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CYCLOPROPYLALLENES II. THERMOLYSIS OF 1-(*cis*-2-METHYLCYCLOPROPYL)-1,2-BUTADIENE

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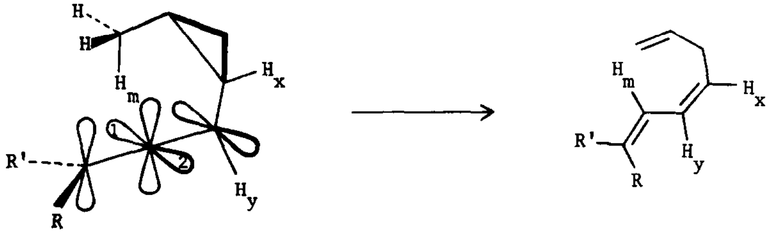
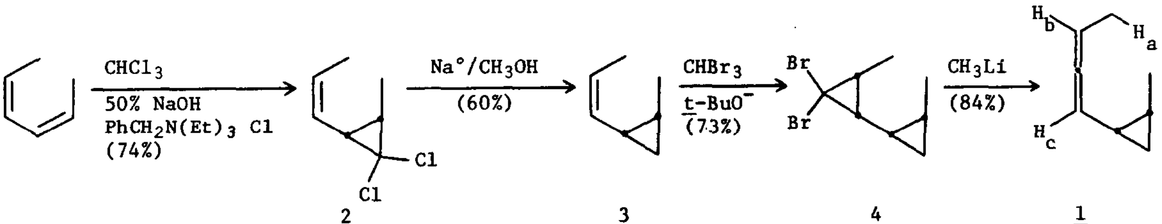
Homodienyl [1,5] hydrogen migration has been studied extensively in a variety of *cis*-2-alkyl-1-vinylcyclopropanes.[1] Transfer of hydrogen to an sp carbon has also been demonstrated in the rearrangement of *cis*-2-methyl-1-ethynylcyclopropane to 1,2,5-hexatriene.[2] However, the use of cyclopropylallene substrates in this reaction has not been appropriately investigated, although we recently described indirect evidence that 3-(*cis*-2-methylcyclopropyl)-1,2-butadiene, produced *in situ* at 380°, does isomerize to the expected triene.[3] We have now observed homodienyl [1,5] hydrogen migration in the diastereomers of the title compound and wish to report that both product structure and reaction rate are dependent on the stereochemistry of the allenic methyl group.

The homodienyl [1,5] hydrogen migration is formally a [σ4s + π2s] process[4] for which the optimum ground state conformation for reaction occurs when H_x and H_y are eclipsed. Consequently,

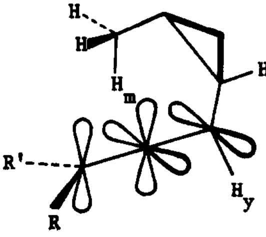


the migrating hydrogen H_m is transferred solely to the *syn* p-orbital lobe 1 of the sp carbon and H_m and R' (as well as H_x and H_y) must therefore have a *cis* relationship in the product. Thus for allenes where R = R', only one product is possible; but in cases where R ≠ R', diastereomeric cyclopropylallenes give mutually exclusive products which differ in stereochemistry at the C_6-C_7 double bond. Cyclopropylallene 1 is an example of the latter type.

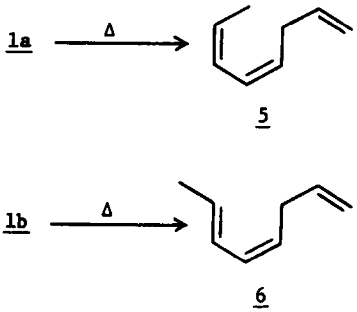


2 3 4 1

The synthetic route shown[5] produces an equimolar mixture of diastereomers as indicated in the PMR spectrum of <u>1</u> (CCl_4) by a doublet of doublets (allylic CH_3, $J_{ab} = 6.5$, $J_{ac} = 3.5$) centered at 1.62 ppm δ and an identical pattern centered at 1.63 ppm δ. These isomers are also discernible by analytical vpc[6] but we have not thus far been able to effect preparative separation.



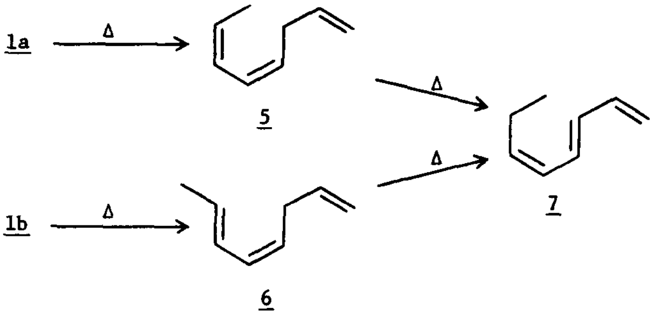
<u>1a</u> R = CH_3, R' = H
<u>1b</u> R = H, R' = CH_3



Molecular models of <u>1a</u> and <u>1b</u> indicate the likelihood that these diastereomers will undergo rearrangement at different rates. The proximity of allenic methyl and ring methyl groups in <u>1b</u> should provide sufficient steric interference in the transition state to retard its rate of isomerization. This expectation appears valid: the observed rate difference is rather large and allows the two reactions, <u>1a</u> → <u>5</u> and <u>1b</u> → <u>6</u>, to be observed independently at appropriate conditions. Low temperature pyrolysis of the mixture of <u>1a</u> and <u>1b</u> (5% solution in benzene, sealed tube, 125°, 3 hours) results in greater than 95% conversion of only one allene diastereomer to a single product. Isomerization of the remaining allene isomer is very slow at this temperature. The data which follow argue strongly that this selective process is indeed the transformation <u>1a</u> → <u>5</u>.

After 3 hours at 125°, the PMR spectrum of the reaction mixture shows that the higher field doublet of doublets (1.62 ppm δ) observed for <u>1</u> is greatly diminished, and the UV spectrum now exhibits a sharp absorption maximum at 232.5 nm (consistent with a conjugated *cis, cis*-2,4-diene). Analytical vpc analysis[6] confirms the homogeneity of the product and establishes its formation at the expense of only one of the allene diastereomers. Extended pyrolysis of the reaction mixture at 150° allows isomerization of the remaining allene (80% complete after 4 hours). During this time, a second product emerges in the gas chromatogram[6] and a prominent shoulder appears on the shorter wavelength side of the UV absorption band (approx. λ 229 nm). Since *cis, trans*-1,4-disubstituted butadienes characteristically absorb at shorter wavelengths in the UV spectrum than do *cis, cis*-1,4-disubstituted butadienes,[7] the initially-formed product must have the structure *cis, cis*-1,4,6-octatriene <u>5</u> and the product of the slower reaction must be the *cis, trans* geometric isomer <u>6</u>. This interpretation is consistent with steric arguments which predict <u>1a</u> to be the more labile diastereomer.

Pure <u>5</u> can be obtained from the mixture of <u>5</u> and <u>6</u> by the following chemical separation. Dienyl [1,5] hydrogen migration is operable in both trienes; but the *cis* C_8 methyl group must hinder the rearrangement of <u>5</u> by destabilizing the s-*cis* conformer such that at 160°, only the triene <u>6</u> isomerizes at a significant rate. The resulting product <u>7</u> is easily separable from <u>5</u> by preparative vpc (10' x ¼" aluminum column packed with 20% squalene on 60/80 Chromosorb G, 90°). The identity of triene 5 is established as *cis, cis*-1,4,6-octatriene by spectroscopic methods.[8] Conjugated triene 7 exhibits spectral characteristics which are in excellent agreement with those reported for 1, *trans*-3, *cis*-5-octatriene.[9]



We have also effected the conversion of 5 to 7 at elevated temperature in an "aged" flow reactor with argon carrier. Pyrolysis of either the mixture 1a and 1b or the mixture 5 and 6 (contact time 3 minutes, 270°) gives 7 (homogeneous by vpc) as the sole product in 94% yield isolated by vacuum transfer. The high stereoselectivity of the dienyl [1,5] hydrogen migration is not unusual. O'Neal and Frey[10] have reported the reaction stereoselectivity for conversion of *cis*-1,3-heptadiene to *cis*-2, *trans*-4-heptadiene to be about 60/1.

The data presented here firmly establish the position of cyclopropylallenes such as 1 on the same energy surface that relates a series of conjugated and non-conjugated acyclic trienes. Aside from the obvious mechanistic importance of these allene rearrangements, we believe that the conversion of 1 to 7 exemplifies a potentially useful method of synthesis for isomer-pure polyenes of predictable geometry—particularly since a large number of precursory vinylcyclopropanes (*cf.* 3) with *cis*-methyl and *gem*-dimethyl ring substituents are readily available.

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5. New compounds 1 - 4 gave satisfactory elemental analyses. Partial physical and spectral data are as follows: Compound 1 - bp 48-9/28 mm, n_D^{20} 1.4754, IR (neat) cm^{-1} 716, 755, 855, 875, 910, 1032, 1077, 1177, 1260, 1282, 1975; Compound 2 - bp 52-4/6 mm, n_D^{20} 1.4860, IR (neat) cm^{-1} 720, 765, 815, 887, 923, 960, 1140, 1390; Compound 3 - bp 53-5/200 mm, n_D^{20} 1.4410, IR (neat) cm^{-1} 712, 755, 816, 889, 928, 950, 1010, 1030, 1077, 1652; Compound 4 - bp 50-1/0.04 mm, n_D^{20} 1.5267, IR (neat) cm^{-1} 731, 778, 855, 911, 1000, 1030, 1080, 1134, 1455.

6. Analysis was done using a 100-ft MBMA capillary column, 70°, with cyclooctane as an internal integration standard.

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8. Compound 5 gave a satisfactory elemental analysis. Partial physical and spectral data are as follows: n_D^{20} 1.4805, IR (neat) cm^{-1} 704 (vvs, *cis, cis* conjugated), 821, 915 (vs, vinyl non-conjugated), 950, 985, 995, 1390, 1440, 1610, 1650; NMR (CCl_4, TMS, ppm δ) 1.72 (d, 3H), 2.87 (t, 2H), 4.75 - 5.17 (m, 2H), 5.18 - 6.55 (m, 5H); UV λ_{max}^{EtOH} 232.5 nm (ε 23,700).

   Compound 5 is further characterized by its failure to give [4 + 2] adducts with maleic anhydride, N-phenylmaleimide, and 4-phenyl-1,2,4-triazoline-3,5-dione in refluxing benzene.

   For additional information concerning the spectroscopic identification of conjugated diene systems, see References 11 and 12.

9. Compound 7 gave a satisfactory elemental analysis. Partial physical and spectral data are as follows: n_D^{20} 1.5243, IR (neat) cm^{-1} 750, 800, 872, 895, 940 (*trans* central double bond), 1005, 1070, 1135, 1183, 1238, 1295, 1320, 1400, 1460, 1585, 1630, 1810; NMR (CCl_4, TMS, ppm δ) 1.00 (t, 3H), 2.20 (quintet, 2H), 4.87 - 6.75 (complex, 7H); UV λ_{max}^{EtOH} 275 nm (ε 35,100), 264.5 nm (ε 43,700), 254 nm (ε 32,700). For literature values, see C. W. Spangler, T. P. Jondahl and B. Spangler, *J. Org. Chem.*, **38**, 2478 (1973).

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