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for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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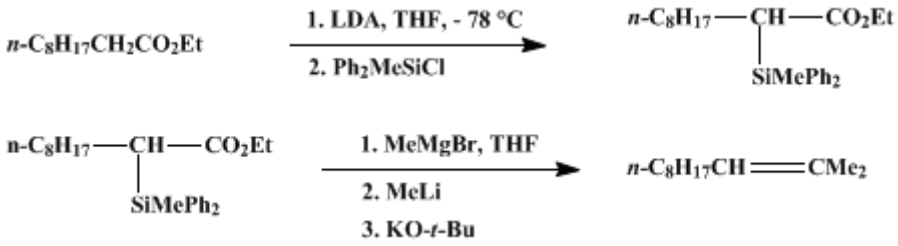
α-DIPHENYLMETHYLSILYLATION OF ESTER ENOLATES: 2-METHYL-2-UNDECENE FROM ETHYL DECANOATE

[2-Undecene, 2-methyl-]



Submitted by Gerald L. Larson, Ingrid Montes de Lopez-Cepero, and Luis Rodriguez Mieles[1].
Checked by Choon Sup Ra and Leo A. Paquette.

1. Procedure

A. *Ethyl 2-(diphenylmethylsilyl)decanoate.* A 500-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, a 100-mL pressure-equalizing dropping funnel, and a no-air stopper is flame-dried under a vigorous flow of nitrogen, cooled under an atmosphere of nitrogen to −78°C with a dry ice–acetone bath, and charged with 39.2 mL (52.5 mmol) of a 1.34 *M* solution of butyllithium in hexane (Note 1). To this solution is added 7.4 mL (5.31 g; 52.5 mmol) of diisopropylamine (Note 2) in 7 mL of tetrahydrofuran (Note 3). The resulting solution is warmed to ambient temperature and held for 30 min. The solution is diluted with 50 mL of dry tetrahydrofuran and cooled again to −78°C. To this solution is added 11.6 mL (10.0 g; 50 mmol) of ethyl decanoate (Note 4) in 45 mL of tetrahydrofuran dropwise over a 30-min period. The mixture is kept at −78°C for 30 min to allow the enolate to form, and then 10.3 mL (11.6 g; 50 mmol) of diphenylmethylchlorosilane (Note 5) in 40 mL of tetrahydrofuran is added over a 5-min period. The reaction mixture is allowed to reach ambient temperature and stir at that temperature for 8 hr. It then is cooled to 0°C, diluted with hexane (150 mL), washed with cold water (2 × 100 mL), dried over magnesium sulfate, filtered, and concentrated at reduced pressure (Note 6). The crude product, which is ca. 95% pure (Note 7), is purified by rapid filtration through 50 g of silica gel (Note 8) with 1% ethyl acetate–hexane (Note 9) as eluant. There is obtained 18.4–18.7 g (93–94%) of ethyl 2-(diphenylmethylsilyl)decanoate (Note 10). Similar results are obtained on a larger scale (Note 11).

B. *2-Methyl-2-undecene*. A 1-L, three-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, a 500-mL pressure-equalizing dropping funnel, and a no-air stopper is flame-dried under vacuum, cooled to room temperature under an atmosphere of nitrogen, and charged with 87 mL (260 mmol) of 3 *M* methylmagnesium bromide in ether (Note 12). This solution is cooled to 0°C (ice bath) and 52 g (130 mmol) of ethyl 2-(diphenylmethylsilyl)decanoate in 260 mL of tetrahydrofuran (Note 3) is added over an 8-min period. After the addition is complete, the reaction mixture is warmed to room temperature and heated to reflux for 24 hr. The reaction mixture is again cooled to 0°C and 244 mL (390 mmol) of 1.6 *M* methyllithium in tetrahydrofuran (Note 13) is added over a 30-min period. After the addition is complete, the reaction mixture is heated to reflux for 24 hr, cooled to 0°C (ice bath), and 29.2 g (260 mmol) of solid potassium *tert*-butoxide (Note 14) is added in three portions (Note 15). The reaction mixture is heated to reflux for 1 hr, cooled to 0°C, diluted with hexane (100 mL), and hydrolyzed by the dropwise addition of 1 *M* hydrochloric acid (240 mL), followed by about 150 mL of 3 *M* hydrochloric acid until a pH of 4 is reached (Note 16). The organic layer is separated and the aqueous layer is extracted with hexane (3 × 100 mL). The combined organic layers are dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure (Note 6) to give 55 g of crude material (Note 17). This material is diluted with 150 mL of dry hexane (Note 18) and applied to a silica gel column (Note 8). The product is obtained by eluting with hexane and collecting 200-mL fractions. This material, which contains small amounts of dimethyldiphenylsilane and

diphenylmethylsilanol, is chromatographed under 3–5 psi on a silica gel column (50 × 2.8 cm) eluting with hexane (Note 19) to give 11.3 g (51.8%) of the olefin (Note 20).

2. Notes

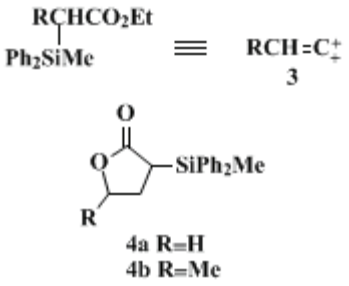
1. Butyllithium was purchased from Foote Mineral Company and titrated by the method of Watson and Eastham.[2]
2. Diisopropylamine was purchased from Aldrich Chemical Company, Inc., and distilled from calcium hydride prior to use.
3. Tetrahydrofuran was a gift from Pfizer Pharmaceuticals of Puerto Rico purchased by them from Dupont Company. It was distilled from sodium/benzophenone prior to use.
4. Ethyl decanoate was purchased from Aldrich Chemical Company, Inc. and used without further purification.
5. Diphenylmethylchlorosilane was purchased from Petrarch Systems, Inc., and distilled from calcium hydride (bp 85°C at 0.1 mm) prior to use. A 187.5-mmol-scale reaction using diphenylmethylchlorosilane purchased from Petrarch Systems and used without purification gave an 89% yield of the α-silyl ester.
6. A high-volume house vacuum system was used for this step.
7. The minor impurities are unreacted ethyl decanoate and diphenylmethylsilanol.
8. Chromatographic silica gel, 70–230 mesh, from Matheson-Coleman-Bell was used.
9. Alternatively, the product can be distilled in an Aldrich Kugelrohr apparatus (pot temperature 130–135°C at 0.2 mm) to give slightly lower (80–90%) yields.
10. The physical properties are as follows: n_D^{20} 1.5190; IR (neat) cm^{-1}: 3068, 3045, 2950–2850, 1714, 1589, 1254, 790; ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.66 (s, 3 H), 0.95 (t, 3 H, J = 1), 1.21 (brs, 14 H), 2.56 (m, 1 H), 3.86 (m, 2 H), 7.29–7.62 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ: 3.39, −5.57, 14.01, 22.63, 25.02, 27.56, 29.20, 29.35, 30.51, 31.87, 36.39, 59.75, 127.71, 129.50, 129.56, 134.32, 134.64, 134.78, 134.83, 175.02; MS 70 eV m/e (relative abundance) 398 (10), 397 (19), 396 (33), 353 (21), 351 (20), 319 (27), 298 (39), 297 (75), 284 (23), 227 (33), 199 (30), 198 (43), 197 (100), 195 (30), 183 (26), 181 (27), 121 (35), 105 (39), 93 (20), 73 (24), 69 (21), 55 (36), 53 (16). Anal. calcd. for $C_{25}H_{36}O_2Si$: C, 75.76, H, 9.09. Found: C, 75.59, H, 9.19.
11. The submitters report that a 187.5-mmol-scale reaction gave an 89% yield of product.
12. Methylmagnesium bromide was purchased from Columbia Organic Chemicals as a 3 *M* solution and used as obtained.
13. Methyllithium was purchased from Aldrich Chemical Company, Inc., and titrated prior to use.[2]
14. Potassium *tert*-butoxide was purchased from Aldrich Chemical Company, Inc., and used without further purification.
15. *Caution! Some foaming occurs because of an exothermic reaction.*
16. Litmus paper was used to determine the pH.
17. Gas-chromatographic analysis of this material (6 ft × 1/8 in. 10% SP-2401 on 100–120-mesh Supelcoport; 100–200°C program at 10°C/min; flow rate of 20 psi) showed the presence of ethyl decanoate, 2-undecanone, dimethyldiphenylsilane, and 2-methyl-2-undecanol in addition to the desired olefin. Small amounts of unidentified products were also present.
18. A mixture of hexanes (Mallinkrodt anhydrous) was used. If the crude product is placed directly on the silica gel column, the column plugs and the compound does not elute.
19. Attempts to purify the product by spinning-band distillation from the crude material gave only about 20% yield.
20. The product is greater than 97% pure by GLC (Note 17). It showed n_D^{20} 1.4360; ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.88 (br t, 3 H), 1.28 (br s, 12 H), 1.61 (br s, 3 H), 1.69 (br s, 3 H), 1.93–2.00 (m, 2 H), 5.14 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ: 14.05, 17.62, 22.74, 25.64, 28.14, 29.41, 29.65, 29.99, 31.98, 125.08, 131.00; MS (70 eV) m/e (relative abundance) 169 (2), 168 (14), 112 (6), 84 (11), 83 (13), 82 (6), 70 (23), 69 (100), 68 (10), 67 (13), 57 (34), 56 (68), 55 (34), 53 (9).

3. Discussion

Compound **1** represents one example of several α-(diphenylmethylsilyl) esters prepared by the method presented herein.[3] Other examples include the α-diphenylmethylsilylated derivatives of ethyl acetate, ethyl propionate, ethyl 10-undecenoate, ethyl palmitate, and ethyl stearate, all obtained in

greater than 70% yield. Other alcohols, principally methyl, isopropyl, *tert*-butyl and 1-menthyl, also have been employed in this reaction without marked differences. The reasons as to why the lithium enolates of esters are silylated at the carbon terminus with diphenylmethylchlorosilane as opposed to the usual silylation on the oxygen terminus is not clear. The direct *C*-silylation of the lithium enolates of α,β-disubstituted esters is not possible, except with ethyl cyclopropanecarboxylate and ethyl cyclobutanecarboxylate.[4]

The α-(diphenylmethylsilyl) esters have been shown to be vinyl dication equivalents 3, and as such are precursors to terminal olefins and deuterated olefins,[5] 1,1-disubstituted olefins,[6] and tri- and tetrasubstituted olefins.[7] They are precursors to β-ketosilanes and ketones,[8] [9] wherein the overall transformation results in an ester to ketone conversion. They can also be deprotonated and the enolate anion condensed with aldehydes and ketones to give α,β-unsaturated esters,[10] in particular α-alkylated-α,β-unsaturated esters.[11] Their γ-lactone counterparts, α-(diphenylmethylsilyl)-γ-butyrolactone **4a** and α-(diphenylmethylsilyl)-γ-valerolactone **4b**, are precursors to 4-oxo acids,[12] 1,4-diketones[13] and α-ylidene-γ-lactones.[14]



This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 530

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

hydrochloric acid (7647-01-0)

ethyl acetate (141-78-6)

ether (60-29-7)

nitrogen (7727-37-9)

carbon (7782-42-5)

Benzophenone (119-61-9)

sodium (13966-32-0)

magnesium sulfate (7487-88-9)

ethyl propionate (105-37-3)

ethyl palmitate (628-97-7)

methylmagnesium bromide (75-16-1)

butyllithium (109-72-8)

Tetrahydrofuran (109-99-9)

hexane (110-54-3)

Methyllithium (917-54-4)

ethyl stearate (111-61-5)

calcium hydride (7789-78-8)

diisopropylamine (108-18-9)

2-Methyl-2-undecene,
2-Undecene, 2-methyl- (56888-88-1)

ETHYL DECANOATE (110-38-3)

diphenylmethylchlorosilane

Ethyl 2-(diphenylmethylsilyl)decanoate

dimethyldiphenylsilane (778-24-5)

diphenylmethylsilanol

2-methyl-2-undecanol

ethyl cyclopropanecarboxylate (4606-07-9)

ethyl cyclobutanecarboxylate (14924-53-9)

potassium tert-butoxide (865-47-4)

α-(diphenylmethylsilyl)-γ-butyrolactone

2-undecanone (112-12-9)

ethyl 10-undecenoate (692-86-4)

α-(diphenylmethylsilyl)-γ-valerolactone