Ruthenium-Catalysed Selective Transetherification of Substituted Vinyl Ethers To Form Acetals and Aldehydes

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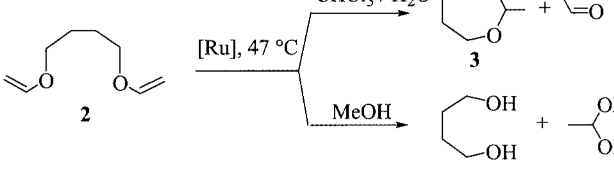
The water-soluble ruthenium allenylidene complex [{RuCl(μ-Cl)(C=C=CPh$_2$)(TPPMS)$_2$}$_2$]Na$_4$ catalyses the selective transformation of substituted linear and cyclic vinyl ethers with MeOH, under mild non acidic conditions, to give acetals, while aldehydes and ketones are obtained in a CHCl$_3$/H$_2$O mixture, which allows for easy recycling of the catalyst. NMR studies showed that the reaction follows a transetherification mechanism rather than simple acid-catalysed hydrolysis.

Introduction

Unsaturated transition-metal carbene complexes, M=C=(C)$_n$=C, such as vinylidenes (n = 0)[1] and allenylidenes (n = 1),[2] are a ubiquitous class of organometallic compounds whose use in catalysis has gained an increasing consideration during the last decade.[3] In this regard, particular emphasis has been placed on ruthenium vinylidene complexes, which have been shown to catalyze several important processes targeting the elaboration of linear and cyclic organic compounds.[3,4] More recently, ruthenium allenylidene species have also started attracting interest as catalysts or catalyst precursors and have been employed to achieve important metal-mediated reactions such as alkene ring closing metathesis (RCM),[5a−5e] ring opening metathesis polymerisation[5f,5h] and propargylation of aromatic compounds.[6]

In a previous communication we have described the first example of a water-soluble transition metal allenylidene complex of formula [{RuCl(μ-Cl)(C=C=CPh$_2$)(TPPMS)$_2$}$_2$]Na$_4$ (**1**) [TPPMS = Ph$_2$P{2-OS(O)$_2$-C$_6$H$_4$}$^-$}].[7] As a first exploratory assessment of its catalytic activity, we have demonstrated that this ruthenium(II) complex may be successfully used in the selective ring-opening metathesis (ROM) of cyclic olefins with methylacrylate as chain-transfer reagent. In order to further evaluate the catalytic activity of this water-soluble unsaturated carbene complex, we decided to investigate its behaviour under the conditions of RCM of acyclic dienes,[8−11] a reaction which is well-known with several Grubbs-type ruthenium catalysts,[12,13] including the few that are soluble in water.[14]

However, in spite of our expectations, the reaction of **1** in a biphasic CHCl$_3$/H$_2$O system with representative substrates such as diethyl diallylmalonate and *N*,*N*-diallyltosylamide failed to give any RCM reaction. Thus, when 1,4-butanediol vinyl ether (**2**) was chosen as substrate, we observed that, although not affording RCM products as reported for other Ru-carbene species,[15] complex **1** was still endowed with catalytic activity, bringing about the selective formation of ethanal and 1,4-butandiol, followed by their intermolecular condensation to generate 2-methyl-[1,3]dioxepane (**3**) in almost quantitative yield. When the same reaction was carried out in methanol, the isolated products were 1,1-dimethoxyethane and 1,4-butanediol (Scheme 1). Although this catalytic method is of little synthetic interest, and the reaction under scrutiny can be performed without the need for expensive transition-metal catalysts, this serendipitous discovery nevertheless represents a completely new reaction to the best of our knowledge, and on this basis we decided to study its general applicability and tried to unravel its mechanism.



Scheme 1

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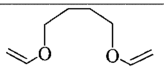
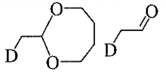
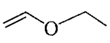
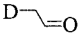
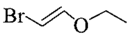
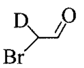
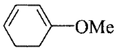
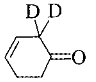
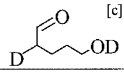
Results and Discussion

In order to explore the scope of the reaction, we applied our catalytic system to a series of linear and cyclic vinyl ethers bearing different functional groups. The nature of the final products depends strictly on whether the reactions are run under monophasic (MeOH) or biphasic ($CHCl_3$/H_2O) conditions. All the tests were run under very mild conditions (47 °C). The results are summarised in Table 1 and 2 for biphasic and monophasic conditions, respectively. Our protocol is highly specific for vinyl ethers, as diallyl, diethyl, dibenzyl and allylpropargyl ethers were recovered intact after the catalytic tests. This indicates a high tolerance of the method for a wide variety of organic substrates and suggests a potential application for the selective deprotection of masked aldehydes protected as vinyl ethers, such as acid sensitive β-hydroxy aldehydes. However, only trivial products were obtained from the ethers of choice as these were deliberately chosen for screening purposes only.

Table 1. Catalytic reactions of linear and cyclic vinyl ethers in the presence of **1** in $CDCl_3$/D_2O[a]

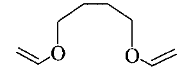
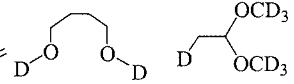
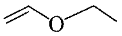
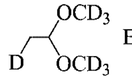
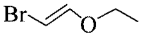
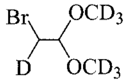
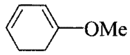
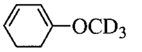
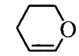
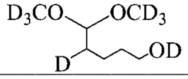
Entry	Substrate	Product(s)
1		
2		 EtOD
3		 [b] EtOD
4		 MeOD
5		 [c]

[a] Reaction conditions: substrate (0.1 mmol), **1** (0.005 mmol), $CDCl_3$ (0.5 mL), D_2O (0.5 mL), 47 °C, 2.5 h, in NMR tube (5 mm) under Ar. [b] Bromoacetaldehyde is not stable under the reaction conditions and cyclotrimerizes to 2,4,6-tris(bromodeuteromethyl)-1,3,5-trioxane (see Exp. Sect.). [c] The aldehyde 5-hydroxypentanal intramolecularly condenses to 3-deuterotetrahydro-2*H*-pyran-2-deuterol, equilibrium yield 84% (see Exp. Sect.).

The reactions were carried out on an NMR-tube scale at first and then repeated in bulk to check for reproducibility and to isolate the products. For all reactions the two methods gave similar results, showing that NMR-scale tests can be representative of the actual catalytic test under the same conditions. Under NMR tube reaction conditions, at 47 °C with a 1:1 $CDCl_3$/D_2O mixture, all vinyl substrates were smoothly converted within three hours, reaching complete selectivity for the products described in Table 1, as determined by NMR spectroscopy and GC-MS techniques. The deep-red coloured catalytically active species remains confined to the water phase and can be recycled up to four times without significant loss of activity (see Exp. Sect.).

An interesting reaction is the selective deuteration of 1-methoxy-1,3-cyclohexadiene to yield 2,2-dideuterocyclohex-3-en-1-one (Table 1, entry 4) where the selective double deuteration at the 2-position follows from H/D exchange via a keto-enol equilibrium (see Scheme 4 in the Exp. Sect.). For linear vinyl ethers the formation of CD_3-diacetals was observed, resulting from the condensation of acetaldehyde and CD_3OD by cleavage of the vinyl carbon-oxygen bond. For example, 2-bromovinyl ethyl ether was converted into 2-bromo-2-deutero-1,1-bis(trideuteromethoxy)ethane (Table 2, entry 8). For cyclic vinyl ethers such as dihydropyran, ring opening and acetalization occur to give the protected 5-trideuteroxy-2-deuteropentan-1-al (Table 2, entry 10). 1-Methoxy1,3-cyclohexadiene was converted into the deuterated OCD_3 analogue (kinetic product) instead of the corresponding diacetal (Table 2, entry 9) which forms only after a week at 47 °C.

Table 2. Catalytic reactions of linear and cyclic vinyl ethers in the presence of **1** in CD_3OD[a]

Entry	Substrate	Product(s)
6		
7		 EtOD
8		 EtOD
9		 MeOD
10		

[a] Reaction conditions: substrate (0.1 mmol), **1** (0.005 mmol), CD_3OD (1.0 mL), 47 °C, 17 h, in NMR tube (5 mm) under Ar

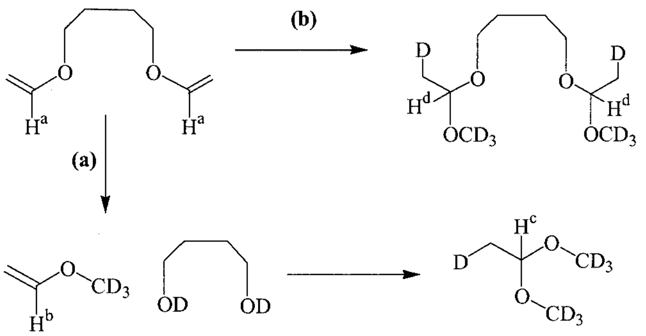
We chose 1,4-butanediol vinyl ether (**2**) to test the effect of catalyst concentration on the rate and selectivity of the reaction. In $CDCl_3$/D_2O, the reaction reached completion in 2.5 hours with 5 mol % of catalyst **1**, 8 h with 1 mol % and 20 h with 0.2 mol %, in all cases with selectivity higher than 99%. In CD_3OD, the reaction is slower (17 h) and normally 5 mol % of **1** are required to complete the reaction in a comparable time scale. The nature of the ruthenium precursor was also found to be crucial for the reaction. A series of precursors was tested for the reaction of **2** under standard conditions; the results are summarised in Table 3. Remarkably, while the classic Grubbs catalyst does not work under these reaction conditions, the water-soluble phenylvinylidene complex $[RuCl_2\{C{=}C(H)Ph\}(TPPMS)_2]Na_2$ (**4**)[7] shows a similar reactivity to **1** in promoting the acetalization of **2**. These results are significant and indicate that ruthenium, TPPMS and *unsaturated carbenes* are necessary ingredients in this reaction either as molecular complexes or to form the catalytic species in situ (Table 3, entries 18 and 19). However, catalytic tests with isolated samples of **4** were not systematically evaluated due to the lower stability and difficulty of isolation of **4** compared to **1**.[7]

Table 3. Blank reactions and effect of Ru precursor on the conversion of **2** to 1,4-D-butanediol and 1,1-D-dimethoxy-2-D-ethane[a]

Entry	Precursor	Yield (%)	Time (h)
11	None	–	70
12	TPPMS	–	70
13	$[RuCl_2(CHPh)(PCy_3)_2]$	–	20
14	$[Cp^*Ru(PEt_3)_2Cl]$	–	20
15	$[RuCl_2(PPh_3)_3]$	–	20
16	$[RuCl_2(TPPMS)_2]_2$	80	1 month
17	$[RuCl_2(PPh_3)_3]$ + 4 TPPMS	30	18
18	$[RuCl_2(PPh_3)_3]$ + 4 TPPMS + $HC{\equiv}CPh$	93	16
19	$[RuCl_2(PPh_3)_3]$ + 4 TPPMS + $HC{\equiv}CC(OH)Ph_2$	95	17

[a] Reaction conditions: substrate (0.1 mmol), precursor (0.005 mmol), CD_3OD (1.0 mL), 47 °C, 17 h, in NMR tube (5 mm) under Ar

We obtained evidence for a transetherification mechanism by monitoring the reaction of **2** with **1** in CD_3OD by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy at 47 °C. The decrease in the intensity of the signal at $\delta = 6.49$ ppm (dd, $J_{H,H}$ = 14.3, 7.0 Hz) due to the vinyl proton H^a (Scheme 2a) was accompanied by an increase in the intensity of a new signal at $\delta = 6.51$ ppm (dd, $J_{H,H}$ = 14.2, 6.8 Hz) that we attribute to H^b, which in turn decreases in intensity with the appearance of the signal due to H^c at $\delta = 4.56$ ppm (dt, $J_{H,H}$ = 5.2, $J_{H,D}$ = 1.8 Hz) belonging to the final product. A parallel experiment, carried out replacing **1** with HOTs, ruled out the possibility of acid-catalysed hydrolysis of the substrate (Scheme 2b).[16–18] Under these conditions, **2** is immediately converted into a new species that does not contain a vinyl group, is stable and is plausibly the product of addition of CD_3OD to the vinyl double bond as evidenced by the diagnostic H^d signal at $\delta = 4.66$ ppm (dt, $J_{H,H}$ = 5.4, J_{HD} = 1.6 Hz). Although a detailed mechanism cannot be proposed on the basis of the NMR study alone, these latter experiments suggest that the reaction occurs as a two-step transformation of the vinyl substrate by exchange of the ether substituent, followed by addition of alcohol to the C=C double bond with regioselective deuteration of the β-carbon. $^{31}P\{^1H\}$ NMR monitoring of the biphasic reaction shows that **1** quantitatively transforms into an unknown ruthenium species (singlet at $\delta = 21.4$ ppm), which remains catalytically active over more than four runs.



Scheme 2. NMR mechanistic experiments: (a) **2**, 0.1 mmol; **1**, 0.005 mmol. CD_3OD 1.0 cm^3; 47 °C; 24 h, in NMR tube (5 mm) under Ar; (b) **2**, 0.1 mmol; HOTs, 0.01 mmol. CD_3OD 1.0 mL; 47 °C; 24 h, in NMR tube (5 mm) under Ar

Conclusion

In summary, our study provides an insight into the reactivity of vinyl ethers in the presence of a Ru-allenylidene complex and an alternative method for the production of acetals, aldehydes and ketones from a wide choice of vinyl ether precursors.[19] Although the present method is certainly not convenient for routine applications, it is important to stress that this protocol affords catalytic solvolysis of vinyl ethers under mild conditions at neutral pH in aqueous phase or anhydrous organic phase, with high tolerance for a variety of functional groups. As a consequence, the present ruthenium catalyst might deserve application in particular cases where the vinyl ether functionality is coupled with acid-sensitive groups. We are currently investigating more interesting applications of the catalytic protocol, such as the synthesis of polyacetals[20] and podands. Preliminary experiments showed that our system is active in the selective catalytic synthesis of a variety of linear polyethers by acetalization of vinyl ethyl ether with various glycols.

Experimental Section

General Remarks: Complex **1** was prepared as described previously.[7] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian VXR300, or Bruker AVANCE DRX300 spectrometers operating at ca. 300 MHz (^1H) and ca. 75.4 MHz (^{13}C). Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at ca. 121 MHz. Chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. A Shimadzu GC-14A/GCMS-QP2000 instrument was employed for GC-MS investigations.

Bulk-Scale Experiments: In a typical macro scale experiment, 3 mmol of substrate were added under argon to 2 mL of MeOH together with 0.03 mmol of **1**. After 2 h whilst stirring at 47 °C the solvent was removed giving the 1,1-dimethoxy-substituted product. When a biphasic system was used, 3 mmol of vinyl ether and

0.03 mmol of **1** were dissolved into 1 mL of $CHCl_3$ and 1 mL of H_2O under argon. The mixture was kept at 47 °C for 1 h under vigorous stirring, then the organic phase was separated and dried over $MgSO_4$. The aldehyde or ketone was obtained in nearly quantitative yield by evaporation at reduced pressure of the solvent.

Typical Experimental Procedure for NMR-Tube Tests. (a) Monophasic Conditions: Compound **1** (11 mg, 5×10^{-3} mmol) was introduced into a 5 mm NMR tube, which was repeatedly evacuated and filled with argon. The substrate (20 equiv., typically 15−18 μL) was then added together with 0.5 mL of CD_3OD, to obtain an orange-red homogeneous solution. The tube was kept in an oil bath at 47 °C for typically 15−17 hours after which ^1H and ^{13}C NMR spectra were collected.

(b) Biphasic Conditions: As above, except for solvent (a mixture of $CDCl_3$, 0.5 mL and D_2O, 0.5 mL was used) and reaction time (typically 3 h). The tube was shaken thoroughly after mixing of the reagents and before taking the NMR spectra.

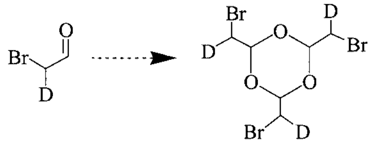
Experimental Procedure for Catalyst Recycling Tests: An NMR tube was charged with **1** (12.5 mg, 5.7×10^{-3} mmol), **2** (18 μL, 0.114 mmol), 0.5 mL of $CDCl_3$ and 0.5 mL of D_2O. The tube containing two separate phases was kept at 47 °C for 3 h, during which time it was shaken approximately every 20 min. After separation of the organic phase, the aqueous phase, which contained the catalyst, was proved to be active in the catalytic reaction during three additional runs carried out by adding 18 μL of **2** to 0.5 mL of $CDCl_3$ (a 100% conversion of **2** was achieved after 2.3 h in the first catalytic run, after 2.5 h in the second catalytic test and after 2.75 h in the third run). Only in the fourth catalytic run was a significant decrease of the catalytic activity observed — the reaction time to transform all of the substrate rose to about 4 h.

NMR and GC-MS Product Characterisation

2-Deuteromethyl-[1,3]dioxepane: (Table 1, entry 1). ^1H NMR (300.13 MHz, $CDCl_3$, room temp.): $\delta = 1.32$ (dt, $J_{H,H} = 5.16$, $J_{H,D} = 1.8$ Hz, 2 H, CH_2D), 1.70 (m, 4 H, OCH_2CH_2), 3.67 (m, 2 H, $OCHH$), 3.93 (m, 2 H, $OCHH$), 4.95 (t, $J_{H,H} = 5.16$ Hz, $OCHO$) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): $\delta = 28.9$ (s, OCH_2CH_2), 66.4 (2 OCH_2), 100.4 (s, $OCHO$), 31.7 (t, $J_{C,D} = 18.5$ Hz, CH_2D) ppm. GC/MS: m/z (%) = 117 (5) [$C_6H_{11}O_2D$], 101 (43) [$C_5H_9O_2$], 71 (87) [C_4H_7O], 55 (53) [C_4H_7], 43 (100) [C_2H_3O].

Deuteroacetaldehyde: (Table 1, entries 1, 2). ^1H NMR (300.13 MHz, $CDCl_3$, room temp.): $\delta = 9.79$ (br. t, $J_{H,H} = 2.80$ Hz, 1 H, CHO), 2.19 (dt, $J_{H,H} = 2.80$, $J_{H,D} = 2.25$ Hz, 2 H, CH_2D) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): $\delta = 200.89$ (s, CHO), 21.49 (t, $J_{C,D} = 19.5$ Hz, CH_2D) ppm. GC/MS: not registered.

Bromodeutero Acetaldehyde: (Table 1, entry 3). Bromoacetaldehyde, which selectively forms from the reaction of **1** with 1-bromo-2-ethoxyethene, is not stable under the reaction conditions and cyclotrimerizes spontaneously to 2,4,6-tris(bromodeuteromethyl)-1,3,5-trioxane (see Scheme 3 below). The NMR analysis of the reaction mixture reveals the presence of both the aldehyde (minor component) and the cyclotrimer. ^1H NMR (300.13 MHz, $CDCl_3$, room temp.): bromoacetaldehyde: $\delta = 9.55$ (d, $J_{H,H} = 2.5$ Hz, CHO), 3.86 (dt, $J_{H,H} = 6.8$, $J_{H,D} = 2.5$ Hz, $CHDBr$) ppm; 2,4,6-tris(bromodeuteromethyl)-1,3,5-trioxane: $\delta = 4.68$ (d, $J_{H,H} = 5.5$ Hz, $CHOO$), 3.61 (dt, $J_{H,H} = 5.5$, $J_{H,D} = 1.9$ Hz, $CHDBr$) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): bromoacetaldehyde: $\delta = 191.9$ (s, CHO), 52.2 (t, $J_{C,D} = 18.5$ Hz, $CHDBr$) ppm. 2,4,6-tris(bromodeuteromethyl)-1,3,5-trioxane: $\delta = 101.36$ (s, $CHOO$), 51.7 (t, $J_{C,D} = 18.5$ Hz, $CHDBr$) ppm. GC/MS: not registered.



Scheme 3

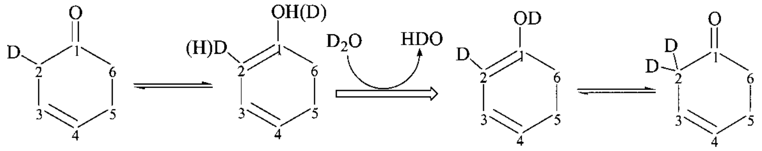
2,2-Dideuterocyclohex-3-enone: (Table 1, entry 4). The product probably forms by selective incorporation of deuterium in position 2 following H/D exchange. The latter is likely to be promoted by the keto-enol equilibrium depicted in Scheme 4.

^1H NMR (300.13 MHz, $CDCl_3$, room temp.): $\delta = 2.34$ [m, 4 H, $CH_{2(5)}CH_{2(6)}$], 6.03 [dt, $J_{H,H} = 10.3$, $J_{H,H} = 1.9$ Hz, 1 H, $CH_{(4)}$], 6.97 [dm, $J_{H,H} = 10.3$ Hz, 1 H, $CH_{(3)}$] ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): $\delta = 205.2$ [$C_{(1)}$],130.9 [s, $C_{(4)}$], 128.2 [s, $C_{(3)}$], 41.9 [s, $C_{(6)}$], 38.0 [quin., $J_{C,D} = 19.7$ Hz, $C_{(2)}$], 22.6 [s, $C_{(5)}$] ppm. GC/MS: m/z (%) = 98 (18) [$C_6H_6D_2O$], 82 (5)[$C_6H_6D_2$], 70 (100%) [$C_5H_6D_2$].

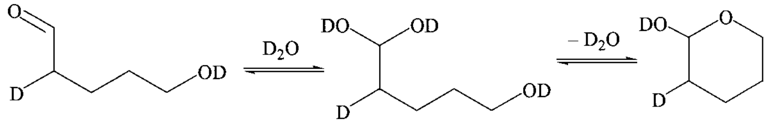
2-Deutero-5-deuteroxypentanal: (Table 1, entry 5). The aldehyde that forms selectively from the cyclic vinyl ether 3,4-dihydro-2*H*-pyran, undergoes acetalization under the present reaction conditions and intramolecularly condenses to yield 3-deuterotetrahydro-2*H*-pyran-2-deuterol. The NMR analysis indicates the formation of an equilibrium mixture with about 84% of the cyclic compound (Scheme 5).

^1H NMR (300.13 MHz, $CDCl_3$, room temp.): 2-deutero-5-deuteroxypentanal: $\delta = 9.79$ (s, 1 H, CHO), 3.46 (m, 2 H, CH_2OD), 1.5−2.1 [m, 5 H, $CH(D)CH_2CH_2$] ppm; 3-deuterotetrahydro-2*H*-pyran-2-deuterol: $\delta = 4.27$ [m, 1 H, $OCH(OD)$], 3.53 (t, $J_{H,H} = 7.4$ Hz, 2 H, CH_2O), 1.5−2.0 (m, CH_2CH_2 + CHD) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): 2-deutero-5-deuteroxypentanal: $\delta = 200.1$ (s, CHO), 62.2 (s, CH_2OD), 30.4 (t, $J_{C,D} = 19.5$ Hz, CHD), 27.2 (s, CH_2CH_2OD), 19.6 (s, $CHDCH_2$) ppm; 3-deuterotetrahydro-2*H*-pyran-2-deuterol: $\delta = 94.5$ [s, $OCH(OD)$], 62.9 (s, CH_2O), 29.7 (t, $J_{C,D} = 36.3$ Hz, CHD), 25.2 (s, CH_2CH_2O), 20.1 (s, CH_2CHD) ppm. GC/MS: m/z (%) = 103 (23) [$C_5H_7O_2D_2$], 85 (10) [C_5H_7OD], 58 (100) [C_3H_4OD], 42 (60) [C_3H_4D].

1,4-Butandeuterol: (Table 2, entry 6). ^1H NMR (300.13 MHz, $CDCl_3$, room temp.): $\delta = 3.67$ (m, 4 H, 2 × OCH_2), 1.64 (m, 4 H,



Scheme 4



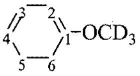
Scheme 5

2 × $OCH_2\mathit{CH_2}$) ppm. $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): δ = 30.2 (s, 2 × OCH_2CH_2), 62.6 (s, 2 × OCH_2) ppm. GC/MS: *m/z* (%) = 92 (2) [$C_4H_8O_2D_2$], 86 (5) [$C_4H_6O_2$], 71 (18) [C_4H_7O], 57 (11) [C_3H_5O], 42 (100) [C_2H_2O].

2-Deutero-1,1-bis(trideuteromethoxy)ethane: (Table 2, entries 6,7). ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ = 4.56 [t, $J_{H,H}$ = 5.2 Hz, 1 H, $\mathit{CH}(OCD_3)_2$], 1.26 (dt, $J_{H,H}$ = 5.2, $J_{H,D}$ = 1.8 Hz, 2 H, $\mathit{CH_2}D$) ppm. $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): δ = 101.2 [s, $\mathit{C}H(OCD_3)_2$], 47.5 (sept, $J_{C,D}$ = 21.3 Hz, $O\mathit{C}D_3$), 17.2 (t, $J_{C,D}$ = 18.7 Hz, $\mathit{C}H_2D$) ppm. GC/MS: *m/z* (%) = 96 (5) [$C_4H_3O_2D_7$], 81 (53) [$C_3HO_2D_6$], 63 (100) [$C_2HO_2D_3$], 44 (27) [CO_2].

1-Bromo-1-deutero-2,2-bis(trideuteromethoxy)ethane: (Table 2, entry 8). ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ = 4.55 [d, $J_{H,H}$ = 5.2 Hz, 1 H, $\mathit{CH}(Ocd_3)_2$], 3.40 (m, 1 H, $\mathit{CH}DBr$) ppm. $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): δ = 103.1 [s, $\mathit{C}H(Ocd_3)_2$], 29.8 (t, $J_{C,D}$ = 23 Hz, CHDBr) ppm. GC/MS: *m/z* (%) = 176 (6) [$C_4H_2O_2D_7Br$], 142 (30) [$C_3H_2OD_4Br$], 108 (5) [C_2H_2DBr], 81 (100) [HBr].

1-Trideuteromethoxy-1,3-cyclohexadiene: (Table 2, entry 9). ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ = 5.86 [m, 1 H, $CH_{(3)}$], 5.40 [br. d, $J_{H4,H3}$ = 7.9 Hz, 1 H, $CH_{(4)}$], 4.97 [d, $J_{H,H}$ = 5.1 Hz, 1 H, $CH_{(2)}$], 2.21 [m, 4 H, $CH_{2(5)}CH_{2(6)}$] ppm. $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): δ = 127.8 (s, C3), 120.1 (s, C1), 113.4 (s, C4), 76.7 (s, C2), 54.8 (sept, $J_{C,D}$ = 21.3 Hz, OCD_3), 25.1 (s, C5), 22.2 (s, C6) ppm. GC/MS: *m/z* (%) = 114 (40) [$C_8H_7O_2D_7$], 96 (100) [C_6H_8O], 80 (62) [C_6H_8].



4-Deutero-5,5-bis(trideuteromethoxy)pentan-1-deuterol: (Table 2, entry 10). ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.): δ = 4.50 [br. s, 1 H, $\mathit{CH}(OCD_3)_2$], 3.68 (br. t, $J_{H,H}$ = 6.2 Hz, $\mathit{CH_2}OD$), 1.53−1.80 (m, 5 H, $CHDCH_2CH_2$) ppm. $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, room temp.): δ = 99.8 [s, $\mathit{C}H(OCD_3)_2$], 61.7 (s, $\mathit{C}H_2OD$), 48.1 (sept, $J_{C,D}$ = 21.8 Hz, OCD_3), 29.8 (t, $J_{C,D}$ = 19.7 Hz, CHD), 18.9 and 25.1 (all s, CH_2CH_2) ppm. GC/MS: *m/z* (%) = [$C_7H_8O_3D_8$] not observed, 120 (30) [$C_6H_6O_2D_5$], 86 (70) [C_5H_8OD], 57 (100) [C_4H_7D], 42 (60) [C_3H_4D].

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