Novel Hydroboration of Highly Substituted Alkenes catalysed by Borohydride Complexes of Uranium, Neodymium and Zirconium

Claude Villiers and Michel Ephritikhine

Service de Chimie Moléculaire, CNRS URA 331, CEA CE Saclay, 91191 Gif sur Yvette, France

Alkenes are hydroborated with $LiBH_4$ in the presence of UCl_4, $NdCl_3$ or $ZrCl_4$, by following the reactivity sequence tetramethylethylene > 1-methylcyclohexene ≫ 2-methylpropene or hex-1-ene (no reaction); treatment of $U(BH_4)_4$ with tetramethylethylene affords the uranium tetrakis(thexylborohydride) $[U(BH_3R)_4]$ (R = CMe_2CMe_2H).

Selective hydroboration of alkenes can be achieved by a variety of reagents and the great utility of this reaction in organic synthesis has been significantly enhanced by the development of transition metal catalysed processes.[1] Besides the classical addition of boranes, the titanium mediated hydroboration of alkenes with $LiBH_4$ or $NaBH_4$ has been reported,[2] but this reaction was envisaged as the Lewis acid promoted decomposition of borohydride to diborane, followed by conventional hydroboration by this reagent.[3] Whatever the hydroborating system, the reactivity of the alkenes follows the sequence tetra- < tri- < di- < mono-substituted C–C double bonds; there is no exception to this trend. We have studied the hydroboration of alkenes with $LiBH_4$ in the presence of UCl_4, $NdCl_3$ or $ZrCl_4$ and, to our surprise, we found that the order of reactivity was opposite to that invariably observed so far: hex-1-ene was inert whereas tetramethylethylene was readily transformed. By examining the behaviour of $U(BH_4)_4$ with tetramethylethylene, we discovered the new reaction depicted by eqn. (1), *i.e.* the simple addition of a borohydride B–H bond to an alkene double bond, giving the corresponding alkylborohydride derivative.

(1)

Tetramethylethylene (0.25 cm^3) was treated with UCl_4 (199.5 mg) and $LiBH_4$ (45.7 mg) in tetrahydrofuran (5 cm^3); the reaction mixture was stirred for 6 h at 20 °C and after evaporation to dryness, the green tetrakis(thexylborohydride) complex $[U(BH_3R)_4(thf)_2]$ **1** (R = CMe_2CMe_2H, thf = tetrahydrofuran) was extracted into toluene and crystallized from this solvent (90% yield). Complex **1** is, after $[U(BH_3Me)_4]$ and its derivatives,[4] a new alkylborohydride compound of uranium; its hydrolysis gave immediately the thexyl boronic acid $RB(OH)_2$ and its oxidation with alkaline hydrogen peroxide afforded 2,3-dimethylbutan-2-ol (92% yield).† The trisubstituted alkenes α-pinene, 2-methylpent-2-ene and 1-methylcyclohexene were found to be less reactive than tetramethylethylene and their complete transformation required 18, 20 and 42 d, respectively, with half-reaction times of 12, 17 and 30 h (Fig. 1). Isopinocampheol (>98% pure), a 95:5 mixture of 2-methylpentan-3-ol and 2-methylpentan-2-ol, and *trans*-2-methylcyclohexanol (>98% pure), respectively, were obtained in almost quantitative yields after the usual oxidative work-up; such anti-Markovnikov hydrations of alkenes *via* hydroboration are classical. Most striking is the order of reactivity of the alkenes, the less substituted (cyclohexene, 2-methylpropene and hex-1-ene) being inert towards this UCl_4–$LiBH_4$ system. The neodymium and zirconium chlorides were also capable of promoting the hydroboration of the most hindered alkenes by $LiBH_4$ and again, no reaction was observed with hex-1-ene. While $ZrCl_4$ was nearly as efficient as UCl_4, $NdCl_3$ was much less reactive, as illustrated in Fig. 2 for tetramethylethylene. After evaporation and extraction into toluene, the zirconium tetrakis (thexylborohydride) $[Zr(BH_3R)_4]$ **2**‡ (R = CMe_2CMe_2H) was isolated as colourless microcrystals in 87% yield.

Treatment of **1** with $LiBH_4$ caused the displacement of the thexylborohydride ligand and revealed the feasibility of a catalytic process. Indeed, hydroboration of tetramethylethylene (0.062 cm^3) by $LiBH_4$ (11.4 mg) in the presence of 10^{-2} equiv. UCl_4 (2.0 mg) in thf (0.5 cm^3) was almost totally achieved after 2 d at 20 °C ($t_{\frac{1}{2}}$ = 1 h), giving lithium thexylborohydride; under the same conditions, 1-methylcyclohexene was half-consumed after 9 d. Similar results were obtained by using $ZrCl_4$ in place of UCl_4 but the reactions with $NdCl_3$ were much slower, 25% of tetramethylethylene being converted after 9 d. In each experi-

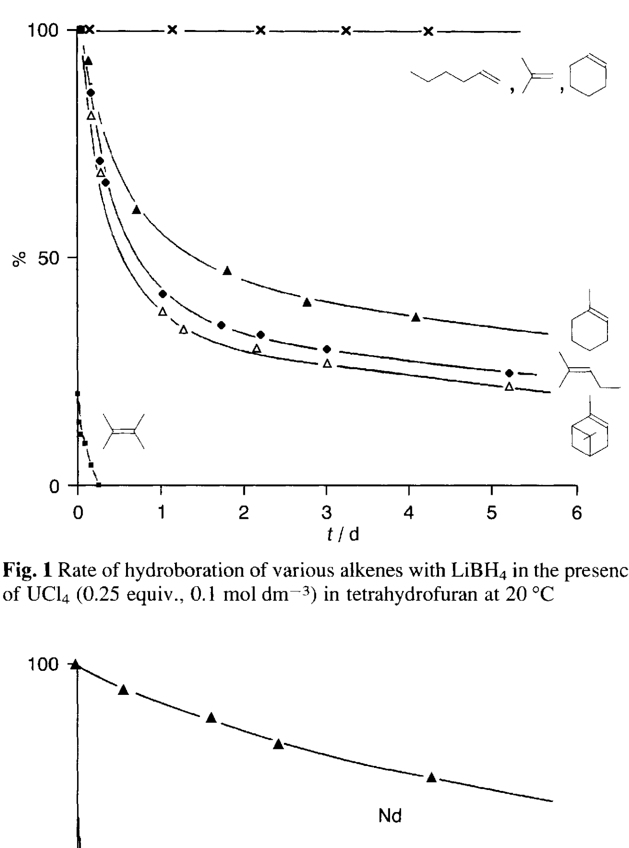

Fig. 1 Rate of hydroboration of various alkenes with $LiBH_4$ in the presence of UCl_4 (0.25 equiv., 0.1 mol dm^{-3}) in tetrahydrofuran at 20 °C

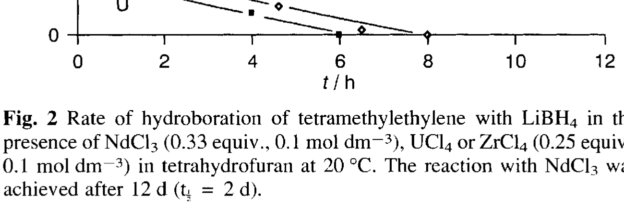

Fig. 2 Rate of hydroboration of tetramethylethylene with $LiBH_4$ in the presence of $NdCl_3$ (0.33 equiv., 0.1 mol dm^{-3}), UCl_4 or $ZrCl_4$ (0.25 equiv., 0.1 mol dm^{-3}) in tetrahydrofuran at 20 °C. The reaction with $NdCl_3$ was achieved after 12 d ($t_{\frac{1}{2}}$ = 2 d).

ment, the reaction mixture was treated with H_2O_2/OH^- to give the expected alcohol in good yield (>85%); hydrogenation, isomerization or polymerization of the alkene were not observed.[5]

The order of reactivity of the alkenes is a clear indication that free BH_3 is not involved in these metal catalysed processes, in contrast to what would occur in the titanium promoted hydroboration of the less substituted alkenes by $LiBH_4$;[3] this difference can be explained by the lower stability of the titanium borohydrides which readily decompose into the corresponding hydrides with liberation of diborane. We believe that the reactions reported here are genuine catalysed hydroborations of alkenes by $LiBH_4$ in which a metal borohydride complex is the active species. This hypothesis was supported by the synthesis of $[U(BH_3R)_4(thf)_2]$ **1**‡ (R = CMe_2CMe_2H) from a 1:4 mixture of $U(BH_4)_4$ (200 mg) and tetramethylethylene (0.32 cm^3) in thf (6 cm^3); after 20 h at 20 °C, the solvent was evaporated off, leaving the product in almost quantitative yield. This reaction was more rapid in toluene [eqn. (1)], requiring 4 h for completion, and afforded pale brown microcrystals of $[U(BH_3R)_4]$ **3**‡ (R = CMe_2CMe_2H) (89% yield). The ^1H NMR spectra revealed that these transformations occurred in a stepwise fashion, *via* the successive intermediates $[U(BH_4)_{4-n}(BH_3R)_n]$ (n = 1, 2 and 3). The pale pink complex $[Nd(BH_3R)_3(thf)_x]$ (R = CMe_2CMe_2H) was obtained after 23 d at 20 °C by treating $Nd(BH_4)_3(thf)_3$ with 3 equiv. tetramethylethylene (NMR experiment). Nevertheless, it is noteworthy that the neutral borohydrides of U, Nd and Zr could not be the true active species in the catalytic hydroboration reactions, since it is known that these are readily transformed into anionic complexes in the presence of lithium salts; for example, $Zr(BH_4)_4$ yielded $Li[Zr(BH_4)_5]$ when treated with $LiBH_4$.[6] While the alkenes exhibited the same reactivity sequence, the rate of their hydroboration with $U(BH_4)_4$ in thf was distinct from that with the UCl_4–$LiBH_4$ system; α-pinene was completely transformed into $[U(BH_3R')_4(thf)_2]$ (R′ = isopinocampheyl) after 6 d at 20 °C, whereas only 5% of 1-methylcyclohexene was converted during this time.

The outstanding selectivity of these hydroboration reactions would reflect the existence of an intermediate or transition state with important cationic character on the alkenic carbon atoms; the pattern of alkyl substituent effects, in particular the great difference of reactivity between tetramethylethylene and 2-methylpropene, is similar to that encountered in the bromination of alkenes, in which a three-centre intermediate is involved.[7] Experimental mechanistic investigations will include the study of the directive effects in the hydroboration of functionalized alkenes.

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Footnotes

† The alcohols and the thexyl boronic acid were identified by comparison of their ^1H NMR spectra and GLC retention times with those of authentic samples; the yields were determined by GLC.

‡ Satisfactory C, H, B analyses were obtained for complexes **1–3**. *Spectroscopic data*: ^1H NMR δ (60 MHz except **2** at 200 MHz, 30 °C in $[^2H_8]$thf except **1**, **2** and **3** in $[^2H_8]$toluene, J and $w_{\frac{1}{2}}$ in Hz) for **1**: 167.2 (12H, $w_{\frac{1}{2}}$ 160, BH_3), 12.93 (4 H, hept, J 6, $\mathrm{C}H\mathrm{Me_2}$), 12.02 (24 H, CMe_2), 9.13 (24 H, d, J 6, $\mathrm{CH}Me_2$), −1.36 (8 H, β-thf) and −9.2 (8 H, $w_{\frac{1}{2}}$ 60, α-thf); for **3**: 156.3 (12 H, $w_{\frac{1}{2}}$ 160, BH_3), 4.24 (4 H, hept, J 6, $\mathrm{C}H\mathrm{Me_2}$), 3.53 (24 H, CMe_2) and 2.28 (24 H, d, J 6, $\mathrm{CH}Me_2$); $[U(BH_4)_{4-n}(BH_3CMe_2CMe_2H)_n]$ (the borohydride resonances are broad with $w_{\frac{1}{2}}$ = 300–350 Hz) for n = 1: 260.1 (3 H, BH_3), 139.2 (12 H, BH_4), 16.53 (1 H, $\mathrm{C}H\mathrm{Me_2}$), 15.25 and 10.38 (6 H + 6 H, Me); for n = 2: 235.8 (6 H, BH_3), 123.1 (8 H, BH_4), 14.72 (2 H, $\mathrm{C}H\mathrm{Me_2}$), 13.56 and 9.13 (12 H + 12 H, Me); for n = 3: 217.2 (9 H, BH_3), 101.3 (4 H, BH_4), 13.71 (3 H, $\mathrm{C}H\mathrm{Me_2}$), 12.53 and 8.14 (18 H + 18 H, Me); for n = 4: 195.0 (12 H, BH_3), 12.43 (4 H, hept, J 6, $\mathrm{C}H\mathrm{Me_2}$), 11.34 (24 H, CMe_2) and 7.23 (24 H, d, J 6, $\mathrm{CH}Me_2$): $[U(BH_3R')_4]$ (R′ = isopinocampheyl): 200.8 (12 H, $w_{\frac{1}{2}}$ 180, BH_3), 23.79 (4 H, m, 3-H), 15.97 (4 H, m, 2-H), 14.96 (4 H, m, 4-H), 11.31 (4 H, t, J 12, 4-H), 7.83 (8 H, m, 1- and 5-H), 7.28 (12 H, d, J 6, 2-Me), 7.13 (8 H, m, 7-H), 5.74 and 3.96 (12 H + 12 H, 6-Me); for **2**: 1.8 (12 H, $w_{\frac{1}{2}}$ 250, BH_3), 1.65 (4 H, hept, J 6, $\mathrm{C}H\mathrm{Me_2}$), 1.22 (24 H, CMe_2) and 1.17 (24 H, d, J 6, $\mathrm{CH}Me_2$); $[Nd(BH_3CMe_2CMe_2H)_3(thf)_x]$: 115.3 (9 H, $w_{\frac{1}{2}}$ 370, BH_3), 5.08 (3 H, hept, J 6, $\mathrm{C}H\mathrm{Me_2}$), 3.75 (18 H, CMe_2) and 2.52 (18 H, d, J 6, $\mathrm{CH}Me_2$). When not specified, the signals are singlets with $w_{\frac{1}{2}}$ = 5–25 Hz.

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