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E-1-LITHIO-1-ALKENES IN HYDROCARBON SOLVENT.

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Trans-alkenyl iodides are treated with *tert*-butyllithium in hexane at room temperature to provide pure *trans*-alkenyllithiums in good yield.

For the synthesis of sphingosine derivatives[1,2] we required various *trans*-alkenyllithiums *in hydrocarbon solution.* Procedures involving the use of alkenyl chlorides or alkenyl bromides, and exchange with Li° or n-BuLi did not seem to be useful, since Et_2O or THF is usually required.[3—5] Solutions of (E)-1-lithio-hexene in hexane or pentane prepared from (E)-1-bromo-1-hexene and Li° metal, including "high sodium" metal, Li° dispersion, and sonication proved unsatisfactory. Published methods for the lithium-iodine exchange reaction of *trans*-alkenyl iodides also require ethereal solvents,[6] low temperatures,[7] or both.[8,9] Thus, we were surprised to find that solutions of *trans*-alkenyllithiums in hexane could be prepared in high yield and purity by the reaction of t-BuLi with the corresponding *trans*-alkenyl iodide[10] at ambient temperature (Figure 1).

Since these intermediates may be of considerable synthetic utility, we would like to report the procedure used for their preparation. Alkenyl iodides **1a**—**1c** were converted to their corresponding lithium compounds **2a**—**2c**, by treatment with two equivalents of t-BuLi in hexane (Table 1). The exchange reaction is extremely sensitive to H_2O, and a variable induction period (10—30 minutes) is observed if the reaction conditions are not scrupulously anhydrous. The

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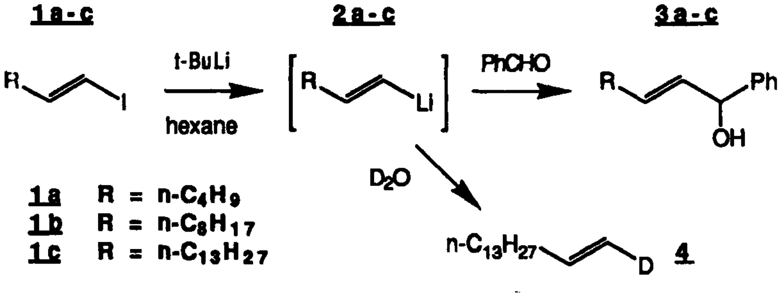

Figure 1

Table 1

	Alkenyliodide[10]	Alcohol	Yield
1a	E-1-iodo-hex-1-ene	**3a**	71%
1b	E-1-iodo-dec-1-ene	**3b**	74%
1c	E-1-iodo-pentadec-1-ene	**3c**	77%

organolithium compounds **2a**—**2c** were treated with an excess of benzaldehyde to provide the benzylic alcohols **3a**—**3c** in 71-77% isolated yield. In addition, to demonstrate complete conversion and stereochemical retention, (E)-1-pentadecenyllithium, **2c**, was quenched *in situ* with D_2O to provide pure (E)-1-*deuterio*-1-pentadecene, **4**[11] in quantitiative yield.

The procedure for the synthesis of **3c** is cited as an example. Freshly distilled (145°/0.76mmHg/CaH_2) 1-pentadecyne (4.30 g, 21 mmol) was taken up in 50 ml of dry hexanes, and treated with 22 ml of a 1.0 M solution of diisobutylaluminumhydride at 50° for 2 hours. The hexanes were removed by rotary evaporation, and the oil was taken up in 50 ml of dry THF. This solution was chilled to -78°, and a solution of I_2 (5.20 g, 21 mmol) in 20 ml of THF was added, and allowed to come to room temperature for several hours. Work-up with dilute

HCl at 0°, followed by extraction with Et_2O, drying (K_2CO_3), and solvent removal gave (E)-1-iodo-1-pentadecene, **1c** in 87% yield (6.11 g, 18.2 mmol).[10]

Iodoalkene **1c**, (336 mg, 1.0 mmol) was passed through a short column (Pasteur pipette) of grade I neutral alumina, and taken up in 2 ml of dry hexanes. t-Butyllithium (2.0 mmol) in pentane (1.2 ml, 1.7 M) was added, and the reaction was stirred for 1 hour. Benzaldehyde (116 mg, 1.1 mmol) in 2 ml of hexanes was added dropwise, and the reaction was quenched with saturated $NaHCO_3$, extracted (Et_2O) dried ($MgSO_4$), and chromatographed on silica gel with 10% EtOAc/pet. ether to provide the alcohol **3c** in 77% yield (243 mg).

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11) 250 MHz ^{1}H-nmr data for **4**: δ 5.76 ppm (dt, 1H, J = 6.2, 17 Hz), 4.92 ppm (d, 1H, J = 17 Hz), 2.05-1.95 ppm (m, 2H), 1.25 ppm (broad s, 22H), 0.88 ppm (t, 3H, J = 6.5 Hz).

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