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Preliminary communication

Ring closure reactions of trienes catalyzed by silver(I) ions

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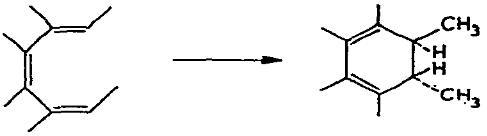
The steric course of the ring closure of the geometric isomer of 3,4,5,6-tetramethyl-2,4,6-octatriene is an intriguing reaction in the light of the Woodward-Hoffmann rules[1]. Thermally *cis,cis,trans*-tetramethyl-2,4,6-octatriene[*] reacts in a conrotatory fashion with respect to *trans*-hexamethylcyclohexa-1,3-diene as is predicted by the symmetry rules. The ring closure is completed in about 5 hours at 150° in methanol.



A study of the stereospecificity under catalytic conditions would have a strong bearing on the theory as advanced by Mango and others[3]. The possible finding of a disrotary ring closure under catalytic conditions would provide strong if not conclusive evidence for the theory, provided that the reaction within the complex occurs in a concerted manner. We investigated the influence of metals on this reaction in order to see whether it would be catalysed in the same way as other valence isomerisations[3,4,5].

The reactions were carried out in toluene and diglyme at temperatures of 90, 120 and 160° with various amounts of catalyst in the case of homogeneous systems and some 10% in heterogeneous systems. The reaction products were studied by NMR and GLC. Typical examples of the catalysts used are CuCl (butadiene), $CuCOOCF_3(CH_3CN)_3$, $AgCOOCH_3$, $AgBF_4$, $PtCl_2$ (ethene), Pt, Ag, $W(CO)_4Py_2$, $[Rh(CO)Cl]_2$, $[RhCl(norbornadiene)]_2$, and $RhCl_3(H_2O)_3$ in CD_3OD.

A fast reaction was found with an equimolar amount of $AgBF_4$ giving 100% yield of hexamethylbenzene (HMB) within 10 minutes. Other catalysts led to a number of products and generally only a very small amount of HMB was found.

HMB may be formed (a) via dehydrogenation after ring closure or (b) via ring closure after hydrogen abstraction from the triene.

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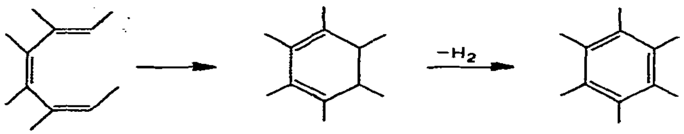
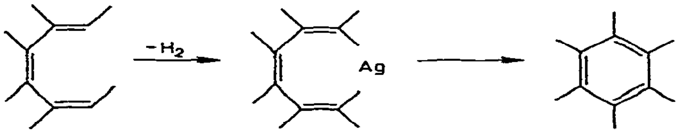
[*] The preparation will be published elsewhere[2].

(a)



(b)



It was found that the *cis*- and *trans*-hexamethylcyclohexadienes are both dehydrogenated under these conditions within 10 minutes, so that both routes (a) and (b) are possible. Since cyclohexadiene was not found among the products and also could not be trapped by adding a dienophile, the question of stereospecificity cannot be answered.

The high activity of $AgBF_4$ seems to be consistent with the results of Pettit[5] and many others[4] in various valence isomerisations. However, all these compounds studied so far contain highly strained three- or four-membered rings and the relief of strain is considered to be a strong driving force for these reactions. There is hardly any strain in *cis,cis,trans*-3,4,5,6-tetramethyl-2,4,6-octatriene and the difference in energy from cyclohexadiene is presumably relatively small. Further work on other non-strained compounds is in progress.

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