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Hydrozirconation of oleyl sulphides and oleyl phenylsulphone

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Abstract

The hydrozirconation of 9-(*Z*)-octadecenylmethyl-sulphide, 9-(*Z*)-octadecenyl phenyl sulphide and 9-(*Z*)-octadecenyl phenyl sulphone have been studied. These compounds underwent substantial elimination of the functional group, yielding after hydrolysis, along with saturated and unsaturated sulphides and sulphones, large amounts of octadecane. The saturated analogues (dodecylmethyl-sulphide, octadecyl phenyl sulphide and octadecyl phenyl sulphone) were unaffected by the hydrozirconation reagent under similar conditions.

Introduction

Conversion of olefins with internal double bonds into terminally functionalised alkanes by hydrozirconation, a procedure developed by Schwartz *et al.* [1] is well known to organic chemists. Isomerisation over several bonds can be achieved, as was illustrated by Gibson [2], who prepared 1-iododotetracontane from 21-dotetracontene. The hydrozirconation–isomerisation reaction could find wider applications in synthesis, provided that it is compatible with common functional groups. We have studied the possible conversion of α-functionalised long chain alkanes, derived from the easily accessible oleic acid, into α,ω-difunctionalised compounds [3–7]. In connection with these studies, it was of interest to investigate the hydrozirconation of internal olefins with terminal sulphur-containing substituents, since nothing was known about their reactivity in this respect.

We report below on a study on hydrozirconation of 9-(*Z*)-octadecenylmethyl-sulphide (**1a**), 9-(*Z*)-octadecenyl phenyl sulphide (**1b**), and 9-(*Z*)-octadecenyl

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Table 1

Hydrozirconation of 9-(*Z*)-octadecenyl sulphides and 9-(*Z*)-octadecenyl phenyl sulphone with 3 equiv. of $Cp_2Zr(H)Cl$ in 1,4-dioxane, followed by hydrolysis [a]

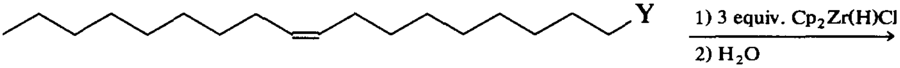
Starting material	Temperature (°C)	Reaction time (h)	Product distribution (%)	
			2	**3+4**
1a	40–45	24	38	62
1b	45	23.5	56	39
1c	40–45	22	33	63

[a] Yields determined by GLC analysis. The saturated **3a–c** and unsaturated **4a–c** sulphides and sulphones could not be separated under the GLC conditions used. The presence of both the unsaturated and saturated compounds was confirmed by MS analysis (*cf*. Experimental).

phenyl sulphone (**1c**), and compare the results with those for the related oxazolines [3,4], tertiary amines [5], alcohols [7] and, in particular, ethers [6].

Results and discussion

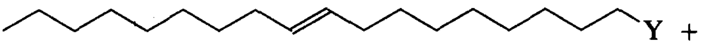
Hydrozirconation of **1a–c** with 3 equiv. of bis(cyclopentadienyl)-zirconium hydrido chloride, $Cp_2Zr(H)Cl$ (prepared as described by Buchwald *et al.* [8]) in 1,4-dioxane at 40–45°C for 22–24 h, followed by hydrolysis, gave considerable amounts of octadecane. In the case of 9-(*Z*)-octadecenyl phenyl sulphide (**1b**) octadecane was the major product, while the methyl-sulphide derivative **1a** and the sulphone **1c** were less prone to undergo cleavage of the carbon–sulphur bond (eq. 1, Table 1) and gave octadecane only as a minor product.



(**1a**: Y = SMe; **1b**: Y = SPh; **1c**: Y = SO_2Ph)

$n\text{-}C_{18}H_{38} + n\text{-}C_{18}H_{37}\text{—}Y\ +$

(**2**) (**3a–c**)



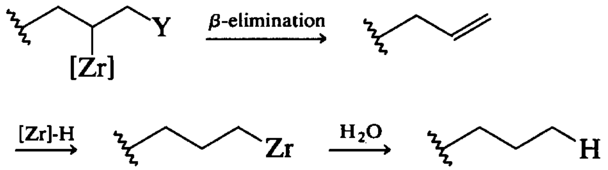
(**4a–c**)

positional double bond isomers (1)

We conclude that the carbon–sulphur bonds are not cleaved by direct reaction of $Cp_2Zr(H)Cl$ with the functional group, since neither dodecylmethyl sulphide (**5**), octadecyl phenyl sulphide (**3b**), nor octadecyl phenyl sulphone (**3c**) produce the corresponding alkane upon hydrozirconation (eq. 2).

$$CH_3\text{—}(CH_2)_n\text{—}CH_2\text{—}Y \xrightarrow[\text{1,4-dioxane}]{\substack{\text{2.1 equiv. }Cp_2Zr(H)Cl\\ \text{26–28 h, 40–45°C,}}} \text{no reaction} \quad (2)$$

(**5**: $n = 10$, Y = SMe;
3b: $n = 16$, Y = SPh;
3c: $n = 16$, Y = SO_2Ph)



$Y = S\text{–}Me, S\text{–}Ph, SO_2\text{–}Ph$, O-tetrahydropyranyl, $O\text{–}CH_2\text{–}Ph, O^tBu$
$[Zr] = Cp_2ZrCl$

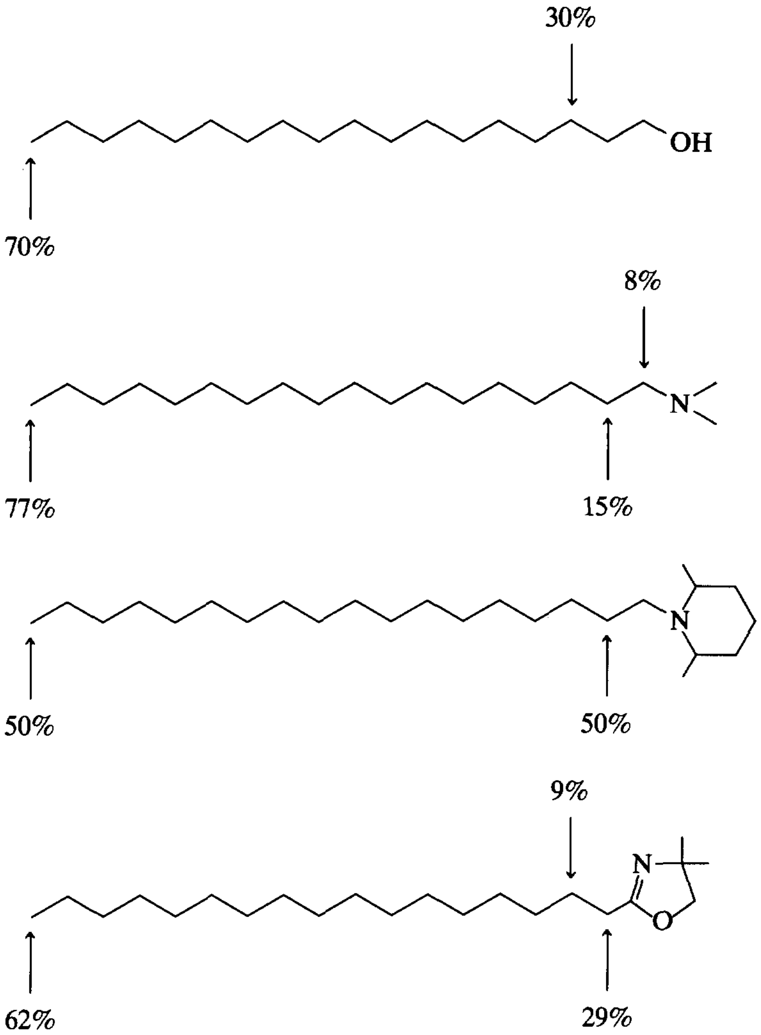
Scheme 1.

This is in agreement with Lipshutz's [9] observation that alkynyl phenyl sulphides and tosylates are compatible with hydrozirconation with commercial $Cp_2Zr(H)Cl$. There are examples of hydrozirconation reactions in which sulphur-containing functional groups give abnormal or unexpected products. For example, hydrozirconation of 2-(1-(*E*)-hexenyl)- and 3-(1-(*E*)-hexenyl)-thiophene [10] resulted in a high degree of hydrogenation, while hydrozirconation of 1-(1-(*E*)-hexenyl)-2-thiomethylbenzene [11] induced cleavage of the methyl group. We believe that the octadecane (**2**) produced by hydrozirconation of compounds **1a–c** is formed after migration of the zirconium moiety to the position beta to the functional group, followed by β-elimination and subsequent hydrozirconation of the 1-octadecene formed (Scheme 1). This mechanism is supported by the formation of thiophenol (GLC) after hydrozirconation of **3b**. We [6] and others [12] have previously suggested a similar pathway to account for cleavage of the carbon–oxygen bond in related alkenyl ethers. There are many examples in the literature of the successful use of ethers as protecting groups [9,13]. Either the elimination reaction does not occur because the site of attack of the zirconium moiety is remote from the ether group and migration of the zirconium is prevented or impossible, or alternatively the structural requirements for elimination are absent.

The high degree of carbon–heteroatom fission that is observed with the sulphur compounds **1a–c** and alkyl ethers severely limits the synthetic use of the hydrozirconation–migration reaction with these substrates. A prerequisite for preparatively useful reactions is not only that the functional group remains intact but also that a regiocontrolled derivatisation of one intermediate carbon–zirconium derivative can be achieved. Oxazoline, tertiary amine, and hydroxyl groups in the terminal position remain intact during hydrozirconation [3–5,7], but unfortunately relatively stable α-, β-, or γ-zirconium derivatives are formed in considerable amounts in addition to the ω-zirconium derivatives, and mixtures of regioisomers are obtained after reaction with electrophiles (Scheme 2).

Attempts to improve the yields of ω-functionalised products by raising the reaction temperature above 40–50°C led to decomposition [2,14] and increased hydrogenation [10], although the ω-selectivity could be improved [10].

Except for the preparation of ω-bromo-oxazolines from internally unsaturated fatty acid oxazolines [4], attempted applications of the hydrozirconation-isomerisation reaction to terminally functionalised long chain olefins have so far been unsuccessful. This is mainly due to carbon–heteroatom cleavage, as exemplified in this report (for $R\text{–}SMe$, $R\text{–}SPh$, $R\text{–}SO_2Ph$, $R\text{–}OR'$) or low regioselectivity ($R\text{–}OH$, $R\text{–}NR'_2$, oxazoline).



Scheme 2.

Experimental

Materials

Amberlyst A-26 (Sigma), bis(cyclopentadienyl)zirconium dichloride (Aldrich), dodecyl bromide (EGA), methyl-trioctylammonium chloride (Merck), octadecyl bromide (Fluka) and thiophenol (Merck) were used as received from the commercial sources indicated. $Cp_2Zr(H)Cl$ [8] and 9-(*Z*)-octadecenyl bromide [15] were prepared by published procedures.

General

The ^1H NMR spectra were recorded on a Varian XL-300 MHz spectrometer at 299.943 MHz; the shifts are given relative to TMS in $CDCl_3$. Mass spectra were recorded on a Jeol SX-102 spectrometer at 70 eV. The GLC analyses were performed on a Varian 3300 gas chromatograph equipped with a 2 m glass column containing 3% Carbowax 20M on Supelcoport 100/120. Pentadecane was used as internal standard for quantitative GLC analyses. Elution band areas were determined electronically with a Varian 4270 integrator. Silica gel 60 (0.040–0.063 (Merck)) was used for flash chromatographic purifications [16]. Melting points are uncorrected.

General procedures

All the hydrozirconation reactions were carried out under dry nitrogen or argon. The solvent (1,4-dioxane (BDH)) was dried by refluxing over sodium wire, and distilled under nitrogen prior to use. Solid transfers to thoroughly dried glassware were performed under nitrogen in a dry-box. Liquid transfers were performed with a syringe or by the septum technique under nitrogen pressure.

9-(Z)-Octadecenylmethyl sulphide (1a)

The method described by Degani *et al.* [17] for related compounds was used. A mixture of 9-(*Z*)-octadecenyl bromide (1.55 g, 4.67 mmol), potassium *O*-methyl dithiocarbonate (0.71 g, 4.85 mmol), methyl-trioctylammonium chloride (0.16 g), and water (5.0 mL) was stirred vigorously for 30 min at ambient temperature. The mixture was diluted with cyclohexane (5.0 mL); then potassium hydroxide pellets (1.32 g, 23.5 mmol) were added with vigorous stirring and the mixture was heated at 70°C for 30 min. Pentane (15 mL) was added and the organic layer was separated and filtered past silica with pentane as eluent. The solvent was removed *in vacuo*. Flash chromatography, with a mixture of pentane and ether (99 : 1) as eluent, gave 0.87 g (62%) of somewhat unpure **1a**. Preparative TLC on 20 × 20 cm plates (Merck), pre-coated with silica (Kiselgel 60 F_{254}), with pentane/ether (99 : 1) as eluent gave 120 mg of purer product per 200 mg of crude material. The isolated compound was approximately 95% pure as indicated by GLC analysis.

^{1}H NMR: δ 0.88 (broad t, 3 H, alkyl-CH_3); 1.20–1.43 (m, 22 H, chain); 1.52–1.65 (quin, 2 H, CH_2–CH_2–S); 1.93–2.06 (m, 4 H, allyl); 2.10 (s, 3 H, CH_3–S); 2.48 (t, 2 H, CH_2–S); 5.35 (m, 2 H, vinyl).

9-(Z)-Octadecenyl phenyl sulphide (1b)

The method described by Herriot and Picker [18] for related compounds was used. A mixture of thiophenol (0.49 g, 4.45 mmol), sodium hydroxide (0.30 g, 7.50 mmol), water (5.0 mL), 9-(*Z*)-octadecenyl bromide (1.50 g, 4.53 mmol), toluene (4.0 mL), and methyl-trioctylammonium chloride (~ 50 mg) was stirred vigorously for 45 min at ambient temperature. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. Flash chromatography with pentane as eluent gave 1.44 g (90%) of the title compound.

^{1}H NMR: δ 0.88 (broad t, 3 H, CH_3); 1.20–1.47 (m, 22 H, chain); 1.65 (quin, 2 H, CH_2–CH_2–S); 1.95–2.06 (m, 4 H, allyl); 2.92 (t, 2 H, CH_2–S); 5.35 (m, 2 H, vinyl); 7.25–7.35 (m, 5 H, arom.). Anal. Found: C, 79.96; H, 11.15. $C_{24}H_{40}S$ (360.646) calc.: C, 79.93; H, 11.18%.

9-(Z)-Octadecenyl phenyl sulphone (1c)

The method described by Manescalchi *et al.* [19] for related compounds was used. A mixture of Amberlyst A-26, benzenesulphinate form (1.66 g, ≈ 5.9 mequiv.), and 9-(*Z*)-octadecenyl bromide (1.50 g, 4.53 mmol) in toluene (15.0 mL) was refluxed with vigorous stirring for 3 h. The resin was filtered off, and washed with CH_2Cl_2. The solvent was removed *in vacuo* from the filtrate and washings. Flash chromatography with a mixture of pentane and ether (9:1) as eluent gave 0.65 g (36%) of the title compound.

^1H NMR: δ 0.87 (broad t, 3 H, CH_3); 1.21–1.40 (m, 22 H, chain); 1.64–1.76 (m, 2 H, CH_2-CH_2-SO_2); 1.90–2.04 (m, 4 H, allyl); 3.03–3.11 (m, 2 H, CH_2-SO_2); 5.35 (m, 2 H, vinyl); 7.53–7.69 and 7.88–7.93 (m, 5 H, arom.). Anal. Found: C, 73.34; H, 10.27. $C_{24}H_{40}O_2S$ (392.645) calc.: C, 73.42; H, 10.27%.

Octadecyl phenyl sulphide (3b)

The procedure described above for the preparation of the unsaturated analogue was used. The amounts of starting materials were as follows: thiophenol (5.00 g, 45.4 mmol); sodium hydroxide (3.00 g, 75.0 mmol); water (50.0 mL); octadecyl bromide (15.2 g, 45.6 mmol); toluene (40.0 mL); methyl-trioctylammonium chloride (0.1 g). Recrystallisation from pentane, followed by drying *in vacuo*, gave 15.8 g (96%) of a white crystalline compound, with a melting point of 55–56°C (lit. 55.5–56.5°C [20]).

^1H NMR: δ 0.88 (broad t, 3 H, CH_3); 1.20–1.35 (m, 28 H, chain); 1.35–1.48 (distorted quin, 2 H, CH_2-CH_2-CH_2-S); 1.64 (quin, 2 H, CH_2-CH_2-S); 2.91 (t, 2 H, CH_2-S); 7.22–7.35 (m, 5 H, arom.).

Octadecyl phenyl sulphone (3c)

The procedure described above for the preparation of the unsaturated analogue was used. The amounts of starting materials were as follows: Amberlyst A-26, benzenesulphinate form (4.40 g, ≈ 15.6 mequiv.); octadecyl bromide (4.00 g, 12.0 mmol); toluene (15.0 mL). Recrystallisation from pentane, followed by drying *in vacuo*, gave 1.77 g (37%) of a white crystalline compound, with a melting point of 62–63°C (lit. 61–62°C [20]).

^1H NMR: δ 0.88 (broad t, 3 H, CH_3); 1.20–1.35 (m, 30 H, chain); 1.65–1.76 (m, 2 H, CH_2-CH_2-SO_2); 3.03–3.11 (m, 2 H, CH_2-SO_2); 7.54–7.70 and 7.88–7.93 (m, 5 H, arom.).

Dodecylmethyl sulphide (5)

A procedure analogous to that described above for 9-(*Z*)-octadecenylmethyl sulphide was used. The amounts of starting materials were as follows: dodecyl bromide (12.5 g, 50.1 mmol); potassium *O*-methyl dithiocarbonate (7.61 g, 52.0 mmol); methyl-trioctylammonium chloride (1.7 g); water (50.0 mL); cyclohexane (50.0 mL); potassium hydroxide pellets (14.0 g, 250 mmol). Distillation under reduced pressure gave 4.22 g (boiling point: 85°C/0.5 mmHg) of somewhat contaminated title compound. Flash chromatography, with pentane as eluent, gave 1.98 g (18%) of approximately 95% pure compound, as indicated by GLC analysis.

^1H NMR: δ 0.88 (broad t, 3 H, alkyl-CH_3); 1.20–1.47 (m, 18 H, chain); 1.59 (quin, 2 H, CH_2-CH_2-S); 2.10 (s, 3 H, CH_3-S); 2.49 (t, 2 H, CH_2-S).

Hydrozirconation of sulphides and sulphones

The hydrozirconation reagent, $Cp_2Zr(H)Cl$, was dissolved in 10–30 mL of dry 1,4-dioxane. A solution of the substrate and internal standard (see General procedures), in 5–10 mL of solvent was added. For hydrozirconation of saturated substrates the amount of substrate was 1.27–1.39 mmol and that of $Cp_2Zr(H)Cl$, 2.10–4.21 mmol, and for hydrozirconation of unsaturated substrates, 0.50–1.38 mmol of substrate and 1.50–4.14 mmol (3.0 equiv.) of $Cp_2Zr(H)Cl$ were used. The mixtures were stirred at 40–45°C for 22–28 h (the reaction temperatures and times for hydrozirconation of the unsaturated compounds are given in Table 1). The mixtures were then treated with 5 mL of water and stirred for 2 h, after which samples for GLC were withdrawn. No reaction was observed in the case of saturated substrates. The results of the GLC analyses of the reactions with the unsaturated substrates are given in Table 1. Since the unsaturated and saturated sulphides and sulphones could not be separated under the GLC conditions used, GLC–MS analyses were performed in order to confirm the presence of these substances. The following peaks were found: substrate **1a**: m/e 285 ($[(C_{18}H_{37}\text{–}SMe) - Me]^+$, **3a**) and 283 ($[(C_{18}H_{35}\text{–}SMe) - Me]^+$, **4a**); substrate **1b**: m/e 362 ($[C_{18}H_{37}\text{–}SPh]^+$, **3b**) and 360 ($[C_{18}H_{35}\text{–}SPh]^+$, **4b**); substrate **1c**: m/e 394 ($[C_{18}H_{37}\text{–}SO_2Ph]^+$, **3c**) and 392 ($[C_{18}H_{35}\text{–}SO_2Ph]^+$, **4c**). No conclusions about the relative proportions of the products could be drawn from these spectra owing to the overlap of the compounds in the chromatogram.

Acknowledgements

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