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CHEMISTRY OF ORGANOSILICON COMPOUNDS

CLXXXVIII *. REACTION OF ORGANODISILANES WITH DIENES CATALYZED BY TRANSITION METAL COMPLEXES. PREPARATION OF 1,8-BIS(TRIMETHYLSILYL)OCTA-2,6-DIENE AND ITS USE IN THE SYNTHESIS OF *dl*-MUSCONE **

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Summary

Organodisilanes, $Me_{3-n}X_nSiSiX_nMe_{3-n}$ (X = Cl and MeO, $n = 0, 1, 2$) undergo efficient 1 : 2 addition reactions with butadiene and isoprene in the presence of a catalytic amount of a suitable palladium complex. One of the products, the title compound, was used as a starting material for a short synthesis of *dl*-muscone.

Introduction

Our new method for silicon–carbon bond formation, based on the $(\sigma + \pi)$ reactions of organodisilanes with unsaturated compounds such as acetylenes [1] and 1,3-dienes [2], has been followed by other studies [3] and now appears very useful. In a previous communication [2], we have reported the formation of 1,8-bis(trimethylsilyl)octa-2,6-diene by the reaction of hexamethyldisilane with butadiene in the presence of some $PdCl_2L_2$ catalysts, but only in 14% yield, while highly reactive disilanes, such as 1,1,2,2-tetramethyl-1,2-disilacyclopentane, gave the corresponding product in high yield. Although our primary interest was the realization of such $(\sigma + \pi)$ reactions for organodisilanes, in view of current interest in the use of organosilicon compounds in organic synthesis [4] we have tried to improve the yield of the reaction. The compounds obtained from the reaction have two allylsilane moieties, and allylsilanes are recognized as one of the most attractive organosilicon compounds, among others, in their application to organic synthesis [5,6].

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* For part CLXXXVII see ref. 24.

** In honor of Professor R. Calas for his outstanding contribution to organosilicon chemistry during more than thirty years on the occasion of his formal retirement from the University of Bordeaux.

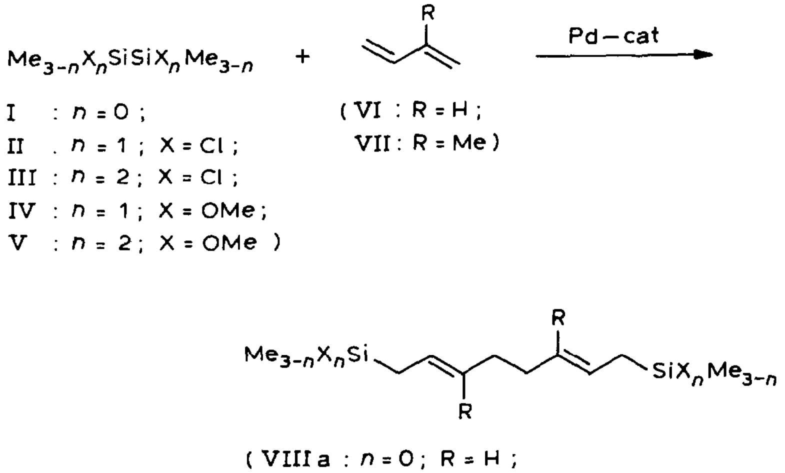
Results and discussion

The outline of the reaction is represented in Scheme 1.

Hexamethyldisilane (I), 1,2-dichlorotetramethyldisilane (II), 1,1,2,2-tetrachlorodimethyldisilane (III), 1,2-dimethoxytetramethyldisilane (IV), and 1,1,2,2-tetramethoxydimethyldisilane (V) were used as the disilane component and 1,3-butadiene (VI) and isoprene (VII) were examined as the diene component in the reaction. Results of reactions of I with VI and VII are listed in Tables 1 and 2, respectively.

As we have reported previously [2], the palladium complex-catalyzed reaction of hexamethyldisilane with isoprene gave 1,8-disilyloctadiene in a regio- and stereospecific manner. The ^{1}H NMR of VIIIb shows signals at δ 0.05 (18H, s, Si–CH_3), 1.46 (4H, d, *J* 8.0 Hz, SiCH_2), 1.65 (6H, s, C=C–CH_3), 2.16 (4H, s, =C(CH$_3$)–CH_2) and 5.22 ppm (2H, t, *J* 8.0 Hz, =CH). A large (12.0%) NOE was observed between methylene (2.16 ppm) and the vinylic hydrogen (5.22 ppm), so that the stereochemistry of double bonds should be *trans*. It is also noteworthy that the isoprene unit dimerizes in the head to head manner.

As shown in Tables 1 and 2, a variety of transition metal complexes are examined under various conditions. Among the complexes examined, divalent palladium complexes, palladium chloride, and palladium acetate were effective as a catalyst. Previously we have used benzene as a solvent to control the reaction, but it is now clear that reactions without solvent give far better yields. A reasonable explanation



(I : n = 0 ;
II : n = 1 ; X = Cl ;
III : n = 2 ; X = Cl ;
IV : n = 1 ; X = OMe ;
V : n = 2 ; X = OMe)

(VI : R = H ;
VII : R = Me)

(VIIIa : n = 0 ; R = H ;
VIIIb : n = 0 ; R = Me ;
VIIIc : n = 1 ; R = H ; X = Cl ;
VIIId : n = 1 ; R = Me ; X = Cl ;
VIIIe : n = 2 ; R = H ; X = Cl ;
VIIIf : n = 2 ; R = Me ; X = Cl ;
VIIIg : n = 1 ; R = H ; X = OMe ;
VIIIh : n = 1 ; R = Me ; X = OMe ;
VIIIi : n = 2 ; R = H ; X = OMe ;
VIIIj : n = 2 ; R = Me ; X = OMe)

SCHEME 1

could be that coordination of solvents such as benzene, THF, acetonitrile and ethanol to the catalyst may retard the reaction, since the silicon–silicon bond of organodisilanes seems to have only a weak coordinative ability towards palladium complexes. Actually the reaction of disilanes with a large excess of diene results only in the formation of oligomers of the diene.

The effect of temperature on the yield of the reaction is very delicate. The reactions of hexamethyldisilane and isoprene catalyzed by $PdCl_2(PhCN)_2$ (Nos. 10–16) show an optimum temperature of 60°C, while a better yield was observed at 120°C (No. 17) than at 60°C (No. 18) in the reactions catalyzed by $Pd(OAc)_2$. However, the reactions of hexamethyldisilane with butadiene catalyzed by $PdCl_2(PhCN)_2$ (Nos. 31–36) show their maximum yield at 90°C.

TABLE 1

TRANSITION METAL COMPLEX-CATALYZED REACTIONS OF HEXAMETHYLDISILANE (I) WITH ISOPRENE (VII)

No.	Catalyst [a,b]	Additive [c]	Solvent [d]	T (°C)	Time (h)	Isolated yield (%)
1	$PdCl_2(PhCN)_2$		PhH	160	16	3
2	$PdCl_2(PhCN)_2$	A	PhH	160	15	4
3	$PdCl_2(PhCN)_2$		PhH	85	17	2
4	$PdCl_2(PhCN)_2$		CH_2Cl_2	85	11	6
5	$PdCl_2(PhCN)_2$	B	CH_2Cl_2	130	19	trace
6	$PdCl_2(PhCN)_2$		EtOH	85	12	–
7	$PdCl_2(PhCN)_2$		THF	85	11	1
8	$PdCl_2(PhCN)_2$		$CHCl_3$	90	11	5
9	$PdCl_2(PhCN)_2$		CH_3CN	90	16	–
10	$PdCl_2(PhCN)_2$			150	17	trace
11	$PdCl_2(PhCN)_2$			100	21	8
12	$PdCl_2(PhCN)_2$			90	12	40
13	$PdCl_2(PhCN)_2$			60	13	60
14	$PdCl_2(PhCN)_2$ [e]			60	12	70
15	$PdCl_2(PhCN)_2$	B		50	19	17
16	$PdCl_2(PhCN)_2$			40	12	14
17	$Pd(OAc)_2$ [e]			120	94	87
18	$Pd(OAc)_2$ [e]			60	35	4
19	$PdCl_2$ [f]			90	13	40
20	$PdCl_2$ [g]			60	19	24
21	$PdCl_2$-PhCN [h]			60	20	18
22	$PdCl_2(PPh_3)_2$		PhH	90	16	–
23	$PdCl_2(PPh_3)_2$	A		85	17	–
24	$PdCl_2(PBu_3)_2$ [i]			60	21	–
25	$PdCl_2(PEt_3)_2$			80	21	–
26	$PdCl(PhCH_2)(Ph_3P)_2$ [j]			60	18	–
27	$Pd(PPh_3)_4$			60	20	–
28	$RhHClPPh_3$(+)DIOP [k]			60	15	–
29	$Fe(acac)_3$ [l]		PhH	85	12	–
30	Pd/C (10%) [m]			85	17	–

[a] Catalysts were used at 1.0 mol% concentration, unless otherwise noted. [b] A mixture of 1 mmole of I and 4 mmole of VII was used, unless otherwise noted. [c] A: 0.4 mol% p-methoxyphenol was added; B: $CuCl_2$ was added in an amount equal to that of the catalyst. [d] 10 ml of solvent was added. [e] A mixture of 1 mmole of I and 2 mmole of VII was used. [f] 16 mole%. [g] 1.7 mole%. [h] 2.5 mole%, $[PdCl_2]/[PhCN] = 1/93$. [i] 1.5 mole%. [j] 0.9 mole%. [k] 0.8 mole%. [l] 5.2 mole%. [m] 7.1 mole%.

TABLE 2

TRANSITION METAL-CATALYZED REACTIONS OF HEXAMETHYLDISILANE (I) AND BUTADIENE (VI)[a]

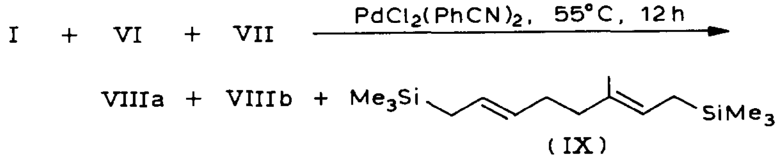
No.	Catalyst	Catalyst concentration (mole%)	T (°C)	Time (h)	Isolated yield (%)
31	$PdCl_2(PhCN)_2$	1.0	110	15	8
32	$PdCl_2(PhCN)_2$	1.0	100	13	13
33	$PdCl_2(PhCN)_2$	1.0	90	15	63
34	$PdCl_2(PhCN)_2$	1.0	80	13	51
35	$PdCl_2(PhCN)_2$	0.8	70	34	44
36	$PdCl_2(PhCN)_2$	0.7	60	20	36
37	$PdCl_2(PhCN)_2$	0.3	60	16	36
38[b]	$PdCl_2(PhCN)_2$	1.0	60	30	52
39[b]	$PdCl_2(p\text{-}MeOC_6H_4CN)_2$	1.0	110	15	46
40[b]	$PdCl_2(p\text{-}MeOC_6H_4CN)_2$	1.0	90	15	85
41[c]	$PdCl_2(p\text{-}MeOC_6H_4CN)_2$	1.1	90	17	80
42[b]	$PdCl_2(p\text{-}MeOC_6H_4CN)_2$	1.0	60	30	38
43[b]	$PdCl_2(p\text{-}MeC_6H_4CN)_2$	1.0	110	15	18
44[b]	$PdCl_2(p\text{-}MeC_6H_4CN)_2$	1.0	90	15	77
45[b]	$PdCl_2(p\text{-}MeC_6H_4CN)_2$	1.0	60	30	55
46[b]	$Pd(OAc)_2$	1.0	120	34	31
47[b]	$Pd(OAc)_2$	1.7	110	6	18
48	$PdCl_2(PPh_3)_2$	1.0	60	7 days	13

[a] A mixture of 1 mmole of I and 4 mmole of VI were used unless otherwise noted. [b] A mixture of 1 mmole of I and 2 mmole of VI was used. [c] A large scale experiment using a mixture of 89.0 mmole of I and 178.0 mmole of VI.

Additives, such as p-methoxyphenol as an antioxidant, or $CuCl_2$ as an oxidant, revealed no dramatic effect on the yield, but there is insufficient information to draw any conclusions from these experimental results only.

Substituents on the benzene ring of the dichloropalladium benzonitrile complex had rather remarkable effects on the yields. Reactions of hexamethyldisilane with butadiene at 90°C catalyzed by the complex with p-methoxybenzonitrile gave the best yields (compare Nos. 33, 44, and 40). Complexes with stronger donor abilities gave better yields. This is also true at a higher temperature (Nos. 31, 43, and 39), but the effect is unclear at lower temperature (Nos. 38, 45, and 42).

The relative reactivity of butadiene and isoprene under fixed conditions was examined. An equimolar mixture of butadiene and isoprene was subjected to reaction with hexamethyldisilane at 55°C in the presence of $PdCl_2(PhCN)_2$:



(IX)

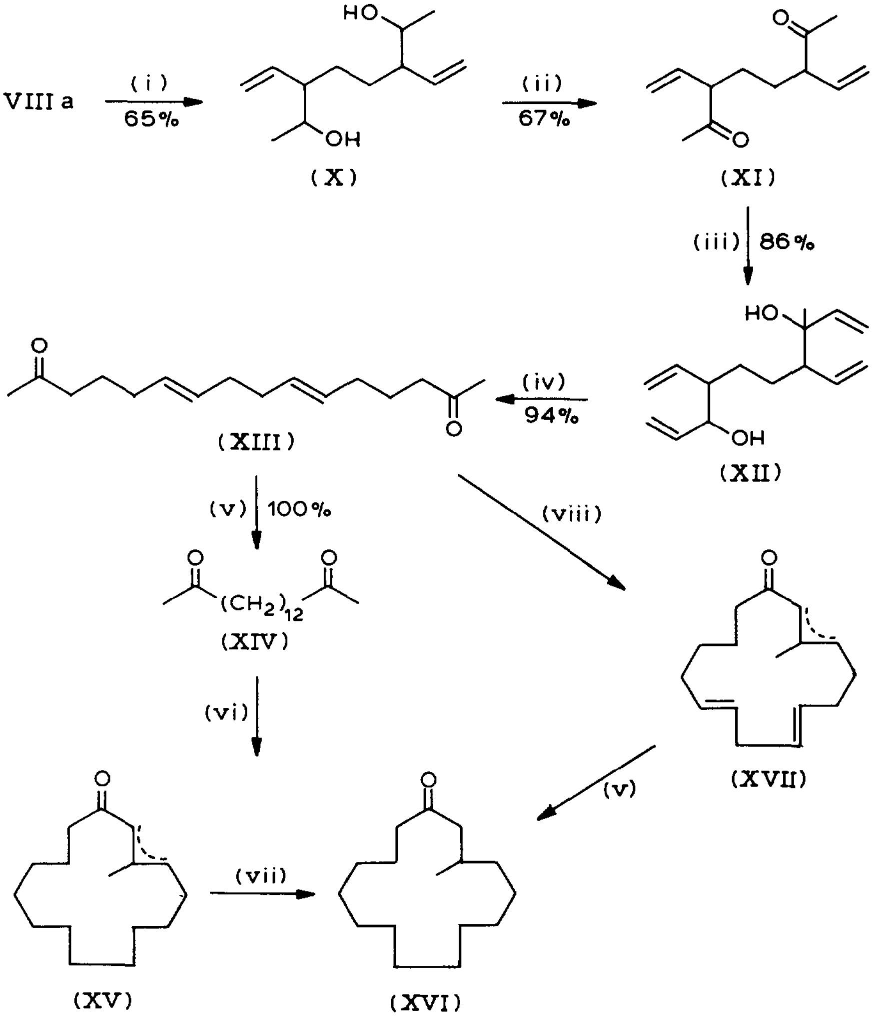
The ratio of VIIIa/VIIIb/IX was 3.0/0.6/2.0. Therefore, butadiene has a higher reactivity than isoprene in the reaction.

1,2-Dichlorotetramethyldisilane (II), 1,1,2,2-tetrachlorodimethyldisilane (III), 1,2-dimethoxytetramethyldisilane (IV), and 1,1,2,2-tetramethoxydimethyldisilane (V)

TABLE 3. $PdCl_2(PhCN)_2$-CATALYZED REACTIONS OF CHLORO- AND METHOXY-SUBSTITUTED DISILANES WITH VI AND VII[a]

No.	Disilane	Diene	Catalyst concentration (mole %)	*T* (°C)	Time (h)	Product and yield (%)
49	II	VI	2.0	60	18	VIIIc 49
50	II	VII	2.0	60	18	VIIId 35
51	III	VI	2.5[b]	60	24	VIIIe 50
52	III	VII	2.5[c]	60	87	VIIIf 41
53	IV	VI	1.0	60	15	VIIIg 69
54	IV	VII	1.0	60	30	VIIIh 37
55	V	VI	1.0	60	77	VIIIi 20
56	V	VII	1.0	60	24	VIIIj 37

[a] 4–5 molar excess diene was used in the reaction and products were methylated with MeMgBr before isolation. [b] 37.5 mole% PhCN was added. [c] 17.5 mole% PhCN was added.



SCHEME 2. (i) CH_3CHO, $TiCl_4$, CH_2Cl_2, −78°C. (ii) CrO_3–3,5-dimethylpyrazole. (iii) $CH_2{=}CHMgCl$, THF. (iv) KH, THF, reflux. (v) H_2, Pd/C, EtOH. (vi) and (vii) see ref. [12]. (viii) i-Bu_2AlOPh, pyridine, THF–n-hexane, reflux.

also gave the corresponding 1 : 2 adducts, as shown in Table 3. 1,2-Difluorotetramethyldisilane was reported to give a 1 : 1 adduct as the main product with isoprene in the presence of a palladium catalyst [7], but 1 : 2 adducts were obtained in the present work.

Further examination of reaction conditions could result in better yields than those reported herein, but we are pleased to report that the yields of isolated pure VIIIa and VIIIb are now 85 and 87%, respectively.

Since both butadiene and hexamethyldisilane [8] are readily available, VIIIa as well as VIIIb is an interesting starting material for organic synthesis. Herein we report a short synthesis of *dl*-muscone from VIIIa. The outline of the synthesis is shown in Scheme 2.

The reaction of VIIIa with acetaldehyde in the presence of titanium chloride [9] gave X regiospecifically. Oxidation, followed by reaction with vinylmagnesium chloride, afforded XII, which was successfully subjected to an anionic oxy-Cope rearrangement [10]. The unsaturated diketone XIII was hydrogenated to give XIV [10]. An efficient route to *dl*-muscone (XVI, 3-methylcyclopentadecanone) from XIV has been described recently [10]. As an alternative, we tried to cyclize XIII to XVII, which was then hydrogenated to XVI, but the total yield of pure XVI was 6%. Although no effort was made to optimize the yield by this route, obviously the route through XIV seems to be better. The MS, IR, and ^{1}H NMR of XVI agreed well with those reported [11].

Experimental

Materials

Hexamethyldisilane [8], 1,2-dichlorotetramethyldisilane [13], 1,1,2,2-tetrachlorodimethyldisilane [14], 1,2-dimethoxytetramethyldisilane [15], and 1,1,2,2-tetramethoxydimethyldisilane [15] were prepared according to literature procedures.

1,3-Butadiene and isoprene were commercially available and were used after being distilled. The following complexes, $PdCl_2(PhCN)_2$ [16], $PdCl_2(PPh_3)_2$ [17], $PdCl_2(PBu_3)_2$ [18], $PdCl_2(PEt_3)_2$ [18], $PdCl(PhCH_2)(PPh_3)_2$ [19], $Pd(PPh_3)_4$ [20], $Fe(acac)_3$ [21], $PdCl_2(p\text{-}CH_3C_6H_4CN)_2$ [22], and $PdCl_2(p\text{-}CH_3OC_6H_4CN)_2$ [22] were prepared according to details given in the references. $Pd(OAc)_2$, $RhHClPPh_3$(+)-DIOP, $PdCl_2$, and Pd/C (10%) were commercial samples and were used without purification.

^{1}H NMR spectra were taken with Varian T-60, EM-390 and XL-200 spectrometers.

General procedure

Reactions were generally carried out using a small stainless steel autoclave (Yuasa-Giken, 50 ml). It was important that all the vessels were carefully washed and dried to obtain reproducible results. Typical examples are as follows. The autoclave containing $PdCl_2(PhCN)_2$ (3.8 mg, 1.0×10^{-2} mmole), and three glass tubes containing hexamethyldisilane (163 mg, 1.11 mmole), isoprene (220 mg, 3.24 mmole), and benzene (10 ml), respectively, were connected to a vacuum line. By using a technique involving freeze-thaw cycles, all the reagents were evacuated and degassed thoroughly and were transferred to the autoclave. After being disconnected from the vacuum line, the autoclave was immersed into an oil bath kept at a fixed temperature.

In the case of the reactions with butadiene, it was transferred from a container to a graduated pressure bottle, which was connected to the vacuum line.

Products of the reaction of hexamethyldisilane (I) were separated by silica gel TLC directly, while those from II, III, IV, and V were methylated with an excess methylmagnesium bromide in ether and then separated by TLC. The methoxysilyl-substituted products, VIIIg, VIIIh, VIIIi, and VIIIj, were also separated by GLC (SE 30–20%, 1 m).

Properties of addition dimers VIII

VIIIa: an oil; n^{23} 1.4564; M^+ 254 (1.6), *m/e* 73 (100); λ_{max} (n-hexane) 211.7 (9,5000); IR (neat, cm^{-1}) 2930, 1250, 850; ^{1}H NMR (CCl$_4$, δ) 0.10 (18H, s, Si-CH_3), 1.46 (4H, d, *J* 7 Hz, Si-CH_2-CH=), 2.10 (4H, t, *J* 3 Hz, CH$_2$-CH_2-CH=), 5.33 (4H, m, =C*H*-). Anal. found: C, 65.95; H, 11.77. $C_{14}H_{30}Si_2$ calcd.: C, 66.06; H, 11.88%.

VIIIb: an oil; n^{23} 1.4630; M^+ 282 (3.2), *m/e* 73 (100); λ_{max} (n-hexane) 212.0 (12,000); IR (neat, cm^{-1}) 2950, 1250, 850; ^{1}H NMR (CCl$_4$, δ) 0.05 (18H, s, Si-CH_3), 1.46 (4H, d, *J* 8 Hz, Si-CH_2-CH=), 1.65 (6H, s, =CH-CH_3), 2.16 (4H, s, -CH$_2$-CH_2-CH=), 5.22 (2H, t, *J* 8 Hz, -C*H*=); NOE 12.0% between peaks at δ 2.16 and 5.22. Anal. found: C, 68.16; H, 12.14. $C_{16}H_{34}Si_2$ calcd.: C, 68.00, H, 12.13%.

VIIIg: an oil; M^+ 286 (3.3), *m/e* 89 (100); IR (neat, cm^{-1}) 3018, 2960, 2835, 1660, 1250, 1095, 965, 840; ^{1}H NMR (CCl$_4$, δ) 0.03 (12H, s, SiCH_3), 1.47 (4H, m, Si-CH_2-CH=), 1.99 (4H, bs, C=C-CH_2CH_2-C=C), 3.36 (6H, s, SiOCH_3), 5.26 (4H, m, -C*H*=C*H*-). Anal. found: C, 58.98; H, 10.51. $C_{14}H_{30}O_2Si_2$ calcd.: C, 58.68; H, 10.55%.

VIIIh: an oil; M^+ 314 (5.4) *m/e* 89 (100); IR (neat, cm^{-1}) 2960, 2930, 2830, 1450, 1250, 1190, 1158, 1092, 835; ^{1}H NMR (CCl$_4$, δ) 0.08 (12H, s, SiCH_3), 1.48 (4H, d, *J* 9.0 Hz, Si-CH_2-C=), 1.59 (6H, t, *J* 0.5 Hz, C=C-CH_3), 2.08 (4H, bs, C=C-CH_2CH_2-C=C), 3.42 (6H, s, SiOCH_3), 5.15 (2H, t, *J* 9.0 Hz, -C*H*=C). Anal. found: C, 60.90; H, 10.93. $C_{16}H_{34}O_2Si_2$ calcd.: C, 61.08; H, 10.89%.

VIIIi: an oil; M^+ 318 (2.3) *m/e* 105(100); IR (neat, cm^{-1}) 2940, 2835, 1260, 1190, 1165, 1090, 965, 845; ^{1}H NMR (CCl$_4$, δ) 0.04 (6H, s, SiCH_3), 1.49 (4H, m, Si-CH_2-C=C), 2.01 (4H, bs, C=CCH_2-CH$_2$-C=C), 3.46 (12H, s, SiOCH_3), 5.29 (4H, m, -C*H*=C*H*-). Anal. found: C, 52.50; H, 9.56. $C_{14}H_{30}O_4Si_2$ calcd.: C, 52.78; H, 9.49%.

VIIIj: an oil; M^+ 346 (5.8), *m/e* 105 (100); IR (neat, cm^{-1}) 2940, 2840, 1263, 1198, 1090, 855, 822, ^{1}H NMR (CCl$_4$, δ) −0.02 (6H, s, SiCH_3), 1.43 (4H, d, *J* 8.5 Hz, SiCH_2-C=), 1.55 (6H, t, *J* 0.5 Hz, C=C-CH_3), 2.02 (4H, bs, C=C-CH_2CH_2-C=C), 3.42 (12H, s, SiOCH_3), 5.09 (2H, t, *J* 8.5 Hz, -CH=CH-). Anal. found: C, 55.17; H, 9.98. $C_{14}H_{30}O_4Si_2$ calcd.: C, 55.44; H, 9.89%.

Competitive reaction of VI and VII with I

Hexamethyldisilane (I) (6.391 g, 43.8 mmole), butadiene (VI) (2.363 g, 43.8 mmole) and isoprene (VII) (2.980 g, 43.8 mmole) were charged in a pressure bottle in which PdCl$_2$(PhCN)$_2$ (247 mg, 0.647 mmole) was placed. After being degassed and evacuated with a vacuum line, the reactor was kept at 55°C for 12 h. After unreacted butadiene had vaporized, the mixture was diluted with hexane and passed through a short column of silica gel to remove the catalyst. A colorless oil (1.455 g) was obtained after distillation. The oil contains VIIIa, VIIIb and IX in a ratio of 3.0/0.6/2.0. Yields based on the starting materials I, VI, and IX are 12.8, 18.2 and 7.3%, respectively.

IX: an oil; M^+ 268 (3.60) m/e 73 (100); IR (neat, cm^{-1}) 3060, 1248, 1154, 962, 855, 690; ^1H NMR (CCl_4, δ), 0.02 (18H, s, $SiCH_3$), 1.35 (2H, d, J 7.0 Hz, $SiCH_2$–C=), 1.37 (2H, d, J 7.0 Hz, $SiCH_2$–C=), 1.54 (2H, d, J 1.0 Hz, C=C–CH_3), 2.00 (4H, m, C=C–CH_2CH_2–C=C), 5.08–5.54 (3H, m, vinyl–H). Anal. found: C, 67.37; H, 11.93. $C_{15}H_{32}Si_2$ calcd.: C, 67.68; H, 12.01%.

Reaction of VIIIa with acetaldehyde

A dichloromethane (250 ml) solution of VIIIa (7.598 g, 29.9 mmole) was cooled to 0°C in a 500 ml three-necked flask. Freshly distilled acetaldehyde (4.5 ml, 80.6 mmole) was added with a syringe under nitrogen. The mixture was cooled to −78°C with a Dry-Ice-methanol bath, and then titanium chloride (8.9 ml, 89.0 mmole) was added over 4 min. After being stirred for an additional 2 min, the pale brown solution was quenched with a saturated sodium hydrogen carbonate solution and was extracted with ether. Usual work-up gave X (3.869 g, 19.5 mmole, 65%: m.p. 57–59°C; $M^+ - 2H_2O$ 162 (4.5) m/e 45 (100); IR (KBr, cm^{-1}) 3030, 3078, 2962, 1638, 1448, 912; ^1H NMR (200 MHz, $CDCl_3$, δ) 1.09 (6H, d, J 6.3 Hz, –CH_3), 1.32 (4H, m, CH_2), 1.50 (2H, m, C=C–CH–), 2.01 (2H, bs, OH), 3.62 (2H, dq, J 6.3, 10.2 Hz, O–C–H), 5.09 (2H, dd, J 16.7, 2.2 Hz, C=CH), 5.13 (2H, dd, J 10.5, 2.2 Hz, C=CH), 5.55 (2H, ddd, J 16.7, 10.5, 5.9 Hz, C=CH–). Anal. found: C, 72.57; H, 11.18. $C_{12}H_{22}O_2$ calcd.: C, 72.68; H, 11.18%.

Oxidation of X

Corey's method [23] was used for the oxidation of X (3.89 g, 19.65 mmole) to give XI (2.56 g, 13.2 mmole, 67%). XI consisted of the *dl*- and *meso*-isomers. Two fractions, *A* and *B*, were separated by HPLC (Lichrosorp Si-60, n-hexane/ethyl acetate = 7/1). *A*: ^1H NMR (CCl_4, δ) 1.30 (2H, m, –CH_2–), 1.60 (2H, m, –CH_2–), 2.05 (6H, s, –CH_3), 2.98 (2H, m, CH), 5.00–5.85 (6H, m, vinyl–H). MS found: 194.1325. $C_{12}H_{18}O_2$ calcd.: 194.1307. *B*: ^1H NMR (CCl_4, δ) 1.05–1.75 (4H, m, –CH_2–CH_2–), 2.05 (6H, s, CH_3), 2.98 (2H, m, CH), 5.00–5.85 (6H, m, vinyl–H). MS found: 194.1310.

The reaction of XI with vinylmagnesium chloride

To a THF solution of vinylmagnesium chloride (50 ml, 2 *M*) was added, dropwise, XI (2.56 g, 13.2 mmole) in THF (30 ml) at 0°C over 15 min under nitrogen. After 30 min, the mixture was quenched with water and worked up as usual, to give XII (2.82 g, 11.3 mmole, 86%). HPLC analysis showed that XII was a mixture of four diastereomers. $M^+ - H_2O$ 232 (2.6), $M^+ - 2H_2O$ 214 (9.4) m/e 71 (100).

Anionic oxy-Cope rearrangement of XII

XII (503 mg, 2.01 mmole) in THF (37 ml) was added to a suspension of potassium hydride (4.00 mmole) at 0°C for 15 min under argon. The mixture was then heated at 80°C for 1 h. Quenching with dilute hydrochloric acid, extraction with ether, and TLC separation (silica gel, n-hexane/ethyl acetate 5/1) gave XIII (474 mg, 1.90 mmole, 94%): m.p. 45–46°C (lit. [10] 47–48°C). ^1H NMR ($CDCl_3$, δ), 1.62 (4H, m, -CH_2-), 1.88–2.20 (8H, m, C=C–CH_2–), 2.14 (6H, s, CH_3), 2.41 (4H, t, J 7.2 Hz, -CH_2CO), 5.30–5.37 (4H, m, =CH–). MS found: 250.1927. $C_{16}H_{26}O_2$ calcd.: 250.1932.

Hydrogenation of XIII

XIII (66 mg, 0.266 mmole) was hydrogenated at room temperature in ethanol (10 ml) with Pd/C (5%, 22 mg) and hydrogen at atmospheric pressure. Recrystallization of crude XIV (67 mg, 0.26 mmole, 100%) from ethanol gave a pure sample: m.p. 82–83°C (lit. [20] 83–85°C); ^{1}H NMR ($CDCl_3$, δ) 1.28 (16H, bs, -CH_2–), 1.55 (4H, m, -CO–CH_2–CH_2), 2.12 (6H, s, -CH_3), 2.30 (4H, t, J 6.6 Hz, CO–CH_2). MS found: 254.2244. $C_{16}H_{30}O_2$ calcd. 254.2244.

Preparation of dl-muscone XVI from XIII

The intramolecular aldol condensation of XIII (180 mg, 0.70 mmole) using diisobutylaluminum hydride (4.0 mmole), phenol (424 mg, 4.5 mmole) and pyridine (393 mg, 3.97 mmole) by a reported procedure [11], was attempted. The expected product XVII (M^+ 232) was obtained in ca. 20% yield, but the pure compound was not isolated. The mixture was hydrogenated by a similar procedure to that used for the reduction of XIII. The crude product (56 mg) was subjected to TLC (silica gel, n-hexane/ethyl acetate 5/1) and GLC (SE 30, 2 m) to give pure XVI (23 mg). The 90 MHz NMR data of XVI agree well with that previously reported [11]. ^{1}H NMR (200 MHZ) ($CDCl_3$, δ) 0.87 (3H, d, J 6.3 Hz, CH_3), 1.00–1.40 (20H, bs, C4–H_2 ~ C13–H_2), 1.57 (2H, m, C14–H_2), 2.00 (1H, m, C3–H), 2.13 (1H, dd, J 15.0, 8.0 Hz, C2–H), 2.37 (1H, dd, J 15.0, 5.0 Hz, C2–H), 2.35 (2H, t, J 6.0 Hz, C15–H_2).

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