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Hydrozirconation of 1-arylalkenes

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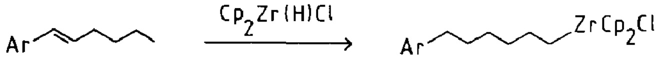
Abstract

The hydrozirconation of 1-arylhexenes with $Cp_2Zr(H)Cl$ has been studied at various temperatures. 1-Phenyl-1-hexene and its *ortho*-methoxyl derivative both react significantly more slowly at room temperature than simple alkenes. Furthermore, the tendency of zirconium to migrate towards the terminal position, in these compounds is very low at room temperature, as concluded from ^2H NMR analysis after deuterolysis. Instead, the α-deuterated arylhexanes predominate. This is in contrast to the behaviour of simple alkenes, which are known to give terminal σ-alkylzirconium compounds. At elevated temperature (60 °C), 1-phenyl-1-hexene gives about 50% of deuterated phenylhexane with a reversed isomer ratio (α-D/ω-D 10/90). 1-Phenyl-3-Z-hexene reacts much faster than 1-phenyl-1-hexene at room temperature, but the reaction is unselective unless the temperature is slightly raised (45 °C; 26 α-D/74 ω-D). 2-(3-Z-Hexenyl)thiophene gives about 55% of deuterated 2-hexylthiophene at 25 °C, with deuterium incorporated almost exclusively at the ω-position. In contrast, 2- and 3-(1-hexenyl)-thiophene, are hydrogenated, and give hexylthiophenes with low deuterium incorporation.

Introduction

During the last decade we have been engaged on a study of the hydrozirconation [1] reaction and we now report our results [2*] on the hydrozirconation of aromatic alkenes [3*]. Our aim was to prepare ω-zirconium-substituted long-chain alkylbenzenes, such as **1**, using di-π-cyclopentadienylzirconium hydridochloride, $Cp_2Zr(H)Cl$.



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* Reference number with asterisk indicates a note in the list of references.

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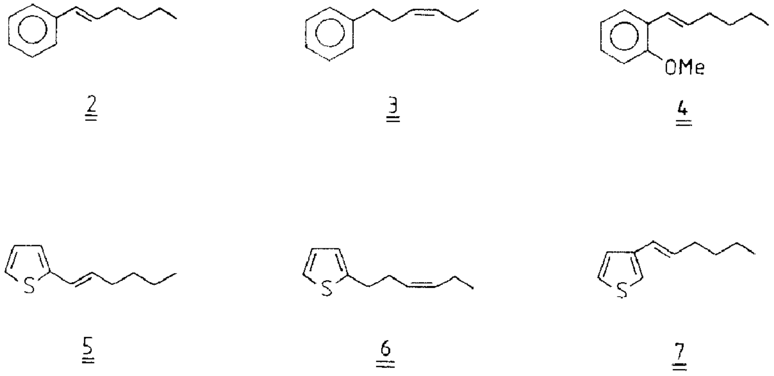
Zirconium may be replaced by other functional groups in various ways [1,4], and so ω-functionalised alkylbenzenes should in principle be accessible by this route provided that the zirconium migrates towards the chain terminus. We reasoned that this would possibly extend the scope of the Heck reaction to include 1-alkenes (a reaction known to give several isomeric phenylalkenes [5]), by allowing conversion of the resulting isomeric mixture into a single major product.

The regioselectivity, as established by analysis of the products after cleavage of the carbon–zirconium bond, depends on the electrophile used for cleavage [6]. In some instances, 2- and 3-deuterated acid oxazolines were obtained after hydrozirconation/deuterolysis of unsaturated acid oxazolines. Use of the same starting materials and conditions for hydrozirconation with subsequent oxidation (H_2O_2/NaOH, t-BuOOH or MCPBA) gave no 2-hydroxylated products. Only 3- or ω-hydroxylated acid oxazolines [6a,b] could be detected. Neither 2- nor 3-zirconium derivatives gave the corresponding bromo compounds, but yielded the α,β-unsaturated oxazolines [6c]. In order to make a more satisfactory determination of the isomeric distribution in the case of alkylzirconium derivatives, and thus enable the determination of factors influencing the direction of migration of the metal, we decided to use deuterium oxide as a trapping reagent.

Results and discussion

The reaction was studied with the 1-arylhexenes shown in Scheme 1 *.

1,4-Dioxane was chosen as solvent since it is known [6c,8] that hydrozirconation is faster in this medium than in toluene or benzene. As is evident from Table 1, the α-deuterated isomer (^{2}H NMR) of phenylhexane predominated almost exclusively after hydrozirconation of **2** at room temperature followed by deuterolysis. The deuterium distribution did not vary with the reaction time. The reaction of $Cp_2Zr(H)Cl$ with **2** is significantly slower than that with simple alkenes, and requires somewhat elevated temperatures. When **2** was hydrozirconated at 60 °C, good ω-selectivity was achieved, but the yield of deuterated phenylhexane was only moderate (~ 50%) owing to increased hydrogenation.



Scheme 1

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* For the hydrozirconation of simpler substrates, e.g. styrene, 2-vinylfuran etc., see ref. 2*, 3*, 4a, 7.

Table 1

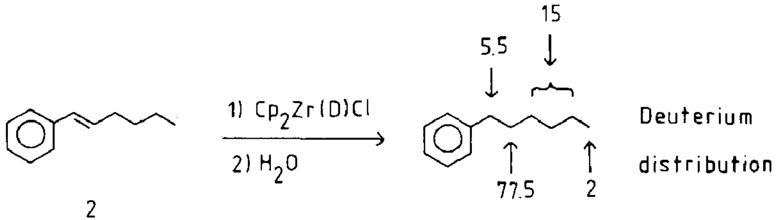
Hydrozirconation[a] of compounds 2, 3 and 4 with subsequent deuterolysis

Hydro-zirconated compound	Equivalent $Cp_2Zr(H)Cl$ [b]	Reaction temp (°C)/ reaction time (h)	Yield [c] of deuterated phenylhexanes (%)	Relative deuterium distribution (%) [d]	
				α-D	ω-D
2	1.1–1.2	20–25/21–24	65 (68) [e]	90–100	0–10 [f]
2	2.0	20–25/74	75 (80)	90– 95	5–10 [f]
2	2.0	20–25/97	75 (81)	90– 95	5–10 [f]
2	2.0	45/24	75 (85)	50	50 [g]
2	2.0	45/97.5	65 (92)	24	76 [g]
2	2.0	60/22	$\leq$ 50 ($\leq$ 80) [h]	10	90
3	1.0–2.0	20–25/20	$\leq$ 60 (88)	50–60	40–50
3	2.0	45/21	76 (88)	26	74
4	1.1–1.2	20–25/24	~ 50 (70) [i]	80–90	10–20 [g]
4	2.0	45/21	55 (78) [i]	40–50	50–60 [g]

[a] Anhydrous 1,4-dioxane was used as solvent. [b] Mole equivalents to olefin, assuming quantitative yield in the reaction of Cp_2ZrCl_2 wit Red-Al (cf. Experimental section). [c] Determined by combination of GLC and MS-analyses (cf. Experimental section). Figures in parentheses are total yields (GLC) of saturated analogues of compounds **2–4**. [d] Determined by ^2H NMR ($CHCl_3$) after filtration and concentration of the reaction mixtures (cf. Experimental section). [e] The yield was not improved when 2 equiv. of $Cp_2Zr(H)Cl$ were used. [f] These figures refer to the total deuterium in the ω-position and other positions. [g] < 5% of deuterium was found in positions other than α and ω. [h] Unknown byproducts were formed. [i] Deuterated 1-hexyl-2-methoxybenzene.

1-Phenyl-3-Z-hexene (**3**) reacted much faster (GLC) than **2** with $Cp_2Zr(H)Cl$. The degree of conversion into phenylhexane was > 80% after 5 h, but even after 20 h no, or only very low, regioselectivity was observed (Table 1). Raising of the temperature to 45°C resulted in the improvement of the ω-selectivity. To achieve the same selectivity with **2** under identical conditions, a reaction time of 4 days was required.

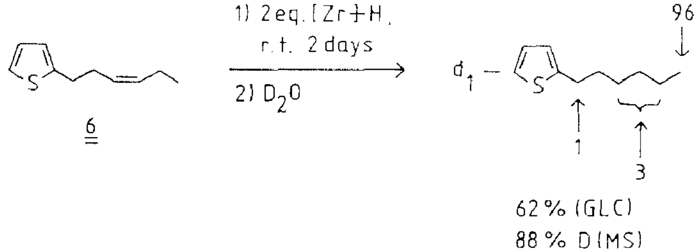
Predominant α-selectivity was also observed in hydroboration of 1-aryl-1-propenes [9], and an explanation for this observation has been offered [9a]. The addition of the zirconium hydride to **2** is propably also governed in such a way as to preferentially produce the α-zirconium intermediate, which apparently is thermodynamically stable. This is also indicated by the results shown in eq. 1. The faster reaction of **3** may be related to steric requirements.



2 (1)

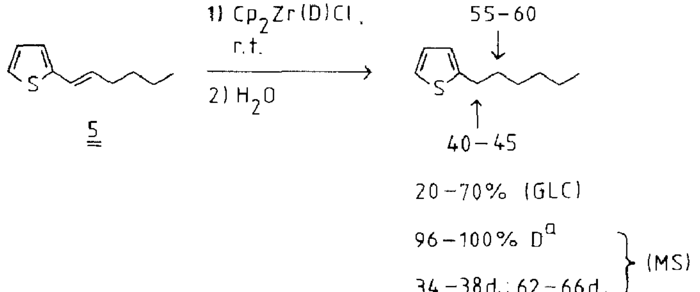
As mentioned above, we previously observed the formation of oxazolines deuterated at the 3-position after hydrozirconation/deuterolysis of unsaturated fatty acid oxazolines [6]. We believe that these isomers stem from 3-zirconium derivatives in which the metal is part of a 5-membered ring formed by coordination to the oxygen in the oxazoline function. The question arose of whether an oxygen atom, as in compound **4**, would stabilize α- and/or β-zirconium intermediates in the same manner *. Thus, a few experiments were carried out with **4** as substrate. Apparently (Table 1), the coordination of zirconium to oxygen is not crucial for stabilization of the zirconium containing intermediates, at least in this particular case, since the deuterium distribution after hydrozirconation is not appreciably different from that observed when **2** was used as substrate.

We considered it of interest to examine the behaviour of the heteroaromatic compounds **5** and **6** (Scheme 1) in this reaction. We found that **5** reacted even more sluggishly than **2** at room temperature, and that hydrogenation mainly occurred. Compound **6**, in which the double bond is not conjugated with the ring, reacted with high selectivity (25 °C) to give the ω-deuterated 2-hexylthiophene (eq. 2).



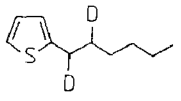
(2)

When **5** was treated with $Cp_2Zr(D)Cl$, most of the 2-hexylthiophene obtained (*a* indicates a fraction with at least one deuterium incorporate) was dideuterated (eq. 3), as indicated by GLC-MS, and deuterium was found only at the α- and β-positions (^2H NMR). The ^{13}C NMR spectrum (Table 2) gave no evidence for



(3)

geminal dideuteration; that is, the dideuterated fraction only consisted of the compound **8** **. The yield of 2-hexylthiophene varied with the amount of $Cp_2Zr(D)Cl$



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* Other functional groups were also used, e.g. NO_2 and SO_2CH_3 (*m*-nitrostyrene and a methylsulphonyl-substituted aromatic alkene). In both cases the compounds did not undergo normal hydrozirconation; both reacted sluggishly, with no evidence for deuterium incorporation. With 3 equiv. [Zr]-H, *m*-aminostyrene was formed (GLC-MS) from *m*-nitrostyrene. Hydroboration, on the other hand, proceeded quite well and no reduction of the nitro group was reported [10]. The methylsulphonyl group was partially cleaved, resulting in about a 20% yield of the corresponding arylalkane (GLC-MS).

** No deuterium was found (MS) in the remaining starting material **5**.

Table 2

NMR analyses after deuterozirconation of compounds **5**, **6** and **7**

Deuterozirconated compound	^{13}C NMR [a] (C_6D_6) (ppm)	^{2}H NMR [b] ($CHCl_3$) (ppm)
5	δ 32.15 (ArCH$_2$*C*H$_2$, absent); 32.05 (ArCHD*C*H$_2$); 31.82; 31.64 (ArC*C*HD, t, *J* 19.3 Hz); 30.17 (Ar*C*H$_2$CH$_2$, absent); 29.72 (Ar*C*HD, t, *J* 19.5 Hz); 29.00 (ArCCH$_2$*C*H$_2$); 28.91 (ArCCHD*C*H$_2$); 22.90; 14.25	δ 2.85 (ArCH*D*) 1.70 (ArCCH*D*)
6	[c]	δ 2.83 (ArCH*D*); 1.69 (ArCCH*D*); 1.32; 0.91 (CH$_2$*D*)
7	[c]	δ 2.62 (ArCH*D*); 1.62 (ArCCH*D*); 1.32 [d]

[a] Thiophene carbons are not assigned. Assignments were made using 2-D HETCOR (^{1}H-^{13}C) spectra of 2- and 3-hexylthiophene. A ^{13}C-DEPT NMR spectrum was also in accordance with the assignments. [b] Assigned after comparison with ^{1}H NMR spectra of 2- and 3-hexylthiophene. For deuterium distribution, see eqs. 3 and 4. [c] The ^{13}C NMR spectra are not given here since information regarding the presence of absence of dideuterated carbons, could not be obtained. No further information concerning the position of deuterium could be obtained (cf. ^{2}H NMR). [d] Weak signal, if present. $>$ 90% of the deuterium incorporated was found at the α- and β-positions.

used and also with the reaction time, but the degree of deuteration and the proportion of dideuterated product, were not influenced by change of these parameters (eq. 3).

Compound **7** was hydrozirconated (25 °C) in the belief that a compound with a conjugated double bond farther away from the heteroatom would be likely to behave like **2**. The only similarity was the rate of conversion into the saturated analogue. After deuterolysis, the amount of deuterium incorporated was found to be almost negligible. The deuterozirconation of **7** also resulted in appreciable dideuteration, with $>$ 90% of the deuterium at the α- and β-positions (Table 2). The amount of dideuterated hexylthiophene formed was somewhat lower than that from **5**, and in contrast to the results for the latter varied with the reaction time. That neither **5** nor **7** gave the fully dideuterated hexylthiophenes implies that more than one hydrogenation mechanism may be operative *. This is not due to a H/D exchange process involving the solvent, since after hydrozirconation of **7** in dioxane-d_8 and quenching with water, no deuterium was found in the 3-hexylthiophene produced.

In keeping with what was said above about the position taken up by the metal when the zirconium hydride is added to the double bond [9], it is most probable that the α-zirconium intermediates **9** and **10** are mainly formed when **5** or **7** are hydro-

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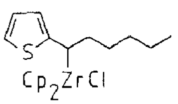
* Usually the proportion of hydrogenation increases with increasing temperature. 2-Vinylpyridine also underwent hydrogenation (25 °C). Upon treatment with $Cp_2Zr(D)Cl$, however, a significantly lower degree of dideuteration was found (only 5–20% of the total amount of deuterated 2-ethylpyridine). This may be due to operation of a different hydrogenation mechanism.



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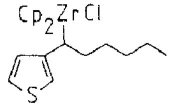

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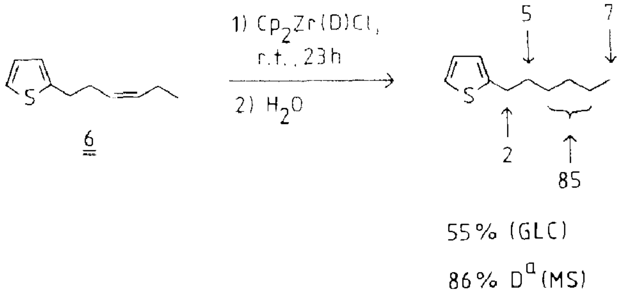
zirconated. The cause of the competing hydrogenation remains unclear, but there may be H/Cl exchange [11] between $Cp_2Zr(H)Cl$ and zirconium in **9** or **10**. The resulting alkylzirconium hydrides could then undergo decomposition [11,12] to yield 2- and 3-hexylthiophene. It should be noted that the presence of added thiophene did not influence the amount of hydrogenation when 1-phenyl-1-hexene (**2**) was hydrozirconated (cf. Experimental).

Equations 2 and 4 (*a* indicates a fraction with at least one deuterium incorporated) show that the tendency of the metal to migrate towards the aromatic ring is very low, when compound **6** is the substrate. The remaining olefins mainly consist of the 3- and 4-isomers ($\geq 90\%$) according to GLC, MS, and ^1H NMR spectroscopy. How the migration towards the α-position is hindered is not clear.



(4)

Our work shows that, although moderate to good ω-selectivity can be achieved, the migration of zirconium towards the terminal position in aryl-substituted olefins usually requires somewhat higher temperature than are needed in the case of simple alkenes. Unfortunately, the degree of deuteration decreases with increasing temperature in the hydrozirconation step. Furthermore, substrates in which the double bond is conjugated with a thiophene ring are hydrogenated even at room temperature.

Experimental

General

^1H, ^2H and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer at 299.943, 46.004, and 75.429 MHz, respectively. The ^1H ($CDCl_3$) and ^{13}C NMR ($CDCl_3$ or C_6D_6) shifts are given relative to TMS. ^2H NMR ($CHCl_3$) shifts are given relative to TMS-d_{12}. Mass spectra were determined with a Finnigan 4021 (Data System Incos 2100) spectrometer operating at 15–20 eV, or a Hewlett–Packard 5970 spectrometer operating at 70 eV. The degree of deuteration after hydrozirconation/deuterolysis was calculated from mass spectra using non-deuterated compounds as references. The reference compounds were either purchased or obtained by hydrolysis of samples withdrawn from the hydrozirconation mixtures. Change from one mass spectrometers to the other did not affect the derived degree of deuteration. Gas chromatographic analyses were performed on a Varian 1400 or a Varian 3300 gas chromatograph equipped with a 2 m glass column containing 3% Carbowax 20M on Suplecoport 100/120, 70–210 °C (10 °C/min). Either heptadecane or octadecane was used as internal standard for quantitative GLC analyses. Elution band areas were determined electronically with a Varian 4270 integrator. For HPLC separations a Polygosil C_{18} column (50 × 0.5 cm) connected to a Constametric pump was used. The column was also connected to an RI-detector (LKB). Acetonitrile (Baker Chemicals BV) was used as eluent. Flowrate: 2 ml/min. Elemental analyses were performed at Dornis und Kolbe, Mikroanalytisches Laboratorium (Mühlheim a.d. Ruhr, West Germany). Since the isolated compounds **6** and **7** darkened upon standing, small samples were further purified by preparative TLC or HPLC before elemental analysis.

Thiophene (Vondelingenplaat) was dried (if it was to be added to hydrozirconations) by refluxing over calcium hydride, distilled, and stored over activated molecular sieves under nitrogen. THF, 1,4-dioxane, and toluene were dried by refluxing over sodium wire and distilled prior to use. Dioxane-d_8 (> 99% D; Ciba-Geigy) was dried over activated molecular sieves under nitrogen. All other solvents used for literature procedures requiring anhydrous conditions were also appropriately dried. Red-Al (Aldrich) was diluted with anhydrous toluene and stored under nitrogen. Hexyl bromide (BDH), 3-bromothiophene (Shell), Cp_2ZrCl_2 (Aldrich), deuterium oxide (99.8% D; Norsk Hydro), and other materials obtained from commercial sources were used as received. Silica (TLC-Kiesel gel 60 H, 15 μm, Merck) was used for flash chromatographic purifications. For preparative TLC, 20 × 20 cm plates (Merck) pre-coated with silica (Kieselgel 60 F_{254}) were used. $Cp_2Zr(H)Cl$ [13], $Cp_2Zr(D)Cl$ [13], $Pd(PPh_3)_4$ [14] and 1-hexenylboronic acid [15] were prepared as described in the literature. Compound **2** (Scheme 1) was made by dehydration [16] of 1-phenylhexanol [17]. Compound **3** and 2-hexylthiophene were made from the relevant aryllithiums and 1-bromo-3-*Z*-hexene [18] or hexyl bromide, as described for related compounds [19] (cf. the preparation of **6** below). Compounds **4** and **5** were made by Suzuki's method [20] (cf. the preparation of **7** below). Glassware used for reactions in an inert atmosphere or for storage of anhydrous solvents and reagents was thoroughly dried.

All hydrozirconation reactions were carried out under nitrogen. Solid transfers were performed under nitrogen in a drybox. Liquid transfers were performed with a syringe or under nitrogen pressure by use of the septum technique. If not otherwise stated, the hydrozirconation reagent, $Cp_2Zr(H)Cl$, was generated in situ from Cp_2ZrCl_2 and Red-Al (1.5 *M* in toluene). Time for generation: 2–3 h.

*2-(3-Z-Hexenyl)-thiophene (**6**)*

A method [19] described for related compounds was used. A dry, nitrogen-flushed 100 ml three-necked flask, fitted with septa, was charged with a solution of 3.0 g (36 mmol) thiophene in dry THF (~ 10 ml). The solution was cooled below −20 °C. Butyllithium (1.5 *M* in hexane, 24–28 ml) was added during 30–60 min by means of a syringe. The mixture was stirred for about 2 h below −20 °C and then 5.0 g (31 mmol) of 1-bromo-3-*Z*-hexene [18] was added dropwise (15 min). The temperature was then allowed to rise slowly and the mixture was stirred overnight under nitrogen. Ether was added and the mixture was hydrolysed. The organic layer was washed with water and dried ($MgSO_4$). The crude product obtained after filtration and evaporation was either distilled (b.p. 64-7 °C/1–1.5 mmHg) of flash chromatographed with pentane as eluent. Yield 29–48%.

^{1}H NMR: δ 7.13 (dd, J 5 Hz, 1 Hz; 1 H, H-5); 6.94 (dd, J 5 Hz, 3Hz; 1H, H-4); 6.82 (m *, 1H, H-3); 5.42 (m, 2H, vinyl); 2.90 (d *t, 2H, α-CH_2); 2.42 (q, 2H, β-CH_2); 2.05 (p, 2H); 0.96 (t, 3H).

^{13}C NMR ($CDCl_3$): δ 144.9; 132.8; 127.5; 126.6; 124.1; 122.9; 30.1; 29.3; 20.6; 14.2.

Mass: (70 eV): m/e (rel. int.) 166 (0.06) M^+; 110 (0.05); 97 (0.89) M^+ – pentenyl.

Anal. Found: C, 72.26; H, 8.56; S, 19.21. $C_{10}H_{14}S$ (166.27) calcd.: C, 72.23; H, 8.49; S, 19.28%.

3-(1-Hexenyl)-thiophene (7)

Suzuki's method [20] for related compounds was used. To a 500 ml three-necked flask, 11.4 g (70 mmol) of 3-bromothiophene and 4.0 g (5 mol-%) of tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) [14] were added. The mixture was stirred for about 15 min and then 12.9 g (~ 1.4 equiv.) of 1-hexenylboronic acid [15] (used without previous recrystallisation) in about 200 ml THF was added, together with 80 ml 2 *M* aqueous sodium hydroxide. The flask was fitted with a reflux condenser and stoppered. The mixture was refluxed for about 3.5 h, then cooled and diluted with pentane. The organic layer was washed with three portions (3 × 35 ml) of 2 *M* sodium hydroxide, then with water, dried ($MgSO_4$), filtered and concentrated. The crude product was flash chromatographed with pentane as eluent. Yield: 55%. The yield can be increased by rechromatographing contaminated fractions.

^{1}H NMR: δ 7.27–7.04 (multiplets, 3 H, arom.); 6.41 (d, J 15.8 Hz, 1H, vinyl.); 6.09 (dt, J 15.8 Hz, 6.9 Hz; 1 H, vinyl.); 2.19 (q, 2H, allyl.); 1.41 (m, 4H); 0.94 (t, 3H).

Mass: (70 eV): m/e (rel. int.) 166 (0.18) M^+; 137 (0.06); 123 (0.54) M^+ – propyl; 110 (0.13); 97 (0.09).

Anal. Found: C, 72.12; H, 8.35. $C_{10}H_{14}S$ (166.27) calcd.: C, 72.23; H, 8.49%.

Hydrozirconation procedure

The aromatic olefin (0.2–0.5 g) and internal standard were dissolved in 2–3 ml of anhydrous 1,4-dioxane. The solution was added to a suspension of the hydrozirconation reagent generated in situ (see General). The total amount of 1,4-dioxane was 10–30 ml. The suspension was then stirred under the conditions given in Table 1 and eq. 2. Samples were withdrawn from the reaction mixture and deuterolysed with deuterium oxide under nitrogen. After about 1 h the deuterolysed samples were analysed by GLC and then filtered through neutral alumina using pentane. The filtrates were washed with 3–4 portions of water, concentrated in vacuo, dissolved in chloroform, dried ($MgSO_4$), and analysed by GLC-MS and ^{2}H NMR spectroscopy. The saturated analogue obtained from compounds **2** and **3** was identified by gas chromatographic and mass spectrometric comparison with authentic phenylhexane.

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* Due to coupling between these protons ($J \approx 1$ Hz).

^2H NMR *: δ 2.65 (benzyl.); ~ 1.6 ** (CHD-CH_2Ph); ~ 1.3 **; 0.94 (CH_2D).

1-Hexyl-2-methoxybenzene, obtained after hydrozirconation of **4**, was identified by GLC-MS analysis (70 eV): *m/e* 193 M^+; 122; 121.

^2H NMR *: δ 2.65 (benzyl.); ~ 1.6 ** ($CHDCH_2Ar$); ~ 1.4 **; 0.94 (CH_2D). For results, see Table 1.

The saturated analogue obtained from compounds **5** and **6** was identified gas chromatographically and by mass spectrometry with authentic 2-hexylthiophene as reference.

^2H NMR * (hydrozirconated **6**): δ 2.85 (1%); 1.33 (3%); 0.92 (96%), cf. eq. 2. This spectrum was recorded after preparative TLC.

3-Hexylthiophene, obtained after hydrozirconation of **7**, was identified by comparison of its ^1H NMR spectrum (recorded after purification by preparative TLC or HPLC) with published NMR data [22].

Deutero- or hydro-zirconation of phenylhexene 2 in the presence of thiophene

Prepared as described above using $Cp_2Zr(D)Cl$ [13] or $Cp_2Zr(H)Cl$ generated in situ. Anhydrous thiophene (3–15 equiv.) was added together with the substrate **2**. After 22–23 h stirring at room temperature the mixture from deuterozirconation was quenched with water and that from the hydrozirconation with D_2O. Analyses were performed as described above. In neither case did the presence of thiophene change the amount of deuterium incorporated (GLC-MS) compared with that from similar runs in its absence. However, the yield (GLC) of phenylhexane was slightly lower in the presence of thiophene. The deuterium distribution after deuterozirconation was the same whether or not thiophene had been added (eq. 1).

Deuterozirconation of compounds 5, 6 and 7

Prepared as described above using 0.3–2.6 equiv. of $Cp_2Zr(D)Cl$ [13]. After 1–4 days stirring at room temperature the reactions were quenched with water. The hydrolysates were analysed by GLC and GLC-MS and then treated as described above. After purification by preparative TLC and/or HPLC, the ^2H and ^{13}C NMR spectra were recorded; see eq. 3 and 4 and text (Results and Discussion). Spectral data are given in Table 2. ^{13}C NMR shift assignments of the products were made by use of 2-D HETCOR (^1H-^{13}C) spectra of 2-hexylthiophene and 3-hexylthiophene (obtained after hydrozirconation, see above) in benzene-d_6. These reference compounds were also used to assign the ^2H NMR shifts of the products.

Hydrozirconation of 7 in dioxane-d_8

Performed as described above using about 2 equiv. of isolated $Cp_2Zr(H)Cl$ [13] in dry dioxane-d_8. After ≥ 24 h the mixture was hydrolysed. Yield of 3-hexylthiophene (GLC) 56%. No deuterium incorporation could be detected (GLC-MS).

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* Assignments of the usually broad singlets were made after comparison with ^1H NMR data, either published [21], or of authentic nondeuterated material.

** If present.

Acknowledgements

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