# The Conjugate Addition of a Silyl Group to Enones and its Removal with Copper(II) Bromide: A Protecting Group for the αβ-Unsaturation of αβ-Unsaturated Ketones †

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Silyl-lithium reagents mixed with copper(I) salts react with enones, including esters and aldehydes, to give β-silyl carbonyl compounds in good yield. The β-silylketones can be used in synthesis without risk to the silyl group and the enone group can be restored by bromination-desilylbromination with copper(II) bromide. The principle is illustrated with syntheses of carvone and dihydrojasmone.

WE have described how a β-silyl carbonyl compound (2) can, by bromination and desilylbromination, be made to give enones (1), in which the C=C double bond is placed specifically between the α-carbon and the carbon to which the silicon was bound.[1] We have also reported, in a preliminary communication,[2] that β-silyl carbonyl compounds (2) can be made from enones (1) by conjugate addition of silylcopper reagents. Here we
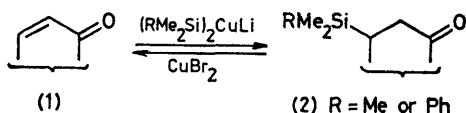
describe the experimental work and add a few more examples. In essence, the sequence provides a method of protecting the C=C double bond of enones with a base-stable group. Still has reported[3] that trimethylsilyl-lithium also undergoes conjugate addition to enones at

in some cases, but ββ-coupled products are also formed, and are often the major products.

Trimethylsilyl-lithium[5] and copper(I) iodide in the ratio 2 : 1 react with enones (Table 1) in reasonable

TABLE 1

Yield of β-trimethylsilylketones (2) from enones (1)

Starting material (1)	Yield of β-trimethylsilyl ketones (2) (%)
3-Methylcyclohex-2-enone	69
Cholest-4-en-3-one	65
Cyclohex-2-enone	64
Pent-3-en-2-one	60
Mesityl oxide	60

yield, but the trimethylsilyl-lithium is troublesome to make free of HMPA, as it has to be here. It cannot be made directly from chlorotrimethylsilane or hexamethyldisilane using lithium, and has to be prepared from bis(trimethylsilyl)mercury.[6] Dimethyl(phenyl)silyl-

TABLE 2

Yields of β-dimethyl(phenyl)silyl compounds (2) from enones (1) and of enones (1) regenerated from β-silylketones (2)

Starting material (1)	Yield of β-dimethyl(phenyl)silyl compound (2) (%)	Yield of enone (1) from reaction with CuBr₂ (%)	Yield of enone (1) from reaction with CuBr₂ and (PhCO₂) (%)
3-Methylcyclohex-2-enone	99 [a] (69—76) [b]	72 (64) [c]	74
5-Methylcyclohex-2-enone	97 (51)	70	66
Isophorone	68		
Cyclohexenone	65		
3-Methylcyclopent-2-enone	94 (62) [b]	66	68
Mesityl oxide	84	69 [d]	
Pent-3-en-2-one	85		
4-Phenylpent-3-en-2-one	68 (54) [b]	43 [d]	
Cholest-4-en-3-one	83		
Methyl vinyl ketone	42		
Ethyl crotonate	81		
Ethyl cinnamate	89		
Cinnamaldehyde	71		

[a] Optimized yield. [b] Yield using tertiary amine and only one equivalent of silicon for each equivalent of enone. [c] Yield using bromine, followed by sodium fluoride in aqueous methanol, in place of CuBr₂. [d] Overall yield after dehydrobromination of the β-bromoketone.
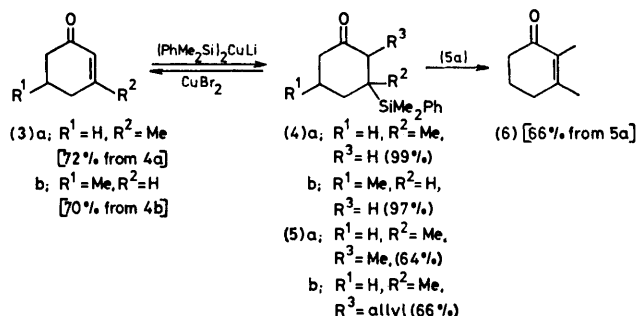
—78 °C in the presence of hexamethylphosphoramide (HMPA); our reagent, however, will add to hindered enones, such as isophorone, towards which his reagent is inert. Otherwise there appears to be little to choose between them. A third method for the introduction of a silyl group is by dissolving-metal reduction of enones in the presence of chlorotrimethylsilane.[4] This works well

† No reprints available.

lithium, however, can easily be made from the chloride or the disilane,[7] and we have used it consistently in all our later work. Again in a 2 : 1 ratio with copper(I) iodide, it adds to the β-position of enones (Table 2). Only one silyl group is transferred in this method, but both can be transferred, with some sacrifice in yield (based on enone), if one equivalent of a tertiary amine is added after ½ h at —23 °C (Table 2).

In several cases (Table 2, column 3) we regenerated the enone from the β-silyl ketones by bromination–desilylbromination. With cyclic ketones, copper(II) bromide in chloroform–ethyl acetate [8] was particularly effective, giving the enones directly in reasonable yield; open-chain ketones, in the same conditions, gave β-bromoketones, presumably as a result of the addition of hydrobromic acid to the first-formed enone. The β-bromoketones were easily converted into the enones with mild base. Copper(II) bromide is probably effective because it is a brominating agent, which can also equilibrate [9] the mixture of α-bromoketones, a step which is necessary if all the β-silylketone is to have a chance to undergo desilylbromination. That the double bond is restored specifically to its original site is proved by the sequences (3a ⟶ (4a) ⟶ (3a) and (3b) ⟶ (4b) ⟶ (3b), which took place without crossover.

In several cases, bromination with bromine followed by treatment with fluoride ion also gave quite good

(3)a; $R^1 =H$, $R^2= Me$
[72% from 4a]
b; $R^1 =Me$, $R^2=H$
[70% from 4b]

(4)a; $R^1 =H$, $R^2= Me$, $R^3= H$ (99%)
b; $R^1 =Me$, $R^2= H$, $R^3= H$ (97%)
(5)a; $R^1 =H$, $R^2= Me$, $R^3= Me$, (64%)
b; $R^1 =H$, $R^2= Me$, $R^3= allyl$ (66%)

(6) [66% from 5a]

yields of enones, even though equilibration of the intermediate bromides is not taking place. These appear to be further examples of a tendency we have noted before,[1] for the ketone to brominate selectively on the side where the silicon is, whatever the level of substitution on each side of the ketone. Another method which may have some advantages (see below), is to use a mixture of benzoyl peroxide and copper(II) bromide.[10] The yields are comparable in the cases we have tried (Table 2, column 4).

In principle, the β-silylketones can be used in synthesis in most of the ways that any ketone can be used, and the αβ-unsaturation can be restored at any stage. In practice, one of the most obvious ways of taking advantage of this possibility is to alkylate directly the enolate produced by the conjugate addition of the silyl group. Thus the enone (3a) can be converted into the methylated enone (6) regioselectively. Methylation and allylation were successful in several cases, but other simple primary alkyl iodides were too unreactive. In a longer sequence, we used this simple method to synthesise carvone (12) (Scheme 1) from the known[11] enone (7). In this sequence, we added benzoyl peroxide to the copper(II) bromide, and carried out the bromination–desilylbromination (10) ⟶ (11) in tetrahydrofuran (THF). This was necessary in order to avoid dehydration of the acid-sensitive tertiary alcohol group in (10). The stereo-

chemistry of the intermediate (8) was revealed by its [1]H n.m.r. spectrum. This stereochemistry is that expected for axial attack by the silylcopper reagent and trans-methylation by the methyl iodide, showing that the silylcopper reagent is similar in this respect to carbon–copper reagents.[12] It should be possible to reverse the order of the last two steps: we were able to add the

(7)
(8) R = O (92%)
(9) R = OCH_2CH_2O (95%)
(10) (88%)
(11) (72%)
(12) [93% from (11)]
[72% from (13)]
(13) (79%)
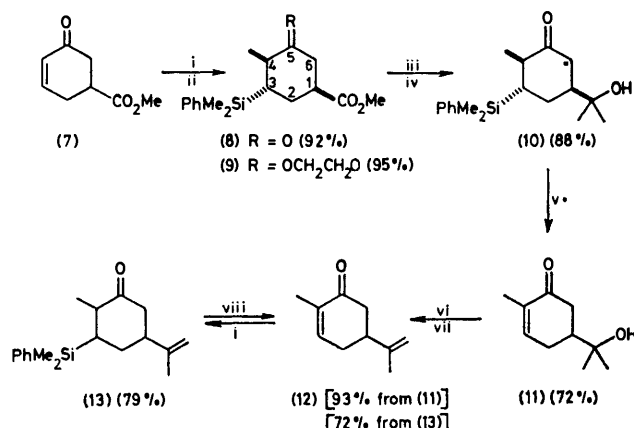
SCHEME 1 *Reagents:* i, $(PhMe_2Si)_2CuLi$; ii, MeI; iii, MeLi; iv, H_3O^+; v, $CuBr_2,(PhCO_2)_2$; vi, Ac_2O; vii, FVP; viii, $PhNMe_3Br_3$

silyl–copper reagent to carvone (12) ⟶ (13), and to return to carvone (13) ⟶ (12) by bromination with trimethyl(phenyl)ammonium tribromide. a reagent known[13] to brominate ketones without adding bromine to the double bond of an isopropenyl group. Indeed, we carried out this synthesis specifically in order to test the compatibility of the bromination–desilylbromination reaction with potentially troublesome functionality such as that found in alkenes like (13) and in tertiary alcohols like (11).

We also used this method for a synthesis of dihydro-jasmone (18) (Scheme 2). This synthesis differs from the great majority of syntheses of that much-synthesised compound[14] by starting with the readily available ketone

(14)
(15) (82%)
(16) (76%)
(17) (99%)
(18) [91% from (17)]
[42% from (16)]
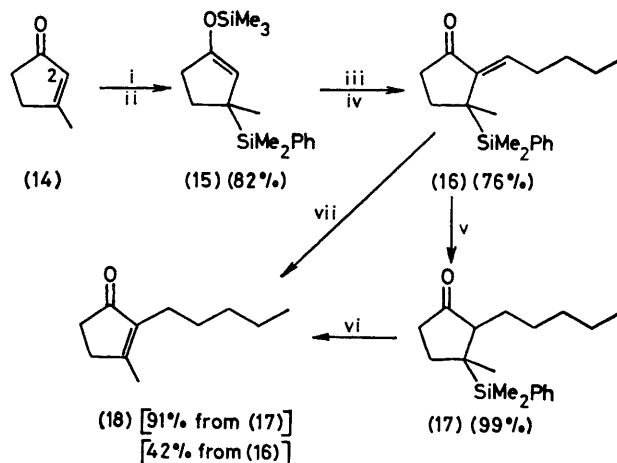
SCHEME 2 *Reagents:* i, $(PhMe_2Si)_2CuLi$; ii, Me_3SiCl, Et_3N; iii, Bu^nCHO, $TiCl_4$; iv, TsOH, C_6H_6; v, H_2, Pd, C; vi, $PhNMe_3Br_3$; vii, BF_3AcOH

(14). It therefore illustrates vividly how the conjugate addition of a silyl group makes an enone such as (14) into the synthetic equivalent of its 2-anion.[15]

The conjugate addition of a removable nucleophile, such as a dimethylamino- or ethylthio-group,[16] has been used before to protect the C=C double bond of an enone. Conjugate addition of a phenylthio-group can even be used to set off an aldol reaction at C-2 of an enone, in the sense (19) ⟶ (20) ⟶ (21); Nu = PhS, E⁺ = RCHO).[17] However, these nucleophiles are inherently
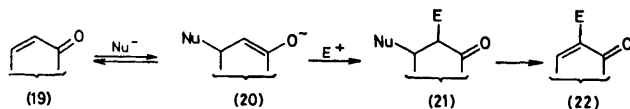
unstable towards base-catalysed elimination in the sense (20) ⟶ (19); although they can work in the sense (19) ⟶ (20) ⟶ (21) in favourable cases, only the silyl group can utterly be relied upon not to leave in the sense (20) ⟶ (19), and yet still be available for the final step (21) ⟶ (22).

EXPERIMENTAL

The Reaction of Trimethylsilyl-lithium and Copper(i) Iodide with Enones.—Copper(i) iodide (1.25 g, 6.56 mmol) was stirred, under argon, at −23 °C with a solution of silyl-lithium [5] in tetrahydrofuran (THF) for 5 min, the enone was added, and the mixture was kept at −23 °C for 1 h. It was then added to a mixture of concentrated hydrochloric acid (60 ml) and ice (150 g), and extracted with chloroform (150 ml, 2 × 50 ml). The extracts were filtered, washed with water (100 ml) and saturated sodium hydrogencarbonate solution (2 × 100 ml), dried (Na$_2$SO$_4$), evaporated *in vacuo* and distilled to give the products. 3-Methylcyclohexenone [18] (500 mg, 4.55 mmol) gave 3-*methyl-3-trimethylsilylcyclo-hexanone* (580 mg, 69%), b.p. 125 °C at 15 mmHg (bulb-to-bulb), $v_{max.}$ (CCl$_4$) 1 710 (C=O) and 1 250 cm⁻¹ (SiMe$_3$), δ (CCl$_4$) 2.2—0.9 (8 H, m, 4 × CH$_2$), 0.77 (3 H, s, CMe), and −0.15 (9 H, s, SiMe$_3$), m/z 184 (16%, M^+) and 169 (100, M-Me); semicarbazone, m.p. 196 °C (from EtOH) (Found: C, 54.9; H, 9.8; N, 17.5. C$_{11}$H$_{23}$N$_3$OSi requires C, 54.7; H, 9.6; N, 17.4%). Cholestenone (1.00 g, 2.60 mmol) gave 5-*trimethylsilylcholestan-3-one*, separated by column chromatography [silica gel, 125 g, 400 × 30 mm, eluting with 3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] (779 mg, 65%) as an oil, $v_{max.}$ (CCl$_4$) 1 710 cm⁻¹ (C=O), δ (CCl$_4$) 2.9—0.5 (43 H, m, steroidal overlaid with singlets at 1.00, 0.84, 0.77, and 0.60) and 0.00 (9 H, s, SiMe$_3$) (Found: M^+, 458.3951. C$_{30}$H$_{54}$OSi requires M, 458.3944), m/z 458 (10%) and 119 (100%). Cyclohexenone (450 mg, 4.69 mmol) gave 3-trimethylsilylcyclohexanone [19] (510 mg, 64%), b.p. 110 °C at 15 mmHg (bulb-to-bulb), $v_{max.}$ (CCl$_4$) 1 710 (C=O) and 1 250 cm⁻¹ (SiMe$_3$), δ (CCl$_4$) 2.3—0.8 (9 H, m, ring) and −0.15 (9 H, s, SiMe$_3$), m/z 170 (12%, M^+) and 155 (100, M − Me). Pent-3-en-2-one (500 mg, 5.9 mmol) gave 4-trimethylsilylpentan-2-one (564 mg, 60%), b.p. 66—68 °C at 15 mmHg, $v_{max.}$ (CCl$_4$) 1 720 (C=O) cm⁻¹, δ (CCl$_4$) 2.46 (2 H, dd, J 7.5 and 2 Hz, CH$_2$), 2.10 (3 H, s, MeCO), 1.38—1.00 (1 H, m, CHSiMe$_3$), and 0.00 (9 H, s, SiMe$_3$), m/z 158 (14%, M^+) and 143 (100, M − Me); semicarbazone, m.p. 183—184 °C (from EtOH) (Found: C, 50.4; H, 9.7; N, 19.8. C$_9$H$_{21}$N$_3$OSi requires C, 50.2; H, 9.8; N, 19.5%). Mesityl

oxide (500 mg, 5.10 mmol) gave 4-methyl-4-trimethyl-silylpentan-2-one [19] (526 mg, 60%), b.p. 65 °C at 15 mmHg (bulb-to-bulb), $v_{max.}$ (CCl$_4$) 1 720 (C=O) cm⁻¹, δ (CCl$_4$) 2.25 (2 H, s, CH$_2$), 2.03 (3 H, s, MeCO), 1.00 (6 H, s, CMe$_2$), and 0.00 (9 H, s, SiMe$_3$), m/z 172 (10%, M^+) and 157 (100, M − Me).

Dimethyl(phenyl)silyl-lithium.[7]—Dimethylphenylchloro-silane [20] (3.4 g, 2 mmol), lithium shot (*ca.* 100 mg, 14 mmol), and dry THF (35 ml) were stirred, under nitrogen, for *ca.* 18 h. The resulting red solution was titrated as described by Whitesides *et al.*,[21] and used without further purification.

Dimethyl(phenyl)silyl-lithium–Copper(i) *Iodide with Enones.*—Dimethyl(phenyl)silyl-lithium (THF solution, 1 mmol), was added to copper(i) iodide (95 mg, 0.5 mmol) at −23 °C under nitrogen and the mixture was stirred at this temperature for 4 h. The enone (0.75—0.5 mmol) was added, and the mixture was stirred at −23 °C for a further 0.5 h, poured onto a mixture of ice (25 g) and hydrochloric acid (5 ml) and extracted with chloroform (3 × 25 ml). The extracts were filtered, washed with 3M-hydrochloric acid (25 ml), water (25 ml), saturated sodium hydrogen-carbonate solution (25 ml), and water (25 ml), dried (Na$_2$SO$_4$), and evaporated *in vacuo* to give, after preparative thin layer chromatography (t.l.c.) [3 : 7 Et$_2$O–light petroleum (b.p. 60—80 °C)] the β-silylketone. The β-silylketones prepared by this method were: 3-*dimethyl(phenyl)silyl-3-methylcyclohexanone* (4a) (99%) as prisms, m.p. 66—67 °C (from EtOH) (Found: C, 72.9; H, 9.2. C$_{15}$H$_{22}$OSi requires C, 73.1; H, 9.0%), R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.4, $v_{max.}$ (CCl$_4$) 1 715 cm⁻¹ (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 2.5—1.4 (8 H, m, ring), 1.00 (3 H, s, CMe), and 0.39 (6 H, s, SiMe$_2$), m/z 246 (7%, M^+), 231 (100, M − Me) and 135 (79, PhMe$_2$Si$^+$); 3-*dimethyl(phenyl)-silyl-5-methylcyclohexanone* (4b) (97%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.45, $v_{max.}$ (CCl$_4$) 1 710 cm⁻¹ (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 2.6—1.4 (8 H, m, ring), 1.20 (3 H, d, J 7 Hz, CMe) and 0.36 (6 H, s, SiMe$_2$), m/z 246 (24%, M^+), 231 (29, M − Me), and 135 (100, PhMe$_2$Si$^+$), semicarbazone, m.p. 173 °C (from EtOH) (Found: C, 63.6; H, 8.3; N, 13.6. C$_{16}$H$_{25}$N$_3$OSi requires C, 63.3; H, 8.3; N, 13.9%); 3-*dimethyl(phenyl)silyl-3,5,5-trimethylcyclohexanone* (68%) as prisms, m.p. 60 °C (from EtOH) (Found: C, 73.6; H, 9.3. C$_{17}$H$_{26}$OSi requires C, 73.9; H, 9.5%), R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.4, $v_{max.}$ (CCl$_4$) 1 710 cm⁻¹ (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 2.5—1.3 (6 H, m, 3 × CH$_2$), 1.16, 1.10, and 1.05 (9 H, 3 singlets, 3 × CMe), and 0.38 (6 H, s, SiMe), m/z 274 (10%, M^+), 273 (10, M − H), 259 (100, M − Me), and 135 (60, PhMe$_2$Si$^+$); 3-*dimethyl(phenyl)silylcyclohexanone* (65%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.3, $v_{max.}$ (CCl$_4$) 1 710 cm⁻¹ (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 2.4—1.2 (9 H, m, ring), and 0.38 (6 H, s, SiMe$_2$), m/z 232 (19%, M^+) and 135 (100, PhMe$_2$Si), semi-carbazone, m.p. 179—180 °C (from EtOH) (Found: C, 62.2; H, 8.0; N, 14.3. C$_{15}$H$_{23}$N$_3$OSi requires C, 62.2; H, 8.0; N, 14.5%); 3-*dimethyl(phenyl)silyl-3-methylcyclopentanone* (94%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.45, $v_{max.}$ (CCl$_4$) 1 730 cm⁻¹ (C=O), δ (CCl$_4$) 7.7—7.3 (5 H, m, Ph), 2.5—1.5 (6 H, m, 3 × CH$_2$), 1.09 (3 H, s, Me), and 0.41 (6 H, s, SiMe$_2$), m/z 232 (13%, M^+), 217 (37, M − Me) and 135 (100, PhMe$_2$Si$^+$), semicarbazone, m.p. 204—205 °C (from EtOH) (Found: C, 62.5; H, 7.9; N, 14.6. C$_{15}$H$_{23}$OSi requires C, 62.2; H, 8.0; N, 14.5%); 4-*dimethyl(phenyl)silyl-4-methylpentan-2-one* (84%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.5,

$\nu_{max.}$ (CCl$_4$) 1 715 cm^{-1} (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 2.30 (2 H, s, CH$_2$), 2.04 (3 H, s, MeCO), 1.10 (6 H, s, CMe$_2$), and 0.39 (6 H, s, SiMe$_2$), m/z 234 (10%, M^+), 219 (100, M − Me) and 135 (94, PhMe$_2$Si$^+$), semicarbazone, m.p. 176—178 °C (from EtOH) (Found: C, 62.0; H, 8.5; N, 14.2. C$_{15}$H$_{25}$N$_3$OSi requires C, 61.8; H, 8.65; N, 14.4%); 4-*dimethyl(phenyl)silylpentan-2-one* (85%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.4, $\nu_{max.}$ (CCl$_4$) 1 720 cm^{-1} (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 2.5—2.2 (2 H, m, CH$_2$), 1.7—1.3 (1 H, m, CHSi), 1.01 (3 H, d, J 7 Hz, CMe), and 0.37 (6 H, s, SiMe$_2$), m/z 220 (7%, M^+), 205 (20, M − Me), and 135 (100, PhMe$_2$Si$^+$), semicarbazone, m.p. 155—156 °C (from EtOH) (Found: C, 60.5; H, 8.4; N, 15.0. C$_{14}$H$_{23}$N$_3$OSi requires C, 60.6; H, 8.4; N, 15.2%); 4-*dimethyl(phenyl)silyl-4-phenylpentan-2-one* (68%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.5, $\nu_{max.}$ (CCl$_4$) 1 710 (C=O) and 1 600 cm^{-1} (aromatic), δ (CCl$_4$) 7.6—7.0 (10 H, m, Ph), 3.30 (1 H, d, J 15 Hz, COCH$_A$-H$_B$), 3.59 (1 H, d, J 15 Hz, COCH$_A$H$_B$), 1.84 (3 H, s, MeCO), 1.55 (3 H, s, CMe), and 1.33 and 1.26 (6 H, 2s, SiMe$_2$), m/z 281 (36%, M − Me) and 135 (100, PhMe$_2$Si$^+$), semicarbazone, m.p. 184—185 °C (from EtOH) (Found: C, 67.5; H, 8.0. C$_{20}$H$_{27}$N$_3$OSi requires C, 67.9; H, 7.7%); 5-*dimethyl(phenyl)silylcholestan-3-one* (83%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.65, $\nu_{max.}$ (CCl$_4$) 1 710 cm^{-1} (C=O), δ (CCl$_4$) 7.7—7.2 (5 H, m, Ph), 3.0—0.6 (45 H, m, overlaid with singlets at 1.17, 1.00, 0.94, and 0.74, steroidal), and 0.40 (6 H, s, SiMe$_2$) (Found: M^+, 520.4092. C$_{35}$H$_{56}$OSi requires M, 520.4100), m/z 520 (50%) and 135 (100, PhMe$_2$Si$^+$); and 4-*dimethyl(phenyl)silyl-butan-2-one* (42%) as an oil, R_F [3 : 7 (v/v Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.4, $\nu_{max.}$ (CCl$_4$) 1 710 cm^{-1} (C=O), δ (CCl$_4$) 7.7—7.2 (5 H, m, Ph), 2.39 (2 H, t, J 8 Hz, CH$_2$CO), 2.10 (3 H, s, COMe), 1.04 (2 H, t, J 8 Hz, CH$_2$Si), and 0.34 (6 H, s, SiMe$_2$), m/z 191 (83%, M − Me) and 135 (100, PhMe$_2$Si$^+$), semicarbazone m.p. 117—119 °C (from EtOH) (Found: C, 57.4; H, 8.6; N, 16.7. C$_{12}$H$_{21}$N$_3$OSi requires C, 57.3; H, 8.35; N, 16.7%).

Dimethyl(phenyl)silyl-lithium–HMPA with Enones.—Dimethyl(phenyl)silyl-lithium (THF solution prepared as described above, 1 mmol) and HMPA (1 ml for every 4 ml THF) were cooled, under nitrogen, to −78 °C. The enone (0.9 mmol) was added and the mixture stirred for 0.5 h at −78 °C. Methanol (1 ml) was added, and the mixture diluted with light petroleum [b.p. 30—40 °C; 60 ml], washed with water (2 × 25 ml), dried (Na$_2$SO$_4$), evaporated *in vacuo* and the β-silylketone isolated by t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)]. β-Silylketones prepared by this method, which is essentially that of Still,[3] were 3-dimethyl(phenyl)silyl-3-methylcyclohexanone (81%), 3-dimethyl(phenyl)silyl-3-methylcyclopentanone (40%) and 5-dimethyl(phenyl)silylcholestan-3-one (12%), all identical with the samples prepared above (n.m.r., t.l.c., and i.r.). Isophorone did not discharge the colour of the anion and was recovered (*ca.* 90%) unchanged. These experiments were carried out to make sure that it was the copper and not the phenyl group which made our reactions work where Still's did not.

Dimethyl(phenyl)silyl-lithium–Copper(I) Iodide and Amines with Enones.—Dimethylphenylsilyl-lithium (THF solution prepared as described above, 1 mmol) was added to copper(I) iodide (95 mg, 0.5 mmol), at −23 °C, under nitrogen, and the mixture was stirred at this temperature for 4 h. The enone (1.05 mmol) was added and the mixture was stirred at −23 °C for 0.5 h. Triethylamine (0.5 ml, 4 mmol)

or tetramethylethylenediamine (TMEDA) was added. After a further 0.5 h, the reaction was worked up as described for the preparation without the amine. β-Silylketones prepared by this route were: 3-dimethyl(phenyl)silyl-3-methylcyclohexanone (76% using TMEDA; 69% using NEt$_3$), 3-dimethyl(phenyl)silyl-3-methylcyclopentanone (67%, using NEt$_3$), 3-dimethyl(phenyl)silyl-3,5,5-trimethylcyclohexanone (62%, using NEt$_3$), 3-dimethyl(phenyl)silyl-5-methylcyclohexanone (51%, using NEt$_3$) and 4-dimethyl-(phenyl)silyl-4-phenylpentan-2-one (54%, using NEt$_3$).

Dimethyl(phenyl)silyl-lithium–Copper(I) Iodide with αβ-Unsaturated Esters and Aldehydes.—Dimethyl(phenyl)silyl-lithium (THF solution prepared as described above, 1 mmol) was added to copper(I) iodide (95 mg, 0.5 mmol) at −23 °C, under nitrogen, and the mixture was stirred at this temperature for 4 h. The αβ-unsaturated compound (0.5 mmol) was added, the mixture stirred at −23 °C, for a further 0.75 h, and worked up in the usual way to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], the product. Compounds prepared by this method were: ethyl 3-*dimethyl(phenyl)silylbutanoate* (81%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.6, $\nu_{max.}$ (CCl$_4$) 1 730 cm^{-1} (C=O), δ (CCl$_4$) 7.6—7.3 (5 H, m, Ph), 4.10 (2 H, q, J 7 Hz, OCH$_2$), 2.6—1.9 (3 H, m, CH, and CH$_2$CO), 1.30 (3 H, t, J 7 Hz, OCH$_2$CH$_3$), 1.05 (3 H, d, J 7 Hz, SiCMe), and 0.36 (6 H, s, SiMe$_2$) (Found: M^+, 250.1385. C$_{14}$H$_{22}$O$_2$Si requires M, 250.1388), m/z 250 (11%), 235 (42, M − Me), and 135 (100, PhMe$_2$Si$^+$); ethyl 3-*dimethyl-(phenyl)silyl-3-phenylpropionate* (89%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.55, $\nu_{max.}$ (CCl$_4$) 1 730 (C=O) and 1 600 cm^{-1} (aromatic), δ (CCl$_4$) 7.6—7.0 (10 H, m, Ph), 4.01 (2 H, t, J 7 Hz, OCH$_2$), 3.1—2.6 (5 H, m, CH, and CH$_2$CO), 1.17 (3 H, t, J 7 Hz, OCH$_2$CH$_3$), and 0.40 and 0.36 (6 H, 2s, SiMe$_2$) (Found: M^+, 312.1533. C$_{19}$H$_{24}$O$_2$Si requires M, 312.1544), m/z 312 (11%) and 135 (100, PhMe$_2$Si$^+$); and 3-*dimethyl(phenyl)silyl-3-phenyl-propanal* (71%) as oil, R_F [3 : 7 (v/v Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.3, $\nu_{max.}$ (CCl$_4$) 2 720 (CHO), 1 720 (C=O), and 1 595 cm^{-1} (aromatic), δ (CCl$_4$) 9.42 (1 H, m, CHO), 7.5—6.8 (10 H, m, Ph), 2.9—2.5 (3 H, m, CH, and CH$_2$), and 0.23 and 0.21 (6 H, 2s, SiMe$_2$) (Found: M^+, 268.1291. C$_{17}$H$_{20}$OSi requires M, 268.1283), m/z 268 (6%), 267 (6, M − H), and 135 (100, PhMe$_2$Si$^+$).

Bromination of 3-Dimethyl(phenyl)silyl-3-Methylcyclohexanone.—Bromine (1.03 ml of a 0.969M solution in carbon tetrachloride, 1 mmol) was added over 5 min to a rapidly stirred solution of the ketone (246 mg, 1 mmol) in carbon tetrachloride (10 ml). After stirring for a further 5 min, the solution was diluted with carbon tetrachloride (40 ml), washed with water (25 ml), sodium thiosulphate solution (20 ml, 10%), saturated sodium hydrogencarbonate solution (25 ml), and water (25 ml), dried (MgSO$_4$), and evaporated *in vacuo* to give an orange oil, which was used without further purification.

Bromination Product of 3-Dimethyl(phenyl)silyl-3-methyl-cyclohexanone with Sodium Fluoride in Aqueous Methanol.—The β-silylketone (529 mg, 2.15 mmol) was brominated as described above. The resulting oil was kept with sodium fluoride (200 mg, 4.76 mmol) in a mixture of methanol (30 ml) and water (3 ml) for 14.5 h, and worked up in the usual way to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], 3-methylcyclohex-2-enone (155 mg, 64%), identical with an authentic sample (n.m.r. and t.l.c.), The brominated ketone also gave the enone after slow chromatography on silica gel using cyclohexane, and with caesium

fluoride in methanol at room temperature for 24 h. The yields were the same with each method.

Regeneration of Enones from β-Silylketones using Copper(II) Bromide in Ethyl Acetate–Chloroform.—The β-silylketone (1 mmol) in chloroform (3 ml) was added to a suspension of copper(II) bromide (447 mg, 2 mmol) in boiling ethyl acetate (3 ml). The mixture was heated under reflux, for 0.75 h, cooled, diluted with carbon tetrachloride (10 ml), and filtered, the precipitate being washed with carbon tetrachloride (3 × 7.5 ml). The filtrate was evaporated *in vacuo* to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], the enone. Enones regenerated by this method were: 3-methylcyclohexenone (3a) (72%), 3-methyl-cyclopentenone (66%), and 5-methylcyclohexenone (3b) (70%), while 4-dimethyl(phenyl)silyl-4-methylpentan-2-one gave 4-bromo-4-methylpentan-2-one (78%), ν$_{max.}$ (liquid film) 1 720 cm^{-1} (C=O), δ (CCl$_4$) 3.05 (2 H, s, CH$_2$), 2.17 (3 H, s, MeCO), and 1.85 (6 H, s, CMe$_2$), identical with an authentic sample prepared by the addition of hydrogen bromide to mesityl oxide in dry ether (n.m.r. and i.r.).

Mesityl Oxide from 4-Bromo-4-methylpentan-2-one.—The bromide (10 g, 56 mmol) and sodium hydrogencarbonate (6 g, 71 mmol) were heated under reflux in a 1 : 1 (v/v) mixture of ethanol and water (20 ml) for 18 g, and worked up in the usual way to give mesityl oxide (4.71 g, 88%), b.p. 125—130 °C, (lit.,^{22} 129.8 °C), identical with an authentic sample (n.m.r. and t.l.c.).

4-Phenylpent-3-en-2-one from 4-Dimethyl(phenyl)silyl-4-phenylpentan-2-one.—The β-silylketone (913 mg, 3.08 mmol) was treated with copper(II) bromide in ethyl acetate–chloroform as described above. The resulting oil was treated with sodium hydrogencarbonate (6 g, 71 mmol) in aqueous ethanol (20 ml, 1 : 1 v/v) also as described above to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], the enone (210 mg, 43%), identical with an authentic sample (n.m.r., i.r., and t.l.c.).

Regeneration of Enones from β-Silylketones using Copper(II) Bromide–Benzoyl Peroxide in THF.—The β-silyl-ketone (1 mmol), copper(II) bromide (223 mg, 1 mmol), and benzoyl peroxide (242 mg, 1 mmol) were stirred together in dry THF (5 ml) for 24 h and the mixture was worked up in the usual way to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], the enone. Enones regenerated by this method were: 3-methylcyclohexenone (74%), 3-methylcyclopentenone (68%), and 5-methylcyclohexenone (66%), all identical with authentic samples.

Dimethyl(phenyl)silyl-lithium–Copper(I) Iodide with Enones followed by Methyl Iodide–HMPA.—The enone (0.5 mmol) was treated with the silylcopper reagent as before and the mixture was stirred, at −23 °C for a further 0.75 h. Methyl iodide (0.12 ml) in HMPA (1 ml) was added and the mixture was kept at −23 °C for 2 h. Methanol (1 ml) was added and the mixture was worked-up in the usual way to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], the alkylated product. Compounds prepared by this method were: 2,3-*dimethyl-3-dimethyl(phenyl)silyl-cyclohexanone* (5a) (64%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], 0.4, ν$_{max.}$ (CCl$_4$) 1 710 cm^{-1} (C=O), δ (CCl$_4$) 7.6—7.2 (5 H, m, Ph), 2.45 (1 H, q, *J* 7 Hz, CHCO), 2.4—1.2 (6 H, m, 3 × CH$_2$), 0.94 (3 H, d, *J* 7 Hz, COCHCH_3), 0.92 (3 H, s, SiCCH$_3$), and 0.40 and 0.38 (6 H, 2s, SiMe$_2$), m/z 260 (9%, M^+), 245 (77, M — Me), and 135 (100, PhMe$_2$Si$^+$), semicarbazone, m.p. 202—202.5 °C (from EtOH) (Found: C, 64.6; H, 8.8; N, 13.3. C$_{17}$H$_{27}$N$_3$OSi requires C, 64.3; H, 8.6; N, 13.2%; 2,3-*dimethyl-3-*

dimethyl(phenyl)silylcyclopentanone (95%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.45, ν$_{max.}$ (CCl$_4$) 1 730 cm^{-1} (C=O), δ (CCl$_4$) 7.7—7.2 (5 H, m, Ph), 2.4—1.5 (5 H, m, CH and 2 × CH$_2$), 1.18 (3 H, d, *J* 8 Hz, COCH-CH_3), 0.98 (3 H, s, SiCMe), and 0.47 (6 H, s, SiMe$_2$) (Found: m/z, 245.1358. C$_{15}$H$_{21}$OSi$^+$ requires M^+ − H, 245.1361. Found: m/z, 231.1205. C$_{14}$H$_{19}$OSi$^+$ requires M − Me, 231.1204), m/z 245 (13%), 231 (42), and 135 (100, PhMe$_2$Si$^+$); and 3,4-*dimethyl-4-dimethyl(phenyl)silylpentan-2-one* (72%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.5, ν$_{max.}$ (CCl$_4$) 1 710 cm^{-1} (C=O), δ (CCl$_4$) 7.65—7.3 (5 H, in, Ph), 2.62 (1 H, q, *J* 7 Hz, COCH), 2.04 (3 H, s, COMe), 1.11 and 1.07 (6 H, 2s, CMe$_2$), 1.04 (3 H, d, *J* 7 Hz, COCH-CH_3) and 0.42 (6 H, s, SiMe$_2$) (Found: M^+, 248.1589. C$_{15}$H$_{24}$OSi requires M, 248.1596), m/z 248 (11%), 233 (51, M — Me), and 135 (100, PhMe$_2$Si$^+$).

Dimethyl(phenyl)silyl-lithium–Copper(I) Iodide with Enones followed by Allyl Bromide–HMPA.—The experiments were carried out as described above for alkylating with methyl iodide–HMPA except that allyl bromide was substituted for methyl iodide. Compounds prepared by this method were: 3-*dimethyl(phenyl)silyl-2-allyl-3-methyl-cyclohexanone* (5b) (66%) as an oil, R_F [3 : 3 (v/v Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.45, ν$_{max.}$ (CCl$_4$) 1 710 (C=O) and 1 640 cm^{-1} (C=C), δ (CCl$_4$) 7.5—7.2 (5 H, m, Ph), 5.9—5.4 (1 H, m, CH=C), 5.0—4.7 (2 H, m, C=CH$_2$), 2.6—1.2 (9 H, m, CH and 8 × CH$_2$), 0.91 (3 H, s, CMe), and 0.40 (6 H, s, SiMe$_2$), m/z (286 (7%, M^+), 245 (100, M − CH$_2$CH= CH$_2$), and 135 (85, PhMe$_2$Si$^+$), semicarbazone, m.p. 208—209 °C (Found: C, 66.7; H, 8.5; N, 12.3. C$_{19}$H$_{29}$N$_3$OSi requires C, 66.4; H, 8.5; N, 12.2%); and 3-*dimethyl-(phenyl)silyl-2-allyl-3-methylcyclopentanone* (54%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.5, ν$_{max.}$ (CCl$_4$) 1 730 (C=O) and 1 640 cm^{-1} (C=C), δ (CCl$_4$) 7.6—7.2 (5 H, m, Ph), 6.2—5.8 (1 H, m, CH=C), 5.1—4.8 (2 H, m, C=CH$_2$), 2.2—1.4 (7 H, m, CH and 3 × CH$_2$), 0.92 (3 H, s, CMe), and 0.39 (6 H, s, SiMe$_2$) (Found: M − 1, 271.1511. C$_{17}$H$_{23}$OSi requires M − 1, 271.1518), m/z 271 (10%), 231 (100, M − CH$_2$CH=CH$_2$), and 135 (100, PhMe$_2$Si$^+$).

2,3-*Dimethylcyclohexenone* (6) *from 2,3-Dimethyl-3-di-methyl(phenyl)silylcyclohexanone.*—The β-silylketone (4) (285 mg, 1.09 mmol) was treated with copper(II) bromide (491 mg, 2.20 mmol) in ethyl acetate–chloroform as described above, to give, after t.l.c. [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)], the enone (88 mg, 66%) as an oil, R_F [3 : 7 (v/v) Et$_2$O–light petroleum (b.p. 60—80 °C)] 0.1, ν$_{max.}$ (CCl$_4$) 1 675 (C=O) and 1 640 cm^{-1} (C=C), δ (CCl$_4$) 2.8—1.7 (12 H, m overlaid with singlets at 1.90 and 1.70, 3 × CH$_2$ and 2 × CH$_3$), semicarbazone, m.p. 223—224 °C (from EtOH) (lit.,^{23} 225 °C).

Methyl 5-Oxocyclohex-3-enecarboxylate (7).—5-Oxocyclo-hex-3-enecarboxylic acid ^{11} was esterified by the method of Ireland.^{24} The acid (3.36 g, 24 mmol), anhydrous potassium carbonate (6.6 g), and methyl iodide (20 ml) were refluxed in dry acetone (50 ml) under nitrogen for 5 h. Every 1.5 h, further methyl iodide (5 ml) was added. Aqueous work-up gave the ester (7) (3.56 g, 97%), b.p. 78—79 °C at 0.1 mmHg (lit.,^{11} 134—137 °C at 2 mmHg).

Methyl 3-Dimethylphenylsilyl-4-methyl-5-oxocyclohexane-carboxylate (8).—Dimethylphenylsilyl-lithium (84.6 ml; 0.52M-solution in THF) was added dropwise to a suspension of copper(I) iodide (4.18 g, 22 mmol) in dry THF (10 ml) under argon at −23 °C and the mixture was stirred for 4 h. The enone (7) (3.08 g, 20 mmol) in dry THF (10 ml) was

added dropwise over 15 min and the mixture was kept at −23 °C for 45 min. Methyl iodide (10 ml) in HMPA (5 ml) was added at −23 °C and the mixture was then allowed to come to room temperature over 3 h. The mixture was diluted with pentane (100 ml), washed with saturated ammonium chloride solution (50 ml, pH 8) and water (25 ml), dried (MgSO$_4$), and evaporated in vacuo. Column chromatography [SiO$_2$; ether–light petroleum (b.p. 30—40 °C), 15 : 85 v/v] gave the ester (8) (5.6 g, 92%), ν$_{max.}$ (film) 1 738 (CO$_2$Me), 1 718 (CO), and 1 250 cm^{-1} (SiMe$_2$) (Found: M^+, 304.1492. C$_{17}$H$_{24}$O$_3$Si requires M, 304.1493) m/z 304 (1%, M^+), 289 (M − Me), and 135 (100, PhMe$_2$Si). The 400 MHz ^{1}H n.m.r. spectrum (CDCl$_3$) gave well separated signals for all the hydrogens on the cyclohexane ring; making only the assumptions that the phenyldimethylsilyl group is equatorial and that the ring is in a chair conformation, the assignments are definitive of the stereochemistry shown: δ 7.48 (2 H, m, ArH), 7.36 (3 H, m, ArH), 3.69 (3 H, s, OMe), 3.28 (1 H, tt, J 5.7 and 4.9 Hz, H-1), 2.92 (1 H, ddd, J 14.5, 4.9, and 1.7 Hz, equatorial H-6), 2.57 (1 H, ddd, J 14.5, 5.7, and 1.1 Hz, axial H-6), 2.48 (1 H, ddq, 10.5, 1.1, and 6.9 Hz, H-4), 2.34 (1 H, dddd, J 14.3, 5.7, 4.0, and 1.7 Hz, equatorial H-2), 2.07 (1 H, ddd, 14.3, 11.4, and 4.9 Hz, axial H-2), 1.51 (1 H, ddd, J 11.4, 10.5, and 4.0 Hz, H-3), 1.25 (3 H, d, J 6.9 Hz, CHMe), and 0.35 (6 H, s, SiMe$_2$).

Methyl 5,5-Ethylenedioxy-4-methyl-3-dimethylphenylsilyl-cyclohexanecarboxylate (9).—Ethylene glycol (10 ml), trimethoxymethane (15 ml), and toluene-p-sulphonic acid (60 mg) were refluxed for 30 min. The ester (8) (4.56 g, 15 mmol) in trimethoxymethane (5 ml) was added and the mixture was refluxed for 2 h, poured into saturated sodium hydrogencarbonate solution (10 ml), extracted with ether (3 × 50 ml), dried (MgSO$_4$), and evaporated in vacuo. Column chromatography (SiO$_2$; ether–cyclohexane, 1 : 1 v/v) gave the acetal (9) (4.96 g, 95%), ν$_{max.}$ (film) 1 740 (CO$_2$Me) and 1 250 cm^{-1} (SiMe$_2$), δ (CDCl$_3$) 7.52 (5 H, m, Ph), 3.91 (4 H, m, OCH$_2$CH$_2$O), 3.72 (3 H, s, OMe), 2.85—1.1 (7 H, m, other CHs), 0.89 (3 H, d, J 6 Hz, CHMe), and 0.39 (6 H, s, SiMe$_2$) (Found: M^+, 348.1760. C$_{19}$H$_{28}$O$_4$Si requires M, 348.1764).

2-(3-Dimethylphenylsilyl-5,5-ethylenedioxy-4-methylcyclohexyl)propan-2-ol.—Methyl-lithium (17.8 ml; 1.4M-solution in ether) was added dropwise to a solution of the acetal (9) (3.48 g, 10 mmol) in dry ether (15 ml) under nitrogen at −78 °C. The mixture was stirred for 2 h at −78 °C, allowed to come to room temperature over 5 h, poured into saturated ammonium chloride solution (10 ml; pH 8), extracted with ether (3 × 50 ml), dried (MgSO$_4$), and evaporated in vacuo. Column chromatography (SiO$_2$; ether–cyclohexane, 1 : 1 v/v) gave the alcohol (3.41 g, 98%), ν$_{max.}$ (film) 3 475br (OH) and 1 250 cm^{-1} (SiMe$_2$), δ (CDCl$_3$) 7.51 (5 H, m, Ph), 3.91, (4 H, m, OCH$_2$CH$_2$O), 1.52—2.05 (7 H, other CHs), 1.21 (3 H, s, MeCOHMe), 1.19 (3 H, s, MeCOHMe), 1.05 (3 H, d, J 7.5 Hz, CHMe), and 0.40 (6 H, s, SiMe$_2$) (Found: M^+, 348.2122. C$_{20}$H$_{32}$O$_3$Si requires M, 348.2120).

2-[3-(Dimethylphenylsilyl)-4-methyl-5-oxocyclohexyl]-propan-2-ol (10).—Oxalic acid (0.9 ml; 10% solution) was added to silica gel (9 g, 70—230 mesh) in dichloromethane (12 ml). After 4 min, the acetal (2.78 g, 8 mmol) in dichloromethane (5 ml) was added and the mixture was stirred for 4 h at room temperature. Sodium carbonate solution was added and the mixture was stirred for 15 min. The solid phase was washed with ether (150 ml) and the

filtrate was evaporated in vacuo to give the pure ketone (10) (2.18 g, 90%), ν$_{max.}$ (film) 3 450 (OH), 1 705 (CO), and 1 250 cm^{-1} (SiMe$_2$), δ (CDCl$_3$) 7.52 (5 H, m, Ph), 2.45 (2 H, m, COCH$_2$), 1.88 (3 H, m, 2 × CH and OH), 1.25 (3 H, m, 3 × CH), 1.2 (6 H, s, CMe$_2$), 1.19 (3 H, d, J 7 Hz, CHMe), and 0.43 (6 H, s, SiMe$_2$) (Found: m/z 286.1757. C$_{18}$H$_{26}$O$_2$Si requires M − H$_2$O, 286.1759), m/z 304 (3%, M^+), 286 (8, M − H$_2$O), 271 (9, M − H$_2$O − Me), and 135 (100, PhMe$_2$Si).

2-(4-Methyl-3-oxocyclohex-4-enyl)propan-2-ol (11).—Copper(ii) bromide (1.12 g, 5 mmol), benzoyl peroxide (1.21 g, 5 mmol), and the ketone (10) (1.52 g, 5 mmol) were stirred in dry THF (20 ml) for 24 h, the mixture was diluted with ether and filtered through Celite, and the filtrate was evaporated in vacuo. Column chromatography (SiO$_2$, ether) gave the enone (11) (0.605 g, 72%), ν$_{max.}$ (film) 3 450 (OH) and 1 662 cm^{-1} (C=O), δ (CDCl$_3$) 6.76 (1 H, m, C=CH), 3.44 (2 H, m, =CHCH$_2$), 2.79—1.82 (4 H, m, other CHs and OH), 1.75 (3 H, d, J 2 Hz, MeC=CH), and 1.21 (6 H, s, CMe_2OH) (Found: m/z 150.1044. C$_{10}$H$_{16}$O$_2$ requires M − H$_2$O, 150.1044), m/z 150 (20%, M − H$_2$O), 135 (4, M − H$_2$O − Me), and 59 (100).

1-Methyl-1-(4-methyl-3-oxocyclohex-4-enyl)ethyl Acetate.—Acetic anhydride (3 ml) and the ketone (11) (0.504 g, 3 mmol) were refluxed for 24 h. The excess of anhydride was evaporated off in vacuo and the residue was chromatographed (SiO$_2$, ether) to give the acetate (0.60 g, 95%), ν$_{max.}$ (film) 1 725 (OAc), 1 675 cm^{-1} (CO), δ (CDCl$_3$) 6.64 (1 H, m, C=CH), 2.62—2.0 (5 H, other CHs), 1.95 (3 H, s, OAc), 1.70 (3 H, d, J 2 Hz, MeC=CH), and 1.48 (6 H, s, CMe$_2$) (Found: m/z, 150.1041. C$_{12}$H$_{18}$O$_3$ requires M − AcOH, 150.1045), m/z 150 (100%, M − AcOH), 135 (20, M − AcOH − Me), and 109 (40, M − AcOH − C$_3$H$_5$).

(±)-Carvone (12).—*Method A.* The above acetate (0.21 g, 1 mmol) was passed at 10^{-3} mmHg through a flash-flow pyrolysis apparatus (glass tube, 20 mm diam., 300 mm long, helices) heated to 550 °C. The product was collected in a trap cooled by liquid nitrogen, and purified by t.l.c. (SiO$_2$, ether) to give carvone (0.147 g, 98%), identical (^{1}H n.m.r., i.r., t.l.c., and g.l.c.) with an authentic sample.

Method B. Trimethyl(phenyl)ammonium tribromide (0.376 g, 1 mmol) was added to a stirred solution of the ketone (13) (see below) (0.286 g, 1 mmol) in dry THF (5 ml) under nitrogen at 0 °C. After 5 min, the mixture was filtered through Celite (2 g) the precipitate was washed with ether (4 × 10 ml), and the filtrate was evaporated in vacuo. Chromatography [SiO$_2$, ether–light petroleum (b.p. 30—40 °C), 1 : 4 v/v] gave carvone (0.108 g, 72%), identical (^{1}H n.m.r., i.r., t.l.c., and g.l.c.) with authentic material.

3-Dimethylphenylsilyl-5-isopropenyl-2-methylcyclohex-anone (13).—Dimethylphenylsilyl-lithium (32.8 ml; 0.67M-solution in THF) was added to a stirred suspension of copper(i) cyanide (0.985 g, 11 mmol) in dry THF (5 ml) under nitrogen at 0 °C. After 20 min, the mixture was cooled to −23 °C and carvone (1.50 g, 10 mmol) in dry THF (5 ml) was added dropwise over 10 min. After 45 min, the solution was warmed to 0 °C and worked up in the usual way, chromatographing [SiO$_2$, ether–light petroleum (b.p. 30—40 °C), 3 : 7 v/v] to give the ketone (13) (2.26 g, 79%) as a mixture of diastereoisomers, ν$_{max.}$ (film) 1 710 (CO), 1 640 (C=C), and 1 250 (SiMe$_2$), δ (CDCl$_3$) 7.29 (5 H, m, Ph), 4.81—4.64 (2 H, m, C=CH$_2$), 2.62—0.83 (7 H, m, 7 × CH), 1.56 (3 H, s, MeC=), 1.50 (3 H, s, MeC=, other diastereoisomer), 1.03 (3 H, d, J 7 Hz, Ac), 1.0 (3 H, d, J 7 Hz, Ac, other diastereoisomer), and 0.42 (6 H, s, SiMe$_2$) (Found: M^+,

286.1755. $C_{18}H_{26}OSi$ requires M, 286.1753), m/z 286 (3%, M^+), 271 (7, M — Me), and 135 (100, $PhMe_2Si$).

3-(*Dimethylphenylsilyl*)-3-*methyl*-1-*trimethylsilyloxycyclopentene* (15).—Dimethylphenylsilyl-lithium (92 ml; 0.72M-solution in THF) was added dropwise to a stirred suspension of copper(I) cyanide (2.95 g, 33 mmol) in dry THF (5 ml) under nitrogen at 0 °C. After 20 min, the red solution was cooled to —23 °C, and 3-methylcyclopent-2-enone (14) (2.88 g, 30 mmol) in dry THF (15 ml) was added dropwise over 15 min. The solution was stirred for 45 min and then allowed to come to 0 °C over 2 h. Triethylamine (12.6 ml, 90 mmol) and chlorotrimethylsilane (11.4 ml, 90 mmol) were added in succession and the resulting mixture stirred for 3 h at room temperature. The mixture was poured into saturated ammonium chloride solution (50 ml, pH 8) and extracted with ether (3 × 75 ml), and the ether was dried ($MgSO_4$) and evaporated *in vacuo*. The residue was distilled to give the *silyl enol ether* (15) (7.48 g, 82%), b.p. 110 °C at 0.01 mmHg, $v_{max.}$ (film) 1 618 (C=C) and 1 250 cm^{-1} (SiMe), δ (CCl_4) 7.55 (5 H, m, Ph), 4.62 (1 H, s, HC=C), 2.25 (2 H, m, CH_2C=C), 1.92—1.22 (2 H, m, CH_2), 1.23 (3 H, s, CMe), 0.50 (6 H, s, $SiMe_2$), and 0.25 (9 H, s, $SiMe_3$) (Found: M^+, 304.1685. $C_{17}H_{28}OSi_2$ requires M, 304.1691), m/z 304 (3%, M^+), 289 (3, M — Me), 231 (7, M — $SiMe_3$), 169 (100, M — $SiMe_2Ph$).

3-(*Dimethylphenylsilyl*)-3-*methyl*-2-*pentylidenecyclopentanone* (16).—n-Pentanal (0.947 g, 11 mmol) and the silyl enol ether (15) (3.04 g, 10 mmol) in dry dichloromethane (10 ml) were added over 15 min to a stirred solution of titanium tetrachloride (1.1 ml, 10 mmol) in dry dichloromethane (15 ml) under nitrogen at —78 °C. After 2 h at —78 °C, the mixture was poured into saturated sodium hydrogencarbonate solution (10 ml), extracted with dichloromethane (3 × 50 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give the β-hydroxyketone as an oil. Toluene-*p*-sulphonic acid (50 mg) and the β-hydroxyketone were refluxed in dry benzene (50 ml) using a Dean–Stark head for 5 h. The benzene was evaporated off and the residue was chromatographed [SiO_2, ether–light petroleum (b.p. 30—40 °C), 5 : 95 v/v] to give a mixture of the *E*- and *Z*-*enones* (16) (2.28 g, 76%), $v_{max.}$ (film) 1 742 and 1 720 (C=O), 1 640 (C=C), and 1 250 cm^{-1} (SiMe$_2$), δ (CCl_4) 7.06 (5 H, m, Ph), 6.15 (1 H, t, J 8 Hz, *Z*-C=CH), 5.16 (1 H, t, J 8 Hz, *E*-C=CH), 1.16 (3 H, s, CMe), 1.50—2.10 (13 H, m, 13 × CH), and 0.10 (6 H, s, SiMe$_2$) (Found: M^+, 300.1909. $C_{19}H_{28}OSi$ requires M, 300.1902), m/z 300 (4%, M^+,) 185 (6, M — Me), and 135 (100, Me$_2$PhSi). This method is essentially that of Mukaiyama and his co-workers [25] and in this instance proved easier than our own method using phenylthioalkylation.[26]

3-(*Dimethylphenylsilyl*)-3-*methyl*-2-*pentylcyclopentanone* (17).—The enone (16) (1.5 g, 5 mmol) in ether (20 ml) was hydrogenated over palladium–charcoal (0.15 g, 10%), the solution was filtered through Celite, and the filtrate was evaporated *in vacuo* to give the *ketone* (17) (1.5 g, 99%) as a pale yellow oil, $v_{max.}$ (film) 1 740 (CO) and 1 252 cm^{-1} (SiMe$_2$), δ (CCl_4) 7.5 (5 H, m, Ph), 2.5—0.9 (19 H, m, 19 × CH), and 0.51 (6 H, s, Me$_2$Si) (Found: M^+, 302.2059. $C_{19}H_{30}OSi$ requires M, 302.2052), m/z 302 (3%, M^+), 187 (7, M — Me), and 135 (100, PhMe$_2$Si).

Dihydrojasmone (18).—*Method A*. Trimethylphenylammonium tribromide (0.376 g, 1 mmol) was added over 2 min to a stirred solution of the ketone (17) (0.302 g, 1

mmol) in dry THF (10 ml) at 0 °C. The solution was stirred for 3 min, diluted with ether (20 ml), filtered through Celite (5 g), and the filtrate was evaporated *in vacuo*. Chromatography [SiO_2, ether–light petroleum (b.p. 30—40 °C) 15 : 85 v/v] gave dihydrojasmone (18) (0.15 g, 91%), identical with an authentic sample (^{1}H n.m.r., i.r., and t.l.c.).

Method B. Boron trichloride–acetic acid (0.85 g, 0.5 mmol) and the enone (16) (0.15 g, 0.5 mmol) were refluxed in carbon tetrafluoride (3 ml) for 1 h under nitrogen. Aqueous work-up and chromatography (as in method A) gave dihydrojasmone (0.035 g, 42%), identical (^{1}H n.m.r., i.r., t.l.c., and g.l.c.) with an authentic sample.

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