J. Chem. Research (S),
1998, 364–365
J. Chem. Research (M),
1998, 1501–1518

The Heterogeneous Catalytic Hydrogenation of Cumulated Allene-cyclopropanes: 1-(2′-Methylpropenylidene)-7-bicyclo[4.1.0]heptane

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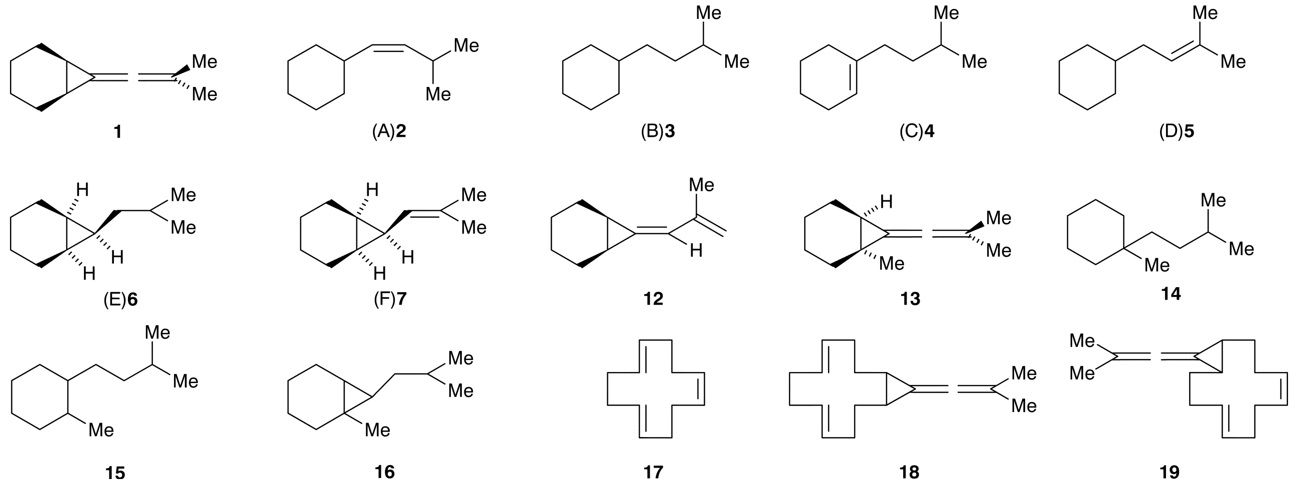
The catalytic hydrogenation of the title allene-cyclopropane **1** is studied, using supported platinum and palladium catalysts, with the aid of 'snapshot analysis' graphs; other related results are reported.

During the competitive heterogeneous catalytic hydrogenation of acetylenes and olefins (isolated, conjugated, cumulative and aromatic) in solution, preferential adsorption of one chemical species may cover the catalyst surface largely or entirely to the exclusion of other chemical species contained in a mixture. Such phenomena can lead to 'molecular queues' being formed to gain access to the catalyst surface, thus leading to an ordered sequence of hydrogenation.[1,2] In many cases however the sequence is not so sharply defined. The catalytic hydrogenation of allenes is particularly responsive to the 'catalyst hindrance' presented by different orientations of the allene to the hydrogen adsorbed on the catalyst surface.[3,4] Indeed such hindrance effects can provide a means of converting molecular dissymmetry into centrodissymmetry, hence allowing an experimental determination of the absolute configuration of an optically active allene.[5]

The hydrogenation of 1-(2-methylpropenylidene)-7-bicyclo-[4.1.0]heptane **1** over Pt was followed using GLC 'snapshot analysis' (Graph 1). Identification and isolation of the major components was by using preparative GLC and examination of the collected material by ^{1}H and ^{13}C NMR and mass spectral analysis, confirming by independent synthesis.



Scheme

It is clear from the products of the first stage of the hydrogenation over Pt (*i.e.* until the starting material has been used up) that the hydrogenation occurs in the 'parallel' mode *i.e.* (F)**7** (68%) and its 1,2-hydrogenation product (E)**6** (13%) are formed in large amount. The former can be readily isolated preparatively. Fully saturated cyclopropane hydrocarbon (E)**6** is being formed during the first stage apparently from (F)**7** either by desorption–readsorption of the initial products or else by reorganisation on the catalyst. The amount of (E)**6** increases during the second stage finally reaching 75% when uptake of hydrogen ceases. In the first stage very little (4%) fully saturated hydrocarbon (B)**3** having a hydrogenolysed cyclopropane is formed, but the curve shows a marked increase during the second phase, apparently through saturation of unidentified minor components formed mainly in stage 1. These soon die away in the second stage leaving 25% of (B)**3** when hydrogen uptake ceases. Towards the end of the hydrogenation the curve for (B)**3** flattens and there is little evidence for anything but very slow conversion of cyclopropane (F)**7** into (B)**3** by direct hydrogenolysis over this catalyst.

The outcome of employing 5% palladium on carbon is shown in Graph 2. As with the platinum catalyst, the *cis*-olefinic cyclopropane (F)**7** reaches its highest concentration (60%) at the end of the first stage. In contrast however, substantial quantities of olefin (A)**2** were found at this point and may be interpreted as a product of 1,4-addition of (F)**7**. The amounts of saturated cyclopropane (E)**6** formed in the first stage are small (~5%) though appreciable quantities of olefin (D)**5** (18%) and a little (C)**4** are present—they are thermodynamically stable olefins and since the equilibrating action of such catalysts is well known, their origin may be (A)**2**, formed first as a kinetic product. At the end of the first stage the mixture is more complex than in the presence of Pt. In the second stage of the Pd hydrogenation the concentration of olefin (A)**2** rapidly falls to zero whilst (D)**5** and (C)**4** increase rapidly to a maximum of 25% and 18% respectively. The more thermodynamically stable olefins in stage 2 can be construed as derived from isomerisation of (A)**2** coming from the conjugated cyclopropane-olefin (F)**7**. This leads ultimately to the large final pool (88%) of saturated aliphatic compound (B)**3** at the end of the hydrogenation. The only other product at the end of the hydro-

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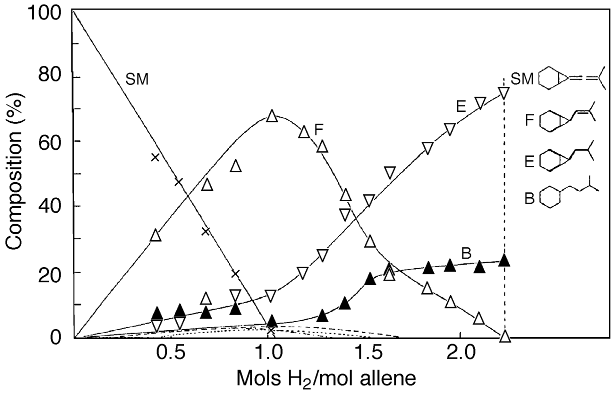
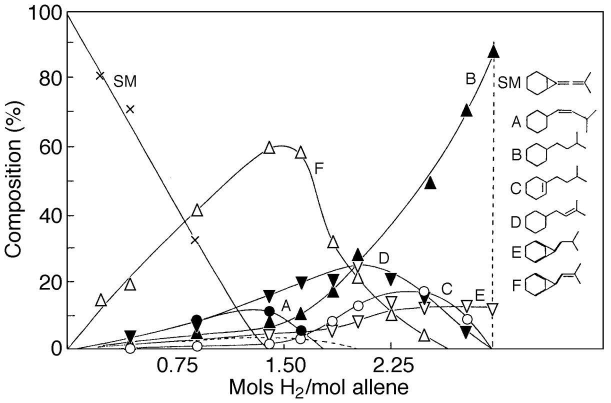


Graph 1 Hydrogenation of 1-(2′-methylpropenylidene)-7-bicyclo[4.1.0]heptane over 5% Pt/C in methanol



Graph 2 Hydrogenation of 1-(2′-methylpropenylidene)-7-bicyclo[4.1.0]heptane over 5% Pd/C in methanol

genation is cyclopropane (E)**6** (12%) which is comparatively resistant to hydrogenolysis to (B)**3**. The palladium catalysed hydrogenation thus contrasts rather sharply with the platinum case in showing preference for 1,4-'edge on' hydrogenation of (F)**7** relative to 1,2-'flat' attitude to the catalyst that leads to (E)**6**. Our results are in agreement with the report that the hydrogenation of conjugated vinyl cyclopropanes over platinum lead mainly to double bond saturation, whilst hydrogenation over palladium involves predominantly ring hydrogenolysis.[16]

The conjugated olefin-cyclopropane (F)**7**, isolated from Graph 2 by preparative GLC, was hydrogenated over palladium (Graph 3—see Full Text) and its behaviour was as expected from Graph 2. The diene-cyclopropane **12**, which was hydrogenated over 5% palladium on carbon with an allowed uptake of 1 mol H_2 gave the olefin-cyclopropane (F)**7**, formed (83% yield) by 1,4-reduction of the diene, the cyclopropane ring not being cleaved. On treatment of the allene-cyclopropane **1** with sodium in liquid ammonia only the *trans*-isomer **8** (corresponding to the *cis*-isomer **7**) of the olefin-cyclopropane was obtained.

Hydrogenation of the unsymmetrically methyl substituted alkenylidene cyclopropane **13** over a 5% palladium on carbon catalyst gave one major product (97%), **14**. Reaction thus takes place from the less hindered side, creating a quaternary carbon centre. On the other hand employment of a 5% platinum on carbon catalyst in the hydrogenation of **13** gave three products, the two largest of which (42 and 40%) were the tetrasubstituted cyclopropane **16** and the same quaternary hydrocarbon **14**. In view of the ease with which alkenylidene cyclopropanes can be made, their hydrogenation is worth considering for reaching structures such as **14**.

During the work, dimethylallene carbene was added using phase transfer methods[18] to other olefins, among them the 1(*Z*),5(*E*),9(*E*)-cyclododeca-1,5,9-triene **17**. This gave a crystalline product and differentiation between the adduct **18** attacked at the (*Z*)-double bond and the adduct **19** attacked at one of the (*E*)-linkages was attained by counting the number of signals in the ^{13}C NMR spectrum. Because of symmetry **18** should have a maximum of 10 signals whereas experimental data showed 16 resonances for the 17 carbon adduct identifying it as **19**.

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

References: 23

Graphs: 3

Received, 18th March 1998; Accepted, 19th March 1998
Paper E/8/02162G

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