Intramolecular Cyclisation of 1,1′,3,3′-Tetramethyl-1,1′-bi-indenyl

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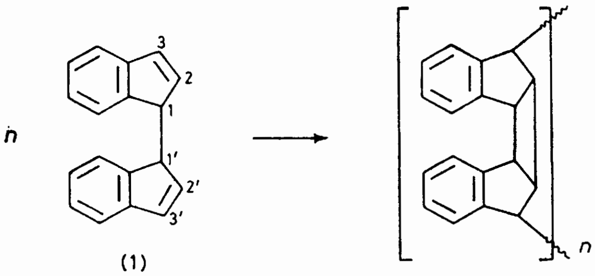
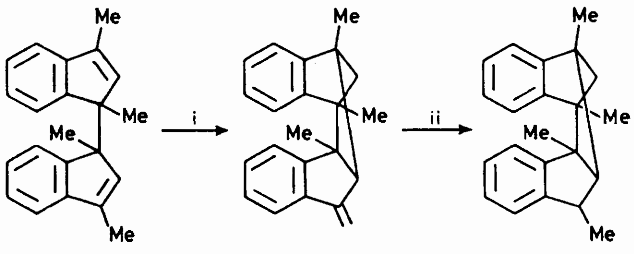
Summary The intramolecular cyclisation of 1,1′,3,3′-tetramethyl-1,1′-bi-indenyl occurs when $TiCl_4$ is used as a catalyst, thus explaining certain unexpected aspects of the polymerisation of 1,1′-bi-indenyl.

The cationic polymerisation of 1,1′-bi-indenyl (**1**) enables the preparation of soluble polymers of high molecular weights. Previous studies[1,2] lead to the hypothesis that the polymerisation involves the simultaneous reaction of two ethylenic systems, as shown in Scheme 1.[1] The mechanism, which involves a primary electrophilic attack at the C-3 position with formation of the carbocation at the C-2 position, does not appear probable. On the contrary, an electrophilic attack at the C-2 position appears more likely since it forms a more stabilized carbocation.



Scheme 1.

Because of the difficulties involved in studying directly the structure of the polymer units, we simplified the problem by using a model molecule susceptible to the same initial electrophilic attack, but not to propagation. We chose 1,1′,3,3′-tetramethyl-1,1′-bi-indenyl (**2**), which has recently been obtained as a mixture of the *meso* and (±)-isomers.[3] We prepared it by a different route and were able to isolate the diastereoisomer (**2**).

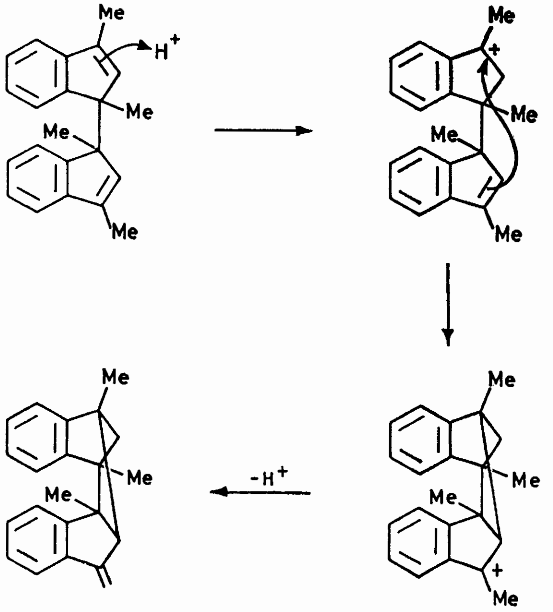


(2) (3) (4)

Scheme 2. i, $TiCl_4$, CH_2Cl_2, −70 °C; ii, H_2–Pd–C, C_6H_6, 25 °C.

The electrophilic attack on (**2**), carried out under the same conditions as for the cationic polymerisation of (**1**), gave compound (**3**) after g.l.c. and h.p.l.c. which was identified by ^1H and ^{13}C n.m.r. spectroscopy. Catalytic hydrogenation of compound (**3**) yielded compound (**4**), identified by ^1H n.m.r. spectroscopy, with regeneration of the fourth methyl group, thus confirming the existence of an exocyclic double bond in compound (**3**) (Scheme 2).

Hence, we propose the mechanism shown in Scheme **3** involving the formation of a five-carbon ring. This mechanism may also be applied to the cationic polymerisation of (**1**) and is essentially an intramolecular cyclisation. Also, the non-conjugated diene leads to non-crosslinked high polymers.



Scheme 3.

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[3] D. W. Jones and G. Kneen, *J. Chem. Soc., Perkin Trans.* 1, 1977, 1313.