A Symmetry-allowed Pericyclic Reaction involving Two 'Forbidden' Processes. The Thermal Rearrangement of (*E*)-2-Benzylidene-(*Z*)-mesityl(phenyl)-methyleneindane into (*Z*)-2-Benzyl-1-mesityl(phenyl)methyleneindene

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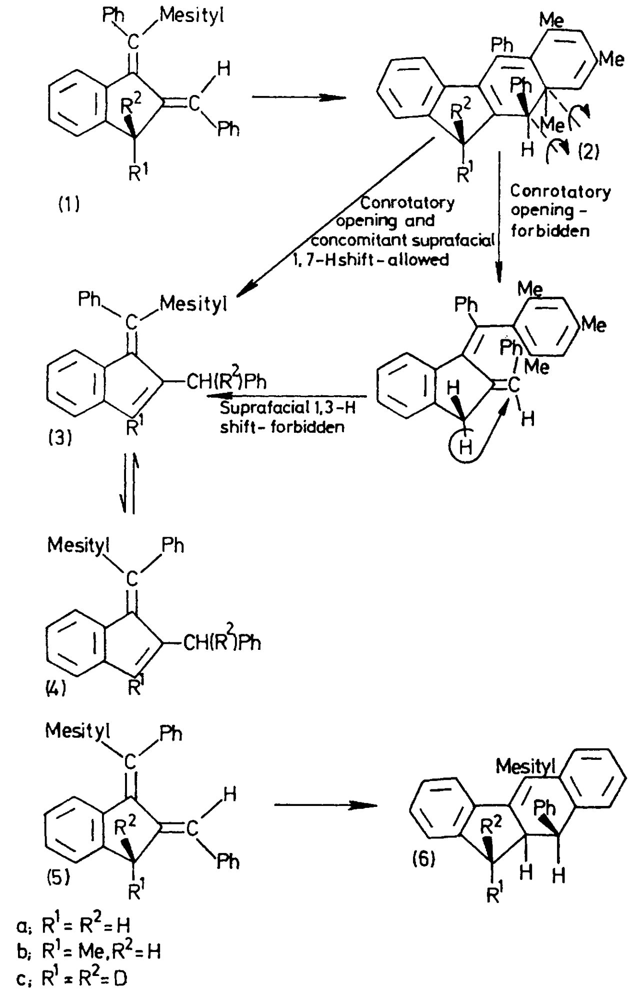
Summary Electrocyclic disrotatory ring closure of (*E*)-2-benzylidene-(*Z*)-1-mesityl(phenyl)methyleneindane occurs at 180° to give (*Z*)-9a,10-dihydro-5,10-diphenyl-6,8,9a-trimethyl-11H-benzo[b]fluorene, which, at this temperature, undergoes conrotatory ring opening and a concomitant suprafacial[1,7]sigmatropic change of hydrogen to yield (*Z*)-2-benzyl-1-mesityl(phenyl)methyleneindene.

CONROTATORY electrocyclic ring opening of a 6-electron system and a suprafacial[1,3]sigmatropic change of hydrogen are symmetry-forbidden thermal processes[1,2] and have not been reported. When two 'forbidden' processes proceed together, the pericyclic reaction can take place with conservation of orbital symmetry in accord with the selection rules. The first example of this type of reaction is reported here.

Diene (**1a**) rearranges at 180° to give the benzofulvene

(**3a**). In contrast, dienes (**1b**) and (**1c**) do not undergo the diene–benzofulvene rearrangement at 180° but isomerise to the dienes (**5b**) and (**5c**) which, like related dienes, undergo thermal disrotatory ring closure followed by a 1,5-hydrogen shift to give the (*Z*)-dihydrobenzofluorenes (**6b**) and (**6c**) respectively. The absence of benzofulvene derivatives in these and previously reported[3,4] indane diene rearrangements precludes an acid or radical catalysed 1,3-hydrogen shift in the reaction (**1a**) → (**3a**).



The thermal rearrangement of diene (**1a**) at 180° to give benzofulvene (**3a**) can only be explained satisfactorily by two consecutive concerted reactions: disrotatory ring closure of diene (**1a**) to the dihydrobenzofluorene intermediate (**2a**), followed by opening of the newly formed σ-bond by the conrotatory mode not prevented by steric constraints with a concomitant suprafacial 1,7-shift of the 11-hydrogen *anti* to the 10-phenyl group and retention of configuration at the migration terminus, as shown in the scheme. This $[\pi^4a + \sigma^2s + \sigma^2s]$ process occurs with conservation of orbital symmetry (Figure 1) and involves a Möbius transition state (Figure 2). The rearrangement (**2a**) → (**3a**) can be broken down into two 'forbidden' processes, a conrotatory electrocyclic ring opening in a 6-electron system, and a suprafacial[1,3]sigmatropic change of order of hydrogen.

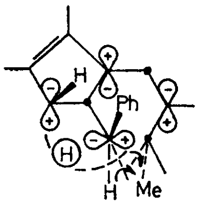


FIGURE 1

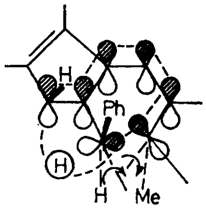


FIGURE 2

M.O. presentation showing conservation of orbital symmetry (1) and Möbius transition state (2) for thermal conrotatory ring opening and a concomitant 1,7-H shift in (**2a**).

The failure to observe product (**3c**) from diene (**1c**) is attributed to the slower migration of the 11-deuterium in the intermediate (**2c**), which will revert back to diene (**1c**) preferentially. In intermediates (**2a**) and (**2b**), migration of the 11-hydrogen *syn* to the 10-phenyl with retention of configuration at the migration terminus is a thermally 'forbidden' process. In diene (**1b**), thermal ring closure is believed to occur by the less sterically hindered disrotatory mode with rotation of the phenyl of the benzylidene group past the 3-hydrogen rather than the 3-methyl, to give intermediate (**2b**) with an *anti* arrangement of the 11-methyl and 10-phenyl groups.[3]

Benzofulvenes (**3a**) and (**4a**) undergo no thermal or photochemical rearrangements other than interconversion. On irradiation, indane dienes yield benzofluorene derivatives. The structures of the hydrocarbons follow from characteristic chemical reactions, and their n.m.r. and u.v. spectra.[3,4] Compounds were crystalline and gave satisfactory analyses.

We thank the S.R.C. for a research studentship (to H. Tucker).

(*Received*, 29*th January* 1974; *Com.* 134.)

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