Reactions of cyclopentadienyl(phosphine)-(α-benzenesulfonylalkyl)nickel complexes; formation of aldehydes and alkenes from sulfones

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Abstract

Three reactions of the cyclopentadienyl(phosphine)(α-benzenesulfonylalkyl)nickel complexes have been investigated: (i) oxidation with oxygen is shown to provide a new and efficient method of preparing aldehydes from sulfones; (ii) treatment with strong Lewis acids gives the corresponding terminal alkenes (the mechanism is briefly discussed); (iii) deprotonation by strong bases gives an anionic species which can in turn be alkylated by iodomethane.

We recently described the new nickel complexes $Cp(PR_3)NiCH(R_1)SO_2Ph$ in which the metal center is linked to a carbon atom bearing a benzenesulfonyl group [1]. These complexes were made in order to provide information about the nature and reactivity of C–Ni bond in such species and to throw some light on the mechanism of the various reactions of α-sulfonyl carbanions promoted by transition metal salts [2,3].

These complexes proved to be fairly stable, decomposing only at about 90°C to give $α,β$-unsaturated sulfones via $β$-elimination [1]. We now report on the reactions of these complexes with dioxygen, Lewis acids, and strong bases.

Oxidation by dioxygen

Few examples of oxidation of alkylnickel complexes by dioxygen have been specifically described although it is well known that these compounds, like many organometallic species, are unstable in air. Oxygen has been shown to induce reductive elimination from a bis(phosphine)(aryl)(methyl)nickel(II) to give toluene [4], whereas it seems to insert into the nickel–carbon bond of bis(triphenylmethyl)nickel to give eventually several products arising from the $Ph_3CO\cdot$ radical [5].

Treatment of a THF solution of $Cp(PPh_3)NiCH(R_1)SO_2Ph$ ($R_1 = n\text{-}C_{11}H_{23}$, Ia) with oxygen was found to yield the corresponding aldehyde in a rather slow reaction.

Table 1

Oxidation of 10 ml of 0.1 M THF solutions of $Cp(PR_3)NiCH(n-C_{11}H_{23})SO_2Ph$ (Ia, R = Ph; Ib, R = n-Bu) by oxygen, with or without added acid

Complex PR$_3$	acid added	duration hours	dodecanal yield	other products
Ia	none [a]	100	70	
Ia	HCl 1 N [b]	0,5	75	
Ib	none [a]	120	37	$\{\begin{array}{l} PhSO_2C_{12}H_{25}\ (20\%) \\ PhSO_2CH=CHC_{10}H_{21}\ (40\%) \end{array}$
Ib	HCl 1 N [b]	2	30	$PhSO_2C_{12}H_{25}$ (65%)

[a] The THF solution was kept under a moisture-free oxygen atmosphere. [b] 5 ml added; stirring under air.


$$(1)$$

(Ia)
(R = n-C$_{10}$H$_{21}$)
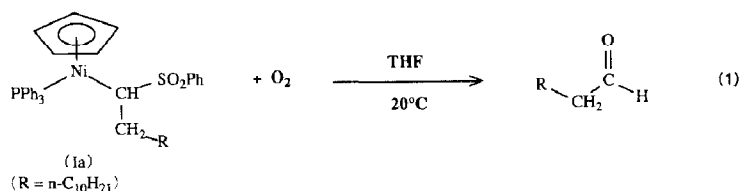
It took as long as 100 hours at room temperature for the reaction to go to completion. However, as can be seen from Table 1, it is very efficiently catalyzed by strong aqueous acids.

Hydrolysis of the triphenylphosphine complex Ia by the aqueous acid does not effectively compete with oxidation; thus it took 15 days to convert this complex into phenyl dodecyl sulfone by treatment with 1 M aqueous H_2SO_4 under argon. The more electron rich tributylphosphine complex Ib is more rapidly hydrolyzed; in this case hydrolysis by 1 M sulfuric acid under argon was complete in 4 days. However in the air the hydrolysis of the complex is much faster (see table 1), a 65% yield of free sulfone being obtained in 2 hours.

In the absence of protons, the reaction of the tributylphosphine complex Ib with oxygen is more complicated than that of Ia. The yield in aldehyde is never high and some type of disproportionation takes place, leading to a mixture of saturated and vinylic sulfones.

Conversion of sulfones into oxygen functions is an important process, as pointed out by Magnus [6]. Several ways of converting them into aldehydes or ketones are known [7*], but each has some disadvantages. Our method does not require isolation of the nickel complexes, thus treatment of the lithium derivative of phenyl dodecyl sulfone with a stoichiometric amount of $Cp(PPh_3)NiCl$ followed by hydrolysis in air gave dodecanal in a 52% yield:


$$(2)$$

(R = n-C$_{10}$H$_{21}$)

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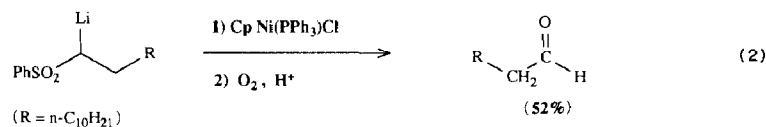
* Reference number with asterisk indicates a note in the list of references

Oxidation of the allylic compound IIa (from phenyl prenyl sulfone) by oxygen under acidic conditions gave the γ-hydroxysulfone in good yield. No aldehyde could be detected.

$$O_2, H^+ \quad THF \qquad (3)$$

(72%)

(IIa)
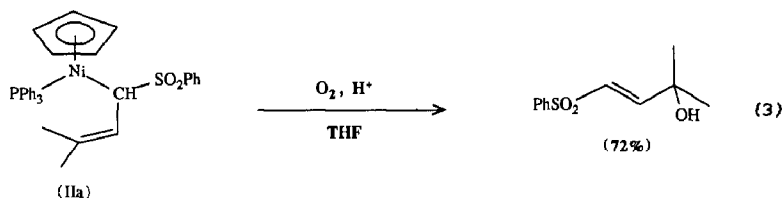
Reaction with Lewis acids

The formation of symmetrical alkenes by nickel(II)-catalyzed coupling of α-sulfonyl carbanions [2] raised the question of the possible carbenoidic behaviour of α-sulfonylalkyl nickel species.

$$2\% \ Ni(acac)_2 \qquad RCH = CHR \qquad (4)$$
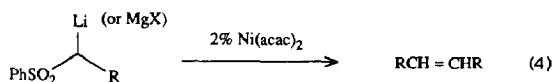
We thus decided to see whether complexes such as Ia or Ib could generate carbene complexes in a way similar to that reported for sulfonium [8] or sulfide [9] derivatives:

$$\qquad ? \qquad PhSO_2^- \qquad (5)$$
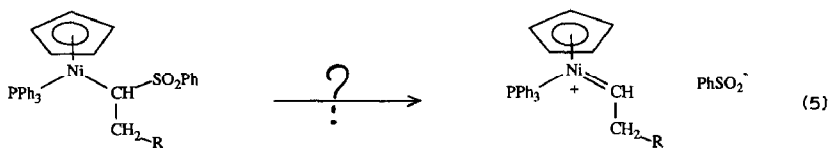
Since thermal decomposition of complexes Ia and Ib gave only α,β-unsaturated sulfones via β-elimination [1], we decided to use Lewis acids to assist the departure of the benzenesulfonyl leaving group [10]. Under these conditions we did, indeed, observe cleavage of the carbon sulfur bond and formation of the terminal alkene:

$$\text{1) } AlCl_3 \qquad R\text{-}CH = CH_2 \qquad (6)$$
$$\text{2) } H_2O$$

(Ia)
$(R = n\text{-}C_{10}H_{21})$
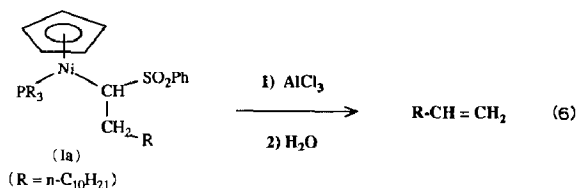
The results in Table 2 show that the reaction requires strong Lewis acids and non-coordinating solvents. Again, better yields are obtained from Ia (PPh₃) than Ib (PBu₃).

In order to gain a better understanding of this reaction, a β,β-bis(deuterated alkyl) sulfone was prepared, converted into the corresponding nickel complex, and finally treated with aluminium chloride in dichloromethane.
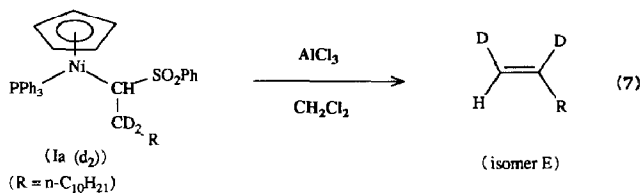
$$AlCl_3 \qquad CH_2Cl_2 \qquad (7)$$

(Ia (d₂))
$(R = n\text{-}C_{10}H_{21})$

(isomer E)

Table 2

Reaction of complexes Ia and Ib with Lewis acids at 20°C

Complex	Lewis acid (equiv.)	Solvent	Duration (h)	Dodecene (%)
Ia	$AlCl_3$ (2)	cyclohexane	3	45
Ia	$AlCl_3$ (2)	CH_2Cl_2	4	60
Ia	$AlCl_3$ (2)	THF [a]	2	0
Ia	BF_3OEt_2 (1)	toluene	48	0
Ia	$TiCl_4$ (2)	CH_2Cl_2	0.25	57
Ib	$TiCl_4$ (2)	CH_2Cl_2	1.5	30 [b]

[a] The same result was obtained when the mixture was heated under reflux. [b] Mixed with 10% of vinylic sulfone.

As expected, the 1,2-bis(deuterated alkene) was formed in a 60% yield, but surprisingly with a pure E stereochemistry as shown by ^{13}C and ^{1}H NMR spectra [11]. This stereoselectivity would be hard to reconcile with the 1,2 H shift from the primary carbene complex to give a π olefin complex. Further evidence against a carbene complex was obtained in that no norcarane was formed when $Cp(PPh_3)NiCH_2SO_2Ph$, IIIa was treated with $AlCl_3$ in the presence of a large excess of cyclohexene.

A possible mechanism for the formation of the olefin from complex Ia could involve decoordination of the phosphine, followed by β-elimination, to give a transient nickel hydride with the E vinylic sulfone [12*] as a π ligand. Displacement of the sulfonyl moiety by the hydride would be expected to take place with retention of stereochemistry (as in the case of hydrogenolysis of vinylic sulfones with Grignards and nickel catalysis [13]) to give the E-bis(deuterated olefin).

Deprotonation and alkylation of complex IIIa

The possibility of using $Cp(PPh_3)NiCH_2SO_2Ph$ (IIIa) as starting material to prepare other complexes by metallation and alkylation of the methylene group was studied next.

Rather few related studies have been described previously for this family of nickel complexes. Barefield showed [8] that in the course of the reaction of $Cp(PPh_3)NiCl$ with trimethyl sulfonium ylide the α-sulfonium complex formed could be deprotonated and then react with another molecule of $CpNi(PPh_3)Cl$, but the deprotonation takes place at a methyl group, not at the methylene α to the nickel atom. Booth and Casey treated some alkyl or α-silylalkyl nickel complexes with n-butyllithium in the presence of an excess of nickelocene to prepare a methylidine trinickel cluster [14]. Deprotonation at the carbon α to nickel atom was suggested as the first step of this reaction.

It was hoped that the electron withdrawing properties of the benzenesulfonyl group would lead to stabilization of the lithium derivative of complex IIIa.
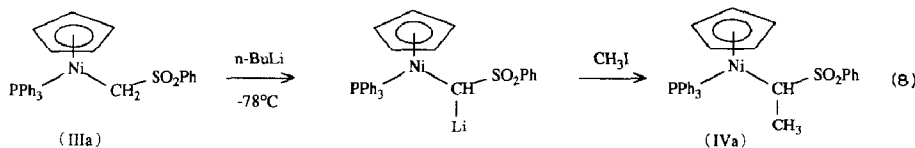
When one equivalent of n-butyllithium was added dropwise to the green THF solution of IIIa at −78° C, the mixture immediately turned red. The red solution appeared to be fairly stable at −78° C but decomposed rapidly on warming up. Upon addition of iodomethane at −78° C, it turned green again. The ethylsulfone complex IVa was obtained as the major product, together with a little unchanged starting material IIIa. More work is needed to characterize this red compound fully, but the reaction seems to involve the formation of a new species in which the same carbon atom bears a sulfonyl group as well as two different metal atoms.

Experimental

Reactions were carried out under dry argon by standard Schlenk tube techniques. Solvents were dried and distilled over suitable reagents (P_2O_5 for pentane and petroleum ether, calcium hydride for dichloromethane, molten sodium for toluene, the benzophenone radical anion for diethyl ether and THF) and deoxygenated prior to use. Chromatography was carried out on neutral alumina (Merck 90, activity I, 0.063–0.200 mm) hydrated with 6% water.

The ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in hexadeuterobenzene or deuterochloroform with TMS as internal standard. The ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer. UV spectra were recorded on a Varian Superscan 3 instrument. Combustion analyses were performed by the "Service de microanalyse de l'Université Pierre et Marie Curie" Paris.

Cyclopentadienyl triphenylphosphine nickel chloride was prepared according by Schroll's procedure [15]. Cyclopentadienyl tributylphosphine nickel chloride was made in 84% yield by the procedure described for the preparation of Cp Ni(PBu$_3$)Br, involving reaction in refluxing DME [15]: m.p. 58° C, lit. [16] 59° C.

The phenyl methyl, phenyl ethyl, phenyl dodecyl and phenyl prenyl sulfones were prepared by reaction of sodium benzenesulfinate with the corresponding halide in DMF; β,β-bis(deuterated dodecyl phenyl) sulfone was prepared from α,α-bis(deuterated dodecanal) [17] by LiAlH$_4$ reduction of the aldehyde followed by PBr$_3$ bromination of the alcohol, and treatment of the β,β-bis(deuterated dodecyl) bromide with sodium benzenesulfinate: it had m.p. 29° C; ^{1}H NMR (CDCl$_3$) 0.91 (t, J 7 Hz, 3H); 1.14–1.42 (m, 18H); 3.08 (s, 2H) 7.56–7.74 (m, 3H); 7.91–8.00 (m, 2H), consistent with the spectrum of phenyl dodecyl sulfone [3], m/z (CI: NH$_3$) 330 [$M + 18$]$^+$.

General procedure for the preparation of α-benzenesulfonylalkyl nickel complexes

The sulfone (2.5 mmol) was dissolved in 15 ml THF and the solution was cooled to −78° C; n-Butyllithium (1.56 ml of 1.6 M solution in hexane, 2.5 mmol) was added, then the mixture was stirred at low temperature for 15 min and allowed to warmed to 0° C. This solution of lithiated sulfone was then added to a red solution of CpNi(PR$_3$)Cl(2.5 mmol) in 20 ml of THF at 0° C. The mixture was allowed to warm to room temperature then stirred for 4 h, during which it gradually changed from red to brownish green. After removal of any remaining carbanion by treatment with 50 μl of water, the solution was dried over magnesium sulfate, filtered, and taken to dryness under vacuum. The product was purified by recrystallization (toluene/petroleum ether or dichloromethane/petroleum ether) for triphenylphos-

phine complexes, or by chromatography on hydrated alumina for tributylphosphine complexes.

Cp(PPh₃)NiCH(n-C₁₁H₂₃)SO₂Ph (Ia). Yield 55%; m.p. (toluene/petroleum ether) 114°C. UV (THF): λ_{max} 454 nm; $\epsilon = 1060$. ¹H NMR (C_6D_6): 1.04 (t, *J* 7 Hz, 3H); 1.17–1.47 (m, 20H); 2.23–2.40 (m, 1H); 5.66 (s, 5H); 7.07–7.14 (m, 3H); 7.15–7.28 (m, 9H); 7.68–7.76 (m, 2H); 7.96–8.08 (m, 6H). Anal. Found: C, 70.37; H, 7.26. $C_{41}H_{49}NiO_2PS$ calcd.: C, 70.79, H, 7.10%.

Cp(PPh₃)NiCH(CD₂-n-C₁₀H₂₁)SO₂Ph (Ia(d₂)). Yield 57%; ¹H NMR (C_6D_6): 1.08 (t, *J* 7 Hz, 3H); 1.19–1.50 (m, 18H); 2.32 (d, *J* 15 Hz, 1H), 5.70 (s, 5H); 7.11–7.18 (m, 3H); 7.20–7.30 (m, 9H); 7.73–7.79 (m, 2H); 7.98–8.11 (m, 6H).

Cp(PBu₃)NiCH(n-C₁₁H₂₃)SO₂Ph (Ib). Yield 62%; green viscous oil. UV (THF): λ_{max} 445 nm; $\epsilon = 919$. ¹H NMR (C_6D_6): 1.03–1.20 (m, 12H); 1.27–1.86 (m, 36H); 1.99–2.20 (m, 3H); 5.71 (s, 5H); 7.19–7.33 (m, 3H); 8.19–8.30 (m, 2H). Anal. Found: C, 65.72; H, 9.72. $C_{35}H_{61}NiO_2PS$ calcd.: C, 66.13; H, 9.67%.

Cp(PPh₃)NiCH(SO₂Ph)CH=C(CH₃)₂ (IIa). M.p. (toluene/petroleum ether): 147–150°C. UV (THF): λ_{max} 461 nm; $\epsilon = 2072$; ¹H NMR (C_6D_6): 0.30 (s, 3H); 1.67 (s, 3H); 3.35 (d,d, *J* 13.5 Hz, 12.5 Hz, 1H); 5.71 (d, *J* 12.5 Hz, 1H); 5.75 (s, 5H); 7.05–7.13 (m, 3H); 7.17–7.32 (m, 9H); 7.85–8.06 (m, 8H). Anal. Found: C, 71.35; H, 5.87. $C_{34}H_{33}NiO_2PS \cdot C_7H_8$ (including one mole of toluene per mole of complex as shown by X-ray structure determination [1]) Calcd.: C, 71.62; H, 6.01%.

Cp(PPh₃)NiCH₂SO₂Ph (IIIa). M.p. (CH_2Cl_2/petroleum ether): 145–150°C dec. UV (THF): λ_{max} 438 nm; $\epsilon = 1098$; ¹H NMR (C_6D_6): 2.06 (d, *J* 8 Hz, 2H); 5.68 (s, 5H); 6.96–7.03 (m, 3H); 7.12–7.21 (m, 9H); 7.80–7.96 (m, 8H). Anal. Found: C, 66.51; H, 4.95. $C_{30}H_{27}NiO_2PS$ calcd.: C, 66.58; H, 4.99%.

Cp(PPh₃)NiCH(CH₃)SO₂Ph (IVa). M.p. (CH_2Cl_2/petroleum ether): 138–140°C dec. UV (THF): λ_{max} 447 nm; $\epsilon = 1150$; ¹H NMR (C_6D_6): 1.02 (d, *J* 7 Hz, 3H); 2.15 (d,q, *J* 14.5 Hz, 7Hz, 1H); 5.69 (s, 5H); 6.98–7.09 (m, 3H); 7.10–7.22 (m, 9H); 7.82–7.97 (m, 8H). Anal. Found: C, 67.11; H, 5.33. $C_{31}H_{29}NiO_2PS$ calcd.: C, 67.06; H, 5.22%.

Oxidation of complexes Ia and Ib. Formation of dodecanal Uncatalyzed oxidation. 1 mmol of the benzenesulfonylalkylnickel complex was dissolved in 10 ml of THF. The argon atmosphere was replaced by oxygen, then 0.5 mmol of tridecane (GLC internal standard) was added and the solution vigorously stirred. Formation of the aldehyde was monitored by GLC. When reaction was complete the solution was washed with aqueous iron(II) solution then dried, and the solvent removed under vacuum. Rapid filtration through silica gel (dichloromethane as eluent) gave a solution of aldehyde free from transition metal salts, when complex Ib was the starting material the solution also contained dodecyl and dodec-1-enyl [3] sulfones.

Acid catalyzed oxidation. A solution of 1 mmol of benzenesulfonyl alkylnickel complex and 0.5 mmol of tridecane (GLC internal standard) in 10 ml of THF was placed in an open conical flask containing 5 ml of 1 *N* aqueous HCl (or in some cases aqueous H_2SO_4). The mixture was vigorously stirred. After a few minutes, the solution turned deep red, and the colour was slowly discharged. Subsequently 10 ml of dichloromethane were added, the liquids were decanted, and the aqueous layer extracted with 10 ml of dichloromethane. The combined organic layers were washed with water then dried. Removal of the solvent gave the crude product mixture, which was analyzed (GLC or NMR) or chromatographed.

Oxidation of complex IIa. Formation of the hydroxysulfone

By use of the acid catalyzed oxidation procedure described above, the hydroxy-sulfone was obtained in 72% yield after crystallization from dichloromethane/pentane. E-3-Methyl-3-hydroxy-1-phenylsulfonyl but-1-ene: m.p. 100–101°C; ^{1}H NMR ($CDCl_3$): 1.39 (s, 6H); 2.50 (m, 1H); 6.59 (d, J 15 Hz, 1H); 7.04 (d, J 15 Hz, 1H); 7.60–7.70 (m, 3H); 7.86–7.93 (m, 2H). Anal. Found: C, 58.31; H, 6.23. $C_{11}H_{14}O_3S$ calcd.: C, 58.41; H, 6.19%.

Procedure for direct transformation of phenyl dodecyl sulfone into dodecanal

The sulfone (2.5 mmol) was dissolved in 15 ml THF and the solution was cooled to −78°C; n-Butyllithium (1.56 ml of 1.6 M solution in hexane, 2.5 mmol) was then added, and the mixture was stirred at low temperature for 15 min then allowed to warm to 0°C. This solution of lithiated sulfone was then added to a red solution of CpNi(PR$_3$)Cl (2.5 mmol) in 20 ml of THF at 0°C. The mixture was allowed to warm to room temperature, then stirred for 2 h, and then treated in air with 10 ml of 1 N aqueous HCl. The solution rapidly became colourless. The usual extraction procedure gave a crude product mixture containing 1.3 mmol (52% yield) of dodecanal, which was isolated by chromatography.

Reaction with Lewis acids

Aluminium trichloride. One mmol of complex Ia was dissolved in 15 ml of solvent (CH_2Cl_2, cyclohexane or THF) containing 0.5 mmol of tridecane (GLC internal standard). The solution was added to freshly sublimed AlCl$_3$ (2 mmol) suspended or dissolved in 3 ml of the solvent. The mixture was stirred at room temperature for a few hours (see table 2), and then hydrolyzed with dilute HCl. After the usual extraction procedure the alkene was isolated by passage through silica gel with pentane as eluent.

Titanium tetrachloride. TiCl$_4$ (2 mmol) was added from a Hamilton syringe to a solution of 1 mmol of complex Ia or Ib in 15 ml of dichloromethane (with or without GLC internal standard). The mixture was stirred at room temperature for about 1 h then worked up as described above.

Reaction of the bis-deuterated complex Ia(d_2) with AlCl$_3$. The procedure described above gave E-1,2-bis(deuterated dodec-1-ene): m/z (electron impact at 70 eV) 170; ^{1}H NMR($CDCl_3$) [18*]: 0.87 (t, J 7.5 Hz, 3H); 1.17–1.33 (m, 16H); 2.03 (t, J 7.5 Hz, 2H); 5.00 (br. s, 1H), in agreement with the reported spectrum of E-1,2-bis(deuterated oct-1-ene) [11]; ^{13}C NMR: 14.11 (CH$_3$); 22.72 (CH$_2$); 28.98 (CH$_2$); 29.21 (CH$_2$); 29.39 (CH$_2$); 29.62 (CH$_2$); 29.71 (2 CH$_2$); 31.96 (CH$_2$); 33.68 (CH$_2$); 113.43–113.67–113.91 (CHD); 138.55–138.77–139.00 (CD).

Deprotonation and alkylation of complex IIIa

To a cold (−78°C) solution of 1 mmol (541 mg) complex IIIa in 20 ml of THF was slowly added 1 mmol of n-butyllithium (0.62 ml of 1.6 M solution in hexane). The colour immediately turned from green to deep red. The solution was stirred at −78°C for 15 min then 2 mmol of methyl iodide were added. The mixture was stirred for 15 min during which it gradually turned back to green. It was then allowed to warm up to room temperature, the solvent was pumped off, and the residue was chromatographed through hydrated alumina to give 380 mg of green crystals, which were shown to consist of a 20/80 mixture of complexes IIIa and IVa

by NMR spectroscopy (spectra of the initial complexes and IIIa and IVa were available).

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18 Compare the spectrum of non deuterated dodec-1-ene under the same conditions: 0.87 (t, J 7.5 Hz, 3H); 1.17–1.33 (m, 16H); 2.03 (q, J 7.3 Hz, 2H); 4.93 (d, J 10.5 Hz, 1H); 5.01 (d, J 18 Hz, 1H); 5.85 (d,d,t, J 18, 10.5, 7.3 Hz, 1H).