Applications of the Xylylmonoalkylboranes to the Stereoselective Synthesis of \textit{trans} Disubstituted Olefins

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In the reaction of the xylylalkyl-1-bromo-1-alkenylboranes (1) with a base, the xylyl group does not migrate from boron to carbon competitively with primary or secondary alkyl groups. Protonolysis of the resulting intermediates (2) with isobutyric acid affords the corresponding \textit{trans} disubstituted olefins in excellent yields (Scheme A).

Scheme A

A current study of the hydroboration of olefins with xylylborane\(^1\) has revealed the reaction is often complicated by dehydroboration of tetramethylethylene\(^2\) and scrambling of the products. Fortunately, at \(-25^\circ\) the reaction can be controlled to provide in nearly quantitative yields xylylmonoalkylboranes derived from a wide variety of olefins, such as isobutylene, 2-butene, 2-methyl-2-butene, cyclohexene, norbornene, and 1-methylcyclopentene\(^3\). Moreover, in certain reactions of the xylyldialkylboranes which presumably involve anionotropic migration, we have observed that the xylyl group does not migrate from boron to carbon competitively with less hindered groups\(^4,5\).

These findings suggested the possibility that the xylylmonoalkylboranes might be valuable in the Zweifel synthesis\(^6\) of \textit{trans} disubstituted olefins (Scheme B).

Scheme B

There are two apparent difficulties in the original procedure. First, it requires dialkylboranes whose availability by simple hydroboration is relatively limited\(^7\). Second, only one of the two alkyl groups on the dialkylborane is utilized. (An alternate two-step route to dialkylboranes has recently been developed\(^8\). However, this still does not solve the problem of utilizing only one of the two groups.)

We now report that both of these difficulties can be circumvented by the use of the xylylmonoalkylboranes\(^9\).
Thus, no difficulty was encountered in synthesizing a wide variety of trans disubstituted olefins (3a-e) in excellent yields by the improved procedure.

![Chemical structures](image)

**trans-3-Propyl-4-nonene (3b):**
To 2.05 M thexylborane\(^1\) (14.7 ml, 30 mmol) in a 100-ml flask equipped with a septum-inlet, a thermometer well, and a mercury bubble and flushed with nitrogen were added sequentially trans-3-hexene (2.52 g, 30 mmol, \(-25^\circ\), 1 hr), 1-bromo-1-hexyne\(^{12}\) (4.83 g, 30 mmol, \(-25^\circ\), 1 hr), and sodium methoxide (2.43 g, 45 mmol, in 30 ml methanol, \(-25^\circ\), 5 min, then \(-25^\circ\), 1 hr). After evaporating the volatile substances (25°, 15 min, 1 hr), isobutyric acid (30 ml) was added. The reaction mixture was refluxed for 1 hr, cooled, poured into water (100 ml), and extracted with pentane (3 x 50 ml). The organic layer was washed with water (2 x 50 ml) and a saturated aqueous solution of potassium carbonate (2 x 50 ml), and was dried with magnesium sulfate. Distillative work-up provided trans-3-propyl-4-nonene; yield: 3.93 g (78%), b.p. 49°/0.4 mm; \(n_d^2\): 1.4319. The product was >99% pure by G.L.C.

I.R. (neat): 970 cm\(^{-1}\).

N.M.R. (CDCl\(_3\), TMS): \(\delta = 0.7, 1.1 (m, 9H), 1.1 - 1.65 (m, 10H), 1.65 - 2.3 (m, 3H), 4.8 - 5.7 (m, 2H) ppm.

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**Table 1. The Stereoselective Synthesis of trans-Disubstituted Olefins via Thexylnonaalkylboranes**

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Product*(^{a})</th>
<th>Yield by G.L.C. %</th>
<th>(n_d^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methyl-1-pentene</td>
<td>3a</td>
<td>94</td>
<td>1.4324</td>
</tr>
<tr>
<td>trans-3-Hexene</td>
<td>3b</td>
<td>93</td>
<td>1.4319</td>
</tr>
<tr>
<td>2-Methyl-2-butenene</td>
<td>3c</td>
<td>86</td>
<td>1.4285</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>3d</td>
<td>85</td>
<td>1.4509</td>
</tr>
<tr>
<td>1-Methyleclopentene</td>
<td>3e</td>
<td>94</td>
<td>1.4501</td>
</tr>
</tbody>
</table>

\(^{1}\) E. Negishi, J. J. Katz, unpublished results.


\(^{4}\) We have not so far been successful in obtaining thexylnonaalkylboranes cleanly from straight-chain terminal olefins.


\(^{6}\) H. C. Brown, Y. Yamamoto, C. F. Lane, Synthesis 1972, 304.


\(^{11}\) Exploration of a related procedure for the synthesis of model compounds of prostaglandins has recently been described [E. J. Corey, T. Ravindranathan, J. Amer. Chem. Soc. 94, 4013 (1972)] and has prompted this report of our independent study of this procedure.

\(^{12}\) It is assumed that equimolar quantities of 3b and 4 would give the same peak areas.


\(^{14}\) It was prepared by the method of Schulte and Goes [K. E. Schulte, M. Goes, Arch. Pharm. 290, 118 (1959)] in 91% yield.