The Preparation and Cyclopolymerisation of *cis*-1,3-Divinylcyclohexane and *cis*-1,3-Divinylcyclopentane

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THE cyclopolymerisation of *cis*-1,3-di-isocyanatocyclohexane has recently been described.[1] *cis*-1,3-Divinylcyclohexane (I) and *cis*-1,3-divinylcyclopentane (II) should present similar and unambiguous examples of cyclopolymerisation and we now report their synthesis and polymerisation.

The dimethyl ester of cyclohexane-*cis*-1,3-dicarboxylic acid was reduced with sodium aluminium hydride in dry tetrahydrofuran at −50° to give cyclohexane-*cis*-1,3-dicarboxyaldehyde in 45% yield, b.p. 94°/1·8mm.†, the low yield being a result of considerable thermal polymerisation in the

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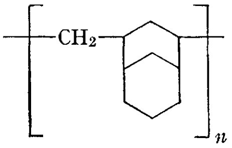
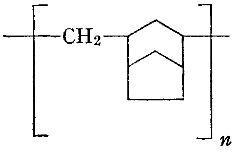
† All new compounds gave satisfactory analyses and spectra.

distillation flask. This dialdehyde was converted by the Wittig reaction, using the ylide (from methyltriphenylphosphonium bromide and sodamide in liquid ammonia) in dry tetrahydrofuran and refluxing under dry nitrogen, into the *cis*-divinyl compound (I) in good yield, b.p. 98—100°/85mm. n_D^{20} 1·4623, with strong absorption bands in the infrared spectrum at 912, 993, and 1645 cm.$^{-1}$ associated with the vinyl groups.



Soluble poly-cis-1,3-*divinylcyclohexane*



Soluble poly-cis-1,3,-*divinylcyclopentane*

Cyclopentane-*cis*-1,3-dicarboxyaldehyde, obtained from bicyclo[2,2,1]hept-2-ene by oxidation with neutral potassium permanganate,[2] similarly underwent the Wittig reaction, with methyltriphenylphosphonium bromide and n-butyl-lithium in n-hexane–tetrahydrofuran solution and refluxing under dry nitrogen to yield the *cis*-divinyl compound (II) in 56% yield, b.p. 63—64°/68mm., $n_D^{24\cdot5}$ 1·4532, with strong absorption bands at 905, 987, and 1620 cm.$^{-1}$ for the vinyl groups.

Both divinyl compounds (I and II) were polymerised with the Ziegler catalyst prepared from tri-isobutylaluminium and titanium tetrachloride in 1: 1 molar ratio in n-heptane solution. The polymerisations occurred at room temperature and the polymers were precipitated from the mixtures by the addition of methanol. The polymer from (I), obtained after 138 hr. in 20% conversion, was a white powder, of which 86% was soluble in cold benzene. This soluble polymer, m.p. about 110°, from its infrared spectrum contained only a trace of residual unsaturation. Similarly, the polymer from (II) (72 hr., 38% conversion) was 65% soluble in hot cyclohexane and the soluble polymer, m.p. 116°, contained only a trace of unsaturation. These soluble, virtually saturated polymers are clearly cyclopolymers and the linear polymer chains will contain bicyclo[3,3,1]nonane and bicyclo[3,2,1]-octane structures, respectively. For the intramolecular step in the cyclopolymerisation to occur almost exclusively, the two vinyl groups must be oriented before or during polymerisation. In (I) this can be achieved by a diaxial arrangement of these groups. In (II) the groups must be close enough in the *cis*-arrangement to make cyclopolymerisation the predominant polymerisation mechanism. There is evidence[3] that interspatial π-orbital interactions occur in acyclic 1,6-dienes which undergo cyclopolymerisation.

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[3] G. B. Butler and T. W. Brooks, *J. Org. Chem.*, 1963, **28**, 2699.