Friedel–Crafts Reactions of Some Vinylsilanes †

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Substituted cyclohexenylsilanes (2), (5), (9), and (13) undergo Friedel–Crafts reactions to give *substitution* products, *site-selectively* at the carbon atom carrying the trimethylsilyl group. β-Trimethylsilylstyrene (17) similarly gives more substitution in Friedel–Crafts reactions with benzoyl chloride and with phenylacetyl chloride than styrene itself. The syntheses of the silanes are reported, and some limitations of the idea identified.

A TRIMETHYLSILYL group is known to be readily replaced in aromatic electrophilic substitution reactions.[1,2] Electrophilic attack takes place, other things being equal, on the carbon atom carrying the silyl group, because the *ipso*-intermediate so produced is stabilised by hyper-conjugative overlap of the orbitals of the carbon–silicon

electrophilic substitution predominantly at the 1-position.[8]

In our preliminary communication,[9] we described the extension of this idea to electrophilic attack using carbon electrophiles on vinylsilanes, and showed that, again, other things being equal, the attack took place on the
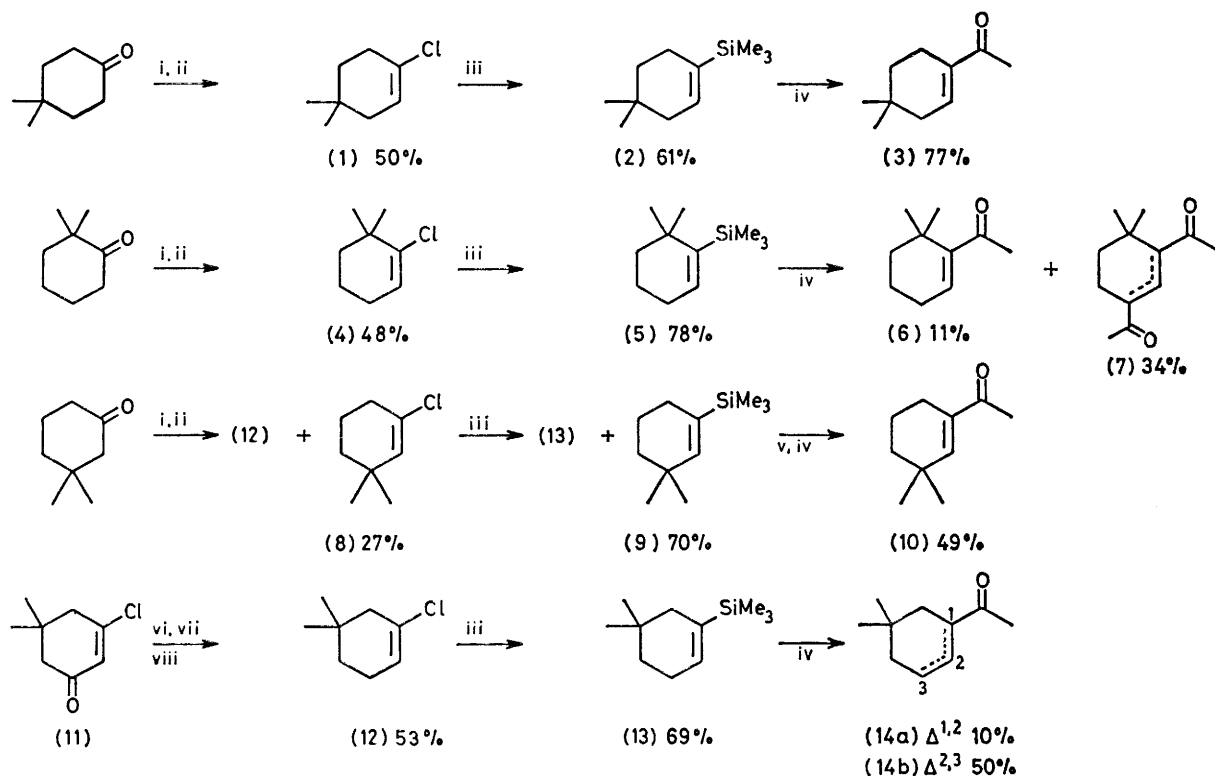
SCHEME 1 *Reagents:* i, PCl₅; ii, NaOEt; iii, Na, Me₃SiCl; iv, AcCl, AlCl₃; v, separate (9) from (13); vi, Al(OPrⁱ)₃, PrⁱOH; vii, Ph₃PCl₂, viii, LiAlH₄

bond and the π-orbitals of the cyclohexadienyl cation system.[3] This site-selectivity has been used to encourage *ortho-* and *para*-substitution to *meta*-directing groups[4,5] and *meta*-substitution to mildly *ortho/para*-directing groups like methyl[6] and acetamido.[5] A more powerfully *ortho/para*-directing group like methoxy, however, was more effective in directing the electrophile *ortho* and *para* to it than a *meta*-silyl group was in directing attack *ipso* to itself.[7] 1-Trimethylsilylbenzocyclobutane, unlike benzocyclobutane itself, undergoes

† There are no reprints of this paper.

carbon atom bearing the silyl group. Furthermore, because trimethylsilyl groups are usually more easily displaced from carbon than are protons,[10] the outcome in the aliphatic series was more often *substitution* than *addition*. Other work, before our preliminary publication, had shown that the vinylsilane (17) underwent electrophilic substitution by hydrogen and halogen electrophiles with retention of configuration,[11] and that Friedel–Crafts reactions were possible with bistrimethylsilylethylene.[12] Since our publication, other work has confirmed that vinylsilanes generally react site-selectively

with a variety of electrophiles [13] and that the reactions are usually stereospecific; retention of configuration is normal, but in a few cases, such as bromination with bromine, inversion of configuration takes place. We record here the experimental details of our work.

The vinylsilanes (2), (5), (9), and (13) were prepared by the routes shown in Scheme 1. Under Friedel–Crafts conditions, the products were the ketones (3), (6), (10),

sent. In the vinylsilane (23), however, the directing effect of the aromatic ring and that of the silyl group are in opposition: the former prevails, as shown by the isolation of the addition product (24a) from reaction with acetyl chloride and aluminium chloride. The structure of this product was confirmed by conversion (24a) ⟶ (24b) ⟶ (25a) ⟶ (25b) into a known compound, in better overall yield, incidentally, than by the direct
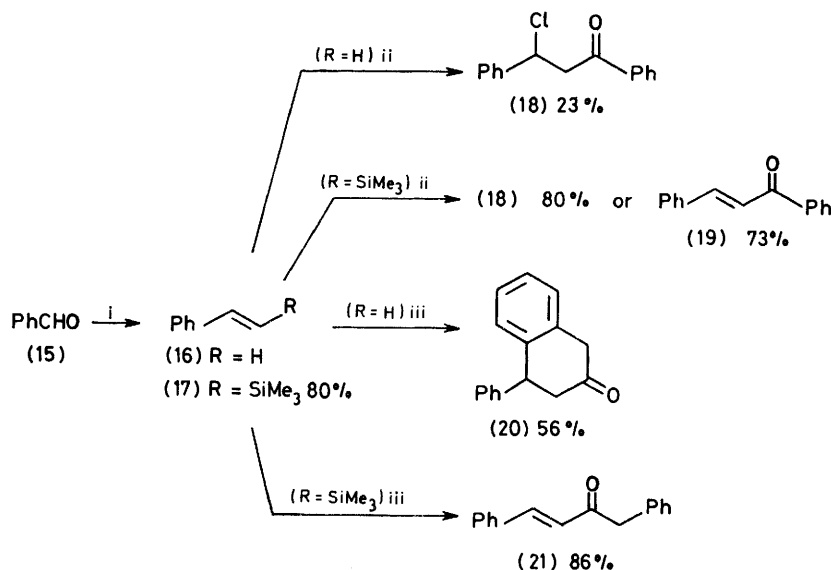
SCHEME 2 *Reagents:* i, Me$_3$SiCH$_2$SiMe$_3$, BuLi, TMEDA; ii, PhCOCl, AlCl$_3$; iii, PhCH$_2$COCl, AlCl$_3$

and (14), respectively. In the case of the hindered silane (5), the yield was poor (11%) and a major by-product (34%) appeared to be the result of further acylation; it was tentatively assigned the structure (7).

Aliphatic Friedel–Crafts reactions often lead to addition rather than substitution. Thus (Scheme 2) we find that styrene (16), aluminium chloride, and benzoyl chloride gave the addition product (18) in 23% yield together with intractable material, and styrene and phenylacetyl chloride under the same conditions gave the cyclic ketone (20) in 56% yield. *trans*-β-Trimethylsilylstyrene (17), on the other hand, gave a 1 : 1 mixture of addition and substitution products (18) and (19) with benzoyl chloride under the same conditions, and, by a suitable choice of work-up procedure, either product could be made the major product. Similarly, the same vinylsilane (17) reacted with aluminium chloride and phenylacetyl chloride to give the simple substitution product (21) in 86% yield. Plainly, the presence of the trimethylsilyl group has encouraged simple substitution and, incidentally, given better yields.

In the case of the vinylsilane (17), the trimethylsilyl group is already on the carbon atom most likely to be the preferred site of attack, and in the vinylsilanes in Scheme 1, the silyl group is effective in controlling the site of attack, because there would not be much bias, except perhaps in the cases (5) and (9), for attack on either carbon atom of the double bond, if the silyl group were not pre-

Friedel–Crafts reaction of acetyl chloride on 1,2-dihydronaphthalene.

We also investigated the possibility that Eschenmoser's electrophile (26) would behave in the same way with
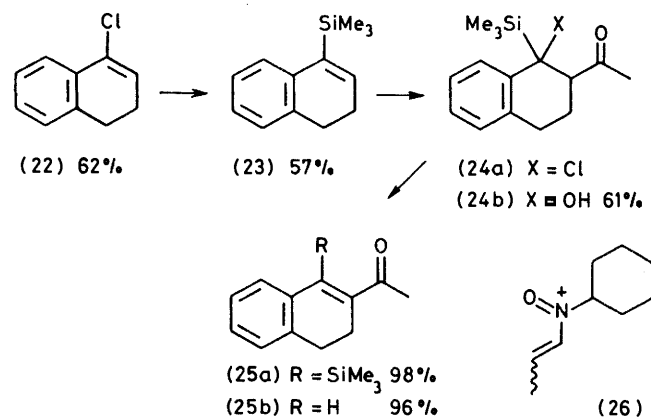
some of our vinylsilanes. It did not do so. Cyclohex-1-enyltrimethylsilane gave no more substitution product than cyclohexene itself, and silicon-containing addition products were isolated. In spite of efforts to keep water out of the reaction mixture, we also isolated the same silicon-free addition products that Eschenmoser and his co-workers got from cyclohexene itself.[14],*

* We thank Dr D. Hall for helpful discussions during this part of our work.

EXPERIMENTAL

Preparation of the Cyclohexenyl Chlorides (1), (4), (8), (12), *and* (22).—We modified the method of Braude and Coles.[15] The crude mixture of *gem*-dichloride and vinyl chloride obtained after treatment of the ketone with phosphorus pentachloride and subsequent work-up (5.6 g) was heated under reflux for 19 h with a solution of sodium (1.7 g) in absolute ethanol (100 ml), cooled, poured into dilute sulphuric acid solution (20 ml) and extracted with ether (3 × 50 ml). The combined organic extracts were washed successively with sodium hydrogencarbonate solution (50 ml, saturated), water (3 × 50 ml), and sodium chloride solution (50 ml, saturated), and then dried (Na_2SO_4), evaporated *in vacuo* and distilled under reduced pressure to give: 1-chloro-4,4-dimethylcyclohexene (1) (50% based on 4,4-dimethylcyclohexanone [16]), b.p. 54—56 °C/11 mmHg; 1-chloro-6,6-dimethylcyclohexene (4) (48% from 2,2-dimethylcyclohexanone [17]), b.p. 56—59 °C/11 mmHg; 1-chloro-3,3-dimethylcyclohexene (8) and 1-chloro-5,5-dimethylcyclohexene (12) as a 1 : 1 mixture, 27% from 3,3-dimethylcyclohexanone, which was prepared by hydrogenation of (11) over 5% palladium on charcoal b.p. 54—58 °C/11 mmHg; and 1-chloro-3,4-dihydronaphthalene (22) (62% from α-tetralone), b.p. 57—58 °C/0.08 mmHg.

1-Chloro-3-hydroxy-5,5-dimethylcyclohexene.—A mixture of 3-chloro-5,5-dimethylcyclohexenone (11) [18] (39.6 g), aluminium isopropoxide (102 g), and isopropyl alcohol (1 000 ml, distilled from calcium hydride) was distilled under nitrogen up a 25-cm column of glass helices so that the distillate was collected at the rate of 4 drops min⁻¹. After 22 h, when *ca.* 100 ml of distillate (b.p. 65—67 °C) had collected, the remainder of the isopropyl alcohol was distilled off. Aqueous work-up and distillation of the residue under reduced pressure gave 1-*chloro-3-hydroxy-5,5-dimethylcyclohexene* (11) (37.8 g, 94%), b.p. 111—113 °C/11 mmHg (Found: C, 59.6; H, 7.90; Cl, 21.8. $C_8H_{13}ClO$ requires C, 59.8; H, 8.30; Cl, 22.1%), $\nu_{max.}$ (CCl_4) 3 340 (OH) and 1 650 cm⁻¹ (C=C); τ (CCl_4) 4.22 (1 H, m, vinyl), 5.60—6.00 (1 H, m, CH), 6.83 (1 H, broad s, OH), 7.8—8.9 (4 H, m, CH_2), 8.94 (3 H, s, CH_3), and 9.03 (3 H, s, CH_3).

1,3-Dichloro-5,5-dimethylcyclohexene.—We used the method of Wiley *et al.*[19] A solution of triphenylphosphine dichloride [prepared from triphenylphosphine (40 g) in carbon tetrachloride (400 ml)] in acetonitrile (400 ml, distilled from phosphorus pentaoxide) under nitrogen at room temperature was treated with a solution of 1-chloro-3-hydroxy-5,5-dimethylcyclohexene (9.63 g) in acetonitrile (10 ml, distilled from phosphorus pentaoxide). After 2.5 h, the mixture was poured into sodium hydrogencarbonate solution (500 ml, saturated) and extracted with light petroleum (b.p. 60—80 °C; 4 × 250 ml). The combined organic extracts were dried (Na_2SO_4), evaporated *in vacuo*, and distilled under reduced pressure to give 1,3-*dichloro-5,5-dimethylcyclohexene* (7.42 g, 72%), b.p. 88—92 °C/10 mmHg (Found: C, 53.4; H, 6.70; Cl, 39.3. $C_8H_{12}Cl_2$ requires C, 53.6; H, 6.80; Cl, 39.6%), $\nu_{max.}$ (CCl_4) 1 640 cm⁻¹ (C=C); τ (CCl_4) 4.15 (1 H, m, vinyl), 5.27—5.67 (1 H, m, CH), 7.67—8.37 (4 H, m, CH_2), 8.91 (3 H, s, CH_3), and 9.01 (3 H, s, CH_3); *m/e* 180/178 (0.2, 0.4%, *M*⁺), 145/143 (2,7, *M*-Cl), 144/142 (5, 16, *M* − HCl), 129/127 (10, 32), 92 (27), and 91 (100).

1-Chloro-5,5-dimethylcyclohexene (12).—A solution of 1,3-dichloro-5,5-dimethylcyclohexene (5.79 g) in dry ether (120 ml) was heated under reflux with lithium aluminium hydride (1.22 g) under nitrogen for 17.5 h. Ethyl acetate was added dropwise to the cooled solution with stirring, and the mixture worked up in the usual way. Distillation gave 1-chloro-5,5-dimethylcyclohexene (12) (3.55 g, 79%), b.p. 57—59 °C/11 mmHg

Preparation of the Vinylsilanes (2), (5), (9), (13), *and* (23) *from the Vinyl Chlorides.*—We used the method of Petrov *et al.*[20] to obtain the following vinyl silanes: 4,4-*dimethyl*-1-*trimethylsilylcyclohexene* (2) (61%), b.p. 73—75 °C/11 mmHg (Found: C, 72.6; H, 12.2. $C_{11}H_{22}Si$ requires C, 72.4; H, 12.2%), $\nu_{max.}$ (CCl_4) 3 230 (C=C–H), 1 630 (C=C) and 1 250 cm⁻¹ ($SiMe_3$); τ (CCl_4) 3.85—4.00 (1 H, m, vinyl), 7.6—8.6 (6 H, m, CH_2), 8.90 (6 H, s, CH_3) and 9.86 (9 H, s, $SiMe_3$); *m/e* 182 (40%, *M*⁺), 167 (100, *M* − Me) and 109 (70, *M* − Me_3Si); 6,6-*dimethyl*-1-*trimethylsilylcyclohexene* (5) (78%), b.p. 72—75 °C/11 mmHg, $\nu_{max.}$ (CCl_4) 3 200 (C=C–H), 1 630 (C=C), and 1 250 cm⁻¹ ($SiMe_3$); τ (CCl_4) 3.90—4.10 (1 H, vinyl), 7.7—8.7 (6 H, m, CH_2), 8.87 (6 H, s, CH_3), and 9.84 (9 H, s, $SiMe_3$) (Found: *M*⁺ 182.151 0. $C_{11}H_{22}Si$ requires *M*, 182.148 9), *m/e* 182 (53%), 167 (100, *M* − Me) and 109 (60, *M* − MeSi); 3,3-*dimethyl- and* 5,5-*dimethyl*-1-*trimethylsilylcyclohexene* (9) and (13) (70% from the corresponding mixture of vinyl chlorides), b.p. 72—74 °C/11 mmHg, separated by preparative g.l.c. (F and M 720, 15% silicone grease on Chromosorb P) to give 3,3-*dimethyl*-1-*trimethylsilylcyclohexene* (9), the first eluted isomer (Found: C, 72.6; H, 12.3. $C_{11}H_{22}Si$ requires C, 72.4; H, 12.2%), $\nu_{max.}$ (CCl_4) 3 250 (C=C–H), 1 630 (C=C), and 1 250 cm⁻¹ ($SiMe_3$); τ (CCl_4) 4.35 (1 H, broad singlet, vinyl), 7.8—9.0 (12 H, m, overlain by a singlet at 9.02 CH_2 and CH_3), and 9.90 (9 H, s, $SiMe_3$); *m/e* 182 (61%, *M*⁺), 167 (100, *M* − Me) and 109 (65, *M* − Me_3-Si), and 5,5-*dimethyl*-1-*trimethylsilylcyclohexene* (13), the second eluted isomer, $\nu_{max.}$ (CCl_4) 3 250 (C=C–H), 1 630 (C=C), and 1 250 cm⁻¹ ($SiMe_3$); τ (CCl_4) 3.90—4.10 (1 H, m, vinyl), 7.5—8.6 (6 H, m, CH_2), 9.00 (6 H, s, CH_3), and 9.92 (9 H, s, $SiMe_3$) (Found: *M*⁺ 182.147 7. $C_{11}H_{22}Si$ requires *M*, 182.148 9), *m/e* (80%), 167 (91, *M* − Me), 109 (66, *M* − Me_3Si) and 73 (100, MeSi); the latter silane (13) was also prepared, by the same method, from the pure chloride (12) in 69% yield; and 3,4-*dihydro*-1-*trimethylsilylnaphthalene* (23) (57%), b.p. 67—71 °C/0.2 mmHg (Found: C, 77.3; H, 8.80. $C_{13}H_{18}Si$ requires C, 77.2; H, 9.00%), $\nu_{max.}$ (CCl_4) 1 625 (C=C), 1 600, 1 580 and 1 505 (aromatic) and 1 249 cm⁻¹ ($SiMe_3$); τ (CCl_4) 2.7—2.9 (4 H, m, Ar), 3.51 (1 H, t, *J* 4 Hz, vinyl), 7.1—7.4 (2 H, m, CH_2), 7.6—7.9 (2 H, m, CH_2), and 9.65 (9 H, s, $SiMe_3$); *m/e* 202 (61% *M*⁺), 187 (83, *M* − Me), 128 (67), and 73 (100, Me_3Si).

Friedel–Crafts Reactions on the Vinylsilanes (2), (5), (9) *and* (13).—The following conditions were typical: 5,5-dimethyl-1-trimethylsilylcyclohexene (13) (364 mg) in dry dichloromethane (100 ml) was added during 6 h under nitrogen at 0 °C with stirring to a mixture of acetyl chloride (0.47 g) and anhydrous aluminium trichloride (0.80 g) in dry dichloromethane (20 ml). The mixture was stirred for a further 15 min at 0 °C and then poured into sodium hydrogencarbonate solution (150 ml, saturated); the aqueous layer was then extracted with dichloromethane (3 × 20 ml). The combined organic layers were washed successively with sodium hydrogencarbonate solution (2 × 50 ml, saturated) and evaporated *in vacuo*. Preparative t.l.c. (silica gel, CH_2-Cl_2) gave 1-*acetyl*-5,5-*dimethylcyclohexene* (14a) (31 mg, 10%) R_F 0.4, $\nu_{max.}$ (CCl_4) 1 670 (C=O) and 1 640 cm⁻¹ (C=C); τ (CCl_4) 3.30—3.42 (1 H, m, vinyl), 7.7—8.8 (9 H, m, overlain by singlet at 7.88, CH_2 and CH_3), and 9.12 (6 H, s, CH_3), *semicarbazone*, m.p. 219—222 °C (from MeOH) (Found: C, 62.9; H, 9.20; N, 20.1. $C_{10}H_{19}N_3O$ requires C, 63.1; H, 9.20; N, 20.1%). This was hydrogenated over 5% Pd–C

in ethanol to give 1-acetyl-3,3-dimethylcyclohexane; $\nu_{max.}$ (CCl$_4$) 1 720 cm^{-1}; semicarbazone, m.p. 189—190 °C (from MeOH–H$_2$O) (lit.,[21] 188.5—189.5 °C); the same preparative t.l.c. gave 3-*acetyl-5,5-dimethylcyclohexene* (14b) (153 mg, 50%), R_F 0.5, $\nu_{max.}$ (CCl$_4$) 1 720 (C=O) cm^{-1}; τ (CCl$_4$) 4.48 (2 H, broad s, vinyl), 7.00—7.25 (1 H, C–H), 7.7—8.7 (7 H, m, overlain by singlet at 7.92, CH$_2$ and CH$_3$), and 9.02 (6 H, s, CH$_3$); *semicarbazone*, m.p. 180—181 °C (from MeOH–H$_2$O) (Found: C, 63.0; H, 9.25; N, 20.2. C$_{10}$H$_{19}$N$_3$O requires C, 63.1; H, 9.20; N, 20.1%). This was hydrogenated over 5% Pd–C in ethanol to give 1-acetyl-3,3-dimethylcyclohexane $\nu_{max.}$ (CCl$_4$) 1 720 cm^{-1}; semicarbazone, m.p. 189—190 °C (from MeOH–H$_2$O) (lit.,[21] 188.5—189.5 °C) mixed m.p. with that derived from the hydrogenated product of 1-acetyl-5,5-dimethylcyclohexene (14a) 188—190 °C. Similar conditions were used in the conversion of 4,4-dimethyl-1-trimethylsilylcyclohexene (2) (364 mg) into 1-acetyl-4,4-dimethylcyclohexene (3) (234 mg, 77%), R_F (CH$_2$Cl$_2$) 0.4, $\nu_{max.}$ (CCl$_4$) 1 670 (C=O) and 1 640 cm^{-1} (C=C); τ (CCl$_4$) 3.24—3.40 (1 H, m, vinyl), 7.8—8.6 (9 H, m, overlain by singlet at 7.86, CH$_2$ and CH$_3$), and 9.12 (6 H, s, CH$_3$); semicarbazone 219—220 °C (from MeOH) (lit.,[22] 220 °C, mixed m.p. with that derived from 1-acetyl-5,5-dimethyl-cyclohexene (14a) 214—221 °C; of 6,6-dimethyl-1-trimethylsilylcyclohexene (5) (364 mg) into 1-acetyl-6,6-dimethylcyclohexene (6) (33 mg, 11%), separated by preparative t.l.c. (SiO$_2$, CH$_2$Cl$_2$), R_F 0.4, $\nu_{max.}$ (CCl$_4$) 1 670 (C=O) and 1 640 cm^{-1} (C=C); τ (CCl$_4$) 3.49 (1 H, vinyl), 7.9—8.9 (9 H, m, overlain by singlet at 7.96, CH$_2$ and CH$_3$), and 8.96 (6 H, s, CH$_3$); semicarbazone m.p. 200—201 °C (from MeOH) (lit.,[23] m.p. 200—201 °C), mixed m.p. with semicarbazone derived from 1-acetyl-3,3-dimethylcyclohexene (10) 190—198 °C [the same preparative t.l.c. gave an unknown compound, probably (7) (133 mg, 34%), $\nu_{max.}$ (CCl$_4$) 1 715 cm^{-1}; τ (CCl$_4$) 4.35—4.60 (2 H, m,), 7.87 (3 H, s), 7.90 (3 H, s), 8.98 (3 H, s) and the usual multiplet in the range 7.0—8.6; *m/e* 194 (30% M^+), 151 (98, M − MeCO), and 107 (100)]; and of 3,3-dimethyl-1-trimethylsilylcyclohexene (9) (106 mg) into 1-acetyl-3,3-dimethylcyclohexene (10) (44 mg, 49%), R_F (CH$_2$Cl$_2$) 0.4, $\nu_{max.}$ (CCl$_4$) 1 670 (C=O) and 1 640 cm^{-1} (C=C); τ (CCl$_4$) 3.67 (1 H, m, vinyl), 7.8—8.9 (9 H, m, overlain by singlet at 7.88, CH$_2$ and CH$_3$), and 8.91 (6 H, s, CH$_3$); semicarbazone m.p. 200—202 °C (from MeOH) (lit.,[21] 201—202 °C).

Bistrimethylsilylmethane.—Sodium sand washed with dry hexane (3 × 50 ml) was suspended in hexane (100 ml) while chloromethyltrimethylsilane [24] (3.7 g) and chlorotrimethylsilane (3.9 g) were added at room temperature under nitrogen. The mixture was heated under reflux with stirring under nitrogen for 1.5 h. The clear supernatant liquid was decanted off, the residue washed with hexane (3 × 20 ml), and the combined extracts distilled using a 37 cm × 2 cm Vigreux column, to give bistrimethylsilylmethane (3.0 g, 62%), b.p. 130—134 °C (lit.,[25] 133.4 °C), τ (CCl$_4$) 10.0 (18 H, s, SiMe$_3$) and 10.3 (2 H, s, CH$_2$).

trans-β-*Trimethylsilylstyrene* (17).—n-Butyl-lithium (90 ml of a 1.5M-solution in hexane) was added under nitrogen at room temperature to a solution of N,N,N',N'-tetramethylethylenediamine (15 ml, distilled from potassium hydroxide) and bistrimethylsilylmethane (10.7 g) in light petroleum (b.p. 60—80 °C distilled from phosphorus pentaoxide). The mixture was heated under reflux for 10 h, cooled, and treated with benzaldehyde (7.0 g, freshly distilled) at 0 °C with stirring until the deep red colour had been discharged. Aqueous work-up and distillation of the residue using a 12-

cm × 1-cm column of glass helices gave *trans*-β-trimethylsilylstyrene (17) (7.2 g, 80%), b.p. 32—34 °C/0.05 mmHg, (lit.,[26] 83—85 °C/6 mmHg), $\nu_{max.}$ (film) 1 635 (C=C), 1 600 and 1 505 (aromatic) and 1 255 cm, (SiMe$_3$); τ (CCl$_4$) 2.5—2.9 (5 H, m, Ph), 3.10 (1 H, d, J 18 Hz, vinyl), 3.65 (1 H, d, J 18 Hz, vinyl), and 9.80 (9 H, s, SiMe$_3$).

Reaction of trans-β-*Trimethylsilylstyrene* (17) *with Benzoyl Chloride.*—*trans*-β-Trimethylsilylstyrene (352 mg) in dry dichloromethane (20 ml) was added during 15 min at 0 °C under nitrogen to a stirred solution of anhydrous aluminium trichloride (0.8 g), and benzoyl chloride (350 mg) in dry dichloromethane (30 ml), and the mixture was stirred for a further 15 min at 0 °C. Aqueous work-up and chromatography on silica gel (40 g) with ether–light petroleum (b.p. 60—80 °C, 1 : 4) as eluant gave a yellow solid (336 mg), which crystallised from 95% ethanol to give 3-chloro-3-phenylpropiophenone (18) (174 mg, 37%), m.p. 114—115 °C (lit.,[27] 114.5—115.5 °C), R_F (C$_6$H$_6$) 0.4, $\nu_{max.}$ 1 685 (C=O), 1 600 and 1 500 cm^{-1} (Ph); τ (CCl$_4$) 2.4—2.8 (10 H, m, Ph), 4.40 (1 H, t, J 6 Hz, CHCl) and 5.80—6.65 (2 H, m, CH$_2$); *m/e* 246/244 (8, 24%, M^+), 209 (13, M − Cl), 208 (12, M − HCl), and 105 (100). The mother-liquors from the crystallisation gave on evaporation *in vacuo* and crystallisation from ether at −78 °C benzylideneacetophenone (19) (117 mg, 27%), m.p. and mixed m.p. 56—58 °C (lit.,[28] 57—58 °C), R_F (C$_6$H$_6$) 0.3, identical (i.r., n.m.r., and t.l.c.) with an authentic sample.

Benzylideneacetophenone (19) *from* trans-β-*Trimethylsilylstyrene.*—The crude product from a similar preparation to that above was heated under reflux in dry ether (70 ml) with dry triethylamine (0.81 g) for 18 h. Aqueous work-up and chromatography on silica gel (40 g) with ether–light petroleum (b.p. 80—80 °C, 1 : 4) as eluant and crystallisation from ether at −78 °C gave benzylideneacetophenone (19) (304 mg, 73%), identical to the sample prepared above.

3-*Chloro-3-phenylpropiophenone* (18) *from* trans-β-*Trimethylsilylstyrene.*—The crude product from a similar preparation to that above was treated at 0 °C in dry ether (20 ml) with dry hydrogen chloride for 1.5 h. The usual aqueous work-up gave 3-chloro-3-phenylpropiophenone (18) (390 mg, 80%), identical to the sample prepared above.

trans-1,4-*Diphenylbut-3-en-2-one* (21).—*trans*-β-Trimethylsilylstyrene (17) (352 mg) in dry dichloromethane (20 ml) was added dropwise under nitrogen at 0 °C during 15 min to a stirred suspension of anhydrous aluminium trichloride (0.4 g) in dry dichloromethane (30 ml) containing phenylacetyl chloride (310 mg) and the mixture was stirred at 0 °C for a further 15 min. Aqueous work-up and chromatography on silica gel (40 g) with ether–light petroleum (b.p. 60—80 °C, 1 : 4) as eluant gave *trans*-1,4-diphenylbut-3-en-2-one (21) (383 mg, 86%), m.p. 69—71 °C (from EtOH) (lit.,[29] 70—71 °C), $\nu_{max.}$ (CCl$_4$) 1 685 (C=O), 1 650 (C=C), 1 600, 1 580, and 1 500 cm^{-1} (Ph); τ (CCl$_4$) 2.65 (1 H, d, J 16 Hz, vinyl), 3.2—3.7 (10 H, m, Ar), 3.38 (1 H, d, J 16 Hz, vinyl), and 6.31 (2 H, s, CH$_2$).

3-*Chloro-3-phenylpropiophenone* (18) *from Styrene.*—In a closely analogous preparation to that immediately above, 3-chloro-3-phenylpropiophenone (18) (112 mg, 23%) was obtained from styrene (208 mg, freshly distilled) and benzoyl chloride (280 mg). The m.p., mixed m.p., i.r. spectrum, and n.m.r. spectrum were identical to those already described. The major proportion of the reaction product was unidentified polymeric material.

4-*Phenyl-2-tetralone* (20) *from Styrene.*—In a parallel preparation to that immediately above, 4-phenyl-2-tetralone

(20) (235 mg, 56%) was obtained from styrene (208 mg, freshly distilled) and phenylacetyl chloride (310 mg). It had b.p. (bulb-bulb) ca. 130 °C/0.1 Torr (bath temperature), (lit.,[29] 127—128 °C/0.07 mmHg), $\nu_{max.}$ (CCl$_4$) 1 720 cm^{-1} (C=O); τ (CCl$_4$) 2.7—2.9 (9 H, m, Ar), 5.65 (1 H, t, J 8 Hz, CH), 6.47 (2 H, s, ArCH$_2$CO), and 7.18 (2 H, d, J 8 Hz, CH$_2$CO); m/e 222 (30%, M^+), 180 (20, M — CH$_2$CO), 179 (20, M — CH$_2$CHO) and 91 (100). This was reduced with sodium borohydride to the corresponding alcohol (92%), m.p. 123—124 °C (from hexane) (lit.,[29] 122—123.5 °C).

Reaction of 3,4-Dihydro-1-trimethylsilylnaphthalene (23) *with Acetyl Chloride.*—A solution of the silane (23) (40 mg) in dry dichloromethane (25 ml) was added during 0.5 h with stirring at 0 °C under nitrogen to a suspension of anhydrous aluminium trichloride (267 mg) in dry dichloromethane (25 ml) and acetyl chloride (0.3 ml, freshly distilled) and the mixture was stirred at 0 °C for a further 10 min. The yellow oil obtained after aqueous work-up contained principally 2-acetyl-1-chloro-1-trimethylsilyltetrahydronaphthalene (24), m/e 282/280 (0.3, 11% M^+), 267/265 (0.3, 1, M-15), 245 (10, M-Cl), 187 (99), 172 (70), and 155 (100), which could not be easily purified by preparative t.l.c. owing to its ease of hydrolysis of silica gel. The chloride was converted into the corresponding alcohol by stirring the crude product in benzene (15 ml) for 2 days with silica gel (10 g) and water (3 ml). The mixture was filtered, dried (MgSO$_4$), and evaporated *in vacuo*. Preparative t.l.c. (SiO$_2$, CH$_2$Cl$_2$) gave 2-*acetyl-1-hydroxy-1-trimethylsilyltetrahydronaphthalene* (24b) (323 mg, 61%), m.p. 99—100 °C (from hexane) (Found: C, 68.6; H, 8.60. C$_{15}$H$_{22}$O$_2$Si requires C, 68.6; H, 8.50%), R_F (CH$_2$Cl$_2$) 0.2; $\nu_{max.}$ (CCl$_4$) 3 480 (OH), 1 705 (C=O), and 1 250 cm^{-1} (SiMe$_3$); τ (CCl$_4$) 2.3—3.0 (4 H, m, Ar), 6.4—6.6 (1 H, m, OH), 6.8—8.0 (8 H, m, overlain by singlet 7.67, CH$_2$ and CH), and 9.98 (9 H, s, SiMe$_3$); m/e 262 (2%, M^+), 247 (20, M — Me), 229 (21), and 172 (100, M — Me$_3$SiOH). The same preparative t.l.c. gave 2-*acetyl-3,4-dihydro-1-trimethylsilylnaphthalene* (25) (37 mg, 7%), R_F 0.6, $\nu_{max.}$ (CCl$_4$) 1 670 (C=O), 1 625 (C=C) and 1 250 cm^{-1} (SiMe$_3$); τ (CCl$_4$) 2.5—2.9 (4 H, m, Ar), 7.0—7.6 (7 H, m, overlain by singlet at 7.57, CH$_2$, and CH$_3$), and 9.70 (9 H, s, SiMe$_3$); m/e 244 (3%, M^+), 229 (82, M — Me) and 84 (100); *semicarbazone* m.p. 235—237 °C (from CHCl$_3$) (Found: C, 63.6; H, 7.70 N, 13.7. C$_{16}$H$_{23}$N$_3$OSi requires C, 63.8; H, 7.70; N, 13.9%).

2-*Acetyl-3,4-dihydro-1-trimethylsilylnaphthalene* (25a).— Toluene-*p*-sulphonic acid monohydrate (234 mg) was azeotropically dehydrated by distillation with dry benzene (50 ml). The anhydrous acid in dry benzene (15 ml) was stirred with 2-acetyl-1-hydroxy-1-trimethylsilyltetrahydronaphthalene (24b) (323 mg) for 5 min. Aqueous work-up gave 2-*acetyl-3,4-dihydro-1-trimethylsilylnaphthalene* (25a) (288 mg, 98%), which had i.r. and n.m.r. spectra identical to those described above.

2-*Acetyl-3,4-dihydronaphthalene* (25b).—Toluene-*p*-sulphonic acid monohydrate (23 mg) was azeotropically dehydrated by distillation with dry benzene (50 ml). The anhydrous acid in dry benzene (15 ml) was heated under reflux with 2-acetyl-1-hydroxy-1-trimethylsilyltetrahydronaphthalene (24b) (32 mg) for 2 h. Aqueous work-up gave 2-acetyl-3,4-dihydronaphthalene (25b) (203 mg, 96%), R_F (CH$_2$Cl$_2$) 0.5, $\nu_{max.}$ (CCl$_4$) 1 668 (C=O), 1 625 (C=C), and 1 500 cm^{-1} (aromatic); τ (CCl$_4$) 2.6—3.1 (5 H, m, aromatic, vinyl), and 7.1—7.7 (7 H, m, overlain by singlet at 7.68, CH$_2$ and CH$_3$); m/e 172 (63% M^+), 155 (19, M — Me) and 129 (100, M — MeCO); semicarbazone m.p. 215—218 °C (from

MeOH–H$_2$O) (lit.,[30] 195—197 °C, lit.,[31] 208 °C, lit.,[32] 176 °C). The ketone was finally characterised by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in 90% yield to 2-acetylnaphthalene, m.p. 54—55 °C (from MeOH–H$_2$O) (lit.,[33] 56 °C).

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