A Probable Two-step Diels–Alder Reaction

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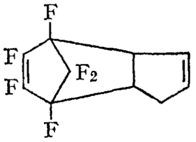
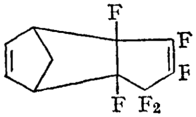
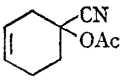
REACTION of perfluorocyclopentadiene[1] with an equimolar amount of cyclopentadiene at 120—125° during 4 days gives an almost quantitative yield of a 16 : 84 mixture of the isomeric Diels–Alder adducts (I) and (II), presumed to have *endo*-configurations, the structures of which have been established by elemental analysis and infrared and nuclear magnetic resonance spectroscopy.



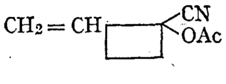
(I) m.p. 37·0–39·5°



(II) m.p. 23·0–25·0°

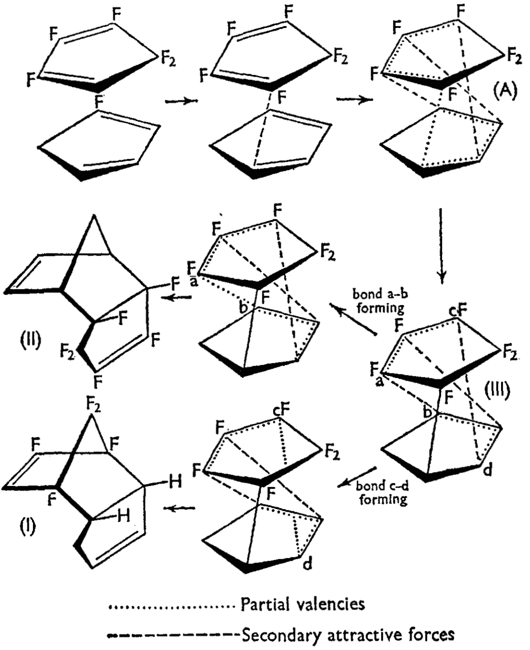


(IV)



(V)

Within the limits of experimental error, the g.l.c.-determined ratio of (I) to (II) in quantitative reactions between equimolar amounts of perfluorocyclopentadiene and cyclopentadiene is unaffected either by change in reaction temperature (*e.g.*, 16 : 84 after 4 days at 110°; 17 : 83 after 5 days at 68° or 7 days at 20°) or by the use of solvents of different polarity (*e.g.*, 17 : 83 after 4 days at 20° in n-hexane; 19 : 81 after 4 days at 20° in nitrobenzene). In addition, both (I) and (II) are unchanged after storage at 20° for several months or at 110°; *i.e.*, they do not undergo interconversion (*e.g.*, by Cope rearrangement).



These facts seem to imply either that (I) and (II) are formed in two simultaneous reactions with pifferent transition states which are influenced in uncommonly like fashion by different solvents, or, and this seems more probable, the reaction involves only one transition state (A) leading to a common transient intermediate (III), which, in steps with low activation energies, collapses to give (I) and (II). This preferred mechanism (see the annexed scheme) follows that proposed by Woodward and Katz[2] for the Diels–Alder reaction. The same type of mechanism has recently[3] been proposed to account for the formation of adducts (IV) and (V) from butadiene and α-acetoxyacrylonitrile in a ratio that is almost unaffected by changes in reaction temperature and solvent polarity.

Since the claim[4] that two isomeric Diels–Alder adducts are obtained when transient cyclopentadienone is trapped with cyclopentadiene has been disputed,[5] the reaction of perfluorocyclopentadiene with cyclopentadiene appears to be the only example of a Diels–Alder reaction between two different cyclic 1,3-dienes in which both dienes play the dual rôle of diene and dienophile.

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