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CYCLOPROPYLALLENES III: STEREOSELECTIVE [1,5] HYDROGEN MIGRATIONS IN *cis*-1,2,4-CYCLODECATRIENE AND *cis*-BICYCLO[7.1.0]DECA-2,3-DIENE

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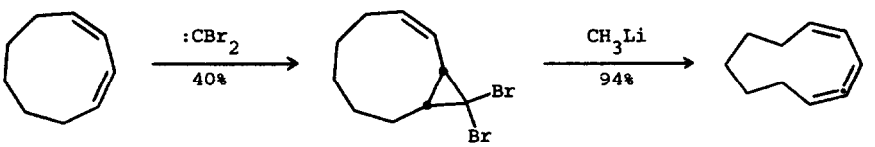
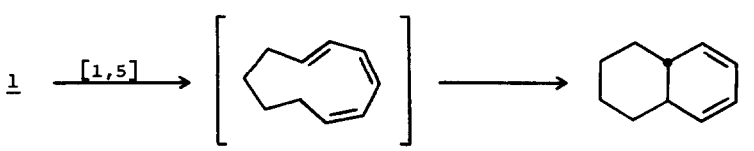
In the course of an ongoing study of the chemistry of substituted cyclopropylidenes, the reactions of *gem*-dibromocyclopropanes with methyllithium have been used recently in our laboratories to generate a variety of highly strained cyclic allenes.[1] We report here the syntheses and thermal rearrangements of two particularly interesting examples, each of which is capable of undergoing structural reorganization *via* [1,5] hydrogen migration. To our knowledge, 1 is the first cyclic, conjugated ene-allene to be isolated and characterized.



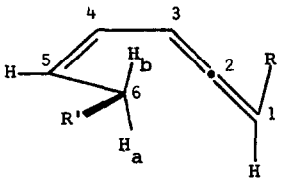
2 1

Allene 1 was prepared as shown from *cis, cis*-1,3-cyclononadiene.[2] The reaction of 2 with methyllithium at -78° gave a single product, which was purified by vacuum transfer (0.01 mm). Pyrolysis of 1 in hexane (sealed tube, 100°, 3 hours) gave *trans*-bicyclo[4.4.0]deca-2,4-diene 3 in quantitative yield.[3] Alternatively, this conversion could be effected by standard preparative vpc injection/collection techniques.[4] We interpret the overall reaction as a two-step process involving the intermediacy of *trans, cis, cis*-1,3,5-cyclodecatriene 4, which undergoes electrocyclic closure.[5] In contrast to results reported for similar [1,5] hydrogen migrations in acyclic systems, as discussed below, the transformation 1 → 4 appears to be completely stereoselective.

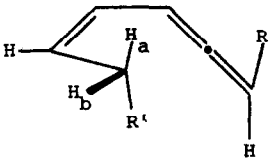


4 3

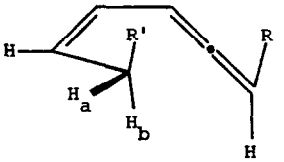
In acyclic ene-allenes of the type 5, dienyl [1,5] hydrogen migration may proceed by suprafacial transfer of either H_a or H_b depending on conformation. For the preferred conformers where R' is directed away from the allene π system (*cf.* 5a), migration of H_a gives the *cis*-1, *cis*-3, *trans*-5 triene (designated *cct*); and migration of H_b gives the *tct* product. Two



5a



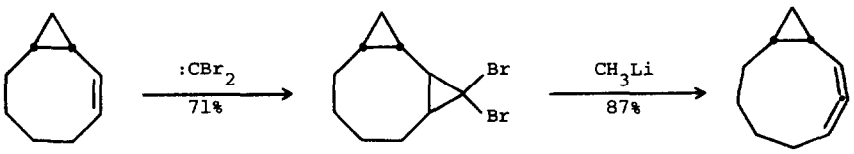
5b



5c

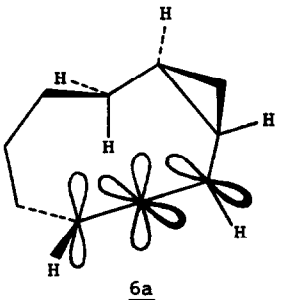
other geometric isomers—*tcc* and *ccc*—arise from 5b and 5c respectively. Thus four distinct modes of hydrogen transfer are possible, each of which simultaneously fixes stereochemistry at both lateral double bonds. Although the preference for a single transfer mode in acyclic systems has been observed when R and R' are large, bulky groups,[6] none of these approach the degree of stereoselectivity that we have observed in the case of 1. Molecular models indicate clearly that for cyclic allene 1, conformations corresponding to 5a cannot be accommodated. Conformer 5c is unfavorable since a ring methylene group must be forced into the allene π system when R,R' = $(CH_2)_4$. In effect, rearrangement of 1 is limited to one of four stereochemical pathways (5b → *tcc*) due to the geometrical restrictions imposed by incorporating the conjugated ene-allene moiety into a ring.

In connection with the study of thermal isomerization in 1, we have also investigated a closely related compound—the cyclopropylallene 6. On the basis of our previous work concerning the stereochemistry of cyclopropylallene rearrangements,[7,8] homodienyl [1,5] hydrogen migration in 6 must give an isomer-pure triene 10. If 10 is capable of subsequent isomerization to 11, then thermolysis of 6 would ultimately give *cis*-bicyclo[4.4.0]deca-2,4-diene 8 and thus complement the behavior of 1. However, examination of molecular models suggests that ring strain might prevent 10 from assuming an appropriate conformation for [1,5] hydrogen migration. In fact, the observed product from pyrolysis of 6 was not the diene 8, but rather the tricyclic hydrocarbon 9.

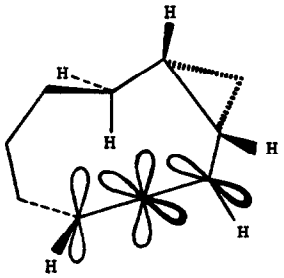


7 6

Allene 6 was prepared[9] as an equimolar mixture of diastereomers, only one of which (6a) can undergo homodienyl [1,5] hydrogen migration. In 6b, the cyclopropane ring is held rigidly in a conformation which does not allow concerted hydrogen migration.[8] Thermolysis of 6 in a flow system at 250° (argon carrier, 45 seconds contact time) gave a pyrolysate which contained

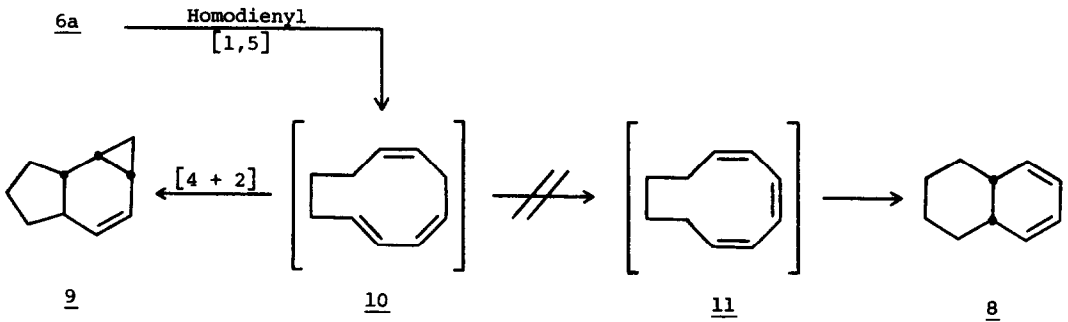


6a



6b

two components in equal amounts.[10] One of these was an allene whose infrared spectrum was virtually identical with that of the mixture 6. This compound must be the pure diastereomer 6b. The remaining component was a vinylcyclopropane assigned the tricyclic structure 9 from spectral evidence and chemical degradation.[11] Final assignment of the cyclopropane stereochemistry follows from the accepted mechanism for [4 + 2] cycloadditions and the fact that one



and only one geometric isomer of the 1,3,6-triene 10 is possible from 6a. The intramolecular Diels-Alder reaction is certainly a reasonable pathway for relief of strain energy in 10.[12] That 9 appears to be a single diastereomer exemplifies again the highly stereoselective nature of unimolecular rearrangements in these conformationally rigid substrates.

In conclusion, the reactions described here are unusually facile when compared with known acyclic cases. Furthermore, the behavior of 1 and 6 may be unique within their respective homologous series. We anticipate that decreased reactivity and perhaps loss of stereochemical control will accompany increased ring size and the inherent increase in ring flexibility. As a case in point, it is interesting to note our preliminary data which show that *cis*-bicyclo-[8.1.0]undeca-2,3-diene is quite stable at conditions described above for quantitative rearrangement of 6a.

ACKNOWLEDGMENT. The authors are grateful to the Robert A. Welch Foundation for predoctoral and research grant support.

REFERENCES AND NOTES

1. M. S. Baird and C. B. Reese, Tetrahedron, 23, 2153 (1976); and references within.

2. See P. N. Newman, Dissertation, The University of Texas at Austin, Austin, Texas (1967) for a synthesis of *cis,cis*-1,3-cyclononadiene. Compounds 1 and 2 gave satisfactory elemental

analysis. Partial physical and spectral data are as follows:

Compound 1 - n_D^{25} 1.5239; IR (neat, cm^{-1}) 660, 683, 714, 725, 735, 754, 770, 849, 870, 973, 1330, 1451, 1953; PMR (CCl_4, TMS, ppm δ) 1.05-1.84 (6H, complex), 1.84-2.80 (4H, complex), 4.90-6.25 (4H, overlapping multiplets).

Compound 2 - bp 80-84°/0.06 mm; n_D^{24} 1.5645; IR (neat, cm^{-1}) 637, 684, 738, 754, 784, 1053, 1122, 1212, 1449, 1639, 1689; PMR (CCl_4, TMS, ppm δ) 0.58-2.78 (12H, complex), 5.25-6.38 (2H, overlapping multiplets).

3. Diene 3 was identified by comparison with an authentic sample prepared by the procedure of K. N. Mehrotra, Dissertation, The University of Texas at Austin, Austin, Texas (1966).

4. Preparative vpc was carried out using a 3/8" x 15' aluminum column packed with 10% Carbowax 20M on 60/80 Chromosorb W, injector - 150°, column - 100°.

5. a) D. S. Glass, J. W. H. Watthey and S. Winstein, Tetrahedron Lett., 377 (1965).
b) E. Vogel, W. Grimme and E. Dinné, Tetrahedron Lett., 391 (1965).

6. a) K. L. Mikolajczak, M. O. Bagby, R. B. Bates and I. A. Wolff, J. Org. Chem., 30, 2983 (1965).
b) M. L. Hammond, A. Mourino and W. H. Okamura, J. Am. Chem. Soc., 100, 4907 (1978).

7. D. E. Minter and G. J. Fonken, Tetrahedron Lett., 1717 (1977).

8. D. E. Minter and G. J. Fonken, Tetrahedron Lett., 4149 (1977).

9. New compounds 6 and 7 gave satisfactory elemental analyses. Compound 7 is homogeneous by tlc and CMR. We have assigned its structure as the *anti* diastereomer by analogy to the reaction of bicyclo[4.1.0]hept-3-ene with dibromocarbene, which gives the *anti* adduct.[13] Partial physical and spectral data are as follows:

Compound 6 (6a + 6b) - bp 33-34°/0.2 mm; n_D^{20} 1.5225; IR (neat, cm^{-1}) 641, 719, 736, 763, 791, 817, 841, 858, 871, 991, 1027, 1336, 1452, 1953; PMR (CCl_4, TMS, ppm δ) (-0.15)-(+0.17) [0.5H, overlapping multiplets (6b)], 0.17-0.43 [0.5H, overlapping multiplets (6a)], 0.55-1.15 (3H, overlapping multiplets), 1.15-2.65 (8H, complex), 4.55-5.30 [1.5H, overlapping multiplets (6a + 6b)], 5.40-5.80 [0.5H, broad, complex (6a)].

Compound 7 - bp 89-91°/0.05 mm; n_D^{20} 1.5646; IR (neat, cm^{-1}) 710, 758, 833, 970, 998, 1029, 1072, 1152, 1443; CMR ($CDCl_3$, TMS, proton noise decoupled, ppm δ) 39.41, 36.42, 32.97, 29.33, 27.77, 27.44, 18.21, 14.31, 13.27.

10. Pyrolysis of 6 also can be carried out using preparative vpc techniques. Thermolysis and separation of components were done in a single operation with a 3/8" x 10' aluminum column packed with 15% diisodecyl phthalate on 60/80 Chromosorb W, injector - 150°, column - 125°. Recovered allene 6b (see spectral data below - ref. 11) was stable and did not undergo rearrangement when re-injected into the gas chromatograph at the same conditions used for the mixture 6. Under forcing conditions in a flow system at 380° (contact time - 6 min.), 6b was converted to a complex mixture containing at least 4 components; and we have not as yet effected preparative separation. These products certainly arise from diradicals.

11. Compounds 6b and 9 gave satisfactory elemental analyses. Partial physical and spectral data are as follows:

Compound 6b - n_D^{20} 1.5202, IR - indistinguishable from that of mixture 6 (See ref. 9 above.) PMR (CCl_4, TMS, ppm δ) (-0.15)-(+0.20)(1H, overlapping multiplets), 0.55-1.12 (3H, overlapping multiplets), 1.12-1.92 (6H, complex), 1.92-2.65 (2H, complex), 4.55-5.10 (2H, overlapping multiplets).

Compound 9 - n_D^{20} 1.5018; λ_{max}^{EtOH} 207 nm (ε 5,400); IR (neat, cm^{-1}) 700, 763, 801, 911, 962, 994, 1026, 1351, 1455, 1623; PMR (CCl_4, TMS, ppm δ) 0.38-2.10 (12H, complex), 5.52 (1H, d, J=10 Hz), 5.86 (1H, d of d, J=10,4); CMR ($CDCl_3$, TMS, proton noise decoupled, ppm δ) 128.75, 127.65, 41.54, 39.79, 29.12, 28.21, 22.81, 16.38, 12.28, 7.08.

The reaction of 9 with one equivalent of aqueous potassium permanganate (25°) followed by drastic oxidation of the resulting mixture with chromic acid under acidic conditions gave *trans*-1,2-cyclopentanedicarboxylic acid as major product (30%).

12. R. T. Taylor and L. A. Paquette, J. Am. Chem. Soc., 99, 5824 (1977).

13. L. A. Paquette and R. T. Taylor, J. Am. Chem. Soc., 99, 5708 (1977).

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