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Reaction of the aromatic olefin 1-(1-hexenyl)-2-thiomethylbenzene with $Cp_2Zr(H)Cl$. Unexpected cleavage of the methyl–sulphur bond

Ulf Annby, Salo Gronowitz and Anders Hallberg

Division of Organic Chemistry 1, Chemical Center, P.O.B. 124, University of Lund, S-221 00 Lund (Sweden)

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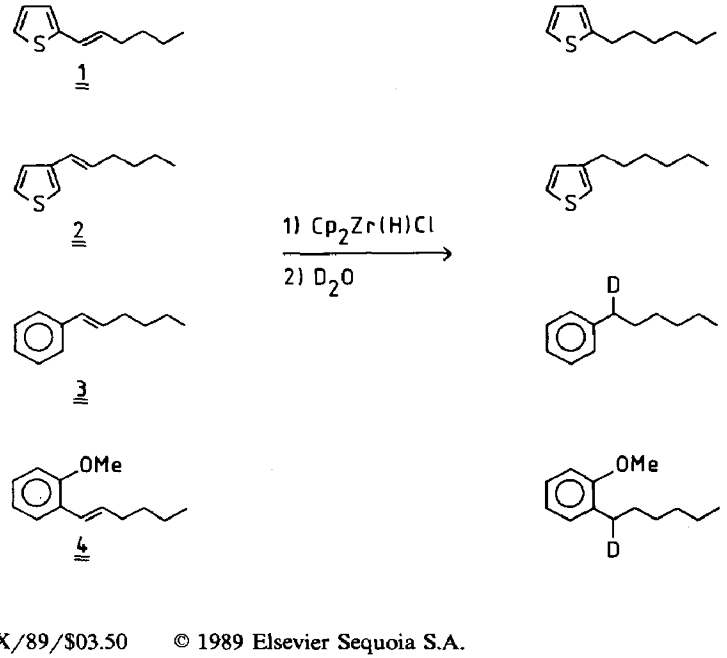
Abstract

Reaction of the aromatic olefin 1-(1-hexenyl)-2-thiomethylbenzene with $Cp_2Zr(H)Cl$ results in cleavage of the sulphur–methyl bond. When the 2-hexylthiophenol thus formed is exposed to air, it is oxidized to the corresponding disulphide, which is produced in about 70% yield (based on starting olefin). Such a reaction does not take place with 1-(1-hexenyl)-2-methoxybenzene as substrate.

Introduction

We recently finished a study of the hydrozirconation of aromatic olefins [1]. We showed that compounds **1** and **2** (eq. 1) mainly undergo hydrogenation, since very

(1)



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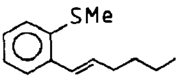
low or negligible amounts of deuterium were incorporated after deuterolysis. This was in sharp contrast to the behaviour of other aromatic alkenes studied, e.g. **3** and **4**, which gave the corresponding deuterated alkanes (almost exclusively the α-D isomer) under identical conditions.

In an attempt to establish whether the hydrogenation is favoured by the sulphur atom and/or electronic differences between the aromatic parts of **1** and **2** on the one hand and **3** and **4** on the other, we decided to prepare and hydrozirconate the thio analogue of **4**, 1-(1-hexenyl)-2-thiomethylbenzene (**5**).



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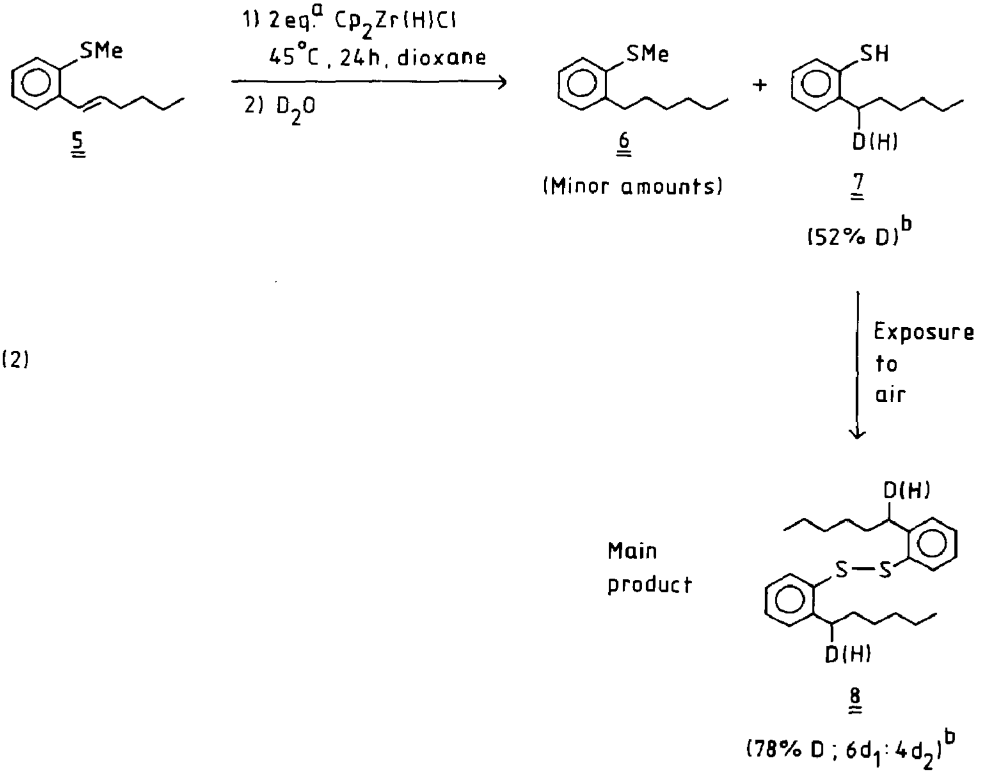
Results and Discussion

The reaction of **5** with $Cp_2Zr(H)Cl$ at 25 °C was very sluggisch, with nearly 90% of the starting material remaining after about 24 h. Since the rate of hydrozirconation is usually higher at slightly elevated temperatures, we conducted a few experi-



(2)

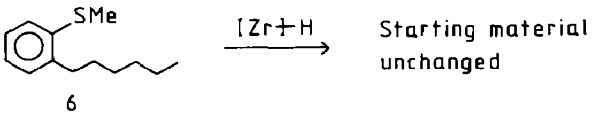
[a] Assuming a quantitative yield in the reaction between Cp_2ZrCl_2 and Red-Al (cf. Experimental).

[b] Relative amount of deuterium incorporated as calculated from ^1H NMR and/or mass spectra. In the case of the disulphide **8**, this means the fraction (78%) with at least one deuterium incorporated.

ments at 45 ° C. Under these conditions, the reaction of the methoxy analogue **4** (eq. 1) gave deuterated 1-hexyl-2-methoxybenzene (~ 80%; 70% deuterium incorporated) [1] whereas reaction of **5** with 2 eq. $Cp_2Zr(H)Cl$ took a totally unexpected course (eq. 2).

The thiol **7***, identified by GLC-MS, was oxidized to disulphide **8** (70% yield by GLC based on **5**) when exposed to air, and so it was difficult to isolate. Products **6** and **8** were identified by GLC-MS and, after HPLC purification, by ^1H and ^2H NMR spectroscopy (cf. Experimental).

No reaction occurred, as indicated by GLC examination, when the saturated analogue of **5** was treated with $Cp_2Zr(H)Cl$ (eq. 3), irrespective of whether isolated or in situ generated zirconium hydride was used. In the latter case, aluminium compounds (from Red-Al used for in situ generation) are present.

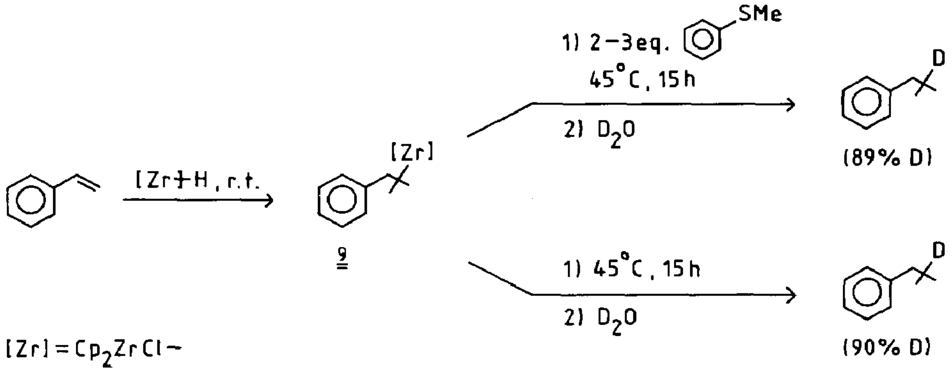
(3) 

6

[Zr] = Cp_2ZrCl–

That no cleavage could be observed in this case indicates that the process is not similar to the corresponding aluminium-mediated cleavage of aryl alkyl ethers [2].

The presence of sulphur in the vicinity of the double bond is apparently crucial, as indicated by the results shown in eq. 4. When thioanisole was added to a solution of **9**, much less than 5% of thiophenol (relative to the amount thioanisole added) was formed, as estimated by GLC. The thiophenol was then oxidized to diphenyldisulphide (GLC-MS). The deuterium incorporation was not influenced to any significant extent by the presence of thioanisole.

(4) 

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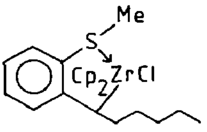
* If *S*-deuterated thiol is formed it probably undergoes H/D exchange during work-up (cf. Experimental). That *S*-deuterated thiol is not present in the crude product is supported by a calculation, taking account of the proportion deuterium in **7**, which gave a degree of deuteration and a d_1/d_2 ratio in **8** in excellent agreement with results obtained by mass spectrometry (eq. 2).

We believe that these observations (equations 3 and 4) imply an intramolecular cleavage of compound **5** (eq. 2), which also would lead to the nondeuterated thiol **7**: We suggest that intermediate **A** is initially formed [1]. A hydride–chloride exchange



A

at zirconium might then occur, in a process involving $Cp_2Zr(H)Cl$ [3]. The resulting alkylzirconium hydride could then undergo reductive elimination, yielding a complex of **6** and biscyclopentadienylzirconium(II) ("Cp_2Zr"), in which sulphur is coordinated to the metal *.

It seemed to us highly likely that such a complex, could undergo insertion of zirconium(II) into the sulphur–methyl bond, since such insertions are known for, e.g., carbon–halogen [4,9], carbon–oxygen [4b], and sulphur–sulphur [10] bonds **.

In order to examine this possibility we carried out the corresponding deuterozirconation of compound **5** (Table 1). It is evident from Table 1 that if the pathway outlined in the text above operates, it cannot account for more than part of the nondeuterated compounds **6** and **7** after reaction with $Cp_2Zr(H)Cl$ (eq. 2). The extents of deuteration (Table 1) after deuterozirconation/hydrolysis of **5** are far too low. Furthermore, the relative amounts of dideuterated **6** and **7** ***, and tri- and tetradeuterated **8** also are too low.

The formation of nondeuterated **6** and **7** in the reaction of **5** with $Cp_2Zr(D)Cl$ can not be easily explained †.

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* Alkane elimination from alkylzirconium hydrides is induced by phosphines [4], acetylenes [5], carbon monoxide [6], and ethylene [7]. These compounds can act as electron donors and can also stabilize the resulting zirconium(II) ("Cp_2Zr"). Both properties seem to be important [4b]. The thiomethyl group would probably function in the same manner, since it has been concluded from IR data that the *d*-orbitals of sulphur are available for back-bonding interaction with a transition metal in a low oxidation state [8].

** Insertion of zirconium into the aryl–sulphur bond would also be expected. Traces (GLC) of phenylhexane (47% D incorporated; GLC-MS) were found after deuterolysis of the reaction mixture.

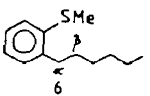
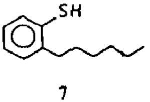
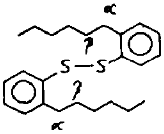
*** We suggest that 19% of the deuterated fraction of **7** refers to the α,β-dideuterio analogue of **7** (Table 1). This would be consistent with the formation of β-deuterated **A** and the pathway proposed. It would then also be reasonable to assume, that the remaining 81% of deuterated thiol corresponds to β-monodeuterated **7**. The disulphide **8** (formed from **7**) would have 16% of its deuterium at the α-position, which is in agreement with what was found (^2H NMR of **8**; 19% α-D). The proportion of d_0, d_1 and d_2 in **7** was used to calculate the amount of nondeuterated **8**. The result (14%) was the same as that determined by mass spectrometry for **8** after deuterozirconation/hydrolysis of **5**.

† It might be suspected that a H/D exchange process is responsible for this. Participation of the solvent in such a process was ruled out in similar cases [1,11]. In one such case [11], $(C_5D_5)_2Zr(H)Cl$ was used. No evidence was obtained for the participation of the cyclopentadienyl hydrogens in H/D exchange. Deuterium could not be detected in the biscyclopentadiene formed by deuterozirconation/hydrolysis of **5**.

When 1-phenyl-1-hexene was treated with 2 eq. $Cp_2Zr(D)Cl$ (same batch), all the phenylhexane formed after quenching with water had at least one deuterium incorporated.

Table 1

Analysis of products obtained after reaction of 5 with $Cp_2Zr(D)Cl$ [a]

Product	Degree of deuteration (%) [b]	Composition of deuterated fraction (%) [c]				Position of deuterium [d]		
		d_1	d_2	d_3	d_4	α	β	γ-ϵ
 6	55	58	30	7	4	30	50	20
 7	63	81	19	–	–			
 8	86	32	42	19	7	19	81	

[a] The experiment was conducted in 1,4-dioxane for 23 h at 45 ° C. ~ 2 eq. $Cp_2Zr(D)Cl$ was used. The reaction was quenched with water. [b] As determined by GLC-MS at 15 eV (cf. Experimental). These figures correspond to the fractions with at least one D incorporated. [c] As determined by GLC-MS (15 eV). [d] Determined by ^2H NMR after HPLC purification (cf. Experimental).

For formation of the α-deuterated thiol in the hydrozirconation (eq. 2), we suspected the intermediacy of an organozirconium species in which the metal is covalently bound to both sulphur and the carbon α to the aromatic ring. Unfortunately, mass spectrometry of the crude organometallic residue after removal of the solvent gave no indication of the presence of such an intermediate. Furthermore, no methyl chloride, which should formally be produced at the same time as this intermediate, could be detected (GLC-MS).

This unexpected sulphur–carbon bond cleavage, and previous results [1,12], show limitations of hydrozirconation as a method for converting olefins into substituted hydrocarbons [13]. Such limitations are of importance when considering the use of hydrozirconation for synthetic purposes.

Experimental

General

The ^1H and ^2H NMR spectra were recorded on a Varian XL-300 MHz spectrometer at 299.943 and 46.004 MHz, respectively. The ^1H NMR ($CDCl_3$) shifts are relative to TMS, and ^2H NMR ($CHCl_3$) shifts relative to TMS-d_{12}. Mass spectra were recorded on a Finnigan 4021 (Data System Incos 2100) spectrometer operating at 15 or 70 eV. The degree of deuteration after hydrozirconation/deuterolysis was calculated from the mass spectra (15 eV) using undeuterated compounds as references; these reference compounds were either purchased or obtained by hydrolysis of samples withdrawn from the hydrozirconation mixtures. Gas chromatographic analyses were performed on a Varian 3300 Gas Chromatograph equipped with (a) a

2 m glass column containing 5% OV17 on Chromosorb W (100–120 mesh); 100–300 °C, 15 °C/min, or (b) a 2 m glass column containing 3% Carbowax 20 M on Supelcoport 100/120; 40(10 min) −200 °C, 30 °C/min. Elution band areas (quantitative GLC analyses) were determined electronically using a Varian 4270 integrator. For HPLC separations a Polygosil C_{18} column (50 × 0.5 cm) connected to a Constametric pump was used. An RI-detector (LKB) was used. The separations were made with acetonitrile (Baker Chemicals BV) as eluent. Flow rate: 2 ml/min. Elemental analyses were performed at Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim a.d. Ruhr, West Germany).

1,4-Dioxane and toluene were dried by refluxing over sodium wire and distilled prior to use. All other solvents used for procedures requiring anhydrous conditions were dried by standard methods. Red-Al (Aldrich) was diluted with anhydrous toluene and stored under nitrogen. Deuterium oxide (99.8% D, Norsk Hydro), 2-bromothioanisole (Aldrich), styrene (Janssen Chimica), Cp_2ZrCl_2 (Aldrich) and other materials obtained from commercial sources were used as received. Thioanisole (Schuchardt) was distilled prior to use. For preparative TLC, 20 × 20 cm plates (Merck), pre-coated with silica (Kieselgel 60 F_{254}), were used. $Cp_2Zr(H)Cl$ [14], $Cp_2Zr(D)Cl$ [14], $Pd(PPh_3)_4$ [15] and 1-hexenylboronic acid [16] were prepared by published methods.

Glassware, used for reactions in an inert atmosphere or for storage of anhydrous solvents and reagents, was thoroughly dried.

Hydrozirconations were carried out under nitrogen or argon. Solid transfers were performed under nitrogen in a drybox. Liquid transfers were performed with a syringe or with nitrogen pressure by the septum technique. Unless 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 2–3 h.

1-(1-Hexenyl)-2-thiomethylbenzene (5)

Suzuki's method [17] for related compounds was used. A mixture of 4.0 g (19.7 mmol) of 2-bromothioanisole and 1.15 g (5 mol-%) of tetrakis(triphenylphosphine)-palladium ($Pd(PPh_3)_4$) was stirred for about 15 min, then 5.0 g (~ 2 eq.) of 1-hexenylboronic acid (used without previous recrystallisation) in 80 ml THF was added, followed by 30 ml of 2 *M* aqueous sodium hydroxide. The mixture was refluxed for 4 h. After cooling, the mixture was diluted with pentane and washed with 2 *M* sodium hydroxide then with water. The organic layer was dried overnight ($MgSO_4$), then filtered and concentrated, and the crude product was flash chromatographed with pentane as eluent. Yield: 88%. A small sample was further purified (preparative TLC) for elemental analysis.

^{1}H NMR: δ 7.47–7.15 (m, 4H, arom.); 6.83 (d, *J* 15.6 Hz, 1H, vinyl); 6.19 (dt, *J* 15.5, 7.0 Hz, 1H, vinyl); 2.47 (s, 3H, $-SCH_3$); 2.30 (q, 2H, allyl); 1.59–1.37 (m, 4H); 0.98 (t, 3H). Anal. Found: C, 75.69; H, 9.11. $C_{13}H_{18}S$ (206.33) calc: C, 75.67; H, 8.79%.

Hydrozirconation of 5

The procedure was as described previously [1]. The conditions are shown in eq. 2. After deuterolysis and mass spectrometric examination, compounds **6** and **8** were isolated by HPLC and analyzed by NMR. The yield of disulphide **8** was found to be ca. 70% (based on **5**) by GLC (column (a)) in a separate run after quenching with water. (Small amounts of finely-divided sodium hydroxide were added before GLC-analysis.) n-Eicosane was used as internal standard. The yield of **6** was about 10–20% as estimated by GLC. See eq. 2 for results.

*Compound **6***

^{1}H NMR: δ 7.22–7.05 (m, 4H, arom.); 2.70 (t, 2H, α-CH_2); 2.46 (s, 3H, -SCH_3); 1.62 (p, 2H, β-CH_2); 1.45–1.25 (m, 6H); 0.90 (t, 3H). ^{2}H NMR: δ 2.73 (α-CH*D*; 32%); 0.91 (-CH_2*D*; 68%).

Mass spectrum (15 eV): m/e 208 M^+; the degree of deuteration was found to be only 8%. Anal. Found: C, 75.02; H, 9.77. $C_{13}H_{20}S$ (208.35) calc: C, 74.94; H, 9.68%.

Compound 7

Mass spectrum (70 eV): m/e 195 (d_1-M^+); 194 (d_0-M^+); 124; 123; the degree of deuteration was found to be 52%.

*Compound **8***

^{1}H NMR: δ 7.55 (dt, J 6.6, 1.5 Hz; 2H, arom.); 7.2–7.1 (m, 6H, arom.); 2.76 (α-CH) *; 1.60 (p, 4H, β-CH_2); 1.44–1.26 (m, 12H); 0.90 (t, 6H). ^{2}H NMR: δ 2.80 (α-CH*D*).

Mass spectrum (70 eV): m/e 388 (d_2-M^+); 387 (d_1-M^+); 386 (d_0-M^+); 195; 194; 193; 123. The degree of deuteration (15 eV) was found to be 78% ($6d_1/4d_2$). Anal. Found: C, 74.35; H, 8.65. $C_{24}H_{34}S_2$ (386.63) calc: C, 74.55; H, 8.86%.

In one experiment the reaction mixture was centrifuged under nitrogen. The clear supernatant liquid was then transferred to a dry Schlenk tube and concentrated in vacuo. Mass spectrometric analysis of the crude organometallic residue gave no indication of the nature of any zirconium intermediates (cf. Results and Discussion).

*Treatment of **6** with $Cp_2Zr(H)Cl$*

This was carried out as previously described for hydrozirconation [1] using isolated or in situ generated $Cp_2Zr(H)Cl$. No reaction occurred (eq. 3), the starting material **6** remaining unchanged as indicated by GLC (column (a), n-eicosane as internal standard).

*Treatment of **9** with thioanisole*

Styrene was hydrozirconated to completion (1,4-dioxane, room temperature) as judged by GLC analysis of a small deuterolysed sample (column (b); propylbenzene as internal standard). Deuterium was incorporated to the extent of 95% in the ethylbenzene formed (GLC-MS). The remaining mixture was split into two parts. Both parts were heated (45 °C) for 15 h, one alone and the other after addition of 2–3 eq. thioanisole. After deuterolysis, much less than 5% of thiophenol (relative to the amount thioanisole added as estimated by GLC) was formed, and was then oxidized to diphenyl disulphide (GLC-MS). Thioanisole had no significant influence on the deuterium incorporation in ethylbenzene (GLC-MS; eq. 4).

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* No integral is given since this carbon was partly deuterated (cf. ^{2}H NMR).

Deuterozirconation of 5

$Cp_2Zr(D)Cl$ (~ 2 eq.) was used. This reaction was performed as previously described [1], except that a dry Schlenk tube, fitted with a cap and a septum on the side arm, was used. The reaction was carried out at 45°C for 23 h. Before quenching with water the reaction mixture was allowed to cool and the vapour in the vessel was analysed by mass spectrometry. Methyl chloride, which formally could be produced, was not detected (cf. Results and Discussion). After hydrolysis, the mixture was treated as described for hydrozirconation above. Results are given in Table 1.

Compound **6**: ^2H NMR δ 2.68 (α-CHD); 1.60 (β-CHD); 1.31 (γ-ϵ).

Compound **8**: ^2H NMR δ 2.76 (α-CHD); 1.60 (β-CHD).

Acknowledgements

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