Hydroalumination of Di- and Triene Hydrocarbons with the $LiAlH_4{\cdot}3AlBr_3$ System

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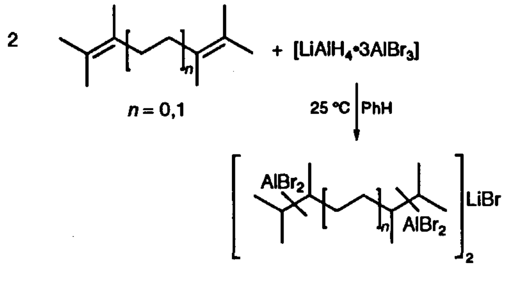
The $LiAlH_4{\cdot}3AlBr_3$ system smoothly hydroaluminates hydrocarbons with conjugated and unconjugated double bonds, resulting in high yields of saturated organoaluminium compounds.

As shown earlier,[1] alkenes with mono-, di- and trisubstituted double bonds undergo smooth hydroalumination with the $LiAlH_4{\cdot}3AlBr_3$ system in benzene or toluene, giving a high yield of related dibromoaluminoalkanes. We continued these studies to show that dienes with either isolated or conjugated double bonds (Schemes 1 and 2, respectively) can be hydroaluminated with the reagent to afford saturated organoaluminium compounds.[†]



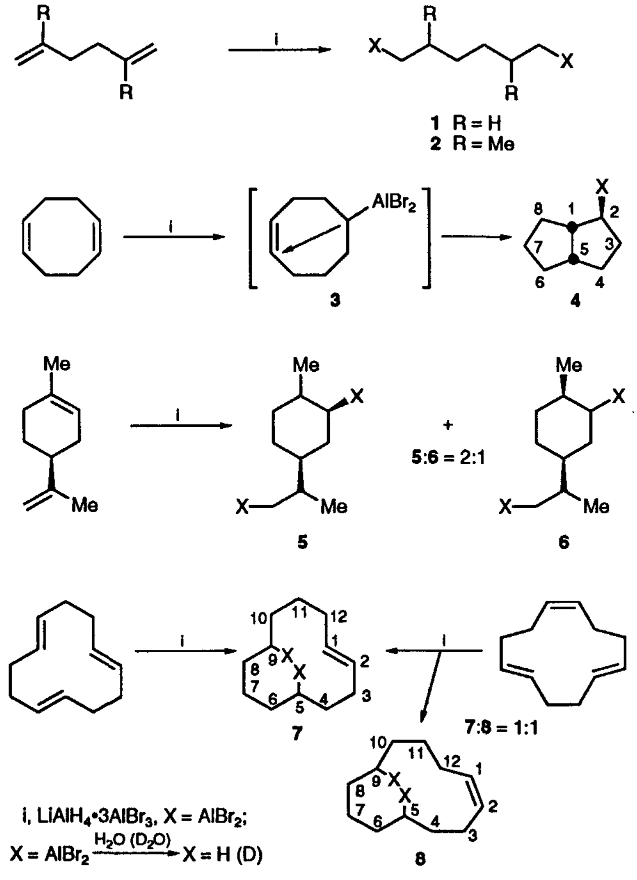
Scheme 1

Thus, hydroalumination of hexa-1,5-diene and 2,5-dimethylhexa-1,5-diene yields 95% of **1** and **2** ($X = AlBr_2$). The latter are then hydrolysed to yield hexane and 2,5-dimethylhexane, respectively. Hydroalumination of the stated dienes with Bu^i_2AlH or Bu^i_3Al is usually accompanied by intramolecular cyclization that leads to cyclopentane alumino derivatives.[2,3]

Cycloocta-1,5-diene reacts with $[LiAlH_4{\cdot}3AlBr_3]$ to yield 95% of a single organoaluminium compound **4** ($X = AlBr_2$). *cis*-Bicyclo[3.3.0]octane results from the hydrolysis of **4**. Intramolecular carboalumination of an intermediate **3** is the most likely route for the formation of **4**. Hydroalumination of cycloocta-1,5-diene with Bu^i_3Al usually leads to dialumino derivatives of 1-ethyl-2-methylcyclopentane.[4]

Hydroalumination of limonene with Bu^i_2AlH is known to occur only at its terminal double bond.[5] In contrast, limonene reacts with $[LiAlH_4{\cdot}3AlBr_3]$ to afford a completely saturated product involving two stereoisomers **5** and **6** ($X = AlBr_2$). The hydrolysis of the latter leads to *trans*- and *cis*-menthanes in 62% and 28% yields, respectively.

As shown earlier, *trans, trans, trans*- and *trans, trans, cis*-cyclododeca-1,5,9-triene react with equimolar amounts of Bu^i_3Al, resulting in perhydro-9b-aluminophenalene.[6] Reaction of the trienes with $[LiAlH_4{\cdot}3AlBr_3]$ affords exclusively dihydroalumination products in 85% total yields. It should be noted here that the *trans, trans, trans*-isomer leads only to an organoaluminium compound **7** ($X = AlBr_2$), whereas the *trans, trans, cis*-isomer gives an equimolar mixture of **7** and **8** ($X = AlBr_2$) after hydrolysis of which *trans*- and *cis*-cyclododecenes are formed, respectively.



i, $LiAlH_4{\cdot}3AlBr_3$, $X = AlBr_2$;
$X = AlBr_2 \xrightarrow{H_2O\,(D_2O)} X = H\ (D)$

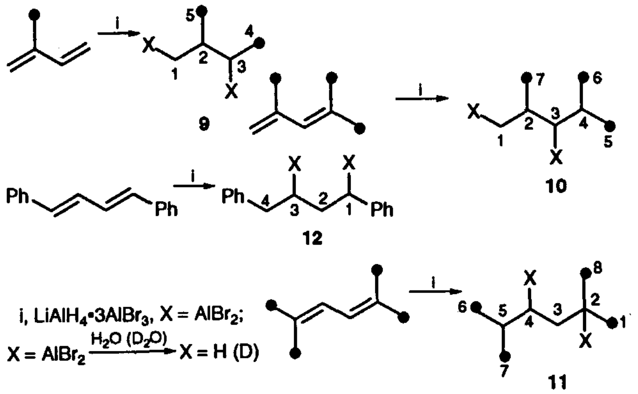
Scheme 2

[†] *General hydroalumination procedure.* A 6 mol dm^{-3} solution of $LiAlH_4$ (1 ml, 6 mmol) in ether was added to benzene (5 ml) in an argon atmosphere with stirring. The greater portion of the solvent was removed at 10–15 Torr. Benzene (20 ml) and a 2.6 mol dm^{-3} solution of $AlBr_3$ in benzene (6.9 ml, 18 mmol) were then added and the mixture was stirred for 1 h at room temperature. A solution of a diene (11 mmol) or a triene (7.6 mmol) in benzene (20 ml) were added dropwise, and the reaction mixture was stirred for 2 h. After excess $LiAlH_4$ had precipitated, a transparent solution of the organoaluminium compound was decanted and used for further transformations. Prior to hydrolysis and deuterolysis of **5–8** and **12**, 20 ml of ether was added to their solution in benzene. With compounds **1, 2, 4, 10** and **11**, benzene was totally replaced by an ether.

^{13}C *NMR spectra* (75.47 MHz, $C_6D_6/C_6H_6 = 1/1$, δ) *for compound* **2** (*threo/erythro* = 1/1): 24.44 (24.48) (C–7,8), 25.38 (C–1,6), 30.53 (30.64) (C–2,5), 39.04 (39.13) (C–3,4); **4**: 26.74 (C–7), 28.12 (C–3), 34.13 (C–2), 34.80 (C–6), 35.52 and 35.61 (C–4.8), 43.89 (C–5), 46.67 (C–1); **9** (*threo/erythro* = 1/1): 13.77 (13.94) (C–4), 25.53 (25.68) (C–5), 25.68 (25.70) (C–1), 33.11 (33.33) (C–3), 34.34 (34.97) (C–2); **10** (*threo/erythro* = 2/1): 24.15 (24.60) and 25.51 (25.21) (q, C–5,6), 26.33 (t, C–1), 26.57 (27.37) (q, C–7), 29.51 (29.82) (d, C–4), 32.08 (31.80) (d, C–2), 50.01 (50.56) (d, C–3); **11**: 23.70 (q, C–1), 24.32 and 24.38 (q, C–6,7), 25.13 (s, C–2), 28.27 (q, C–8), 33.13 (d, C–5), 36.64 (d, C–4), 45.63 (t, C–3).

^{13}C *NMR spectra* (75.47 MHz, $CDCL_3$, δ) *for deuterated products* **4**: 26.36 (C–3), 26.44 (C–7), 33.99 (C–2, $^1J_{^{13}C\text{-}D} = 19.58$ Hz), 34.27 (C–4,6,8), 43.19 (C–1), 43.27 (C–5); **7**: 24.36 (C–5, $^1J_{^{13}C\text{-}D} = 19.73$ Hz), 24.62 (C–10), 24.97 (C–4), 25.02 (C–11), 25.26 (C–9, $^1J_{^{13}C\text{-}D} = 19.24$ Hz), 25.66 (C–6), 26.23 (C–8), 26.31 (C–7), 32.16 (C–3), 32.21 (C–12), 131.47 (C–1,2); **8**: 21.78 (C–9, $^1J_{^{13}C\text{-}D} = 18.87$ Hz), 22.12 (C–6), 24.04 (C–3,12), 24.08 (C–5, $^1J_{^{13}C\text{-}D} = 19.30$ Hz), 24.42 (C–10), 24.67 (C–8), 24.75 (C–7), 26.99 (C–4), 27.04 (C–11), 130.47 (C–1,2); **9**: 11.73 (C–4), 22.02 (C–1, $^1J_{^{13}C\text{-}D} = 18.90$ Hz), 22.31 (C–5), 30.06 (C–2), 31.55 (C–3, $^1J_{^{13}C\text{-}D} = 18.90$ Hz); **10**: 22.44 (C–1, $^1J_{^{13}C\text{-}D} = 19.62$ Hz), 22.73 (C–5,6,7), 25.61 (C–2,4), 48.71 (C–3, $^1J_{^{13}C\text{-}D} = 19.62$ Hz); **11**: 22.05 (C–1,8), 22.12 (C–6,7), 27.67 (C–2, $^1J_{^{13}C\text{-}D} = 19.57$ Hz), 27.91 (C–5), 36.11 (C–4, $^1J_{^{13}C\text{-}D} = 19.64$ Hz), 36.30 (C–3); **12**: 30.66 (C–3, $^1J_{^{13}C\text{-}D} = 19.62$ Hz), 31.02 (C–2), 35.50 (C–1, ^1J = 19.38 Hz), 35.80 (C–4)

Exhaustive hydroalumination of butadiene, isoprene and piperylene with Bu^i_2AlH, Et_2AlH or AlH_3 are known to occur under rigid conditions, when sufficient amounts of polymer products may be formed.[7,8] With [$LiAlH_4 \cdot 3AlBr_3$], conjugated dienes give high yields of dihydroalumination products. Thus, isoprene, 2,4-dimethylpenta-1,3-diene, 2,5-dimethylhexa-2,4-diene and 1,4-diphenylbuta-1,3-diene result in saturated compounds **9**–**12** ($X = AlBr_2$) in 90%, 80%, 85% and 95% yields, respectively. After hydrolysis of the organoaluminium compound, 2-methylbutane, 2,4-dimethylpentane, 2,5-dimethylhexane and 1,4-diphenylbutane are formed, respectively.



i, $LiAlH_4 \cdot 3AlBr_3$, $X = AlBr_2$;
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The structures of the organoaluminium compounds prepared were unambiguously confirmed from the ^1H and ^{13}C NMR spectral assignments of their deuterolysis and hydrolysis products. In addition, ^{13}C NMR spectra were recorded for compounds **1**, **2**, **4** and **9**–**11** ($X = AlBr_2$), those being in line with the expected structures.

References

1 E. V. Gorobets, A. V. Kutchin, L. M. Khalilov and G. A. Tolstikov, *Metalloorg. Khim.*, 1991, **4**, 198 (*Organomet. Chem. USSR*, 1991, **4**, 105).
2 K. Ziegler, *Angew. Chem.*, 1956, **68**, 721, 727.
3 A. A. Antonov, N. S. Nametkin and V. I. Smetanyuk, *Neftekhimiya*, 1969, **9**, 722 (in Russian).
4 E. Marcus, D. L. MacPeek and S. W. Tinsley, *J. Org. Chem.*, 1971, **36**, 381.
5 K. Ziegler, F. Krupp and K. Zosel, *Liebigs Ann. Chem.*, 1960, **629**, 241.
6 V. P. Yuriev, G. A. Tolstikov, I. M. Salimgareeva, A. V. Kutchin, V. I. Khvostenko and A.Kh. Gazizov, *Zh. Obshch. Khim.*, 1973, **43**, 2071 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1973, **43**, 2053].
7 L. I. Zakharkin and L. A. Savina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 78 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, 72).
8 L. I. Zakharkin, L. A. Savina and L. M. Antipin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1962, 996 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1962, 2053).

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