

Stereoselective hydrogenation reactions in chloroaluminate(III) ionic liquids: a new method for the reduction of aromatic compounds

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Stereoselective hydrogenation reactions in the ionic liquid system 1-ethyl-3-methylimidazolium chloride–AlCl₃ can be performed with excellent yields and selectivities, using electropositive metals and a proton source.

The hydrogenation of aromatic compounds can be achieved by a number of methods, including high pressure catalytic hydrogenation,¹ dissolving metal reductions,² and ionic hydrogenations with TFA and silanes.³ Here, we report a new, highly stereoselective method for the reduction of carbocyclic aromatic compounds in chloroaluminate(III) ionic liquids at ambient temperatures.

Room temperature ionic liquids such as [emim]Cl–AlCl₃ (*X* = 0.67)⁴ ([emim]⁺ = 1-ethyl-3-methylimidazolium cation, see Fig. 1),[†] have been found to be excellent solvents for a number of reactions, such as the Friedel–Crafts reaction,⁵ isomerisations,⁶ polymerisation of alkenes such as refinery waste gas,⁷ and catalytic hydrogenation reactions.^{8,9}

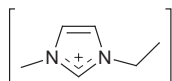
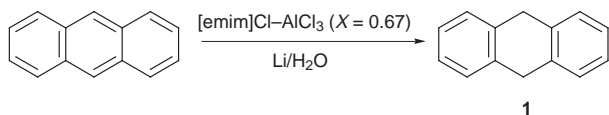


Fig. 1 Structure of the [emim]⁺ cation.

When polycyclic aromatic compounds, such as anthracene, are dissolved in solvents containing dissolved aluminium(III) chloride, deeply coloured paramagnetic solutions are formed.¹⁰ Authors such as Olah¹¹ have referred to these compounds as AlCl₃ π-complexes, but the precise structure and bonding of these complexes has yet to be elucidated.¹⁰ It has also been observed that carbocyclic aromatic compounds are readily protonated in the [emim]Cl–AlCl₃ (*X* = 0.67) ionic liquid.¹² It was thus envisaged that the interaction of an electropositive metal with a protonated aromatic hydrocarbon would result in reduction of that compound. A preliminary investigation led to the observation that when moist air was introduced to a deep green solution of anthracene in [emim]Cl–AlCl₃ (*X* = 0.67), containing lithium metal, the green colour faded and 9,10-dihydroanthracene **1** was formed in 98% yield (Scheme 1).



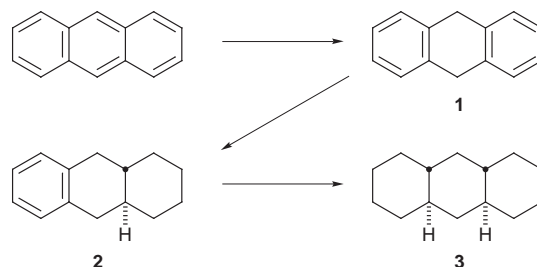
Scheme 1

Following on from this initial observation, a more detailed investigation was carried out with anthracene, pyrene and 9,10-dimethylantracene, in order to examine the stereochemical outcome of this reaction. The results of this investigation are summarised in Table 1 and Schemes 2–4.

The partial reduction of anthracene and pyrene was achieved by using the ionic liquid [emim][HCl₂] as a proton source.¹³ For complete reduction to the alicyclic products (**3** and **7**), anhydrous HCl gas was found to be the most effective proton source. In general, this reaction was successful with electroposi-

Table 1 The reduction of aromatic compounds in [emim]Cl–AlCl₃ (*X* = 0.67) at 20 °C

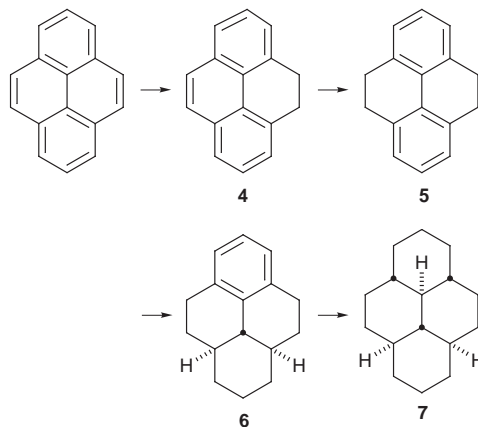
Substrate	Metal	H ⁺ source	t/h	Products (% yield)
Anthracene	Al	[emim][HCl ₂] (l)	24	1 (25), 2 (25), 3 (25)
Anthracene	Zn	excess HCl (g)	6	3 (90)
Pyrene	Li	[emim][HCl ₂] (l)	1	4 (2), 5 (18), 6 (20), 7 (25)
Pyrene	Al	excess HCl (g)	4	7 (84)
9,10-Dimethyl-anthracene	Al	HCl (g)	0.5	8 (81), 9 (14)



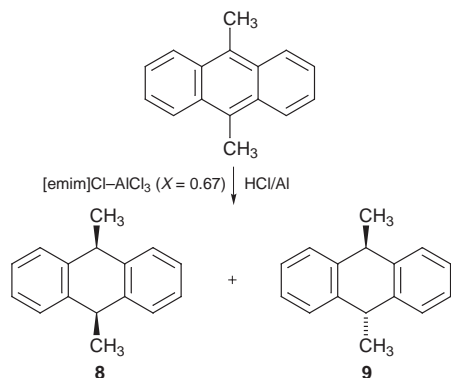
Scheme 2

tive metals (*e.g.* Na, Li, Mg, Al and Zn). The metal of choice was found to be aluminium, since the aluminium(III) chloride by-product of the reaction is precipitated and the composition of the ionic liquid remained largely unaffected. It should be noted that this reaction differs from other dissolving metal reductions, such as the Birch reduction,² in that products containing unconjugated double bonds are not observed.

The reduction of anthracene was found to proceed sequentially, as shown in Scheme 2. It should be noted that **2** and **3** are the thermodynamically most stable isomers.



Scheme 3



Scheme 4

The reduction of pyrene occurs in a similar manner to that of anthracene (see Scheme 3): the two most reactive bonds are reduced first. Again, the subsequent reduction gave rise to the thermodynamically most stable intermediate **6** and ultimately the product **7** as single diastereomers.¹⁴ The structure of **7** was confirmed by X-ray crystallography¹⁵ and was found to be identical to the published structure.¹⁶

The partial reduction of 9,10-dimethylanthracene (see Scheme 4) gave rise to two isomers (**8** and **9**) in a 6:1 ratio respectively. In contrast to the products from the reduction of pyrene and anthracene, the major product **8** was the *cis*-isomer and the minor product **9** was the *trans*-isomer. This difference from the behaviour of anthracene and pyrene can be explained by the enthalpies of formation of the two products **8** and **9**. The *cis*-isomer **8** is 16 kJ mol⁻¹ more stable than the *trans*-isomer **9**.¹⁷ Hence, as with the pyrene and anthracene reductions, the thermodynamic product predominates.

The reductions of simpler aromatic compounds such as benzene and naphthalene were found to behave in a more complex manner. In both these cases, the expected products [cyclohexane (2%) and decalin (15%, as a 5:1 *trans*- to *cis*-isomer mixture)] were obtained, but in low yields. In these two cases, polymerisation reactions occur in addition to reduction reactions. In the reduction of benzene, products such as phenylcyclohexane and bi(cyclohexyl) were detected, presumably from the Friedel–Crafts reaction between benzene and cyclohexene (a postulated intermediate in the reduction reaction): the major product was a non-volatile colourless oil—polycyclohexane—obtained in 70% yield.

In conclusion, reduction by a metal–acid combination in a chloroaluminate(III) ionic liquid provides an effective means of hydrogenating aromatic compounds in a highly selective manner. This contrasts with the catalytic hydrogenation of

anthracene or pyrene, which requires high temperatures and pressures, and usually gives rise to isomeric mixtures.^{1,18}

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Notes and references

† The composition of a tetrachloroaluminate(III) ionic liquid is best described by the apparent mole fraction of AlCl₃ {X(AlCl₃)} present. Ionic liquids with X(AlCl₃) < 0.5 contain an excess of Cl⁻ ions over [Al₂Cl₇]⁻ ions, and are called 'basic'; those with X(AlCl₃) > 0.5 contain an excess of [Al₂Cl₇]⁻ ions over Cl⁻, and are called 'acidic'; melts with X(AlCl₃) = 0.5 are called 'neutral'.

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