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SILICON MIGRATION AND RING CLEAVAGE REACTIONS OF 2-ALKYL-2-TRIMETHYLSILYLMETHYL-1,3-DITHIANES

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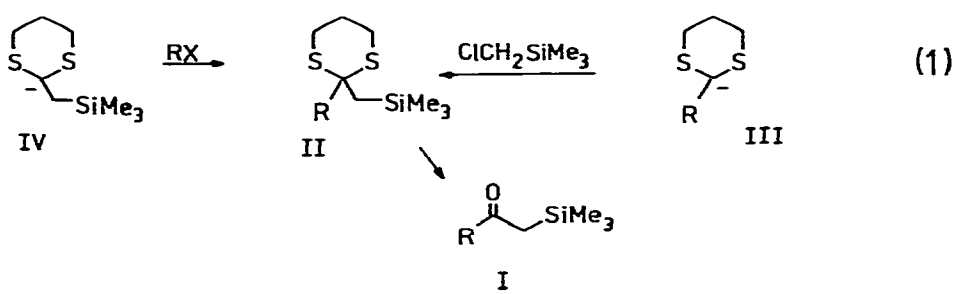
Summary

The synthesis and ring cleavage reactions of 2-alkyl-2-trimethylsilylmethyl-1,3-dithianes are described. The cleavages lead to 2-alkylthio-1-vinylsilanes and, via silicon migration, to 2-[3-alkylthio-3-(trimethylsilyl)propylthio]-1-alkenes.

The α-silylated ketones (or β-ketosilanes) (I) are versatile starting materials for the stereoselective synthesis of alkenes either via C=O reduction [1,2] or alkylation [3–5], and of β,γ-unsaturated esters, amides and nitriles [6]. Recent syntheses * of β-ketosilanes I start from carboxylic acids and derivatives [1,2,6–8], or involve the oxidation of β-hydroxysilanes [1,2,6,7], the rearrangement of α,β-epoxysilanes [4,7,9]; or special routes [7,10,11]. It seemed to us that standard 1,3-dithiane-based umpolung chemistry should furnish another general route (eq. 1) to β-ketosilanes I, provided that the final unmasking step II → I is feasible.



(1)

Indeed, dithianes II were readily obtained from 2-lithio-2-alkyl-1,3-dithianes (III) but the carbonyl generating step II → I proved, perhaps not unexpectedly, troublesome. None of the methods tried (e.g., SO_2Cl_2 on wet silica [12], the various

* For additional references to earlier work, see ref. 8, 11.

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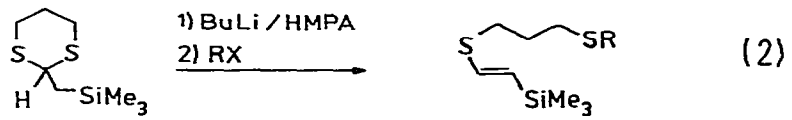
mercury(II) [13,14], copper(II) [13] or thallium(III) [15] based procedures or methyl fluorosulfonate [16]) gave isolable amounts of ketosilanes I.

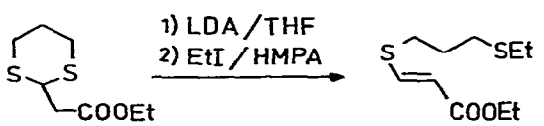
However, as far as the synthesis of II is concerned, we were intrigued by the fact that the more general route to these compounds, i.e., the alkylation of the dithiane anion IV gave only low yields of II at best. n-Butyilithium alone or with TMEDA was used for lithiation, and large amounts of unreacted starting material were always present in the reaction products. The poor outcome of this approach is presumably a result of incomplete anion formation at dithiane C(2), due to electronic and steric interference of the neopentyl-like Me_3SiCH_2 substituent. There is also a previous example of the low reactivity of IV: reaction with benzaldehyde gives a 30% yield of the addition product [17].



(2)

IIa V

As indicated in our preliminary communication [18], the alkylation of IIa in the presence of hexamethylphosphoric triamide (HMPA) does not give any alkylation products II but results in an unexpected ring cleavage (eq. 2). The alkylthiovinylsilanes (V) are obtained in up to 60% yield, with RX = MeI, BuBr or $MeOCH_2Cl$, or R = D (from D_2O). The (*E*) geometry to the products is assigned from the ^1H NMR spectra which show a characteristic *trans J* value (18 Hz) for the olefinic protons. Also, the olefinic proton shifts (δ 5.56 and 6.43 ppm) are in good agreement with values reported in the literature [19]. Obviously, these products arise via proton abstraction from the CH_2 group bonded to silicon, followed by thiolate elimination and alkylation. Significantly, no dithiane 2-alkylation products were observed among the products. It appears that the dithiane C(2) protons are thermodynamically more acidic but that kinetic control takes over when the BuLi/HMPA complex is used, resulting in deprotonation at CH_2Si. This behaviour, although of different origin, is reminiscent of that shown by 2-(1,3-dithiane)acetic esters (VI) which are known to give analogous alkylthiovinyl products VII (eq. 3) [20]. However, it is interesting that whereas in reaction 2 products V with R=H or D are also accessible, aqueous quench of the first formed thiolate anion in reaction 3 regenerated the starting material, showing that the vinylsilanes are very inferior Michael acceptors.



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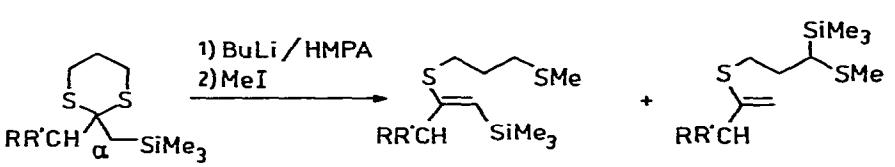
VI VII



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VIII IX X

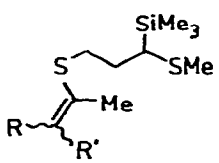
TABLE 1

RING CLEAVAGE PRODUCTS FROM 2-TRIMETHYLSILYLMETHYL-1,3-DITHIANES II AND VIII

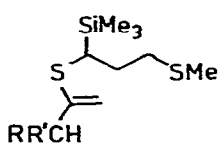
Starting material	R	R	Products (yield %) [a]			
IIa	D		Va (36)			
IIa	Me		Vb (60)	XIIIb (10)		
IIa	Bu		Vc (61)			
IIa	$MeOCH_2$		Vd (54)	XIId (10)		
VIIIa	H	H		Xa (12)	XIIIb (53)	XIV (9) *
VIIIb	H	Me	IXb (27) *	Xb (35)	XIIIb (10) *	XIV (16)
VIIIc	H	Et	IXc (26) *	Xc (38)	XIIIb (8) *	XIV (10) *
VIIId	H	Pr	IXd (30) *	Xd (33)	XIIIb (11) *	XIV (9) *
VIIIe	Me	Me	IXe (6) *	Xe (65)		
VIIIf	H	i-Pr	IXf (10) *	Xf (45)		XIV (7) *
VIIIg	Me	Et		Xg (65)		
VIIIh	$(CH_2)_5$			Xh (73)		

[a] Isolated yields are shown, excluding those marked * which are GC based estimates.

To find out whether the dithiane 2-alkyl homologues (VIII) would behave similarly, a number of them were treated with BuLi/HMPA and alkylated. Alkylthiovinylsilanes (IX) with a trisubstituted C=C bond indeed arise (see Table 1), judging from GC/MS and ^1H NMR, although they proved to be too unstable to allow preparative isolation. However, a competing ring cleavage reaction also occurs, leading to the Me_3Si-migrated products X (eq. 4). These 2-alkylthio-1-alkenes are highly acidic labile compounds, and are readily isomerised to the more stable 2-alkylthio-2-alkenes (XI); for example, on standing in chloroform solution.



XI



XII

It is readily seen in Table 1 that with branched and relatively large dithiane-2-alkyl substituents, the yields of the vinylsilanes IX decrease while those of the Me_3Si-migrated products X increase. This is presumably a result of the α-CH_2 groups of VIII being less accessible towards base owing to steric hindrance. Instead, proton abstraction occurs at the thermodynamically less acidic ring C(4) site. In the 1,3-dithiane ring system, carbanion formation at C(4), although unusual, is known, this behaviour being shown by 2-cyclohexylidene-1,3-dithiane on treatment with BuLi in THF [21]; proton abstraction at the alternative, i.e., allylic, site could also be effected by LDA/HMPA.

In the present case, the next step involves an attack of the C(4) carbanion at silicon. This is obviously only possible when the Me_3SiCH_2 substituent is axial. We have 500 MHz ^1H NMR evidence [22] that our dithianes exist in the two chair

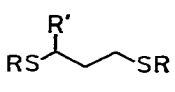
conformations, although the bulkiness of a 2-alkyl substituent does not appear to affect the conformer ratio very much. Thus, for example, VIII (R = H, R′ = Et) is estimated to have Et(eq)/Et(ax) = 25/75 while in VIII (R = Me, R′ = Et), sec-Bu(eq) sec-Bu(ax) = 38/62. In the event, this trend is certainly in keeping with the changes in product distribution in reaction 4.

Following the attack by the C(4) carbanion at silicon, the Si–$CH_2(\alpha)$ bond is cleaved, leading to C(2)-to-$CH_2(\alpha)$ double bond formation and thiolate expulsion. Inspection of molecular models reveals that S(3), and not S(1), should be involved in the elimination, as only then are the substituents at $CH_2(\alpha)$ and C(2) both properly aligned for the latter to become sp^2 hybridised. The alternative mode, i.e., S(1) thiolate elimination leading to XII would require rotation about the C(α)–C(2) bond after C(α) anion formation.

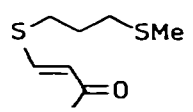
Indeed, we can only observe one type of Me_3Si-migrated products from reaction 4 by GC and NMR. Experimentally, the argument that the products are X and not XII is based on the mass spectra, which in every case show an intense peak at *m/z* 147, corresponding to $^+CH_2CH(SMe)SiMe_3$. Peaks at *m/z* 75 ($^+CH_2CH_2SMe$) or 61 ($^+CH_2SMe$) or at $M-61$ ($M-CH_2SMe$) are absent from the mass spectra. Further support is available from ^1H NMR: a two-proton, virtually coupled triplet at ca. δ 2.8 ppm is assignable to the CH_2–S–C=C moiety in X; in XII, the $MeSCH_2$ triplet should appear at ca. δ 2.4 ppm as observed in the spectra of compounds IX.

A synthon analysis of the above results makes it clear that the overall transformation RR′CHX → X (or XI) provides the equivalent of the acyl anion CH_3CO^-, insofar the vinylic thioethers can be easily hydrolysed to methyl ketones. However, relatively large number of steps is involved, and many shorter routes are available [23] for acetyl anion synthons.

Regarding the same compounds X, the silicon-bearing side chain would seem to give access to synthons such as $RSCH_2CH_2CO^-$, or $HSCH_2CH_2CO^-$. Unfortunately, it is known that the compounds RCH(SR′)$SiMe_3$ cannot be deprotonated unless R = phenyl [24], and we have also not succeeded in deprotonating X or XI.



	R	R′
XIIIb	Me	H
XIIId	$MeOCH_2$	H
XIV	Me	$SiMe_3$



XV

The clean stereoselective formation of the (*E*)-2-alkylthiovinylsilanes (V) makes these compounds available for the first time in pure form. Previously, simple 2-alkylthiovinylsilanes have been obtained as (*E*) + (*Z*) mixtures from the homolytic addition of RSH to trimethylsilylacetylene [19]. As an indication of the potential of these compounds for synthetic purposes, we have acylated V(R = Me) under the usual vinylsilane Friedel–Crafts conditions to give XV, although only in moderate yield (46%) owing to competing vinylthio C–S bond cleavage. Previous routes to β-alkyl- or β-aryl-thioenones include thiolate addition to ynones, or to β-haloenones [25], and thiolate addition to enones followed by dehydrogenation [26].

Experimental

All reactions were performed under Ar using solvents distilled over CaH_2. Preparative TLC separations were made using Merck's 60 PF 254 + 366 silica gel. ^1H (60 MHz, Me_4Si reference, JEOL JNM-PMX-60) and ^{13}C (15 MHz, $CDCl_3$ reference, JEOL JMM-FX-60) NMR spectra are from CCl_4 and $CDCl_3$ solutions, respectively. GC/MS instrumentation was comprised of Carlo Erba Fractovap 2900 (with 12-m SP-1200 quartz or 25-m OV-101 glass capillary column), JEOL JMS-D300 and JMA-2000 computer. ^{13}C NMR assignments are from C–H coupled spectra.

General procedure for the preparation of VIII

n-BuLi in hexane (1.05 eq) was added within 10 min to a solution of the 2-alkyl-1,3-dithiane (20 mmol) in THF (60 ml) at −20°C. After 5 h, the solution was cooled to −60°C, and chloromethyltrimethylsilane (3.6 ml, 26 mmol) was added. The mixture was then allowed to reach ambient temperature (ca. 20 h), poured into water and extracted with ether (3 × 50 ml). The combined extracts were washed with a saturated NaCl solution, followed by drying, evaporation and distillation.

2-Methyl-2-trimethylsilylmethyl-1,3-dithiane (VIIIa): b.p. 98°C/1 torr; ^1H NMR δ (ppm) 0.12 (9 H s), 1.40 (2 H s), 1.72 (3 H s), 1.9 (2 H m), 2.8 (4 H m); ^{13}C NMR δ (ppm) 0.8 ($SiMe_3$), 25.1 (C-5), 27.4 (C-4,C-6), 30.5 (Me), 33.8 (CH_2Si), 48.4 (C-2); *m/z* (rel. int. %) 220 (22), 205 (10), 146 (47), 131 (22), 93 (20), 73 (100).

2-Ethyl-2-trimethylsilyl-1,3-dithiane (VIIIb): b.p. 100°C/0.7 torr; ^1H NMR δ (ppm) 0.12 (9 H s), 0.95 (3 H t), 1.26 (2 H s), 1.8 (4 H m), 2.7 (4 H m); ^{13}C NMR δ (ppm) 0.8, 9.4, 25.1, 26.6, 29.2, 32.9, 53.1; *m/z* 234 (20), 219 (10), 205 (12), 160 (44), 145 (12), 106 (12), 93 (38), 73 (100).

2-Propyl-2-trimethylsilylmethyl-1,3-dithiane (VIIIc): b.p. 120°C/1.0 torr; ^1H NMR δ (ppm) 0.12 (9 H s), 0.94 (3 H t), 1.32 (2 H s), 1.7 (6 H m), 2.7 (4 H m); ^{13}C NMR δ (ppm) 0.8, 14.0, 18.2, 25.1, 26.8, 29.8, 42.5, 52.5; *m/z* 248 (25), 233 (10), 205 (15), 174 (50), 165 (16), 146 (50), 93 (17), 73 (100).

2-Butyl-2-trimethylsilylmethyl-1,3-dithiane (VIIId): b.p. 119°C/0.8 torr; ^1H NMR δ (ppm) 0.12 (9 H s), 1.32 (2 H s), 1.2 (7 H m), 1.9 (4 H m), 2.7 (4 H m); ^{13}C NMR δ (ppm) 0.8, 14.0, 22.7, 25.1, 26.7, 26.9, 29.8, 40.0, 52.6; *m/z* 262 (11), 247 (6), 205 (9), 188 (36), 146 (53), 106 (24), 93 (88), 73 (100).

2-(1-Methylethyl)-2-trimethylsilylmethyl-1,3-dithiane (VIIIe): b.p. 120°C/0.6 torr; ^1H NMR δ (ppm) 0.13 (9 H s), 1.07 (6 H d), 1.22 (2 H s), 1.9 (2 H m), 2.36 (1 H septet), 2.7 (4 H m); ^{13}C NMR δ (ppm) 1.2, 17.9, 25.2, 25.5, 26.2, 34.8, 57.9; *m/z* 248 (5), 233 (9), 205 (59), 174 (27), 165 (14), 93 (10), 91 (13), 73 (100).

2-(2-Methylpropyl)-2-trimethylsilylmethyl-1,3-dithiane (VIIIf): b.p. 120°C/0.7 torr; ^1H NMR δ (ppm) 0.14 (9 H s), 1.01 (6 H d), 1.42 (2 H s), 1.9 (5 H m), 2.8 (4 H m); ^{13}C NMR δ (ppm) 1.0, 24.9, 25.0, 25.3, 26.9, 30.3, 49.3, 52.9; *m/z* 262 (25), 247 (13), 205 (15), 188 (36), 165 (18), 146 (75), 93 (29), 73 (100).

2-(1-Methylpropyl)-2-trimethylsilylmethyl-1,3-dithiane (VIIIg): b.p. 106°C/0.7 torr; ^1H NMR δ (ppm) 0.13 (9 H s), 1.1 (8 H m), 1.18 (2 H s), 2.0 (3 H m), 2.8 (4 H m); ^{13}C NMR δ (ppm) 0.9, 13.0, 13.8, 24.3, 24.9, 25.3, 25.9, 41.5, 58.2.

2-Cyclohexyl-2-trimethylsilylmethyl-1,3-dithiane (VIIIh): b.p. 143°C/0.7 torr; ^1H NMR δ (ppm) 0.12 (9 H s), 1.26 (2 H s), 1.5 (13 H m), 2.8 (4 H m); ^{13}C NMR δ (ppm) 1.1, 25.4, 26.2, 26.3, 26.7, 27.0, 27.8, 45.2, 57.9, *m/z* 288 (3), 214 (59), 205 (62), 140 (22), 106 (23), 93 (59), 73 (100).

General procedure for the ring cleavage reactions

To a solution of the dithiane IIa or VIII (2 mmol) and HMPA (0.7 ml, 4 mmol) in THF (6 ml) at 0°C BuLi/hexane (4 mmol) was added within 1 min, followed by 4 mmol of the alkyl halide (or D_2O in excess for Va). After 2 h the reaction mixture was poured into water, extracted with ether (3 × 20 ml), and the combined extracts washed with a saturated NaCl solution, dried and evaporated. Preparative TLC (elution with 10/1 petroleum ether 40–60°C/CH_2Cl_2) gave pure Va, Vc, Vd and Xa–Xh.

(E)-2-(3-Mercaptopropylthio)ethenyl(trimethyl)silane (Va): ^{1}H NMR δ (ppm) 0.08 (9 H s), 1.9 (2 H m), 2.7 (4 H m), 5.62 (1 H d 18 Hz), 6.47 (1 H d 18 Hz). In a reaction where H_2O instead of D_2O was used for quenching, the SH signal appears at δ 1.20 ppm (t 8 Hz).

(E)-2-[3-(Methylthio)propylthio]ethenyl(trimethyl)silane (Vb) was prepared on an 11 mmol scale and distilled: b.p. 128°C/2.0 torr; IR 1548, 1250, 965, 870, 845 cm^{-1}; ^{1}H NMR δ (ppm) 0.08 (9 H s), 1.8 (2 H m), 2.05 (3 H s), 2.43 (2 H t 7 Hz), 2.77 (2 H t 7 Hz), 5.56 (1 H d 18 Hz), 6.43 (1 H d 18 Hz); *m/z* 220 (54), 205 (31), 179 (12), 105 (19), 91 (13), 90 (12), 89 (92), 88 (16), 73 (100), 61 (35). A distillation forerun was identified as 1,3-bis(methylthio)propane (XIIIb) ^{1}H NMR δ (ppm) 1.85 (2 H quintet 7 Hz), 2.07 (6 H s), 2.56 (4 H t 7 Hz); *m/z* 136 (85), 121 (100), 88 (61), 61 (90).

(E)-2-[3-(Butylthio)propylthio]ethenyl(trimethyl)silane (Vc): ^{1}H NMR δ (ppm) 0.08 (9 H s), 0.9 (9 H m), 2.45 (4 H t 7 Hz), 2.79 (2 H t 7 Hz), 5.60 (1 H d 18 Hz), 6.46 (1 H d 18 Hz).

(E)-2-[3-(Methoxymethylthio)propylthio]ethenyl(trimethyl)silane (Vd): ^{1}H NMR δ (ppm) 0.08 (9 H s), 2.0 (2 H quintet 7 Hz), 2.60 (2 H t 7 Hz), 2.70 (2 H t 7 Hz), 3.32 (3 H s), 4.57 (2 H s), 5.62 (1 H d 18.5 Hz), 6.50 (1 H d 18.5 Hz).

IXb–IXf could not be isolated by preparative TLC due to decomposition, and were only shown to be present by GC/MS. The crude reaction product mixtures all gave a singlet at ca. δ 5.0 ppm in ^{1}H NMR, assigned to the vinylic proton.

2-[3-(Methylthio)propylthio]-1-butenyl(trimethyl)silane (IXb): *m/z* 248 (12), 233 (3), 201 (12), 179 (43), 160 (26), 105 (13), 89 (12), 73 (100).

2-[3-Methylthio)propylthio]-1-pentenyl(trimethyl)silane (IXc): *m/z* 262 (13), 215 (10), 179 (27), 174 (15), 146 (26), 121 (11), 105 (12), 89 (12), 73 (100).

2-[3-(Methylthio)propylthio]-1-hexenyl(trimethyl)silane (IXd): *m/z* 276 (5), 229 (3), 187 (34), 179 (28), 146 (27), 105 (9), 89 (9), 73 (100).

3-Methyl-2-[3-(methylthio)propylthio]-1-butenyl(trimethyl)silane (IXe): *m/z* 262 (5), 219 (12), 215 (4), 179 (17), 174 (20), 121 (7), 105 (7), 99 (8), 89 (10), 73 (100).

4-Methyl-2-[3-(methylthio)propylthio]-1-pentenyl(trimethyl)silane (IXf): *m/z* 276 (17), 229 (9), 188 (14), 187 (32), 179 (30), 146 (30), 121 (10), 105 (10), 89 (12), 73 (100).

2-[3-Methylthio-3-(trimethylsilyl)propylthio]propene (Xa): ^{1}H NMR δ (ppm) 0.10 (9 H s), 1.9 (3 H m), 1.93 (3 H br s), 2.09 (3 H s), 2.8 (2 H m), 4.67 (1 H br s), 4.90 (1 H br s); *m/z* 234 (5), 147 (10), 114 (65), 113 (22), 105 (16), 99 (20), 87 (17), 73 (100).

2-[3-Methylthio-3-(trimethylsilyl)propylthio]-1-butene (Xb): ^{1}H NMR δ (ppm) 0.08 (9 H s), 1.12 (3 H t), 2.08 (3 H s), 2.0 5 H m), 2.8 (2 H m), 4.67 (1 H br s), 4.97 (1 H br s); *m/z* 248 (16), 233 (2), 147 (18), 128 (48), 127 (19), 105 (18), 99 (37), 73 (100).

2-[3-Methylthio-3-(trimethylsilyl)propylthio]-1-pentene (Xc): IR 3105, 1605, 1255, 875, 850, 755 cm^{-1}; ^{1}H NMR 0.10 (9 H s), 0.92 (3 H t), 1.8 (7 H m), 2.09 (3 H s), 2.8

(2 H m), 4.64 (1 H br s), 4.92 (1 H br s); *m/z* 262 (18), 247 (3), 147 (20), 142 (38), 114 (29), 105 (19), 99 (33), 73 (100).

2-[3-Methylthio-3-(trimethylsilyl)propylthio]-1-hexene (Xd): ^{1}H NMR δ (ppm) 0.10 (9 H s), 1.6 (12 H m), 2.10 (3 H s), 2.8 (2 H m), 4.66 (1 H br s), 4.94 (1 H br s); *m/z* 276 (11), 261 (2), 156 (23), 147 (24), 114 (66), 105 (23), 99 (25), 73 (100).

3-Methyl-2-[3-methylthio-3-(trimethylsilyl)propylthio]-1-butene (Xe): ^{1}H NMR δ (ppm) 0.10 (9 H s), 1.12 (6 H d 7 Hz), 2.10 (3 H s), 2.2 (4 H m), 2.8 (2 H m), 4.62 (1 H br s), 4.97 (1 H br s); ^{13}C NMR δ (ppm) −2.1, 17.3, 22.5, 29.4, 29.6, 33.6, 35.9, 102.4, 152.4; *m/z* 262 (18), 247 (3), 147 (19), 142 (44), 141 (16), 105 (16), 99 (52), 73 (100).

4-Methyl-2-[3-methylthio-3-(trimethylsilyl)propylthio]-1-pentene (Xf): ^{1}H NMR δ (ppm) 0.10 (9 H s), 0.91 (6 H d 6 Hz), 2.0 (6 H m), 2.10 (3 H s), 2.9 (2 H m), 4.70 (1 H br s), 4.93 (1 H br s); ^{13}C NMR δ (ppm) −2.4 ($SiMe_3$), 17.2 (SMe), 22.1 (Me_2), 26.9 ($CHMe_2$), 29.3 and 29.4 (CH_2CH_2S), 33.4 (CH-S), 47.1 (CH_2-Pr-i), 105.8 ($=CH_2$), 144.3 (S-C=); *m/z* 276 (21), 156 (24), 155 (13), 147 (18), 114 (41), 105 (21), 99 (26), 73 (100).

3-Methyl-2-[3-methylthio-3-(trimethylsilyl)propylthio]-1-pentene (Xg): ^{1}H NMR δ (ppm) 0.09 (9 H s), 1.0 (8 H m), 1.9 (3 H m), 2.08 (3 H s), 2.7 (3 H m), 4.60 (1 H br s), 4.94 (1 H br s).

1-[3-Methylthio-3-(trimethylsilyl)propylthio]-1-cyclohexylethene (Xh): ^{1}H NMR δ (ppm) 0.08 (9 H s), 1.6 (13 H m), 2.08 (3 H s), 2.8 (3 H m), 4.60 (1 H br s), 4.94 (1 H br s); *m/z* 302 (11), 182 (27), 153 (20), 147 (19), 105 (20), 99 (34), 73 (100).

Isomerisation X → XI

3-Methyl-2-[3-methylthio-3-(trimethylsilyl)propylthio]-2-butene (XId). A sample of Xd was quantitatively isomerised to XId on standing $CHCl_3$ solution for 3 days: ^{1}H NMR δ (ppm) 0.10 (9 H s), 1.77 (3 H br s), 1.93 (3 H br s), 2.10 (3 H s), 2.9 (3 H m), 2.8 (2 H m); ^{13}C NMR δ (ppm) −2.4, 16.9, 19.2, 21.0, 22.7, 30.2, 30.8, 32.8, 120.9, 134.3.

1,3-Bis(methylthio)-1-(trimethylsilyl)propane (XIV): ^{1}H NMR δ (ppm) 0.10 (9 H s), 1.85 (2 H m), 2.10 (1 H m), 2.07 (3 H s), 2.13 (3 H s), 2.65 (2 H m); *m/z* 208 (14), 193 (12), 147 (22), 105 (30), 88 (57), 73 (100), 61 (43).

(E)-4-[3-(Methylthio)propylthio]-3-buten-2-one (XV): To a solution of $AlCl_3$ (0.27 g, 2 mmol) and acetyl chloride (0.14 ml, 2 mmol) in CH_2Cl_2 (20 ml) at 0°C, Vb (0.44 g, 2 mmol) in CH_2Cl_2 (30 ml) was added during 2 h. After 15 min, the reaction mixture was poured into saturated $NaHCO_3$ solution and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried. Evaporation and preparative TLC (elution with petroleum ether 40–60°C/ethyl acetate 4/1) gave XV (0.17 g, 46%) as an oil: IR 1665, 1550, 1360, 955 cm^{-1}; ^{1}H NMR δ (ppm) 1.8 (2 H m), 2.07 (3 H s), 2.12 (3 H s), 2.91 (2 H t 7 Hz), 6.00 (1 H d 15 Hz), 7.40 (1 H d 15 Hz).

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