **1993**, 814. – [3g] F. Jin, Y. Xu, W. Huang, *J. Fluorine Chem.* **1995**, *71*, 1. – [3h] D. Saleur, T. Brigaud, J.-P. Bouillon, C. Portella, *Synlett* **1999**, 432.
[4] [4a] R. Plantier-Royon, C. Portella, *Synlett* **1994**, 527. – [4b] R. Plantier-Royon, C. Portella, *Tetrahedron Lett*. **1996**, *37*, 6113. – [4c] T. Brigaud, O. Lefebvre, R. Plantier-Royon, C. Portella, *Tetrahedron Lett*. **1996**, *37*, 6115.
[5] [5a] J. S. Nowick, R. L. Danheiser, *Tetrahedron* **1988**, *44*, 4113. – [5b] A. Degl′Innocenti, A. Capperucci, L. Bartoletti, A. Mordini, G. Reginato, *Tetrahedron Lett*. **1994**, *35*, 2081. – [5c] A. Fürstner, G. Seidel, B. Gabor, C. Kopiske, C. Krüger, R. Mynott, *Tetrahedron* **1995**, *51*, 8875. – [5d] A. Capperucci, A. Degl′Innocenti, C. Faggi, A. Ricci, *J. Org. Chem.* **1988**, *53*, 3612. – [5e] T. Mandai, M. Yamaguchi, Y. Nakayama, J. Otera, M. Kawada, *Tetrahedron Lett*. **1985**, *26*, 2675. – [5f] B. F. Bonini, M. Comes-Franchini, M. Fochi, G. M. Azzanti, C. Nanni, A. Ricci, *Tetrahedron Lett.* **1998**, *39*, 6737.
[6] T.-H. Chuang, J.-M. Fang, W.-T. Jiaang, Y.-M. Tsai, *J. Org. Chem*. **1996**, *61*, 1794.
[7] [7a] J.-P. Bouillon, C. Portella, *Tetrahedron Lett*. **1997**, *38*, 6595. – [7b] D. Saleur, J.-P. Bouillon, C. Portella, *Tetrahedron Lett.* **1999**, *40*, 1885.
[8] [8a] A. G. Brook, J. M. Duff, P. F. Jones, N. R. Davis, *J. Am. Chem. Soc*. **1967**, *89*, 431. – [8b] E. J. Corey, D. Seebach, R. Freedman, *J. Am. Chem. Soc.* **1967**, *89*, 434.
[9] $Et_3O \cdot BF_4$: [9a] T. Oishi, K. Kamemoto, Y. Ban, *Tetrahedron Lett*. **1972**, 1085. – $(NH_4)_2Ce(NO_3)_6$: [9b] T.-L. Ho, H. C. Ho, C. M. Wong, *J. Chem. Soc., Chem. Commun*. **1972**, 791. – [9c] Y.-M. Tsai, S.-Y. Chang, *J. Chem. Soc., Chem. Commun*. **1995**, 981. – $(CF_3CO_2)_2IC_6H_5$: [9d] G. Stork, K. Zhao, *Tetrahedron Lett*. **1989**, *30*, 287; see also ref.[9c] – Anodic oxidation: [9e] K. Suda, J.-I. Watanabe, T. Takanami, *Tetrahedron Lett*. **1992**, *33*, 1355. $Tl(NO_3)_3 \cdot 3\ H_2O$: [9f] R. A. J. Smith, D. J. Hannah, *Synth. Commun*. **1979**, *9*, 301. – 1,3-*N*,*N*-Dibromo-5,5-dimethylhydantoin (DBH): [9g] G. Foulard, T. Brigaud, C. Portella, *J. Org. Chem*. **1997**, *62*, 9107. – $Cu(NO_3)_2/Al_2O_3 \cdot 4\ SiO_2$: [9h] M. Balogh, A. Cornelis, P. Laszlo, *Tetrahedron Lett*. **1984**, *25*, 3313. – [9i] A. Cornelis, P. Lazslo, *Synthesis* **1985**, 909.
[10] [10a] D. W. Emerson, H. Wynberg, *Tetrahedron Lett*. **1971**, 3445. – [10b] W. F. J. Huurdeman, H. Wynberg, D. W. Emerson, *Tetrahedron Lett*. **1971**, 3449. – [10c] H. J. Reich, J. J. Rusek, R. E. Olson, *J. Am. Chem. Soc*. **1979**, *101*, 2225. – [10d] H. J. Reich, R. C. Holtan, C. Bolm, *J. Am. Chem. Soc*. **1990**, *112*, 5609. – [10e] B. Dondy, P. Doussot, C. Portella, *Synthesis* **1992**, 995.
[11] [11a] B.-T. Gröbel, D. Seebach, *Synthesis* **1977**, 357. – [11b] R. Bernardi, D. Ghiringhelli, *J. Org. Chem*. **1987**, *52*, 5021. – [11c] R. L. Danheiser, D. M. Fink, *Tetrahedron Lett*. **1985**, *26*, 2509. – [11d] G. A. Molander, C. S. Siedem, *J. Org. Chem*. **1995**, *60*, 130; see also refs.[4a,4b]
[12] H. C. Kolb, S. V. Ley, A. M. Z. Slawin, D. J. Williams, *J. Chem. Soc., Perkin Trans. 1* **1992**, 2735.
[13] [13a] G. A. Russell, L. A. Ochrymowycz, *J. Org. Chem*. **1969**, *34*, 3618. – [13b] W. A. Szarek, A. Zamojski, K. N. Tiwari, E. R. Ison, *Tetrahedron Lett*. **1986**, *27*, 3827; see also refs.[4b,9g]
[14] A. G. Brook, *Acc. Chem. Res.* **1974**, *7*, 77.
[15] [15a] A. T. Nielsen, W. J. Houlihan, *Org. React. (N.Y.)* **1968**, *16*, 1. – [15b] C. H. Heathcock, *Comprehensive Organic Synthesis* (Ed.: B. M. Trost), Pergamon Press, **1991**, p. 133.
[16] [16a] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, W. H. McLamore, *J. Am. Chem. Soc*. **1952**, *74*, 4223. – [16b] N. Mishriky, F. M. Asaad, Y. A. Ibrahim, A. S. Girgis, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 35; see also ref.[15b]
[17] T. Mukaiyama, *Org. React. (N.Y.)* **1982**, *28*, 203.
[18] [18a] A. Alexakis, M. J. Chapdelaine, G. H. Posner, A. W. Runquist, *Tetrahedron Lett*. **1978**, 4205. – [18b] A. Ishida, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161.
[19] [19a] S. Murata, M. Suzuki, R. Noyori, *J. Am. Chem. Soc*. **1980**, *102*, 3248. – [19b] G. A. Molander, C. S. Siedem, *J. Org. Chem*. **1995**, *60*, 130.

[20] T. Sato, M. Arai, I. Kuwajima, *J. Am. Chem. Soc*. **1977**, *99*, 5827.
[21] J. Berthelot, C. Guette, F. Fournier, D. Davoust, *Tetrahedron Lett*. **1987**, *28*, 1881.
[22] J. L. Soto, C. Seoane, A. M. Mansilla, M. C. Pardo, *Tetrahedron Lett*. **1981**, *22*, 4845.
[23] R. Grigg, G. J. Reimer, A. R. Wade, *J. Chem. Soc., Perkin Trans. 1* **1983**, 1929.
[24] [24a] K. Tanabe, R. Hayashi, R. Takasaki, *Chem. Pharm. Bull. (Tokyo)* **1961**, *9*, 1 (*Chem. Abstr.* **1964**, *60*, 9331). – [24b] K. Tanabe, Y. Morisawa, *Chem. Pharm. Bull. (Tokyo)* **1963**, *11*, 536 (*Chem. Abstr.* **1963**, *59*, 7600). – [24c] R. B. Turner, G. D. Diana, G. E. Fodor, K. Gebert, D. L. Simmons, A. S. Rao, O. Roos, W. Wirth, *J. Am. Chem. Soc*. **1966**, *88*, 1786. – [24d] P. Magnus, P. Pye, *J. Chem. Soc., Chem. Commun.* **1995**, 1933. – [24e] P. Magnus, J. Booth, L. Diorazio, T. Donohoe, V. Lynch, N. Magnus, J. Mendoza, P. Pye, J. Tarrant, *Tetrahedron* **1996**, *52*, 14103.
[25] [25a] I. Flemming, A. Pearce, *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485. – [25b] K. Nakatani, T. Izawa, Y. Odagaki, S. Isoe, *J. Chem. Soc., Chem. Commun.* **1993**, 1365. – [25c] K. Nakatani, T. Izawa, S. Isoe, *J. Org. Chem*. **1994**, *59*, 5961.
[26] J. Mirek, M. Gaweda, B. Kawalek, *Polish J. Chem.* **1981**, *55*, 987.

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