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THERMAL ISOMERIZATION OF 1,1-DISUBSTITUTED CYCLOHEXA-2,4-DIENES

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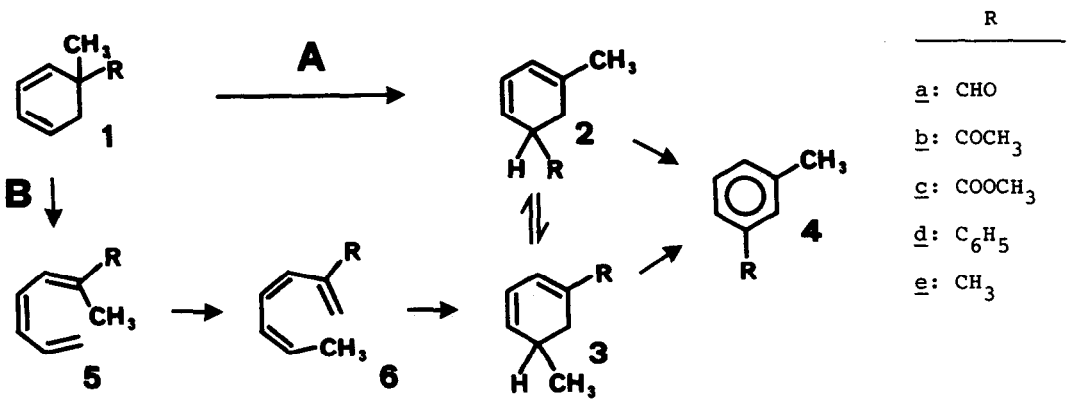
1,1-disubstituted cyclohexa-2,4-dienes (1) rearrange to mixtures of 1,3-isomers such as 2 and 3 at elevated temperature [1]. We have shown that in the case of compound 1a this rearrangement involves a 1,5-shift of the formyl group [2]. Similar activation entropies for the rearrangement of 1a - 1c have been taken as evidence for the same mechanism in these three examples. In a recent report [3] the isomerization of 1e has been claimed to follow the same mechanistic pathway as that of 1a (A in chart 1) and an alternate reaction course proposed previously [4], involving acyclic intermediates 5 and 6 (B in chart 1) has been dismissed.

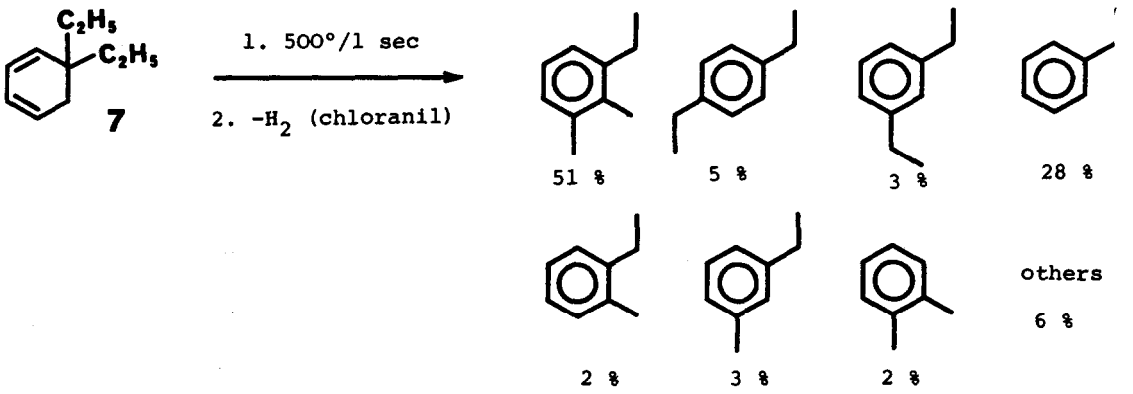
Chart 1



We wish to report experiments undertaken with the aim to establish the extent to which the two possible reaction pathways A and B participate in the isomerization of 1,1-disubstituted cyclohexa-2,4-dienes [5]. It is known that the ethyl group shows a higher tendency to participate in thermal migration than methyl [6]; 1,1-diethyl-cyclohexa-2,4-diene (7) therefore was expected to rearrange faster than 1e. This indeed was found to be the case ($k_7/k_{1e} \cong 8$, 404°/

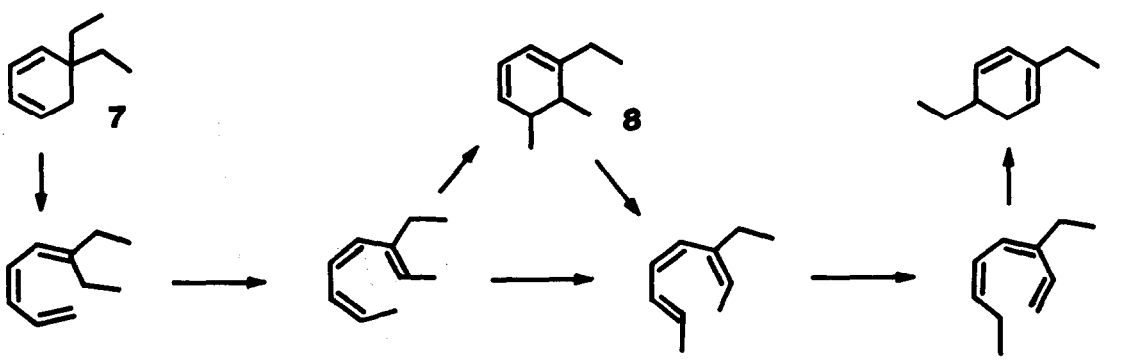
25 sec). Chloranil dehydrogenation of the more than 30 primary products obtained upon flash pyrolysis of 7 (500°/1 sec) leads to the aromatic hydrocarbons shown in chart 2:

Chart 2



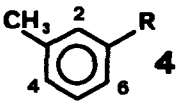
The major C_{10}-compounds can only arise through reaction sequence B (see chart 3). 1,3-diethyl-benzene, the product expected if path A were followed, amounts to less than 3 %. It could equally well have been formed by recombination of radicals generated from 7. The formation of ethylbenzene (28 %) indicates that in 7 bond cleavage indeed competes effectively with rearrangement [7]. Furthermore CC-bond cleavage from intermediate 8 accounts easily for the formation of other, minor fragmentation products. We conclude that compounds such as 1e and 7 rearrange by reaction sequence B as proposed by Pines [4]. 1,5-alkylshifts, known to occur reluctantly [8], at most participate to a very minor extent in product formation. Cleavage of allylic CC-bonds however is a competing side reaction. The increased rate of rearrangement of 7 with respect to that of 1e can be accounted for by the higher ground state steric strain in 7.

Chart 3



At 404° the rate of rearrangement of 7 is comparable to that of 1c and 1d. It therefore became important to learn to which extent the latter two compounds rearrange by a 1,5-shift of the functional group R (path A) or by a sequence of steps involving electrocyclic and 1,7-hydrogen shift reactions (path B). Accordingly 1c and 1d labeled in the methyl group by ^{13}C were prepared by standard procedures starting with $^{13}CH_3J$.

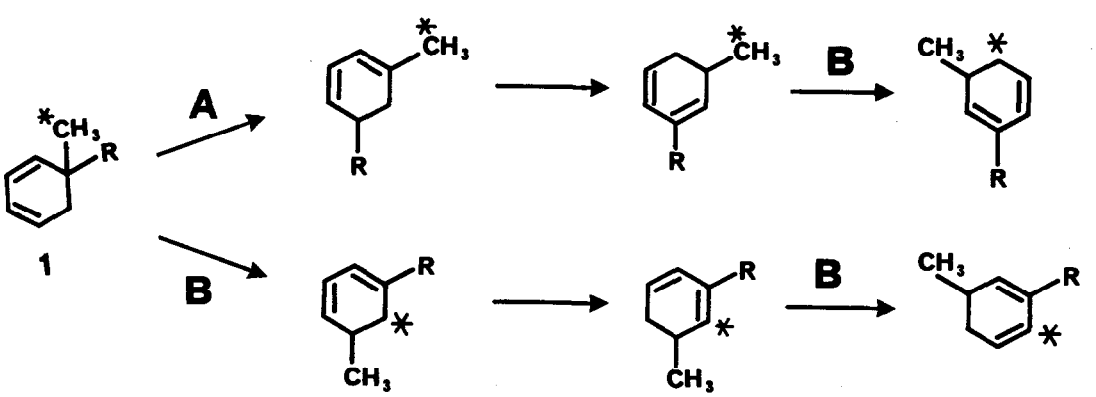
Results are given in table 1. It is evident that at 520° the ester 1c rearranges to the extent of 75 % by a 1,5-shift of the carbomethoxy group (path A), whereas 25 % takes pathway B leading to product 4c having the label in the aromatic ring at position 2. A small amount of label is transferred to positions 4 and 6 by a further reaction sequence of type B preceded by 1,5-hydrogen shifts (chart 4). At 300° rearrangement is more selective, the concerted pathway A now amounting to 85 % vs. only 15 % for path B.

Table 1 ^{13}C-distribution in  obtained upon thermolysis and aromatisation of CH_3-labeled 1 [a]

	thermolysis	% of label at $CH_3C(3)$	C(2)	C(4)	C(6)
1c: R = $COOCH_3$	520°/1 sec	75	24	0.5	0.5
	300°/10 hrs [b]	85	15	-	-
1d: R = C_6H_5	550°/1 sec	4	84 [c]		12

a) Determined through integration of appropriate signals in CMR and HMR spectra. b) In heptane solution. c) Label at C(2) and C(4) combined.

Chart 4



The rearrangement of 1d though proceeding at a similar rate as that of 1c follows a different course [9]. At 550° only 4 % of the label appears in the methyl group of 4d and 96 % is located in the ring. Furthermore a substantial amount of ^{13}C is transferred to position 6 and presumably to 4 indicating multiple rearrangement of type B having occurred.

The phenyl group has been reported to participate in sigmatropic 1,5-shifts in preference to methyl [10]. Our experiments now show that the migration aptitude of phenyl is considerably lower than that of the carbomethoxy group. Compounds of type 1 which have two pathways available for rearrangement apparently follow path A only when R is a group with high migration aptitude such as hydrogen or a carbonyl group.

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[9] Products after flash thermolysis (550°/1 sec) and dehydrogenation: 4d (72 %), biphenyl (26 %), others (2 %).

[10] L.L. Miller and R.F. Boyer, J. Amer. chem. Soc. 93, 650 (1971).