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CYCLOPROPYLALLENES I. PYROLYSIS OF 3-(*trans*-2-METHYLCYCLOPROPYL)-1,2-BUTADIENE; EVIDENCE FOR [1,7] HYDROGEN MIGRATION

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Relatively few cases of [1,7] hydrogen migration in polyene systems are known outside the classic isomerization of precalciferol to calciferol.[1] At this time we wish to describe the thermolysis of 3-(*trans*-2-methylcyclopropyl)-1,2-butadiene 4 and the reactions which take place in the products therefrom. These transformations provide further insight and evidence for the [1,7] hydrogen migration in simple acyclic heptatrienes.

Cyclopropylallene 4 was prepared from alcohol 1.[2] Partial physical and spectral data for new compounds 2, 3, and 4 are shown in Table I.[3]

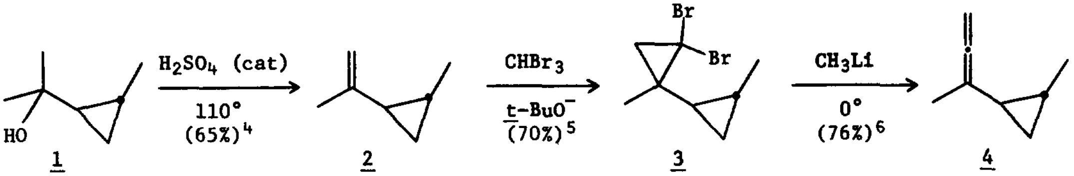
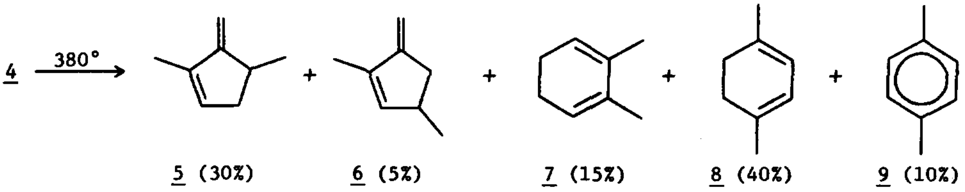


TABLE I

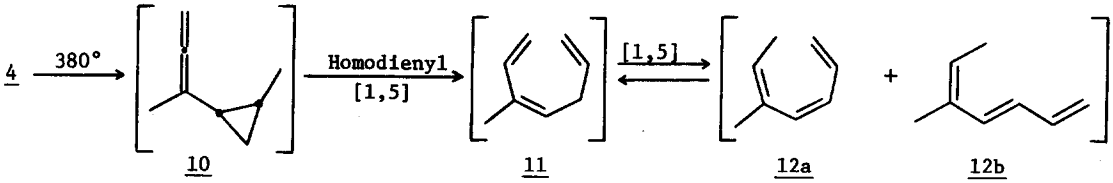
Compound	bp °C/mm	n_D^{20}	IR (neat) cm^{-1}
2	91-2/760	1.4253	790, 875, 1025, 1080, 1645
3	46-7/0.03	1.5206	693, 795, 890, 1027, 1058, 1085, 1380
4	63-4/85	1.4597	790, 850, 1075, 1160, 1290, 1380, 1450, 1960

Thermal isomerization of 4 was effected in an "aged" flow reactor with argon carrier. After a contact time of approximately 2 minutes at 380°, the allene was greater than 95% converted to a mixture of 5 components (90% yield of monomeric material). Products were separated and purified by preparative vpc (10' x 1/4" aluminum column packed with 20% squalene on 60/80 Chromosorb G, 90°). Structures 5 - 9 were assigned by comparison of analytical data with literature values[7] or authentic samples.

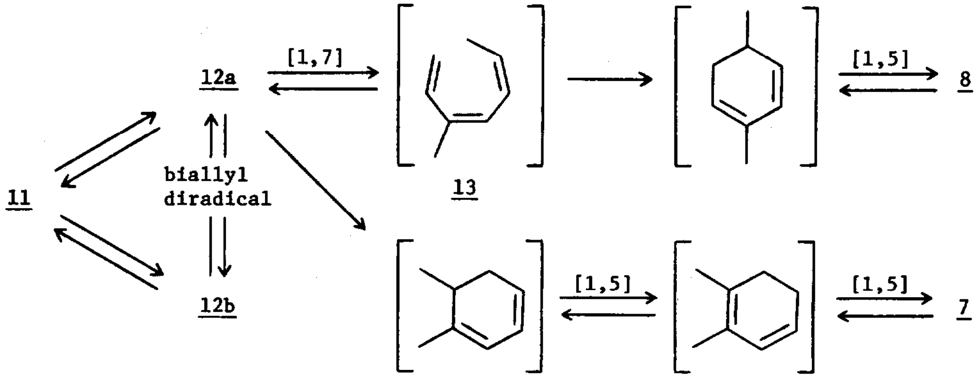


Methylenecyclopentenes 5 and 6 are normal rearrangement products.[8,9] Of these, the major isomer 5 corresponds to migration of the more highly substituted carbon. This result is not unexpected from analogy with well-known vinylcyclopropane thermal chemistry.[10] However, of particular mechanistic interest is the observation of cyclohexadienes 7 and 8 (and resulting 9).[11] We believe that these products emanate from *trans* to *cis* isomerization of 4 competitive with cyclopentene formation and that the presence of 8 (plus 9) cannot be explained without invoking a facile [1,7] hydrogen migration.

Roth[9] has demonstrated the *cis/trans* isomerization of *cis*-1-allenyl-2-deuteriocyclopropane at 313°. In our system, a similar epimerization reaction leads to 10, which would not be expected to survive at elevated temperature.[12,13] Triene 11, the homodienyl [1,5] hydrogen shift product, is certain also to be transitory.[13]

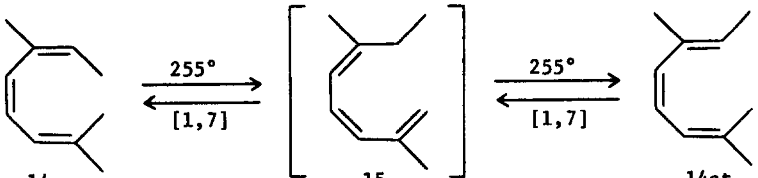


Of the two suprafacial [1,5] hydrogen migrations open to 11, formation of 12b is much more favorable on steric arguments; and in fact, 12b may be the only isomer produced. Nevertheless, 12a, which is likely the precursor to both of the observed cyclohexadienes, is easily accessible at 380° by way of the biallyl diradical mechanism.[14] Direct closure of 12a leads ultimately to 7, the most stable double bond positional isomer.[14] Cyclohexadiene 8 must arise *via* analogous transformations from the [1,7] hydrogen-shifted congener 13. Thus 12a is partitioned between electrocyclic and sigmatropic processes. These pathways are shown below.[15]



We find it surprising that 7 is a minor product compared to 8 + 9, particularly since 12a is formed at conditions which normally allow the quantitative closure of trienes exhibiting a *cis* central double bond.[11,16,17] This indicates clearly that the [1,7] hydrogen migration is faster than the electrocyclic reaction—a conclusion which is also consistent with a recent report by Crowley and Traynor[18] on the thermochemistry of alloocimenes 14. The process

14cc ⇄ 14ct was shown to be reversible *via* 15 at 255°. Cyclohexadienes were observed only at



14cc 15 14ct

temperatures above 300°. Consequently, if in our case, 12a and 13 are in equilibrium, then the predominance of 8 + 9 implies that the cyclization rate for 13 is larger than for 12a. Analogous systems have been investigated by Spangler *et al.*,[17] who reported the activation enthalpy for electrocyclization of 3-methyl-*cis*-1,3,5-hexatriene to be approximately 3 kcal/mole less than for *cis, trans*-1,3,5-heptatriene. This result probably reflects, to some extent, the influence of a 3-alkyl group on the relative amounts of s-*trans* and s-*cis* conformers. The same argument is applicable to 13 as well.

The paucity of documented [1,7] hydrogen migrations has generally been attributed to the fact that existing methods for triene synthesis do not allow adequate control of stereochemistry at the central double bond. Our findings indicate that central double-bond stereochemistry is irrelevant at elevated temperatures and that *cis* C_5,C_6 geometry is crucial. Judiciously-alkylated cyclopropylallenes are therefore ideal precursors to trienes capable of undergoing [1,7] hydrogen migration since one of the lateral double bonds of the derived conjugated triolefin will always be *cis* by virtue of its origin from consecutive stereospecific reactions.

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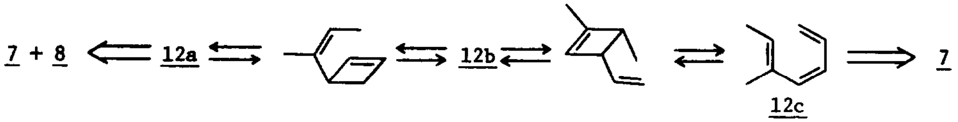
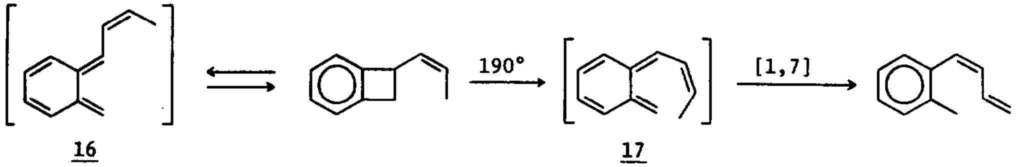
15. Pathways such as 12b → 12c and 12b → 12a shown below are presumably inoperative. Although there is evidence for the intermediate formation of trimethylcyclobutene in the thermal isomerization of *cis*-2,3-dimethyl-1,3-pentadiene,[19] the intervention of vinylcyclobutenes in the geometrical isomerizations of conjugated trienes has been discounted.[14] One notable exception has been reported by Jones[20] for o-xylylene 16. The reaction 16 → 17 is, however, a special case for which there is considerable driving force.





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