Synthesis of Tri- and Tetravinylmethane Derivatives using Penta-2,4-dienyl(dipropyl)borane

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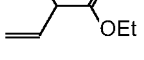
Sequential deprotonation, borylation and allylboration reactions, starting from penta-1,4-diene, provide a general approach to the synthesis of branched polyenes and polyenynes, including the tetravinylmethane derivatives.

β,γ-Unsaturated (allylic) boron derivatives add smoothly to carbonyl compounds, thioketones, imines, nitriles, some olefins and acetylenes.[1,2] All these allylboration reactions involve rearrangement through a six-membered transition state (2π + 2π + 2σ-process). The deborylation of the adducts formed provides homoallylic alcohols, thiols, amines or penta-1,4-dienes.[1,2]

In 1985 K. Smith and co-workers[3] obtained a series of penta-1,4-diene derivatives (2-vinylbut-3-enols) by treating pentadienyl(diphenyl)borane with carbonyl compounds. M. Schlosser and co-workers[4] have used the penta-2,4-dienylboron derivatives (without isolation) for the conversion of 1,4-dienes to penta-2,4-dien-1-ols.

This paper deals with the synthesis of some new derivatives of trivinylmethane **1** and **2** and tetravinylmethane **3** through ethoxyacetylene allylboration with penta-2,4-dienyl(dipropyl)-borane **4** as a key step.



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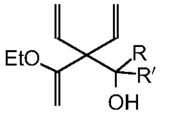
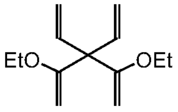


2a R = H, R′ = Me
2b R = R′ = Me



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Borane **4** was isolated[5] in more than 80% yield after treatment of pentadienyllithium[6] in THF with chloro(dipropyl)borane. At room temperature **4** exists as a ~4:1 mixture of *E*- and *Z*-isomers; its dynamic properties (fast 1,3-boron shift), as well as thermal cyclization, have been investigated earlier by means of NMR techniques.[5]

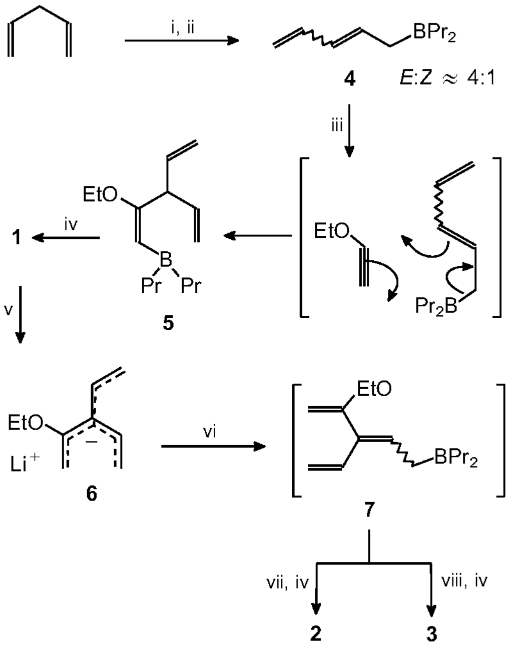
Borane **4**, like other β,γ-unsaturated boron derivatives,[1,2] undergoes *cis*-addition to the triple bond of ethoxyacetylene under mild conditions (−50 °C). This affords the trienic compound **5**, which yields the trivinylmethane derivative **1** (49%) upon deborylation with triethanolamine (by cleavage of the B—C$_{sp^2}$ bond).

The triene **1**, like trivinylmethane,[7] is readily metallated with BuLi in THF (−78 °C); the Li derivative **6**[†] formed gives triene **7**[‡] upon treatment with chloro(dipropyl)borane.

On treatment with excess carbonyl compound (acetaldehyde, acetone) at −78 °C, **7** gave the corresponding allylboration products – trienic alcohols **2a**,**b** – in 40–60% yield.

As expected,[1,2] the reaction of borane **7** with ethoxyacetylene proceeded at −78 °C with rearrangement; the *cis*-addition product formed was deborylated with triethanolamine to give the tetravinylmethane derivative **3** in 45% yield. To date the only existing method for tetravinylmethane preparation is rather difficult,[8] while its derivatives such as **3** have not been described.

Thus, a general approach to the synthesis of branched polyenes and polyenynes, including the tetravinylmethane derivatives, has been elaborated based on sequential deprotonation-borylation-allylboration reactions.



Scheme 1 *Reagents and conditions*: i, BuLi/THF, −30 °C; ii, Pr$_2$BCl, −78 → 20 °C, 83%; iii, EtOC≡CH, −78 → 20 °C; iv, N(CH$_2$CH$_2$OH)$_3$; v, BuLi/THF, −78 °C; vi, Pr$_2$BCl, −78 → 20 °C; vii, RCOR′, −60 °C; viii, EtOC≡CH, −78 → 20 °C.

The structures of all compounds synthesized have been established by physicochemical methods.[§]

[†] Compound **6** does not undergo β-elimination below 40 °C.

[‡] Compound **7** was used in further transformations without isolation. According to the ^{1}H and ^{13}C NMR data, **7** is a ~1:2 mixture of *syn*- and *anti*-isomers.

[§] 2-Ethoxy-3-vinylpenta-1,4-diene **1**. Yield 49%; b.p. 60 °C (16 Torr); n_D^{20} 1.4437; ^{1}H NMR (CDCl$_3$): δ 1.25 (t, 3H, Me of ethoxy-group), 3.44 (br.t, 1H, H-3), 3.71 (q, 2H, OCH$_2$ of ethoxy-group), 3.90 (dd, 2H, H-1, $J \approx J$ 2 Hz), 5.05 m, 5.12 m (4H, H-5), 5.8–6.0 (2H, H-4); ^{13}C NMR (CDCl$_3$): δ 14.2 (Me of ethoxy-group), 53.1 (C-3), 62.8 (OCH$_2$ of ethoxy-group), 81.3 (C-1), 115.4 (C-5), 137.9 (C-4), 163.5 (C-2).

2-Ethoxy-3,3-divinylpent-1-en-4-ol **2a**. Yield 63%; b.p. 48–53 °C (0.04 Torr); n_D^{20} 1.4612; ^{1}H NMR (CDCl$_3$): δ 1.17 (d, 3H, Me, *J* 7.8 Hz), 1.32 (t, 3H, Me of ethoxy-group, *J* 8 Hz), 3.78 (q, 2H, OCH$_2$ of ethoxy-group, *J* 8 Hz), 4.04 (m, 1H, CHOH), 4.14 and 4.20 (AB-system, *J* 2.5 Hz), 5.06–5.35 (m, 2H, =CH$_2$), 5.8–6.1 (m, 1H, =CH); ^{13}C NMR (CDCl$_3$): δ 14.3 (Me of ethoxy-group), 18.2 (C-5), 56.7 (C-3), 63.1 (OCH$_2$), 71.1 (C-4), 86.3 (C-1), 116.7 and 116.8 (=CH$_2$), 137.6 and 138.3 (=C), 163.4 (C-2).

2-Ethoxy-3,3-divinyl-4-methylpent-1-en-4-ol **2b**. Yield 40.5%; b.p. 45–48 °C (0.05 Torr); n_D^{20} 1.4645; ^{1}H NMR (CDCl$_3$): δ 1.18 (s, 6H, Me), 1.31 (t, 3H, Me of ethoxy-group, *J* 7 Hz), 3.77 (q, 2H, OCH$_2$ of ethoxy-group, *J* 7 Hz), 4.16 and 4.21 (AB-system, *J* 2.5 Hz), 5.07 and 5.24 (dd, 4H, =CH$_2$), 5.94 (dd, 2H, =CH); ^{13}C NMR (CDCl$_3$): δ 14.3 (Me of ethoxy-group), 26.3 (Me), 61.2 (C-3), 63.2 (OCH$_2$), 74.0 (C-4), 87.4 (C-1), 116.9 (=CH$_2$), 137.8 (=C), 163.9 (C-2).

2,4-Diethoxy-3,3-divinylpenta-1,4-diene **3**. Yield 45%; b.p. 53–55 °C (1 Torr); n_D^{20} 1.4700; ^{1}H NMR (CDCl$_3$): δ 1.26 (t, 3H, Me of ethoxy-group), 3.76 (q, 2H, OCH$_2$, *J* 7 Hz), 4.11 and 4.15 (AB-system, H-1, *J* 2.5 Hz), 5.12 and 5.22 (m, 2H, =CH$_2$), 6.14 (m, 1H, =CH); ^{13}C NMR (CDCl$_3$): δ 14.2 (Me of ethoxy-group), 59.5 (C-3), 63.0 (OCH$_2$), 84.0 (C-1), 115.3 (=CH$_2$), 139.1 (=C), 162.9 (C-2).

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