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The Heterogeneous Catalytic Hydrogenation of Cumulated Allene-cyclopropanes: 1-(2′-Methylpropenylidene)-2-phenylcyclopropane

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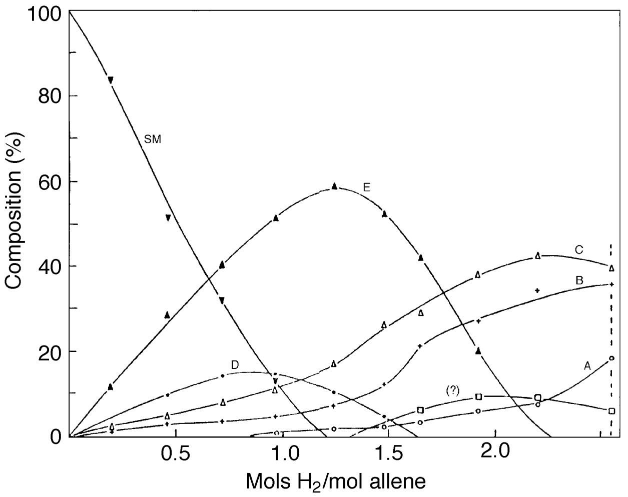
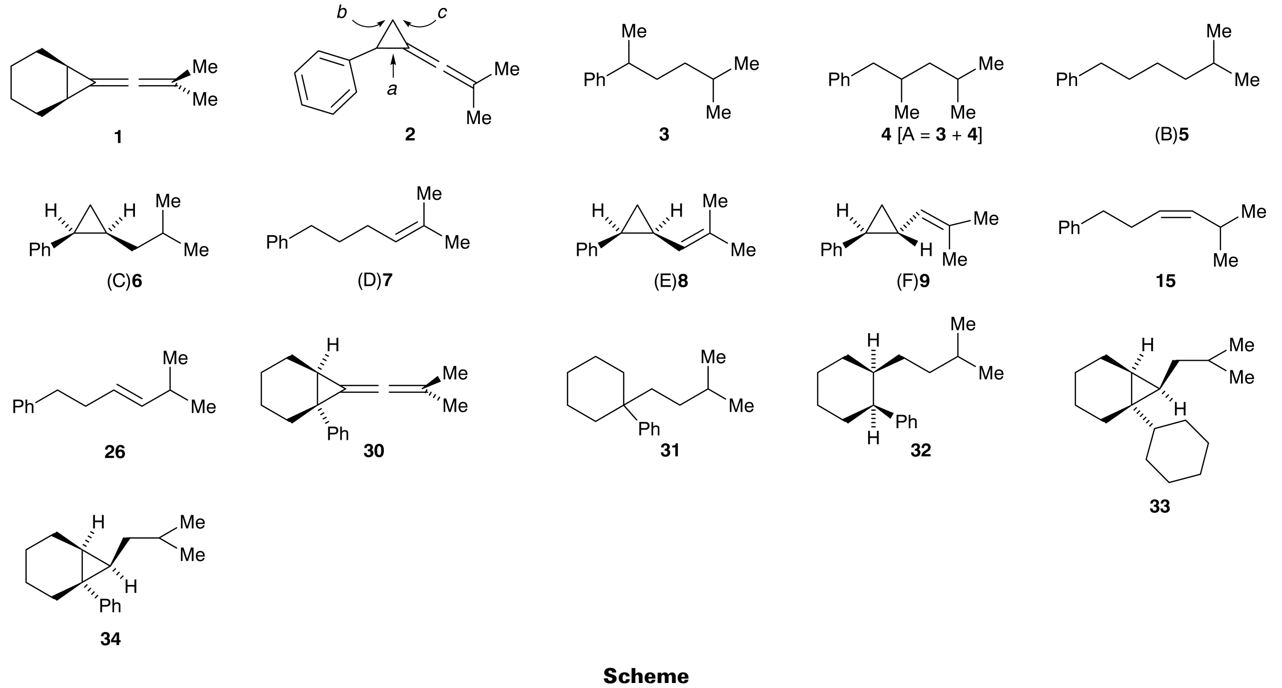
Hydrogenation of the unsymmetrical title allene-cyclopropane **2** is studied graphically using 'snapshot analysis' and supported platinum, palladium and Raney nickel catalysts.

In the accompanying study[1] we have examined the low pressure heterogeneous solution phase catalytic hydrogenation of 1-(2′-methylpropenylidene)-7-bicyclo[4.1.0]heptane **1** using carbon supported platinum and palladium as catalysts. In this paper we report on the catalytic hydrogenation of 1-(2′-methylpropenylidene)-2-phenylcyclopropane **2** which is unsymmetrical and contains an activating aryl group. Identification of the major products **3**–**9** was carried out analytically and by synthesis, and product A was shown to be a mixture of **3** and **4** (~1 : 1).

Graph 1 shows that the major event of the first stage (*i.e.* disappearance of the starting material) of hydrogenation over platinum is the formation in 60% yield of the *cis*-conjugated cyclopropane (E)**8**, the product of presentation of the molecule **2** to the catalyst in the least hindered orientation with phenyl away from the catalyst. The process is not highly selective. In the second stage the formation of (B)**5** builds up a final concentration of 37%. The occurrence of the mono-olefin **7** in the first stage only (14% maximum) may result from a competitive rearrangement product involving the 'half hydrogenated'[3] stage. It is perhaps significant that the formation is a first stage process, and that (D)**7** rapidly dies away, being hydrogenated to (B)**5** when allene-cyclopropane **2** is exhausted. The formation of the mixture (A)**3** + **4** over Pt is negligible during the first phase of the hydrogenation but there is a gradual increase during the second phase leading to a final concentration of 17%. There is a small decline in the amount of saturated cyclopropane (C)**6** towards the end of the hydrogenation, possibly slow direct hydrogenolysis of bonds *b* and *c*, leading to **4**, and **3**.



Graph 1 Hydrogenation of 1-(2′-methylpropenylidene)-2-phenylpropane over 5% Pt/C in methanol. For identities of A–F see formulae in the Scheme



Scheme

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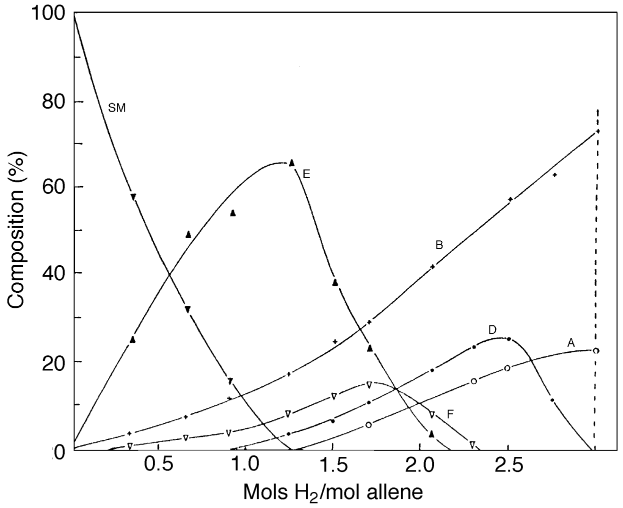
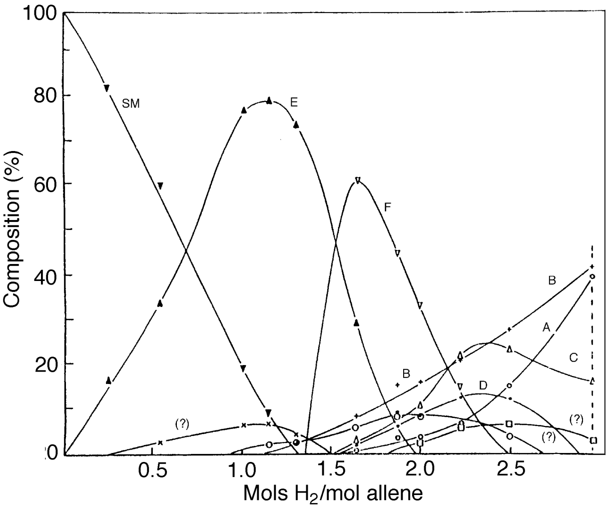


Graph 2 Hydrogenation of 1-(2′-methylpropenylidene)-2-phenylpropane over 5% Pd/C in methanol. For A–F see Scheme



Graph 3 Hydrogenation of 1-(2′-methylpropenylidene)-2-phenylpropane over Raney nickel in ethanol. For A–F see Scheme

A GLC–MS run on the completely hydrogenated product from the platinum experiment confirmed the four major compounds **3**–**6** in isolates (A)–(C) (Graph 1), and revealed a set of minor products corresponding to **3**, **4** and **5** in which benzene rings had also been reduced to cyclohexane.

The most striking thing noted on comparing Graph 2 for Pd with Graph 1 for Pt is that no cyclopropane-containing component remains when hydrogen uptake ceases in the palladium experiment. whilst an isolated cyclopropane ring is not readily hydrogenated in the presence of Pd, it becomes susceptible when conjugated with a double bond.[6] A second comparative feature is that whilst the first stage is dominated in the platinum case by the conversion of the allene **2** into the *cis*-conjugated cyclopropane-olefin (E)**8**, in the case of the palladium there is epimerisation (for the mechanism see full text) into the *trans*-**9**, mainly in the second stage.

As with the platinum case, in the palladium experiment the formation of (A), the mixture of **3** and **4**, finally reaching 24% but not formed until all starting material has been completely hydrogenated, may indicate some direct hydrogenolysis of bonds *b* and *c*. Since no cyclopropane ring component survives to the end of the hydrogenation, direct hydrogenolysis of the third cyclopropane bond '*a*' also seems possible as the origin of some (B)**5**. On the other hand 1,4-hydrogenation of the olefin-cyclopropane (E)**8** would lead to the *cis*- or *trans*-olefin **15**, it being rapidly hydrogenated to (B)**5** or isomerised to the less rapidly hydrogenated (D)**7**.

GLC–MS of partially hydrogenated material over palladium confirmed the presence of A, B, D, E and F and suggested that a minor component was **15**. Hydrogenation of the allene-cyclopropane **2** over Raney nickel (Graph 3) gives a very selective reduction of the 'inner' allenic double bond, producing the *cis*-conjugated olefin (E)**8** in some 80% yield. *cis*- to *trans*-Isomerisation does not occur in the first stage when the surface of the nickel is covered by allene, but sets in apace early in the second phase when the catalyst has been cleared of allene. The two isomers can be distinguished by the positions of their olefinic proton signals in the NMR. The major events are similar to the precious metal hydrogenations in as much as (B)**5** and the mixture (A) **3** + **4** are formed. As in the platinum case the trisubstituted olefin (D)**7** forms and disappears in the second stage but unlike the palladium case some cyclopropane ring material does survive at the end of the hydrogen uptake. However in the case of platinum catalysis it is the *cis*- isomer whilst here it is mainly *trans* because of the epimerisation.

During the present work the reduction of the cumulated allene-cyclopropane **2** with sodium in liquid ammonia was examined. Two products were observed. That with the lower R_t (24.5% of the mixture) was shown to be the disubstituted olefin **26** (not observed in the catalytic hydrogenations) whilst the second component (75.5%) was the trisubstituted olefin **7**. A formation scheme for the two compounds is suggested (see full text).

We have carried out hydrogenation to saturation of the phenyl compound **30** to assess the effect of replacing methyl by the more reactive phenyl. Two major products, **31** (66%) and **32** (23%) were obtained. As in the methyl example, the major hydrogenation is from the least hindered side of the cumulated allene-cyclopropane, though in this case not exclusively so. An orientation in which the aromatic ring lies flat on the catalyst surface and stabilises the radical position of the 'half hydrogenated' intermediate may account for the appearance of **32** in competition with **31**. A similar hydrogenation of **30** over a platinum catalyst gave **33** (26%), **31** (35%), **34** (10%) and **32** (22%).

Techniques used: ^{1}H NMR, IR, MS, elemental analysis, GLC

References: 10

Schemes: 3

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