

## Thermal Rearrangement of 1,1,2,2-Tetraphenylcyclopropane

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*Summary* The thermal rearrangement of 1,1,2,2-tetraphenylcyclopropane (**1**) to 1,1,3-triphenylindan (**2**) involves formation of an intermediate triene (**3**) which has been detected by u.v. spectroscopy and trapped by reaction with enophiles.

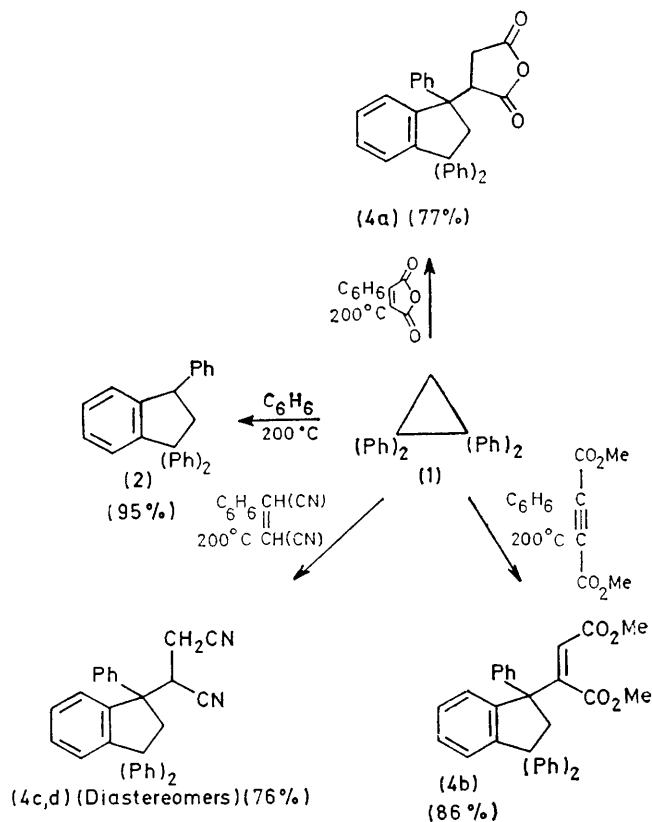
IN view of the axioms that ring-strain leads to thermodynamic instability, and that bond dissociation energies

decrease as a function of the increasing stability of the incipient radicals, the fact that 1,1,2,2-tetraphenylcyclopropane<sup>1</sup> (**1**) is a readily prepared, relatively stable, high melting (167 °C) compound requires some explanation. The thermal reactions of (**1**), and other multiphenylated cyclopropanes have, however, received little attention.<sup>2</sup>

When a benzene solution of (**1**) was heated at 200 °C, the rearranged product, 1,1,3-triphenylindan (**2**) was formed in

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quantitative yield (Scheme 1).<sup>‡</sup> The disappearance of (1) was followed by <sup>1</sup>H n.m.r. and even at this high temperature, the rate of rearrangement was slow; complete reaction required over one week.<sup>§</sup>



When (1), in a benzene solution containing 1 mol. equiv. of maleic anhydride, was heated at 200 °C, the adduct (4a) was obtained in 77% yield.<sup>§</sup> This reaction was considerably faster than the rearrangement of (1) to (2); an equivalent quantity of (1) was consumed after only 24 h. However, the rate of disappearance of (1) was essentially the same when the concentration of maleic anhydride was increased by a factor of five. The rate is also relatively insensitive to solvent polarity; (4a) was formed at a similar rate when acetonitrile was the solvent. Control experiments prove that (2), 1,1,3,3-triphenylindene, and 1,1,3,3-tetraphenylpropene do not react with maleic anhydride in benzene at 200 °C.

<sup>‡</sup> In a typical reaction (1) (0.06 g) was dissolved in the solvent (0.5 ml) in a thick-walled n.m.r. tube. The tube was sealed and heated in a constant temperature oil bath. Known compounds were identified by comparison of spectra (i.r. and <sup>1</sup>H n.m.r.) with those of an authentic sample.

<sup>§</sup> Adduct (4a) was crystallized from the reaction mixture and (4b—d) were isolated by column chromatography. These new compounds were characterized by i.r. and <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy, as well as by mass spectrometry and elemental analysis. Details will be reported in the full paper.

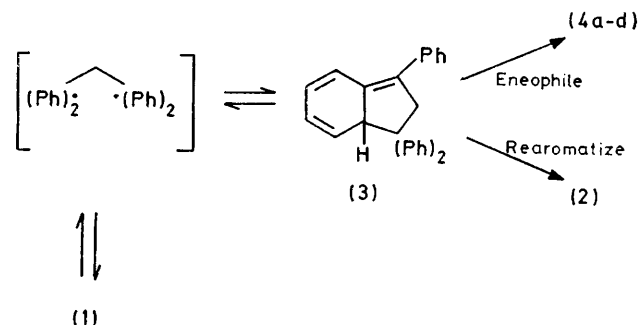
<sup>1</sup> J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, 1962, **27**, 4187.

<sup>2</sup> R. J. Crawford and T. R. Lynch, *Canad. J. Chem.*, 1968, **46**, 1457; Th. Martini and J. A. Kampmeier, *Angew. Chem. Internat. Edn.*, 1970, **9**, 236; phenylcyclopropane has received considerable attention: J. T. Wood, J. S. Arney, D. Cortes, and J. A. Berson, *J. Amer. Chem. Soc.*, 1978, **100**, 3855.

<sup>3</sup> The acid catalysed isomerization of (1) to (2) occurs rapidly at this temperature (ref. 1).

<sup>4</sup> W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, 1962, **27**, 3476; K. R. Kopecky and M.-P. Lau, *J. Org. Chem.*, 1978, **43**, 525. 3-Methylenecyclohexene has  $\lambda_{\text{max}}$  231 nm (W. J. Bailey and J. C. Gossens, *J. Amer. Chem. Soc.*, 1956, **78**, 2804) and 3-benzylidene-cyclohexene has  $\lambda_{\text{max}}$  281 nm (E. A. Broude and J. A. Coles, *J. Chem. Soc.*, 1950, 2014); therefore,  $\lambda_{\text{max}}$  350 nm is reasonable for (3).

The reactions of (1), in benzene at 200 °C, with dimethyl acetylenedicarboxylate, to give (4b) (86%), and with the mixture fumaronitrile–maleonitrile, to give the diastereomeric adducts (4c) and (4d) (76%) also go to completion after 24 h. The rate of the formation of adducts (4a—d) was similar in each case.



These results can be accounted for in terms of Scheme 2, where (1) and (3) are in equilibrium at 200 °C and the net rate of reaction of (1) with the trapping agents (enophiles) is controlled by the rate of formation of (3) from (1). The rate of reaction of (3) with the trapping agents is also fast in comparison with the rate of conversion of (3) into (2) (an orbital symmetry-forbidden reaction). In support of this scheme, we observe absorption in the u.v. region of a solution of (1) at high temperatures which we tentatively attribute to the triene (3). When a degassed solution of (1) in Nujol was heated to 200 °C in a variable temperature quartz u.v. cell, a new absorption with a maximum at 350 nm gradually increased to a constant absorbance. Increasing the temperature resulted in an incremental increase in absorbance. When the cell was cooled rapidly to room temperature, the absorption at 350 nm did not completely disappear; however, if dimethyl acetylenedicarboxylate was then added, this absorption disappeared as the mixture was slightly warmed.

Comparison with model compounds leads to the conclusion that a 350 nm maximum is reasonable for the triene (3). For example, 1-methylenecyclohexa-2,4-diene (5) exhibits a maximum at 303 nm.<sup>4</sup> Furthermore, (5) is stable in solution (hexane) at 20 °C and reacts with enophiles in a manner analogous to that we suggest for (3).

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