The fascinating stereopreferences and stereodynamics of pentadienyl-type organometallics have been reviewed some years ago.\(^1\) Fundamental facts shall nevertheless be briefly summarized. Whereas 2,4-pentadienyllithium\(^2\) in tetrahydrofuran and 2,4-pentadienylpotassium in liquid ammonia\(^3\) or in paraffinic suspension\(^4\) adopt the zigzag-like outstretched “W-form”, 2,4-pentadienylpotassium coils up to produce the horseshoe-like “U-form” when dissolved in tetrahydrofuran.\(^5,6\) The conformational population of pentadienyls carrying a primary alkyl chain at the 1-position again depends on the nature of the metal and the solvent.\(^7\) In contrast, all 3-methyl-2,4-pentadienyls\(^8\) exist in the “W-shape” and all 2,4-dimethyl-2,4-pentadienyl\(^9\) in the “U-shape” regardless whether combined with lithium or potassium and dissolved in tetrahydrofuran or suspended in hexanes. The third privileged structure, the equally coplanar and hence again optimally resonance-stabilized “S-form” has so far been identified only in mobility-restricted cyclic structures.\(^9,10\)

The principal features of the scenario thus being known, numerous details remain to be elucidated. In view of their immense practical importance, the following issues will now be addressed specifically:

- How regioselectively do 2,4-pentadienylmetals and 3-methyl-2,4-pentadienylmetals react with a wide variety of electrophiles?
- How stereoselectively can the metalation of (Z) - and (E)-1,4-hexadiene and 2,6-dimethyl-2,5-heptadiene be accomplished?

The stereopreferences of pentadienyl-type organometallics were probed either by NMR spectroscopy\(^2,3,6,8\) or by correlation of the stereocomposition of the reactive intermediates with that of their final, isolable products.\(^4,5,7,9,10\) The latter approach relies on the availability of “well-behaved” electrophiles, such as silanes or boranes, which attack preferentially or exclusively terminal positions of the delocalized area. If, on the contrary, the electrophile becomes attached to the central carbon atom, most if not all stereochemical information inherent in the organometallic intermediate gets lost. Therefore, virtually all trapping studies performed so far employed either chlorotrimethylsilane or fluorodimethoxyborane,\(^11,12\) both electrophiles being reputed to exhibit the required regioselectivity.

As a more systematic investigation has now revealed, the latter assumption is only partially fulfilled. Whereas all halotrialkylsilanes investigated reacted with 2,4-pentadienylpotassium, if suspended in hexanes, almost exclusively at the terminal positions and the 3-substituted isomer was formed only in traces (≤ 3%), the amount of the latter increased significantly (to 11–44%) whenever tetrahydrofuran was used as the solvent. Carbon dioxide, formaldehyde, oxirane and ethylene sulfate afforded regioisomeric mixtures \(1,\ 2,\ \text{see Scheme 1}\) in all solvents (Table 1). In contrast, fluorodimethoxyborane\(^11,12\) and 2-methoxy-1,3,2-dioxaborolane\(^13,14\) gave only primary derivatives (Z-I or E-I) regardless of the reaction medium (Table 1).

A substituent at the 3-position as present in 3-methyl-1,4-pentadienylmetals tends to hinder the approach of an electrophile. After deprotonation of the hydrocarbon precursor with butyllithium in the presence of potassium tert-butoxide (“LIC-KOR”) in tetrahydrofuran and subsequent interception with silanes or boranes, only the end-on products 3 were found (Scheme 2, Table 2). When oxirane or 1-iodobutane served as the trapping reagents, both the chain-lengthened and the doubly branched regioisomers,
When the metalation was carried out with ethylene sulfate (1,3,2-dioxathiolane 2,2-dioxide) instead of oxirane.

Followed by neutralization at 0 °C. The branched γ-product underwent partial isomerization to its conjugated isomer (see Ref.17).

When the metalation was carried out with tert-butoxide, 93% of products were formed in a γ/a-ratio of 12:88 and a Z/E-ratio of 5:95. After the immediately ensuing treatment with alkaline hydrogen peroxide the allyl alcohol was isolated.

The configuration of the end-on products 3 was invariably E.

The 1,4-pentadiene derived products 1 were trans-isomers when prepared in petroleum ether and cis-isomers when prepared in tetrahydrofuran (Table 1). The 3-methyl-1,4-pentadiene derived products 3 had invariably the E-configuration (Table 2). We wanted to include in the present study also “5-methyl-2,4-pentadienylmetals” (2,4-hexadienylmetals) which we expected to show, qualitatively at least, the same stereochemical dynamics and preferences as already reported for 2,4-decadienylmetals.7 This was indeed found to be the case. For well intelligible reasons, the internal double bond retained the configuration inherited from its hydrocarbon precursor and the or- ganometallic intermediate generated upon deprotonation with sec-butyllithium adopted the “W-form”. However, after the interception with standard electrophiles, some 2Z,4Z-isomer (2Z,4Z-5) was inevitably isolated along with the 2E,4Z-isomer (2E,4Z-5) in an approximate ratio of 1:12 (Table 3). Since admixtures of the sterically unre-
The metalation of 5-methyl-1,4-hexadiene with sec-butyllithium or superbasic mixed metal reagent followed by treatment with chlorotrimethylsilane invariably produced stereomixtures suggesting the coexistence of a “W-conformer” and an “S-conformer.” On the contrary, a neat “W-structure” can be attributed to the organometallic species generated by metalation of 2,6-dimethyl-2,5-heptadiene with “LIC-KOR” in tetrahydrofuran. Although its condensation with chlorotrimethylsilane mainly takes place at the 4-position (51% of isomer 6) and only to a small extent (6%) at the 2-position, the exclusive trans-configuration of the latter isomer 7 has been unequivocally established (Scheme 4).

To our knowledge, fluorotrimethylsilane (see Table 1) has never been used before as a trapping agent for polar organometallics. It proved to be far less reactive than the heavier halotrimethylsilanes. For example, when chlorotrimethylsilane was added to a solution of 2,4-pentadienylpotassium in tetrahydrofuran kept at −75 °C, the characteristic red color disappeared in the course of a few seconds while a steep temperature rise indicated an exothermic process. In contrast, fluorotrimethylsilane was found to be inert at −75 °C and to react only slowly at −50 °C. Judging on this basis, the relative chloride/fluoride ratios must be situated between 10 and 100, thus falling in the same range which is typical for bimolecular nucleophilic substitutions (SN 2). In contrast, one would expect to encounter reversed ratios if a nucleophilic addition/nucleofugal elimination mechanism featuring an ate complex intermediate were operative. 4-Fluoronitrobenzene undergoes irreversible nucleophilic aromatic substitutions up to 400 times faster than the chloro analog does.

For laboratory routine and abbreviations, see previous publications emanating from this laboratory (e.g., Ref. 21). 1H NMR spectra were recorded of solutions in CDCl3 at 400 MHz.

Starting Materials and Reagents: 1,4-Pentadiene, 3-methyl-1,4-pentadiene and cis-1,4-hexadiene are commercial. trans-1,4-Hexadiene20 and 2,7-dimethyl-2,6-heptadiene21 were prepared according to literature procedures. The same holds for the reagents fluorodimethoxyborane11,12 and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and the solution of formaldehyde in tetrahydrofuran.15,16

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Metathesis and Trapping Reactions; General Procedures

a) At 0 °C, BuLi (25 mmol) was added to a suspension of potassium tert-butoxide (2.8 g, 25 mmol) in hexanes (25 mL). After 20 min of vigorous stirring at 0 °C, the electrophile (25 mmol) was added to the mixture at −75 °C or the latter was poured onto an excess of freshly crushed dry ice. If the reagent was a trialkylsilane or 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, the precipitate formed was removed by filtration or centrifugation and the product isolated by distillation. The alcohols and carboxyls obtained in reactions with formaldehyde, oxirane or carbon dioxide were neutralized with a slight excess of HCl in Et2O before the workup continued as described above. The dimethyl boronates resulting from the reaction with fluorodimethoxyborane were oxidized with 35%aq H2O2 in alkaline medium11 to afford allylic alcohols, which were extracted with Et2O and distilled. The composition of crude reaction mixtures was always checked by gas chromatography using calibrated reference compounds (“internal standards”) for the assessment of yields. To make acids more volatile, they had beforehand been converted into their methyl esters by exhaustive treatment with etheral diazomethane.

b) If the reaction between the dienyl type organopotassium compound and the electrophilic reagent was to be performed in homogeneous solution, the metatilation was carried out as described in the preceding paragraph. Then the hexanes were stripped off under reduced pressure. At 75 °C, precooled THF (125 mL) was added, followed 20 min later, still at −75 ºC, by the electrophile.

c) If the organolithium derivative was to be generated in THF, the hydrocarbon (25 mmol) was dissolved in this solvent (125 mL) and was treated with sec-BuLi (25 mmol) for 1 h at −50 ºC. The electrophile (25 mmol) was added at −75 ºC.

Products Derived from 1,4-Pentadiene

(Z)- and (E)-Trimethyl-2,4-pentadienylsilane (Z- and E-1a),10 triethyl-1-(1-vinyl-2-propenyl)silane (2a),21 (Z)2- and (E)2-2,4-pentadienyl-1-ol (Z- and E-1e), (Z)6-3,5-hexadien-1-ol (Z- and E-1g), 2-vinyl-3-buten-1-ol (2g),36 (Z)2- and (E)2-4,6-heptadien-1-ol (Z- and E-1b), 3-vinyl-4-penten-1-ol37,39 and methyl (E)-3,5-hexadienoate30 (2h) have been reported previously.

(Z)-Triethyl-2,4-pentadienylsilane (Z-1b)

Purified by preparative gas chromatography (2 mL, 10% SE-30, 125 ºC); bp 90–91 ºC/12 mmHg; nD20 1.4786.

1H NMR: δ = 6.63 (1 H, ddd, J = 16.9, 11.0, 10.4 Hz), 5.93 (1 H, t, J = 10.8 Hz), 5.52 (1 H, q, J = 9.4 Hz), 5.13 (1 H, d, J = 16.5 Hz), 5.03 (1 H, d, J = 9.7 Hz), 1.69 (2 H, d, J = 8.9 Hz), 0.96 (9 H, s), 0.55 (6 H, q, J = 7.7 Hz).

MS: m/z = 183 (100, M+ + 1), 182, (9, M+), 132 (64), 115 (73), 104 (32), 87 (97).


(E)-Triethyl-2,4-pentadienylsilane (E-1b)

Purified by preparative gas chromatography (2 mL, 10% SE-30, 125 ºC); bp 90–91 ºC/12 mmHg; nD20 1.4792.

1H NMR: δ = 6.29 (1 H, dt, J = 17.1, 10.2 Hz), 5.94 (1 H, dd, J = 15.1, 10.2 Hz), 5.72 (1 H, dt, J = 15.1, 8.3 Hz), 4.98 (1 H, d, J = 17.1 Hz), 4.84 (1 H, d, J = 10.2 Hz), 1.57 (2 H, d, J = 8.3 Hz), 0.93 (9 H, t, J = 8.0 Hz), 0.53 (6 H, q, J = 8.0 Hz).

Methyl 2-Vinyl-3-butenoate (2F)
Workup and gas chromatographic isolation as described in the preceding paragraph; colorless liquid; bp 54–55 °C/12 mmHg; $n_0$ 1.4911.

$^1$H NMR: δ = 6.56 (1 H, d, $J = 16.6$, 11.2, 10.3 Hz), 6.17 (1 H, t, $J = 7.0$ Hz), 5.62 (1 H, dt, $J = 10.7$, 7.1 Hz), 5.28 (1 H, d, $J = 16.6$ Hz), 5.20 (1 H, d, $J = 9.6$ Hz), 3.70 (3 H, s), 3.24 (2 H, d, $J = 7.5$ Hz).

MS: $m/z$ (%) = 209 (89, $M^+$ + H), 208 (61, $M^+$), 151 (22), 108 (95), 84 (100).


Products Derived from 3-Methyl-1,4-pentadiene

(E)-3-Methyl-2,4-pentadien-1-ol, 41 3-methyl-3-vinyl-4-penten-1-ol and (E)-3-methyl-1,3,3,4-tetramethylsilane have been reported previously. Therefore, these compounds were only characterized by their physical constants (bp, $n_0$), their $^1$H and $^13$C nuclear magnetic resonances and mass spectra.$^{44}$

(E)-Trimethyl(3-methyl-2,4-pentadienyl)silane (E-3a)
Configurational assignment on the basis of $^1$H-NOESY; colorless liquid; bp 59–60 °C/8 mmHg; $n_0$ 1.4706.

$^1$H NMR: δ = 6.40 (1 H, dd, $J = 17.2$, 10.7 Hz), 5.58 (1 H, t, $J = 8.9$ Hz), 4.99 (1 H, d, $J = 17.2$ Hz), 4.84 (1 H, d, $J = 10.7$ Hz), 1.69 (3 H, s), 1.60 (2 H, d, $J = 9.0$ Hz), 0.01 (9 H, s).

Anal. Calcd for C$_9$H$_{14}$Si (145.3): C, 70.04; H, 11.76. Found: C, 70.48; H, 11.76.

(E)-Triethyl(3-methyl-2,4-pentadienyl)silane (E-3b)
Colorless liquid; bp 108–110 °C/8 mmHg; $n_0$ 1.4826.

$^1$H NMR: δ = 6.38 (1 H, dd, $J = 17.4$, 10.4 Hz), 5.58 (1 H, t, $J = 8.9$ Hz), 4.98 (1 H, d, $J = 17.4$ Hz), 4.84 (1 H, d, $J = 10.7$ Hz), 1.72 (3 H, s), 1.63 (2 H, d, $J = 8.9$ Hz), 0.95 (9 H, t, $J = 7.9$ Hz), 0.54 (6 H, q, $J = 7.9$ Hz).

Anal. Calcd for C$_{11}$H$_{22}$Si (196.4): C, 73.38; H, 12.32. Found: C, 72.80; H, 12.02.

(E)-4,4,5,5-Tetramethyl-2-(3-methyl-2,4-pentadienyl)-1,3,2-dioxaborolane (E-3e)
Colorless liquid; bp 100–102 °C/13 mmHg; $n_0$ 1.4648.

$^1$H NMR: δ = 6.38 (1 H, dd, $J = 17.0$, 10.4 Hz), 5.62 (1 H, t, $J = 7.8$ Hz), 5.02 (1 H, d, $J = 17.0$ Hz), 4.86 (1 H, d, $J = 10.4$ Hz), 1.76 (2 H, d, $J = 7.8$ Hz), 1.70 (3 H, s), 1.22 (12 H, s).

MS: $m/z$ (%) = 209 (89, M$^+$ + H), 208 (61, M$^+$), 151 (22), 108 (95), 85 (100).

Anal. Calcd for C$_{11}$H$_{22}$BO$_2$ (208.1): C, 68.08; H, 9.87. Found: C, 67.82; H, 9.87.

(E)-4-Methyl-3,5-hexadienoic Acid (E-3f)
Configurational assignment on the basis of $^1$H, $^1$H-NOESY; monoclinic colorless crystals; mp 32–33 °C; bp 108–110 °C/0.2 mmHg.

$^1$H NMR: δ = 6.43 (1 H, dd, $J = 17.5$, 10.6 Hz), 5.66 (1 H, t, $J = 7.2$ Hz), 5.20 (1 H, d, $J = 17.5$ Hz), 5.05 (1 H, d, $J = 10.6$ Hz), 3.26 (2 H, d, $J = 7.2$ Hz), 1.78 (3 H, s).

MS: $m/z$ (%) = 126 (36, M$^+$), 111 (12), 84 (100).

Methyl (E)-2-Methyl-3,5-hexadienoate
Workup and gas chromatographic separation as described in the preceding paragraph: 16%; colorless liquid; bp 71–72 °C/12 mmHg; nD20 1.4735.

\[ \text{MS: } m/z = 158 (68, M^+ + NH}_4), 140 (22, M^+), 81 (100), 79 (18) \]

Anal. Calcd for C8H12O2: C, 68.54; H, 8.63. Found: C, 68.74; H, 8.86.

Methyl (Z)-2-Vinyl-3-pentenoate
Workup and gas chromatographic separation as described above (see 3E,5Z-5d); 6%; colorless liquid; bp 72–74 °C/12 mmHg; nD20 1.4749.

\[ \text{MS: } m/z = 158 (43, M^+ + NH}_4), 140 (12, M^+), 81 (100), 79 (19) \]

Anal. Calcd for C8H12O2: C, 68.54; H, 8.63. Found: C, 68.78; H, 8.45.

Products Derived from trans-1,4-Hexadiene: Metallation with Butyllithium and Potassium tert-Butoxide; (2Z,4E)-2-(2,4-Hexadienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2Z,4E-5E)
Isolated by distillation; (2Z,4E/2E,4E) ratio 96:4; colorless liquid; bp 100–101 °C/12 mmHg; nD20 1.4709.

\[ \text{MS: } m/z (\%) = 158 (74, M^+ + NH}_4), 141 (52), 107 (48), 73 (100). \]

Anal. Calcd for C12H21BO2: C, 68.08; H, 9.87. Found: C, 68.75; H, 8.82.

Methyl (3Z,5E)-3,5-Heptadienoate (3Z,5E-5Gr)
After carboxylation of the organometallic intermediate, by extraction and treatment of the resulting 3:2 mixture of acids with diazomethane; main component (minor component: see directly below) 24%; separation by preparative gas chromatography (2 m, 5% C20M, 125 °C), (3Z,5E/3E,5E) ratio 92:8; bp 75–77 °C/12 mmHg; nD20 1.4776.

\[ \text{MS: } m/z (\%) = 196 (3, M^+), 122 (38), 107 (48), 73 (100). \]

Anal. Calcd for C12H23Si: C, 73.38; H, 12.32. Found: C, 73.29; H, 12.24.

(E)-Trimethyl(1,1,5-trimethyl-2,4-hexadienyl)silane (E-5)
Minor component (6%) as mentioned in the preceding paragraph: (Z/E) < 2.98; bp 114–115 °C/12 mmHg; nD20 1.4438.

\[ \text{MS: } m/z (\%) = 94 (3, M^+), 5.06 (2, H, d, J = 10.6 Hz), 2.78 (1, H, t, J = 10.6 Hz), 1.72 (6, H, s), 1.61 (6, H, s), -0.04 (9, H, s). \]

Anal. Calcd for C12H23Si: C, 73.38; H, 12.32. Found: C, 73.26; H, 12.25.

Acknowledgement
This work was financially supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Bern (grant 20-55'303-98) and the Bundesamt für Bildung und Wissenschaft, Bern (grant 97.0083 linked to the TMR project FMRXCT970129).
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