First-stage Antimony Pentafluoride Intercalated Graphite: a Mild and Efficient Catalyst for Hydrocarbon Isomerisation at Low Temperature

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Summary First-stage SbF_5 intercalated graphite has been used to isomerise a series of cyclic and bicyclic saturated hydrocarbons at or below room temperature, and the thermodynamically most stable isomer has been obtained selectively in all cases.

THE acid-catalysed isomerisation of saturated hydrocarbons has been continuously used on a large scale by the petroleum industry since the 1940s, and has been the subject of numerous theoretical and practical investigations.[1] The majority of the published work so far is devoted to the mechanism of the isomerisation and to the thermodyanmics of the isomeric equilibria. The major inconvenience of these reactions, whichever catalyst is chosen (Lewis acid, Brönsted acid, or acidic oxide), arises from the relatively high temperatures necessary to activate the reagents. An increase in temperature means both an unfavourable thermodynamic equilibrium for the branched isomer, and favourable conditions for cracking and polycondensation reactions yielding side-products.

Since the pioneering work of Olah and his group,[2] showing that hydrocarbons can be activated at low temperature by the 'magic acid' system $HSO_3F:SbF_5$ (1:1), a new area of hydrocarbon chemistry has been opened. The HF–SbF_5

system has recently been shown to be a selective and efficient catalyst for the isomerisation of hydrocarbon skeletons in the steroid field.[3] The room-temperature isomerisation of pentane with HF–SbF$_5$ has been studied as a heterogeneous system.[4]

In our laboratory we have found that pure SbF$_5$, inserted into graphite to form the first-stage insertion compound, is very efficient as a solid superacid for low-temperature, gas-phase hydrocarbon isomerisation[5] and we present here our results on the potential of this catalyst to isomerise cyclic and bicyclic alkanes in the liquid phase at room temperature and below. The hydrocarbons which have been tested are the decalins, perhydroindanes, methylcyclopentane, and cyclohexane. As a part of the molecular structure of steroids, the decalins and perhydroindans are interesting synthetic intermediates.

Starting with a commercial mixture of 61·5% *cis*- and 38·5% *trans*-decalin in the presence of SbF$_5$-intercalated graphite in the molar ratio (hydrocarbon to catalyst) of 10 : 1, we noticed that the isomerisation of *cis*- to *trans*-decalin is too fast at room temperature to be conveniently followed by g.l.c. By increasing the molar ratio to 17 : 1, and operating at 0 °C, the reaction can conveniently be followed. After 3 h contact time, the reaction had reached equilibrium. We obtained 98% of *trans*-decalin, which is in agreement with the thermodynamic ratio (99·3% : 0·7%) extrapolated from Allinger's data.[6a] No methylbicyclononanes or dimethylbicyclo-octanes could be detected under these conditions. In this example the use of SbF$_5$-intercalated graphite shows two major advantages over previous methods: (i) the formation, at room temperature and below, of the thermodynamically most stable isomer with negligible side reactions, and (ii) the separation of the products from the catalyst by simple filtration.

The same procedure has been tested with perhydroindan. Starting again with a commercial mixture comprising 8% *trans*- and 92% *cis*-isomer in the presence of catalyst in the molar ratio 8 : 1 (hydrocarbon to catalyst) we obtained, after 3 h at 0 °C, 62% of *trans*- and 38% of *cis*-perhydroindane, a ratio which is close to the thermodynamic ratio (69 : 31) extrapolated from ref. 6b.

When methylcyclopentane is mixed with the catalyst in the ratio 15 : 1 at room temperature, it yields 91% of cyclohexane in about 4 h (the half-life being 1 h). This reaction, which is mechanistically quite different from the previous examples as it involves a change in branching, can be dramatically accelerated by adding 1% of cyclohexene at the start, in which case the half-life is reduced to 5 min at the same temperature. That the methylcyclopentane to cyclohexane ratio obtained (91% : 9%) is indeed the equilibrium ratio at room temperature was shown by the reaction of cyclohexane with the catalyst, which yielded the same mixture after 3 h. The ratio was not affected by addition of olefin or longer contact times.

The mechanism of oxidation of hydrocarbons by SbF$_5$ has been much discussed in recent years,[7] and the initial step is still not very clear, but if the addition of traces of olefin has such an activating effect, it is difficult to exclude the possibility that some protons are still present, even in twice distilled SbF$_5$.

The intercalation of SbF$_5$, and the advantages of handling the insertion compound, were first described by Lalancette,[8a] but Herold and co-workers have more closely investigated the various stages of insertion.[8b]

The results which are described here are very much in agreement with the prediction of Ebert *et al.*,[9] which was based on wide-line and pulsed ^{19}F n.m.r. experiments; in the intercalated compound there is probably little interaction between SbF$_5$ and the graphite layers which can roughly be considered as the solvent. This could explain why graphite reduces the activity of the Lewis acid without affecting its chemistry, and from our point of view this may be the main reason why the above-studied reactions can be conducted smoothly, without the local overheating which leads to the generally observed side-products.

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