The Effect of Ring Size on Threading Reactions of Macrocycles

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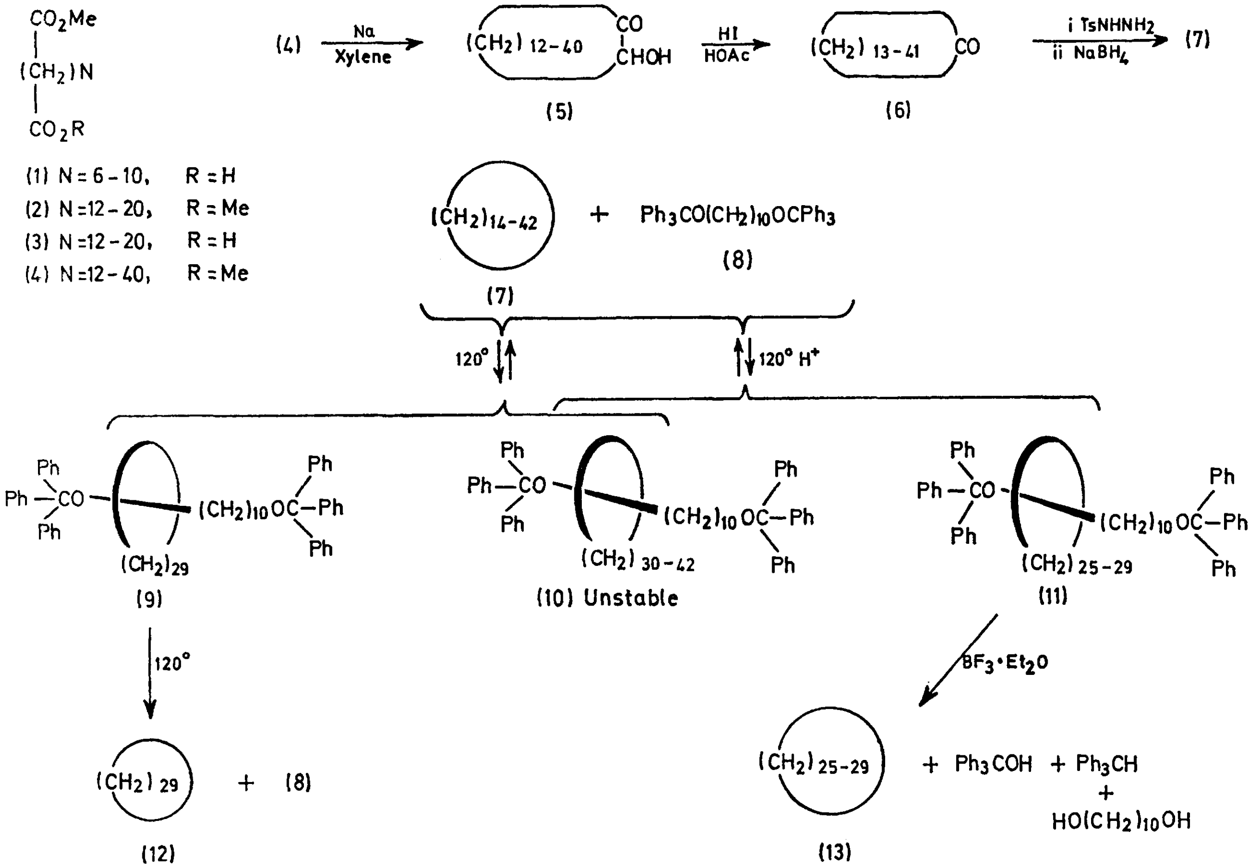
Summary 1,10-Bis(triphenylmethoxy)decane forms stable threaded compounds with macrocyclic hydrocarbons in the range C_{25}–C_{29} only.

Statistical and directed syntheses of compounds consisting of macrocycles threaded by methylene chains bearing large end groups, such as (**9**), have been described[1] previously. Described here is the application of the statistical method to the determination of the effect of macrocycle ring size on the formation and stability of threaded compounds.

A mixture of cyclic hydrocarbons (**7**), containing all homologues from cyclotetradecane to cyclodotetracontane, was first prepared as follows. A mixture of the five dicarboxylic acid monoesters (**1**) was subjected to a crossed Kolbe electrolysis in methanol–benzene containing sodium methoxide, forming the ester mixture (**2**) which was hydrolysed[2] to the monoester mixture (**3**). A mixture of (**1**) and (**3**) was further electrolysed forming the ester mixture (**4**) containing all homologues from dimethyl dodecane-1,12-dicarboxylate to dimethyl tetracontane-1,40-dicarboxylate. Cyclisation of (**4**) with sodium in refluxing xylene in the presence of chlorotrimethylsilane[3] gave, after acid hydrolysis, the acyloin mixture (**5**). Hydrogen iodide in acetic acid converted (**5**) into the ketone mixture (**6**) which was purified through the Girard derivative. Borohydride reduction[4] of the tosylhydrazone of (**6**) yielded the hydrocarbon mixture (**7**) which was freed from unsaturated impurities by treatment with alkaline sodium permanganate solution and purified by filtration of a solution in hexane through silica gel.



The macrocycle mixture (**7**) and 1,10-bis(triphenylmethoxy)decane (**8**) were heated together at 120° rapidly forming a small equilibrium concentration of the threaded compound (**9**), formed from the C_{29} macrocycle only (t.l.c.). Separation by column chromatography or by t.l.c. gave the compound (**9**) as well as the unchanged starting materials (**7**) and (**8**). Heating (**9**) to 120° caused the expected extrusion of the threading piece (**8**), $t_{1/2}$ *ca.* 10 min, releasing the C_{28} macrocycle (**12**) (g.l.c.). Since only the C_{29} macrocycle forms a stable threaded compound it appears that the C_{28} and smaller macrocycles do not allow passage of the blocking group at 120° while the C_{30} and higher macrocycles form only transient compounds (**10**) which separate into their components even at room temperature.†

In contrast to the above thermal synthesis of threaded compounds, the reaction of (**7**) with (**8**), catalysed by small quantities of trichloroacetic acid at 120° which reversibly cleaves the triphenylmethyl group allowing insertion‡ by the unblocked chain, formed a small amount of the macrocycle mixture (**11**), containing all rings from C_{25} to C_{29}. Acid hydrolysis of this product gave a mixture (**13**) of the five macrocycles cyclopentacosane to cyclononacosane (relative weight yields 1, 9, 23, 43, and 57) (g.l.c.–m.s.).§ Very small peaks in the gas chromatogram possibly correspond to the C_{23} and C_{24} macrocycles. However, no traces of the C_{30} and higher macrocycles were observed.

Molecular models¶ are consistent with the above results; a ring of 22 methylenes and a threaded methylene chain are in close contact, while the limiting ring size for passage of a triphenylmethyl group is about C_{29}. Models also show that the triphenylmethyl group does not pass through the C_{29} macrocycle by a symmetrical transition state but rather that the group must tilt relative to the ring allowing one or a group of two phenyls to pass first.

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† Previous work (ref. 1) has shown that stable threaded compounds can be prepared using the triphenylmethyl blocking group and C_{30} macrocyclic acyloins.

‡ The inserting species is presumably the monotriphenylmethyl ether of decane-1,10-diol.

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¶ Constructed from Corey-Pauling (CPK) atomic models.

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