

REACTIONS OF STRAINED TRICYCLIC HEXANES WITH TRANSITION METALS

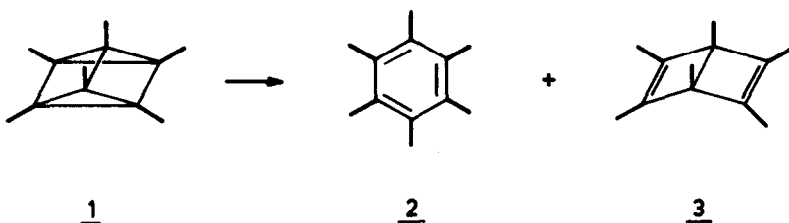
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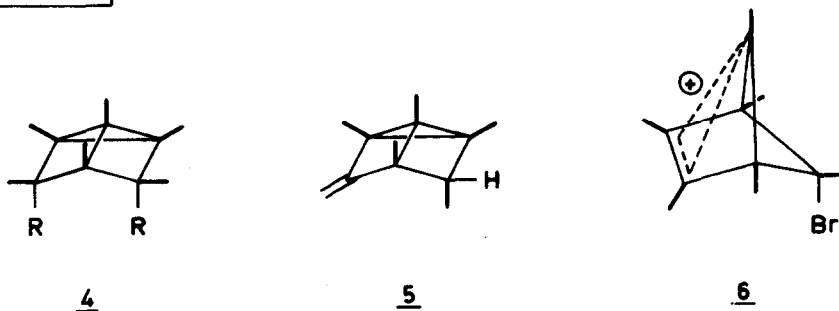
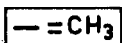
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Valence isomerizations of hexamethyltetracyclo[2.2.0.0^{2,6},0^{3,5}]hexane (1) have been found to give hexamethylbenzene (2) and hexamethyldewarbenzene (3). It was found that by suitable choice



of reaction conditions either isomer could be obtained as the major product.¹

In continuing our investigations of the catalytic effects of transition metals on (valence) isomerizations of strained molecules, we have been studying the action of AgClO_4 and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ on exo-1,2,3,4,5,6-hexamethyltricyclo[2.2.0.0^{2,6}]hexane (4)² and 1,2,4,5,6-pentamethyl-3-methylene-tricyclo[2.2.0.0.^{2,6}]hexane (5).³

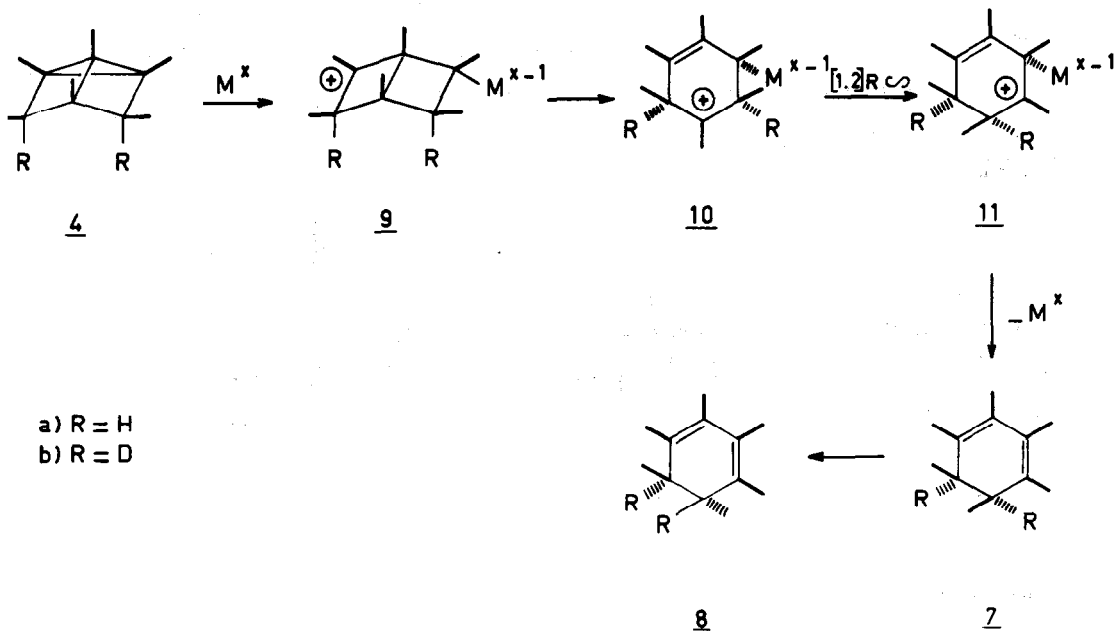


- a) R = H
b) R = D

Compound 4b was synthesized in 60% yield from the reaction of endo-5-bromo-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cation (6) with LiAlD_4^4 as described previously for the undeuterated compound 4a.^{2b} The structure of 4b follows from its nmr spectrum (CDCl_3): 4 singlets at δ (ppm): 1.21 (3H); 1.05 (6H); 0.93 (6H); 0.68 (3H); ir (CCl_4 , $c = 1 \text{ mg/ml}$): strong CD-stretch at 2150 cm^{-1} ; m/e ($\text{C}_{12}\text{H}_{18}\text{D}_2$): 166.

When 4 or 5 were treated at room temperature with AgClO_4 (5 mol% in chloroform) or $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (15 mol% in chloroform) 2 was formed nearly quantitatively within three minutes.⁵ We were able, however, to trap the intermediates from the reaction 4 \rightarrow 2 and 5 \rightarrow 2 at low temperature. The present report describes the results of this study, which demonstrates again the specific effect of transition metals on catalytic processes of strained compounds. At -50°C 4 was transformed under the influence of transition metal catalysts stereospecifically into cis-hexamethylcyclohexadiene (7) (observed by nmr⁶), which at 20°C isomerized rapidly to the more stable trans-isomer 8. Nevertheless, 8 could not be isolated from the reaction product mixture, e.g., on distillation only 2 was obtained. It was found, however, that if the catalyst was deactivated by adding anhydrous Na_2S to the reaction product mixture at -50°C followed by warming to room temperature, 8 could be isolated in about 70% yield. It was identified by nmr, ir and uv data which were identical with those of an authentic sample.⁷

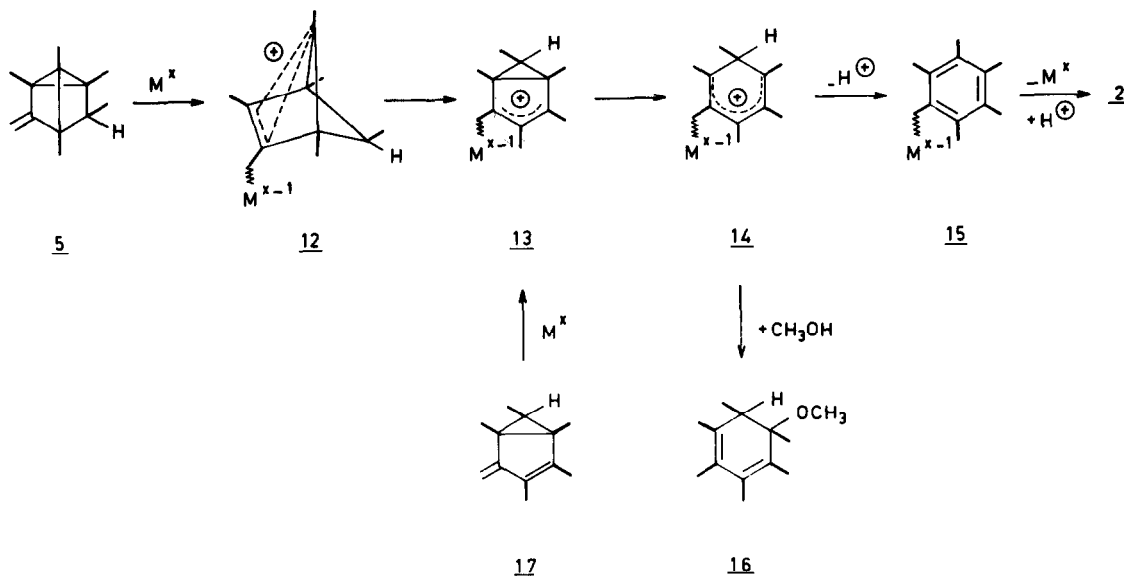
The formation of 7 from 4 is rationalised in terms of the mechanistic scheme outlined below ($\text{M}^x = \text{Ag}^\oplus$ or Rh^I):



Steric considerations lead us to expect that attack of the catalyst takes place on the C₂-C₆ bond from the sterically least hindered side of the compound to form 9. Subsequent cleavage of the C₁-C₄ bond proceeds in a fashion similar to that described previously⁸ to form 10, which after intramolecular[1,2]H-shift and loss of the metallic catalyst gives the cis-cyclohexadiene 7. Evidence for the intramolecular nature of the hydrogen shift in the case of the silver ion catalyzed reaction of 4 is obtained from an experiment in which a 1:1 mixture of 4a and 4b gave only undeuterated and dideuterated trans-hexamethylcyclohexadienes 8. Mass spectra which were taken before and after the reaction was carried out showed a constant ratio (100:15:100) for the molecular ion peaks at m/e 164 (due to 4a, respectively 8a), at m/e 165 (due to ¹³C isotopes of 4a, respectively 8a) and at m/e 166 (due to 4b, respectively 8b). The peak at m/e 165, which would correspond also to the monodeutero trans-hexamethylcyclohexadiene, showed no increase in intensity, demonstrating that no scrambling of deuterium occurs between the undeuterated and dideuterated compounds during the reaction. Attempts to trap one of the proposed intermediates (9, 10 or 11) as a methoxy derivative by carrying out the reaction in methanol (instead of chloroform) failed, suggesting that either the intramolecular reaction steps are rapid compared to attack of the nucleophilic solvent or that the reaction proceeds via a concerted mechanism.

In contrast to 4, the unsaturated compound 5 reacts with AgClO₄ (5 mol%) or Rh₂(CO)₄Cl₂ (15 mol%) in chloroform at -50°C rapidly to give 2. However, when 5 was treated at -50°C with these catalysts in methanol, a complex mixture of methoxylated compounds was observed in the nmr spectrum, suggesting that the transition metal catalyzed rearrangement of 5 → 2 is a stepwise process in which the catalyst acts as a Lewis acid.⁹ Product 16, present in the reaction mixture in 50% yield (according to nmr), was isolated by glc^{10a} and identified by comparison with published spectral properties of authentic material.^{10b} We were unable to isolate the other methoxylated compounds, because of their instability in the glc column.

We assume that the reaction 5 → 2 proceeds via the mechanistic picture outlined below. Significantly, M^x (Ag⁺ or Rh^I) attacks 5 at the double bond rather than at the cyclopropane ring to give the carbonium ion 12, in a manner similar to the protonation of 5 with FSO₃H.¹¹ A subsequent 1-2 carbon shift would lead to 13, which is followed by a ring opening process to give 14, in the same fashion as described earlier.³ In chloroform 14 would lose a proton to give 15 which, on protonolysis^{9a} of the carbon metal bond, affords 2, whereas in methanol solution, the carbonium ion 14 is trapped to give 16. Support for the proposed mechanism^{9b} is found in the fact that 1,2,3,5,6-pentamethyl-4-methylene-bicyclo[3.1.0]hex-2-ene (17)^{10b} which is an isomer of 5, gives



also **2** (80%) upon reaction with $AgClO_4$ in chloroform at $-50^\circ C$ and gives **16** when the reaction is carried out in methanol (70%). This implies that attack of the catalyst occurs on the exocyclic double bond (in preference to the endocyclic double bond or cyclopropane ring) to give initially **13** ($M^{x-1} = Ag$), which subsequently leads to the observed products as described above.

References and footnotes:

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- a. P. Tauchner and R. Hüttel, *Tetrahedron Lett.*, 4733 (1972).
- b. H. Hogeveen and P.W. Kwant, *ibid.*, 1151 (1973).
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- In addition, a new $C_{12}H_{18}D_2$ isomer has been found in 25-30% yield; the structure of this compound is still under investigation.
- A thermolytic ($130^\circ C$ in toluene) or acid catalysed (1 mol% $AlCl_3$ in pentane at $-30^\circ C$) reaction of **4** leads rapidly to the thermodynamically very stable compound **2**. Attempts to trap an intermediate in the thermal reaction with acetylenedicarboxylate dimethyl ester lead to a complex product mixture which has not been analysed further.
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- a. P.G. Gassman and T.J. Atkins, *J.Amer.Chem.Soc.*, **94**, 7748 (1972), and literature cited therein.
 - An alternative explanation in terms of a proton-catalyzed process has very recently been advanced for rearrangement of tricyclo[4.1.0.0^{2,7}]heptanes (L.A. Paquette, S.E. Wilson, G. Zon, and J.A. Schwartz, *J.Amer.Chem.Soc.*, **94**, 9222 (1972); P.G. Gassman and R.R. Reitz, *ibid.*, **95**, 3058 (1973)).
- a. Analytical glc as well as isolation of **16** was carried out using a SE 30 column at a temperature of $100^\circ C$.
- b. W. Schäfer and H. Hellmann, *Angew.Chem.*, **79**, 565 (1967).
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