

STEREOSPECIFIC PREPARATION OF TERMINAL VINYL LITHIUM DERIVATIVES BY  
 Br/Li-EXCHANGE WITH T-BUTYLLITHIUM

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(Received in UK 29 October 1976; accepted for publication 8 November 1976)

Hitherto, there is no generally applicable procedure of preparing the vinyl lithium compounds 2 from terminal bromides 1 by Br/Li-exchange with  $R\text{Li}$ <sup>1, 2)</sup>. Previous attempts caused dehydrobromination with formation of products derived from acetylenes<sup>3)</sup>. Reagents 2 are therefore made by reacting Li metal with the corresponding bromides<sup>4)</sup>, by carrying out  $R_3\text{Sn/Li}$  transmetalations<sup>3, 5)</sup> or by switching to the less readily available vinyl iodides<sup>1, 6)</sup>. Also, vinylic organomagnesium<sup>7)</sup> and -aluminium<sup>8)</sup> derivatives are used for this type of stereospecific olefin synthesis.

We have now found, that terminal alkenyllithiums 2 can be generated from the easily accessible<sup>9)</sup> bromides 1 in high yields and with clean retention of configuration by employing 2 equivalents of *t*-butyllithium<sup>10)</sup> at  $-120^\circ\text{C}$  in the Trapp-solvent mixture<sup>11)</sup>.

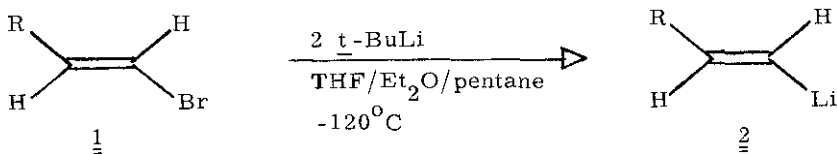
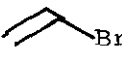
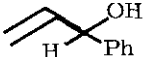
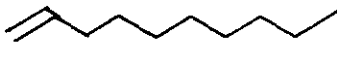
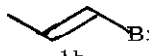
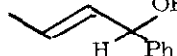

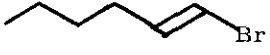
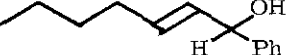


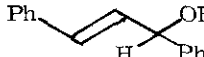
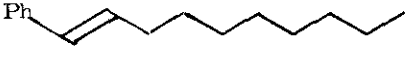
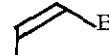
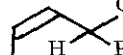
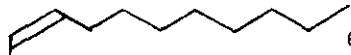


Table 1 shows the products with yields obtained from different vinyl bromides by trapping 2 with benzaldehyde and 1-haloctanes. In the case of the *cis-trans* isomeric  $\omega$ -bromo-styrenes 1d and 1e we have proved by GC-analysis that the E-olefin synthesized from 1d and bromooctane did not contain any Z-isomer and that 1e was converted to better than 99.7% configurationally pure Z-olefin<sup>12)</sup>.

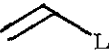
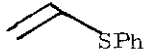
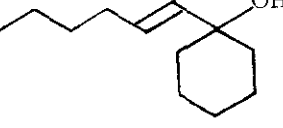
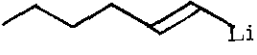
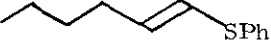
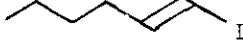
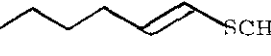
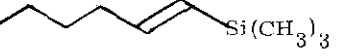
The unsubstituted vinyl lithium (2a) and E-1-lithio-1-hexene (2c) were also derivatized with the heteroelectrophiles diphenyl and dimethyl disulfide, iodine, and chloro

Table 1: Stereospecific coupling of terminal vinylbromides 1 with benzaldehyde and 1-haloctane through the vinyl lithium derivatives 2.

Vinylbromide	Product with Ph-CHO	Yield [%]	Product with $n-C_8H_{17}X^a)$	Yield [%]
 <u>1a</u>		76		52
 <u>1b</u>		72		62
 <u>1c</u>		87		77
 <u>1d</u>		73		73
 <u>1e</u>		81.5		65

a) With 1a and 1b X=I, in all other cases X=Br

Table 2: Miscellaneous conversions of 1a and 1c

Li-derivative generated	Product with RSSR	Yield [%]	other Products	Yield [%]
 <u>2a</u>		74		79
 <u>2c</u>		93		76
		66		46

trimethylsilane; cyclohexanone and 2c gave the expected allylic alcohol. The yields and product structures are shown in Table 2.

Since there is no organic halide present after the Br/Li-exchange and the mutual destruction of t-butyl bromide and t-butyllithium at  $-120^{\circ}\text{C}$ , the solutions of 2 can be warmed up to room temperature if desired for reactions with electrophiles. To avoid acetylene formation, however the bath temperature during the exchange step 1  $\rightarrow$  2, must not be above  $-110^{\circ}\text{C}$ .

All yields given in the tables are those of distilled products; the IR and NMR data are fully compatible with the structures shown; new compounds analyzed correctly, the physical properties of known products agreed with the literature data.

Procedure: A magnetically stirred solution of 10 mmoles of 1 in 42 ml of Trapp-mixture (THF/Et<sub>2</sub>O/pentane 4:1:1) was cooled under an argon atmosphere in a  $-120^{\circ}\text{C}$  bath [ligroin (30-50), isopropanol, acetone (4:1:1)/liquid N<sub>2</sub>] and combined within 10 min . with 20 mmoles of t-butyllithium (in pentane). The temperature was kept between  $-120^{\circ}\text{C}$  and  $-110^{\circ}\text{C}$  for 1 hr, and then raised to  $-90^{\circ}\text{C}$ . 9.9 mmoles of benzaldehyde were added, and stirring was continued for 15 min at  $-78^{\circ}\text{C}$  and for 20 min at room temperature. The mixture was quenched by pouring into a separatory funnel containing 10 mmoles of acetic acid, saturated aqueous NaCl solution and methylene chloride<sup>10</sup>).

To achieve alkylation, sequential addition of 9 mmoles of 1-bromo or 1-iodo octane and of 50 ml of THF at  $-90^{\circ}\text{C}$  was followed by stirring at room temperature for 18 hr.

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