Electrocyclisation of the 1,5-Diphenylpenta-1,4-dienyl Anion

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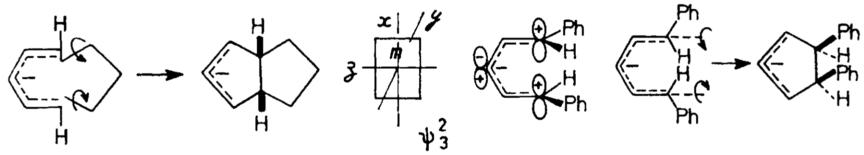
Summary Thermal disrotatory electrocyclisation of the 1,5-diphenylpentadienyl anion gives the *cis*-1,2-diphenylcyclopentenyl anion leading to *cis*-1,2-diphenylcyclopent-3-ene.

THE only recorded example of the thermal ground-state electrocyclisation of a pentadienyl anion is the disrotatory conversion by Bates and McCombs[1] of the cyclo-octadienyl anion (**1**) into the *cis*-bicyclo[3,3,0]octene anion (**2**). We report the thermal, ground-state, symmetry-allowed, six-electron $[{}_{\pi}2_s + {}_{\omega}2_s + {}_{\pi}2_s]$ disrotatory electrocyclisation of the 1,5-diphenylpentadienyl anion (**3**) to the *cis*-1,2-diphenylcyclopentenyl anion (**4**).



(1) (2) (3) (4)

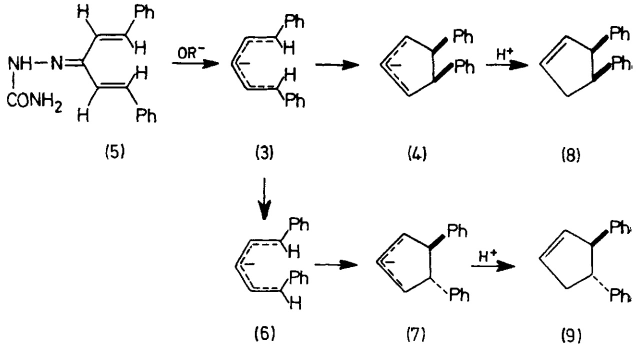
FIGURE. *m* = mirror plane σ^{xz} normal to the plane of the paper in formulae (**1**)—(**4**).

Brenner and Klein[2] found that a mixture of *trans,trans*-, *cis,trans*-, and *cis,cis*-1,5-diphenylpenta-1,4-dienes,[3] and also a mixture of the isomeric 1,5-diphenylpenta-1,3-dienes,[4] by treatment with a solution of Bu^nLi in ether gave a single 1,5-diphenylpentadienyl anion, whose ^1H n.m.r. spectrum was unchanged after 5 days at 38° and after heating to 70°. In our hands generation of the 1,5-diphenylpentadienyl anion with sodamide or with Bu^nLi in diglyme at 160° or with Bu^nLi in decalin at 190° failed to yield after quenching either *cis*- (**8**) or *trans*-1,2-diphenylcyclopent-3-ene (**9**) as shown by g.l.c. of the product, and gave intractable polymers of unknown structure.

TABLE. Cyclisation products from the semicarbazone (**5**) at 225°.

Base	(**8**) (%)	(**9**) (%)	1,2-Diphenylcyclopent-2- and -1-ene (%)
$KOBu^t$	7	25	68
NaOMe	23	73	4
KOH	17	74	9

In the belief that polymerisation processes exclude cyclisation under the above conditions, we have generated the 1,5-diphenylpentadienyl anion *in situ* at 225° by treatment of *trans,trans*-dibenzylideneacetone semicarbazone[5] (**5**) with powdered alkoxides or with powdered potassium hydroxide: $NH_2CO{-}NH{-}N{=}C{<}\rightarrow\overline{N}H{-}N{=}C{<}\rightleftharpoons\overline{N}{=}N{-}CH{<}\rightarrow N_2 + \overline{C}H{<}$. The initial product, the pentadienyl anion (**3**), and its stereoisomer (**6**), by disrotatory cyclisation yield respectively the cyclopentenyl anions (**4**) and (**7**), which afford the products isolated. These, *cis*- and *trans*-1,2-diphenylcyclopent-3-ene (**8**), (**9**) [and the cyclopent-2-ene and cyclopent-1-ene isomers derived from the former], were



(5) (3) (4) (8)

(6) (7) (9)

isolated by preparative g.l.c., and identified by comparison of their retention times, ^{1}H n.m.r. spectra, and mass spectra with those of genuine specimens. The results are given in the Table.

Since we have shown that *cis*-1,2-diphenylcyclopent-3-ene (**8**), but not the *trans*-isomer (**9**), undergoes conversion into the conjugated isomers 1,2-diphenylcyclopent-2- and -1-ene with base, the initial yields of *cis*-1,2-diphenylcyclopent-3-ene (**8**) are 75, 27, and 26% rather than 7, 23, and 17% as shown in the Table. There is appreciable loss of stereochemistry with NaOMe and KOH in the anion (**3**), leading to the anion (**6**), which by disrotatory electrocyclisation gives the anion (**7**), yielding *trans*-1,2-diphenylcyclopent-3-ene (**9**).

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