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BOND-MAKING IN THE 1,5-SIGMATROPIC MIGRATION OF UNSATURATED GROUPS

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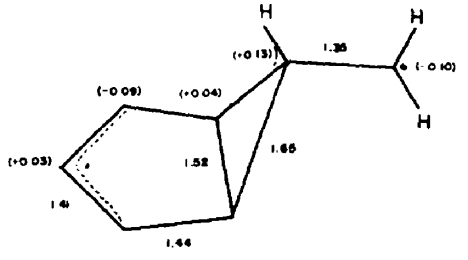
Abstract—1,5-Shifts of vinyl and related groups occur by a mechanism in which σ-bond-making is almost complete before bond-breaking begins; in at least one case (the rearrangement of *cis*-9,10-dihydronaphthalenes) a discrete intermediate is involved.

There is now extensive experimental evidence[1] that in 1,5-sigmatropic shifts vinyl, formyl, and similar unsaturated groups migrate with exceptional ease. Many, but not all,[2] examples involve cyclopentadienes and related systems and in some cases reaction even occurs at room temperature.[3,4] Explanations for this behaviour range from secondary orbital interactions[1b,1c,1e] to vinylogous di-π-methane [4a + 2a + 2a] transition states.[4]

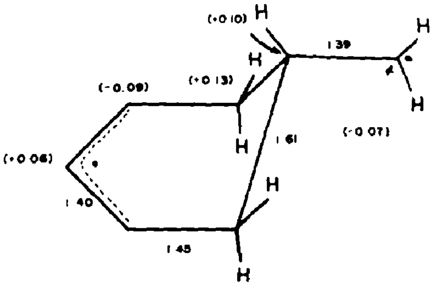
We propose that the *simplest* explanation is that the major process occurring on the way to the transition state is formation of the new σ-bond at the expense of the relatively weak π-bonds, the old σ-bond being almost broken.

MINDO/3 calculations were performed on several cyclopentadienes and on the C_S symmetrical species (transition state or intermediate) which is the mid-point in their 1,5-shift (Table 1). These calculations give a good account of the energetics for the migration of the various groups with the possible exception of the propargyl shift where $\Delta H_f(B) - \Delta H_f(A)$ seems surprisingly high (propargyl was studied in preference to allyl in order to preserve C_S symmetry in (B)). The charge distribution (see the figures in parenthesis on 1) on the C atoms of the transition state (or intermediate) nicely rationalises the substituent effects observed[1b] for migration of a series of –CH=CHX groups on an indene framework. However the most interesting parameter is the distance r between the migrating atom and the migration terminus (or origin) in the C_S species (B). The bond length r is substantially shorter for vinyl and formyl migration than for Me migration and is longer again for the propargyl shift. In the formyl and vinyl cases, formation of the new σ-bond can run ahead of breaking of the old σ-bond, the transition state (or intermediate) resembling a bicyclic biradical (1). With propargyl, the tendency is for separation into cyclopentadienyl and propargyl radicals. In the transition state for vinyl migration on an acyclic pentadiene (2) r is even shorter (1.61 Å).

This is indeed reasonable, since the new σ-bond is not now part of a strained ring. The biradicals (1 and 2) are very similar in structure to the interesting biradical (3) with D_{2d} symmetry discussed by Bischof, Gleiter and Haider.[5] Gleiter *et al.* emphasise the through-bond coupling in 3 which has a MOMO–LUMO separation of 6.23 eV. The HOMO–LUMO gaps for 1 and 2 are calculated to be 7.48 eV and 5.37 eV respectively, so the biradical charac-



(1)



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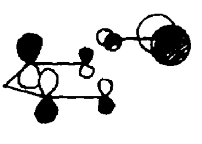
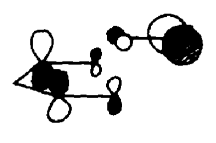
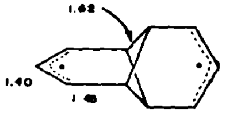


(2)HOMO

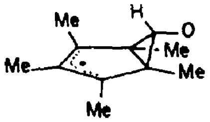


(2)LUMO



(3)

ter[6] of these species increases in the order **1** < **3** < **2**, which is the order of decreasing r and, presumably, decreasing through-bond coupling. The HOMO and LUMO for both **1** and **2** (see diagram) are antisymmetric with respect to the symmetry plane and this treatment can be reconciled with the secondary orbital interaction picture. However we suggest that **1**, **2** and **3** are best viewed as biradicals; the *simplest* view is that σ-bonding between the migrating carbon and the migration terminus is the major process in their formation. This viewpoint also has the merit of suggesting a continuum of possibilities as we move via **4**[1c] to **5**[7] and **6**;[8] with **6** we reach the situation where **6** is the ground state with the cyclopentadiene being the transition state or intermediate. The continuum of possibilities can be neatly summarised on a More O'Ferrall-Jencks[9] diagram (Fig. 1).



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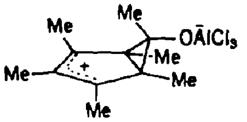

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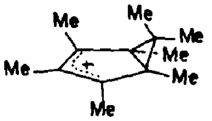


(6)

Non-synchroneity of bond-making and -breaking hints at the possibility of a true intermediate, though it certainly does not logically require it. We wish to suggest that **3** is a true intermediate, which can partition to different products, in the rearrangements of *cis*-9,10-dihydronaphthalenes. These rearrangements were first observed in 1964[10] and it was then suggested that cyclodecapentaenes were intermediates.

In the most sophisticated study, Paquette and Carmody[2] showed that the primary products from **7** (R = Me or COOMe) were **8** and **9**; no **10** was formed initially. Product composition was temperature independent over the (limited) range studied. The activation parameters were E$_a$ 26.0 ± 0.8 and log A 12.8 ± 0.6 for **7** R = Me and E$_a$ 26.7 ± 0.7 kcal mol^{-1} and log A 12.1 ± 0.4 sec^{-1} for **7** R = COOMe. The authors proposed that **8** was formed by a 1,5-shift and **9** via a *cis*^{5}-cyclodecapentaene. There are several problems with this interpretation. (i) It is very doubtful if ring opening of **7** could be rapid enough to account for the formation of **9**. It can be estimated[11] that E$_a$ for ring opening of cyclohexa-1,3-diene itself is 46.4 kcal mol^{-1}, so the ring opening of **7** has to be 20 kcal mol^{-1} easier than that of cyclohexa-1,3-diene itself to account for the reaction. In fact, *cis*^{5}-cyclodecapentaene[12] is surely more strained, relative to hexatriene, than **7** is, relative to cyclohexadiene, and it is therefore likely that ring opening of **7** will be *slower* than that of cyclohexadiene itself. (ii) If the reaction goes via a cyclodecapentaene, **10**, as well as **9**, could be formed. Paquette and Carmody advanced some reasons why **9** might be preferred, but the complete absence of **10** is surprising. (iii) The lack of temperature dependence of product composition implies similar $\Delta S^\dagger$ for the sigmatropic shift and the ring opening, which is also rather surprising.

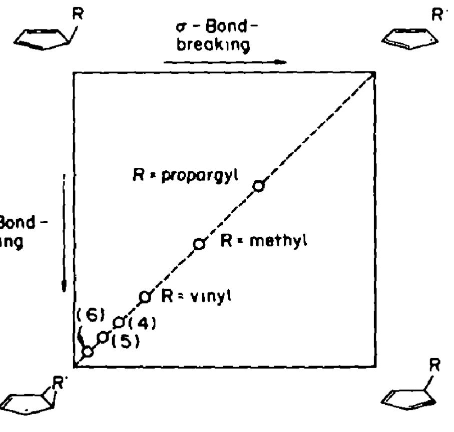
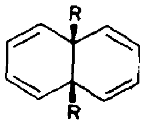
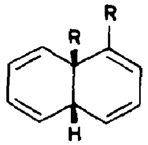


Fig. 1. More O'Ferrall–Jencks diagram for rearrangement of a series of cyclopentadienes (diagrammatic).



(7)



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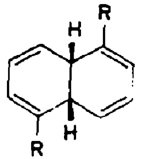

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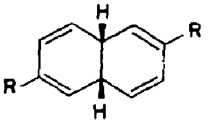
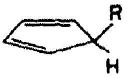


(10)

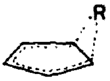
We propose that both **8** and **9** arise by alternative cleavages of the cyclobutane ring in an *intermediate* of type **3**. This proposal satisfies Occam's razor, and accounts for the lack of formation of **10** and the constancy of the **8**:**9** ratio with temperature. It is also thermochemically reasonable. Formation of the octa-2,6-dien-1,8-diyl biradical from two butadiene molecules, the prototype of this process, is endothermic by only[13] 17–25 kcal mol^{-1}. In intramolecular variants of this reaction, the activation energy may be affected by the compression of the π-clouds. Examination of Drieding models of cyclooctatetraene, *cis*-9,10-dihydronaphthalene and **11**[3] show quite well the increasing ease with which these compounds can form biradicals by transannular bond formation.

There seems to be no need to invoke any special stability[5] for **3** in order for it to be a viable intermediate in the rearrangement of **7**.[15] If our interpretation is correct, we detect it as an intermediate simply because of its high symmetry. The species **1** and, especially, **2** should now be seriously considered as potential intermediates rather than transition states in 1,5 shifts of vinyl groups, with similar intermediates possibly occurring in shifts of related groups. A traditional way to detect non-concerted reaction via an intermediate is through loss of stereospecificity. However stereochemistry within the migrating vinyl group may well be retained even if **1** and **2** are intermediates, since bond rotation in **1** or **2** will destroy the through-bond coupling (*cf* the dimethylcyclopropyl carbonium ion). MINDO/3 calculation showed a rise in energy of 4.5 kcal mol^{-1} on 45° methylene rotation in **2**.

Table 1.



(A)



(B)

	C_s symmetry[a]	C_s symmetry[a]		Observed	
R	ΔH_f(A)	ΔH_f(B)	ΔH_f(B)-ΔH_f(A)	$\Delta H^{\ddagger}$	r in Å
H	41.7 (32.4)[b]	69.4	27.7	23.6[c]	1.31
CH_3	39.7 (25.6)	86.1	46.4	44.4[d]	1.72
$CH_2C\equiv CH$	88.5 (85.4)	139.0	50.5	-	1.75
$CH=CH_2$	65.9 (50.5)	102.1	36.2	26.7[e]	1.65
CHO	12.9 (6.1)	43.1	30.2	(13.2)[f]	1.65

[a] Full geometry optimisation within C_s symmetry was carried out for both A and B; $CH=CH_2$ etc. groups were oriented *exo*.

[b] The figures in brackets are the values of ΔH_f calculated from the Benson additivity scheme: S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, 1969, 69, 279.

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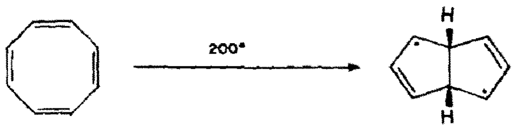
[e] Data for spiro |4.4|nona-1,3,6-triene from reference 1e.

[f] Data for 5-formyl-1,2,3,4,5-pentamethylcyclopentadiene from reference 1c. The pentamethyl substitution should significantly lower $\Delta H^{\ddagger}$.



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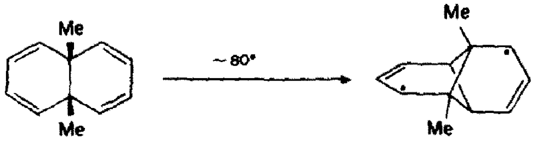
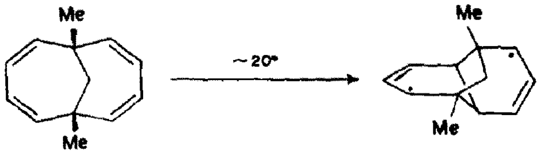


(ref. 2)



(II)

(ref. 3).

We end, however, by reiterating our main point, that in these rearrangements formation of the new σ-bond at the expense of π-bonding is the major process occurring on the way to the transition state.

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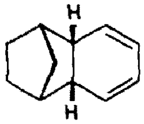
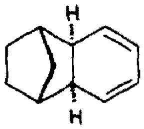


(i)



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[15] The arguments advanced here against the involvement of *cis*^{5}-cyclo-decapentaene in the rearrangement of **7** apply to other similar cases: see G. Maier, I. Fuss and M. Schneider, *Tetrahedron Letters* 1057 (1970); R. M. Acheson, P. J. Abbott, J. K. Stubbs, and M. Yu.Kornilov, *Khim. Getersikl. Soedin* 1701 (1975), *Chem. Abs.* **84** (1976), 150043 for two heterocyclic examples which are better interpreted in terms of intermediates similar to **3**.