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Reciprocal Tests of Steric Opposition to Down-Disrotatory Thermal Decyclization of [3.2.1] Propellanes. The Cycloreversion Stereochemistry of the 6,7,8-Trimethyltricyclo[3.2.1.0^{1,5}]octanes

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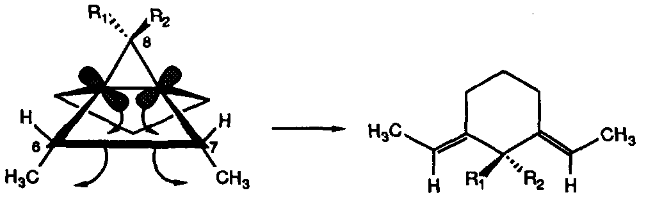
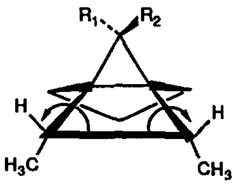
Abstract.- The syntheses and thermal decompositions of the isomeric title compounds are described. The cis, endo isomers undergo down-disrotatory cycloreversion to*E,E* -2-methyl-1,3-*bis*-(ethylidene)-cyclohexane with high stereospecificity, regardless of the stereochemistry of the C_8-methyl group. Both 8-*syn* - and 8-*anti* - 6,7-*trans* -trimethyl isomers decyclize with low stereochemical preference, suggesting that the orbital overlap factors favoring the down-disrotatory path in the cis cases may be overcome easily by steric effects.

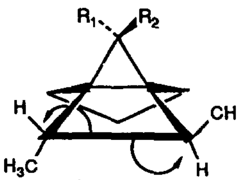
A previous study from this Laboratory[1] found the surprising preference for down-disrotatory thermal cycloreversion of *cis, endo* -6,7-dimethyl[3.2.1]propellane (**1**, see Table 1) stereospecifically to *E,E* -1,3-*bis* -(ethylidene)cyclohexane (**8**), a reaction that is formally forbidden by orbital symmetry. Since the stereospecificity did not survive in the corresponding reactions of the *cis, exo-* or *trans-* dimethyl isomers (**2** or **3**), which gave mixtures of 1,3-*bis-* (ethylidene)cyclohexanes, it was plausible to conjecture that the "normal" down-disrotatory pathway was being blocked in the latter two instances by a steric clash between the inwardly rotating C_6 and/or C_7 methyl(s) and the 8-syn hydrogen in the transition state.



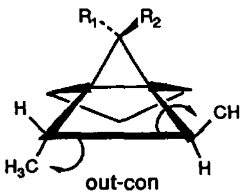
down-disrotatory



up-disrotatory



in-con



out-con

We now have examined this hypothesis in a test series of the 6,7,8-trimethyl[3.2.1]propellanes. The attachment of a syn -methyl group at C_8, as in 8-*syn* - 6,7-*cis,endo* -trimethyl[3.2.1]propellane (**4**), generates a potential 8-syn- Me/6-exo- H interaction. If this interaction were sterically reciprocal to[2] (that is, a satisfactory mimick of) the 8-syn -H/6-exo -Me interaction in the trans dimethyl compound **3**, and if a steric blockade by the latter interaction really were the cause of the departure from the down-disrotatory cycloreversion of **3**, one would predict a similar blockade in the case of the cis, endo trimethyl compound **4**.

The syntheses of the trimethyl derivatives of Table 1 were achieved by the cuprous chloride catalyzed[3] reaction of diazoethane with the *cis-* and *trans-* 6,7-dimethylbicycloheptenes**14** and **15** (Scheme 1). The latter olefins in turn were prepared by the reaction of cyclopentyne with *cis-* and *trans* -2-butene, respectively, by the method of Fitjer and co-workers.[4] The cis olefin **14** gave a 3:1 mixture of syn, endo and anti, endo products, **4** and **5**, while the trans olefin **15** gave a 1:1 mixture of syn, trans and anti, trans products, **6** and **7**.[5] Although our packed columns failed to separate either mixture in preparative gas chromatography (GC), a 25-m, 5% phenyl methyl silicone fused silica capillary column achieved baseline analytical separations.

Independent syntheses of two (**11** and **12**) of the three (**11-13**) expected pyrolysis products were achieved by a six-step synthesis from cyclohexanone.[3b]

Flash vacuum pyrolysis (FVP) of the mixture of trans isomers **6** and **7** at temperatures of 538, 581, and 620 °C with residence times of about 0.02 s resulted in 22, 56, and 82% conversions, respectively. The rates of reaction of the individual isomers **6** and **7** did not differ significantly, since the ratios of propellanes recovered after pyrolysis (1.2, 1.2, and 1.6) were similar to those of the starting material (1.2, 1.0, and 1.0). The diene products **11**, **12**, and **13**[5] were formed in ratios of 75:24:<1, 73:27:<1, and 74:26:<1(see Table 1). The reaction in the trans trimethylpropellane series thus is only feebly stereospecific for a *conrotatory* pathway in which the C_6 and C_7 methyl groups both turn outwards. These results are similar to those found[1] in the dimethyl propellane series, where the trans isomer **3** gave the corresponding olefins **8**, **9**, and **10** in ratios of 55:41:4(see Table 1).

In the cis, endo trimethyl series, the syn and anti isomers **4** and **5** at 523, 535, and 670 °C gave conversions of 32, 58, and 100%. The ratios of recovered propellanes after the two partial pyrolyses were 0.56 and 0.39 as compared to the starting ratios of 0.59. The products **11**, **12**, and **13** were formed in ratios of 98:2:<1 at all three temperatures.

These data indicate that the rates of reaction of the 8-syn- and 8-anti-methyl isomers **4** and **5** do not differ significantly and that both of them react in a highly stereospecific manner in a down-disrotatory mode.[7] Since the previously studied[1] cis, endo -propellane **1**, which lacks the 8-methyl group, also reacts by a stereospecific down-disrotation (see Table 1), it is apparent that unless the assumption of steric reciprocity (8-syn-Me/6-exo-H of **4** about equal to 8-syn-H /6-exo-Me of **3**) is unexpectedly invalid, the diversion of the reactions of the trans compounds **3**, **6**, and **7** into other stereochemical channels cannot be blamed on the latter interaction. This suggests a transition state geometry in which C_8 and its attached substituents remain clear of the trajectory of the inwardly rotating groups at C_6 and C_7. The structural feature that interferes with the down-disrotatory pathway seems to be an exo methyl group at C_6 and/or C_7. This effect may be related to the retardation of the (conrotatory) ring-opening of cyclobutenes by a methyl

Scheme 1

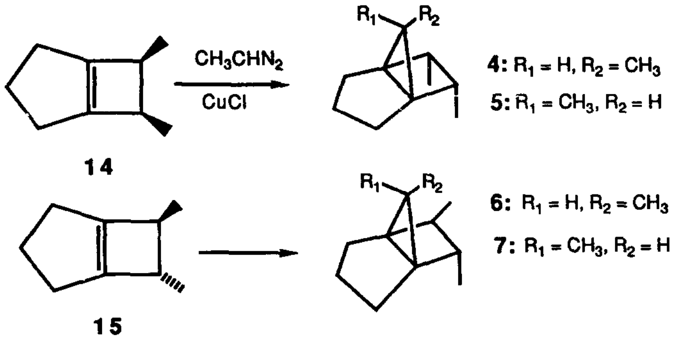
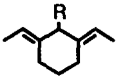
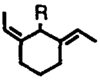
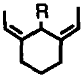
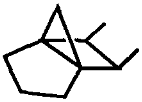
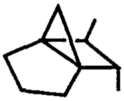
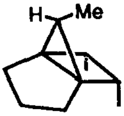
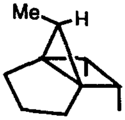
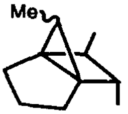


Table 1. Products of pyrolyses of propellanes at 535 °C.

Reactant	**Product** (%) [pathway]		
	 **8: R = H** **11: R = Me**	 **9: R = H** **12: R = Me**	 **10: R = H** **13: R = Me**
1[a] 	**8** (99) [down-dis]	**9** (1) [con]	**10** (<1) [up-dis]
2[a] 	**8** (13) [up-dis]	**9** (48) [con]	**10** (40) [down-dis]
3[a] 	**8** (55) [out-con]	**9** (41) [dis]	**10** (4) [in-con]
4[b] 	**11** (98) [down-dis]	**12** (2) [con]	**13** (<1) [up-dis]
5[b] 	**11** (98) [down-dis]	**12** (2) [con]	**13** (<1) [up-dis]
6[b] 7[b] 	**11** (75) [out-con]	**12** (24) [dis]	**13** (<1) [in-con]

[a]Ref. 1a. [b]This work.

group that is forced to turn inward (compare *cis*-1,2,3,4-tetramethylcyclobutene, E_a = 37.4 kcal/mol, and its trans isomer, E_a = 33.6 kcal/mol[9]).

In the absence of this retardation, the down-disrotatory preference is robust enough to control the stereochemistry. Favorable alignment of the canted cyclopropane Walsh orbitals with the breaking C_6-C_7 bond, as depicted above,[1] remains one factor that can mitigate the formally "forbidden" nature of this pathway.

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References and Notes.-

(1)(a) Blaustein, M.A.; Berson, J.A. *J. Am. Chem. Soc.* **1983**, *105*, 6637. (b) For the pyrolysis of the parent compound, see Aue, D.H.; Reynolds, R.N. *J. Org. Chem.* **1974**, *39*, 2315. See also Caringi, J.J. Ph.D. Thesis, Yale University, New Haven, Connecticut, 1987 (with K.B. Wiberg).
(2) (a) For rare cases in which this kind of assumption has been tested, see refs. 2b,c. Instances in which the assumption would be expected to break down include those in which the switch of substituents creates significant differential buttressing effects. (b) Leung, P.T.; Curtin, D.Y. *J. Am. Chem. Soc.* **1975**, *97*, 6790. (c) Holubec, Z.; Jonas, J. *J. Am. Chem. Soc.* **1968**, *90*, 5986.
(3)(a) Diazoethane was prepared and handled by modifications(ref. 3b) of procedures for diazomethane (refs. 3c-e). Detonations occurred only infrequently in our work, but one should not forget that *diazoethane is an extremely hazardous reagent and must be treated with great caution*: (b) Stevens, L.L., Ph. D. Dissertation, Yale University, New Haven, Conn., 1988.(c) Doering, W. von E.; Roth, W.R. *Tetrahedron*, **1963**, 715. (d) Pizey, J.S. "Synthetic Reagents", Vol. 2, Wiley, New York 1974, p. 65. (e) Amstutz, E.D.; Myers,R.R. "Organic Syntheses", Collective Vol. II, Wiley, New York, 1943, p. 165.
(4) (a) Fitjer, L.; Kliebisch, U.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* **1982**, 1661. (b) Fitjer, L.; Modaressi, S. *ibid.* **1983**, 5495.
(5) The hydrocarbons were characterized by exact mass spectrometric elemental composition, ^{13}C NMR and ^{1}H NMR spectroscopy, and nuclear Overhauser experiments(ref. 3b).
(6) Control experiments showed that the ratios of diene products did not change under the pyrolysis conditions.
(7) Molecular mechanics calculations by the MM2[8] procedure give no indication of any significant thermochemical bias toward formation of any one of the diene products. The steric energies of **11**, **12**, and **13** are 11.5, 11.3, and 11.0 kcal/mol.
(8) Burkert, U.; Allinger, N.L. *Molecular Mechanics*, ACS Monograph 177; American Chemical Society; Washington, D.C., 1982.
(9) Branton, G.R.; Frey, H.M.; Skinner, R.F. *Trans. Faraday Soc.* **1966**, *62*, 1546.

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