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GEOMETRIC ISOMERIZATION OF SPIROPENTANE[1]

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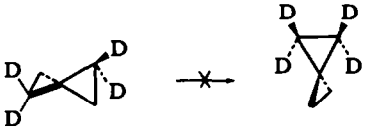
Abstract—A degenerate reaction of spiropentane has been elucidated by the synthesis and thermal interconversion of *cis*- and *trans*-1,2-dideuteriospiropentane. The activation parameters for the isomerization have been obtained.

SEVERAL investigations have revealed that the energy surfaces relating the C_5H_8 species, spiropentane, methylenecyclobutane and ethylene-allene, are remarkably complex. Thus, methylenecyclobutane thermally undergoes both a degenerate rearrangement in which the allylic and vinylic methylene groups are interchanged (1)[2] and a retrocycloaddition to produce allene and ethylene,[3] whereas spiropentane, on thermolysis, rearranges to methylenecyclobutane or decomposes to allene and ethylene[3c, 4] but does not undergo a reaction in which the ring methylene groups become interchanged (2).[2] Our interest in attempting further definition of the energy surfaces relating C_5H_8 hydrocarbons has prompted synthesis and thermolysis of *cis*-1,2-dideuteriospiropentane (I).

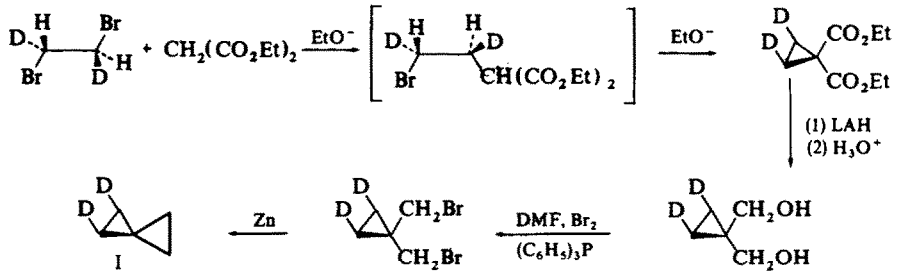
(1)



(2)

The synthesis of I was accomplished by ethoxide-catalyzed reaction of *meso*-1,2-dibromo-1,2-dideuterioethane with diethyl malonate, reduction of the resulting *cis*-2,3-dideuterio-1,1-dicarboethoxycyclopropane to the diol with LAH, and conversion of this diol through the dibromide to the dideuteriospiropentane.[2] The *meso* dibromide was itself prepared by bromination of *trans*-1,2-dideuterioethylene[5] according to the method described by Bernstein *et al.*[6] In agreement with their work, we find that this reaction provides *meso* dibromide contaminated with 5% of the *rac* isomer. On the basis of the synthetic sequence employed, the stereochemical purity of I is dependent upon the stereoisomeric purity of the *meso*-1,2-dibromo-1,2-dideuterioethane and upon the stereospecificity of the cyclization reaction between the dibromide and diethyl malonate. Thus, I should have contained no more than 5% of its geometric isomer, *trans*-1,2-dideuteriospiropentane (II), on the assumption

that both displacement reactions occurring during cyclization are stereospecific with inversion of configuration.



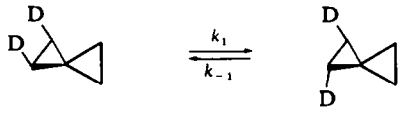
That the crucial cyclization is a stereospecific reaction was subsequently confirmed by the synthesis of authentic II, starting with diethyl malonate and *rac*-1,2-dibromo-1,2-dideuterioethane. The *rac* dibromide was available from bromination of *cis*-1,2-dideuterioethylene[7] and, on the basis of IR analysis,[6] was contaminated with no more than 8% of the *meso* isomer. Analysis of the IR spectra[8] of the diastereomeric 1,2-dideuteriospiropentanes revealed that I contained 5% of II and that II contained 7% of I. Expectations were thus realized; the cyclization is stereospecific.*

A remaining question is that concerning the amount of deuterium present in I and II. Mass spectrometric determination of the deuterium content of these hydrocarbons is made complicated by the fact that spiropentanes produce molecular ion minus one peaks having intensities greater than those of the molecular ions themselves, even if low ionizing voltages are used. However, an indirect but accurate measure of the deuterium content of the dideuteriospiropentanes was available from an analysis of the mass spectra of the diesters which served as their precursors. This analysis gave an isomer distribution for *cis*-2,3-dideuterio-1,1-dicarboethoxycyclopropane of 94·5% d_2, 5·1% d_1 and 0·4% d_0; the corresponding result for the *trans* isomer was 93·8% d_2, 5·7% d_1 and 0·5% d_0. Qualitative support for these distributions was obtained from an analysis of the integrated NMR spectra of the two diesters that indicated that the *cis* and *trans* isomers contained 97% and 94%, respectively, of the theoretical amount of deuterium. That the deuterium label was not diluted upon subsequent transformations of the diesters to the spiropentanes was determined by integration of the NMR spectra of the intermediates involved.

When *cis*-1,2-dideuteriospiropentane (I) is heated at 355° and 270 mm for 3·5 hr in a Pyrex ampoule, *ca.*, 10% rearrangement to methylenecyclobutane-d_2 and 4% decomposition to (allene-ethylene)-d_2 occurs. The NMR and mass spectra of the spiropentane-d_2 recovered after thermolysis are identical to those of I (Experimental). The IR spectrum, however, exhibits several significant differences, primarily in the fingerprint region where several new bands can be detected. Of particular interest, for analytical purposes, is the appearance of a new band at 820 cm^{-1}, a frequency at which I is virtually transparent but at which II has an intense absorption,[8] along with the concomitant diminution in the strong absorption of I at 920 cm^{-1}. That the

* Although the stereospecificity of the cyclization has now been demonstrated, the stereochemistry of the nucleophilic displacements given the cyclic diester has not. It is conceivable that *meso*-dibromide ultimately yields II rather than I. This possibility not only is considered highly unlikely but also would not change the conclusions to be drawn in this paper.

changes noted are the result of the establishment of an equilibrium was demonstrated by the observation that the IR spectra of samples of spiropentane-d_2 recovered after heating I at 355° for 3·5 and 5 hr are superimposable. These data, combined with the demonstrated absence of the degenerate reaction (2) under these conditions,[2] are consistent with a process in which I enters into thermal equilibrium with its geometric isomer, *trans*-1,2-dideuteriospiropentane (II), at an overall rate which is approximately ten times greater than that for structural rearrangement.



I II

A more quantitative evaluation of the *cis-trans* isomerization of spiropentane is available from investigation of the kinetics of the equilibration. The rate of the isomerization is that of a strictly first-order, reversible process over a range of 29–91% of completion of reaction and is insensitive to an approximately six-fold change in the ratio of surface to volume and to a twofold change in the pressure. The unimolecularity and homogeneity of the process are thus assured.

Determination of the temperature dependence of the rate constant for the equilibration gave the results tabulated in Table 1. A least-squares analysis of this data showed

TABLE 1. VARIATION OF RATE CONSTANT WITH TEMPERATURE FOR EQUILIBRATION OF *cis*- AND *trans*-1,2-DIDEUTERIOSPIROPENIANI

T (°C)[a]	t (sec)[b]	I (%)	$(k_1 + k_{-1})\,10^5$
304·6[c,d]	23383	81·2	1·566
304·9[d]	23400	80·8	1·592
304·4[d]	34398	76·6	1·518
314·0[e]	10090	82·3	3·286
313·2[e]	33906	66·7	2·924
314·0[e]	35173	64·2	3·279
335·4[f]	4904	71·2	15·25
336·0[f]	14878	54·4	15·49

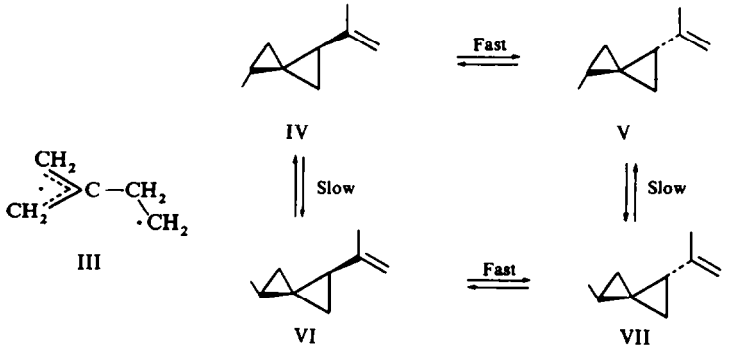
[a] Corrected temp.
[b] Corrected for thermal equilibration.
[c] Ampoule loosely packed with Pyrex glass wool.
[d] Benzophenone, b.p. 305·8, used as refluxing solvent.
[e] Octadecane, b.p. 316·1, used as refluxing solvent.
[f] Phenanthrene, b.p. 340·2, used as refluxing solvent.

that the rate of the reaction fits the expression, $\log (k_1 + k_{-1}) = (14{\cdot}81 \pm 0{\cdot}4) - (51{,}500 \pm 1000/2{\cdot}303\ RT)$. In terms of transition state theory, the activation parameters for the equilibration are $\Delta H^{\ddagger}_{298^\circ} = 50{\cdot}9 \pm 1{\cdot}0$ kcal/mole and $\Delta S^{\ddagger}_{298} = 7{\cdot}3 \pm 2$ e.u.

The availability of the activation parameters for the interconversion of I and II

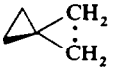
permits consideration of some of the potential relationships between the geometric isomerization and the structural rearrangement of spiropentane. The magnitude of the difference between the activation energies for geometric isomerization (51·5 kcal/mole) and for structural rearrangement (55·5 kcal/mole)[3c] is significantly greater than the experimental error present in the values. The observation of such a difference is strong evidence that the two known modes of molecular reorganization of spiropentane do *not* represent partitioning of a common transition state. Rather the two reactions involve separate transition states, that must be energetically, if not structurally, distinct entities in multi-dimensional space.

This conclusion does not exclude the possibility that the two modes of reaction result from partitioning of a common intermediate, as is thought to be the case for geometric and structural isomerization of cyclopropane itself,[9] and knowledge of the nature of this intermediate would aid in definition of the mechanism of the reactions. One fascinating possibility for such a common intermediate is the tetramethylene diradical, III, which is proposed to intervene in the structural rearrangement of spiropentane[3c] and in the degenerate isomerization of methylenecyclobutane.[2] The generation of III from spiropentane, however, requires cleavage of both of the 3-membered rings of the hydrocarbon, and the available evidence renders this unlikely in the case of the geometric isomerization. Thus, Gajewski has found that the 1-isopropenyl-4-methylspiropentanes, IV and V, are thermally interconvertible at a rate that is at least 50 times greater than that for their isomerization to VI and VII.[10] If an intermediate analogous to III intervened, the relative rates of formation of VI and VII from IV and V would be expected to be significantly greater than is observed. These results are consistent with the conclusion that the geometric isomerization, if it is not concerted, involves an intermediate in which one 3-membered ring remains intact. Whether the structural rearrangement also proceeds by initial development of this same type of intermediate, with subsequent rupture of the second 3-membered ring to produce either III or an activated methylenecyclobutane,[2, 3c] or whether a different pathway is followed in this rearrangement is not known at present.

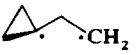


The detailed mechanism of the geometric isomerization of spiropentane thus is thought to involve initial homolysis of either the C_1–C_2 (peripheral) or the C_1–C_3 (radial) carbon–carbon bond to provide either VIII or IX, respectively, as an inter-

mediate.* An anticipated value of the enthalpy of activation for such process may be approximated by subtracting the "incremental strain" of 8·8 kcal/mole present in spiropentane[2] from the enthalpy of activation for geometric isomerization of cyclopropane (64·5 kcal/mole).[12] The result (55·7 kcal/mole) is somewhat greater than the observed enthalpy of activation (50·9 kcal/mole). Although this disparity may simply reflect the approximate nature of the calculation, it may also indicate that the transition state leading to production of XIII or IX is stabilized, by factors presently not understood, relative to the corresponding state leading to trimethylene itself. In any case, the low enthalpy of activation as well as the positive entropy of activation for the geometric isomerization are consistent with a transition state in which considerable strain has been released by ring-opening.



VIII



IX

Arguments based on relative bond strengths and on differences in stabilities of radicals could be made in regard to the relative favorability of VIII or IX as the intermediate in the geometric isomerization of spiropentane.† However, since experimental verification of the possibility of selectivity in cleavage of a peripheral versus a radical bond is possible, any such arguments are better deferred until the appropriate experiments are completed.

EXPERIMENTAL‡

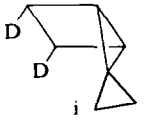
1. cis-1,2-*Dideuteriospiropentane* (I)

meso-1,2-*Dibromo*-1,2-*dideuterioethane*. The procedure of Bernstein *et al.*,[6] was used to convert *trans*-1,2-dideuterioethylene[5] to the dibromide. The IR spectrum of the dibromide was consistent with that reported[6] except that absorptions at 1509 (s) and 1550 (m) cm^{-1} were absent. Analysis of the spectrum indicated that no more than 5% of the *rac* dibromide was present.

cis-2,3-*Dideuterio*-1,1-*dicarboethoxycyclopropane*. This compound, b.p. 86–88°/5·5 mm, was prepared in 60% yield by reaction of the *meso* dibromide and diethyl malonate, according to the procedure of Dox and Yoder.[14] Analysis of the NMR spectrum (CCl_4) [4·15 ppm, quartet (4·00 protons); 1·31 ppm, singlet and 1·26 ppm, triplet (8·06 protons)] showed that the cyclopropane was greater than 95% dideuterated. Comparison of the mass spectra of this diester and its undeuterated analog showed that one mode of fragmentation of the molecular ion involved loss of a total mass of 56, which corresponds to elimination of

* Whether the transition states for the formation of VIII and IX are visualized as diradicals in which there is little or no bonding interaction between the radical-bearing carbons or as "expanded-ring" cyclopropanes[11] in which there is significant bonding between the incipient radical centers does not seriously alter the argument to be presented.

† In the case of the geometric isomerization of the bicyclo-[2.1.0]pentane-5-spirocyclopropane, *i*,[13] a peripheral bond undoubtedly is cleaving.



i

‡ B.ps are uncorrected. NMR spectra were measured on a Varian A-60 NMR spectrometer and IR spectra with a Beckman IR 7 Spectrophotometer unless otherwise noted. Mass spectra were obtained with a CEC Model 21-102 Mass Spectrometer.

ethylene from both ester functions. No deuterium is lost in the process, so that the peaks in the region of *m/e* 132 reflect the deuterium content of the diester. The relative peak heights in this region were *m/e* 132, 100·0; *m/e* 131, 5·4; *m/e* 130, 0·5.

The diester was converted to *cis*-1,2-dideuteriospiropentane in the manner described previously.[2] The physical constants and NMR spectra of intermediates isolated are given below.

cis-2,3-*Dideuterio*-1,1-*bis*(*hydroxymethyl*)*cyclopropane*. B.p. 94–98°/3 mm; NMR ($CHCl_3$): 3·92 ppm, singlet (2·12 protons); 3·45 ppm, singlet (4·00 protons); 0·35 ppm, singlet (2·00 protons).

cis-2,3-*Dideuterio*-1,1-*bis*(*bromomethyl*)*cyclopropane*. B.p. 84–87°/18 mm; NMR (CCl_4): 3·49 ppm, singlet (4·00 protons); 0·92 ppm, singlet (1·96 protons).

cis-1,2-*Dideuteriospiropentane* (I). B.p. 35–38°/760 mm; NMR (neat): 0·77 ppm. The IR and mass spectra of I are tabulated in Tables 2 and 3, respectively.

2. trans-1,2-*Dideuteriospiropentane* (II).

rac-1,2-*Dideuterio*-1,2-*dibromoethane*. *trans*-1,2-Dideuterioethylene[7] was converted to the dibromide by the method of Bernstein *et al.*[6] Analysis of the IR spectrum of the dibromide indicated that no more than 5 % of the *meso*-isomer was present.

The conversion of the dibromide to trans-1,2-dideuteriospiropentane was accomplished according to the procedures described above. Relevant physical and spectral data on intermediates isolated are given below.

trans-2,3-*Dideuterio*-1,1-*dicarboethoxycyclopropane*. B.p. 122–124°/38 mm; NMR (CCl_4): 4·15 ppm, quartet (4·00 protons); 1·31 ppm, singlet, and 1·26 ppm, triplet (8·22 protons); mass spectrum in the region of *m/e* 132: *m/e* 132, 100·0; *m/e* 131, 6·1; *m/e* 130, 0·6.

trans-2,3-*Dideuterio*-1,1-*bis*(*hydroxymethyl*)*cyclopropane*. B.p. 82–84°/0·2 mm; NMR ($CHCl_3$): 3·96 ppm. singlet (2·24 protons); 3·45 ppm, singlet (4·00 protons); 0·35 ppm, singlet (1·98 protons). The IR spectrum of this compound was notably different from that of the *cis* isomer in the fingerprint region.

trans-2,3-*Dideuterio*-1,1-*bis*(*bromomethyl*)*cyclopropane*. B.p. 85–88°/18 mm; NMR (CCl_4): 3·49 ppm, singlet (4·00 protons); 0·92 ppm, singlet (1·99 protons).

TABLE 2. TABULATED IR SPECTRA OF *cis*- AND *trans*-1,2-DIDEUTERIOSPIROPENTANE

Frequency in cm^{-1}	% Transmission[a,b]			Frequency in cm^{-1}	% Transmission[a,b]		
	I[c]	II	I and II[d]		I	II	I and II[d]
3082	24	34	24	1050	60	61	72
3023	13	82	15	1015	23	(26)	(44)
3015	10	82	15	1008	(51)	9	28
2950	63	63	70	980	86	(84)	87
2845	(89)	86	92	967	(94)	57	81
2348	(98)	87	(100)	925	24	74	45
2320	92	88	93	872	(34)	21	(40)
2267	48	35	48	867	7	34	21
2200	93	91	94	822	89	9	33
2100	93	91	95	793	52	59	62
2060	89	82	91	770	(89)	73	75
1425	70	60	73	720	(90)	66	74
1296	67	(75)	—	712	83	(89)	84
1294	—	—	75				
1292	(81)	61	—				
1157	78	53	78				
1105	65	51	67				
1080	(82)	64	82				

[a] Spectra obtained on a neat sample contained in a 0·025 mm cell.

[b] All values, except those in parentheses, apply to absorption maxima.

[c] Spectrum measured with a Perkin–Elmer Model 257 Spectrophotometer.

[d] The 50–50 mixture obtained by thermal equilibration.

trans-2,3-*Dideuteriospiropentane* (II). B.p. 36–38°/760 mm; NMR (neat): 0·77 ppm. The IR spectrum is tabulated in Table 2.

3. *Rearrangement of* cis-1,2-*dideuteriospiropentane* (I)

a. *Equilibration studies.* A 200-μl. sample of I was distilled via a vacuum line into an evacuated 600-ml Pyrex ampoule which had been seasoned by prior thermolysis of two 100-μl. samples of I. The ampoule was heated at 355 ± 5° for 2 hr. The resulting pyrolysis mixture was analyzed by GLPC using a 2-m silver fluoroborate–Carbowax column operating at room temp and was found to consist of ca. 88% spiropentane-d_2 and 12% methylenecyclobutane-d_2 (the percentages of allene-d_x and ethylene-d_x present were not determined). Isolation of the spiropentane-d_2 was accomplished using the same column. The IR spectrum of the recovered hydrocarbon is given in Table 2. Repetition of the above experiment, with the single exception that a 5-hr period of heating was used, produced a pyrolysis mixture containing spiropentane-d_2 (40%) and methylenecyclobutane-d_2 (60%). The IR spectrum of the recovered hydrocarbon was superimposable with that obtained above, indicating that the equilibration of I and II was complete. The NMR spectrum was essentially identical to that of I as was the mass spectrum (Table 3) of the equilibrated spiropentane-d_2.

b. *Calibration mixtures.* For purposes of obtaining 10·0% solns in CS_2 of known mixtures of *cis*- and *trans*-1,2-dideuteriospiropentane, 30·0 μl. of I, which contained 5% of II (*vide supra*), and 30 μl. of the 50–50 mixture of I and II, obtained by thermal equilibration, were separately dissolved in 270 μl. of CS_2. Aliquots of the two standard solns were used to prepare calibration mixtures of the compositions given in Table 4. The IR absorbances of the solns were determined at 920 and 820 cm^{-1} and were found to obey

TABLE 3. MASS SPECTRA OF DIDEUTERIOSPIROPENTANES

	Intensities[b]	
m/e[a]	I	I and II[c]
71	1·3	1·3
70	22·5	24·4
69	100·0	100·0
68	28·8	26·9
67	3·8	3·8

[a] Ionizing voltage of 12 eV.
[b] Given relative to *m/e* 69 as the base peak.
[c] The 50–50 mixture obtained by thermal equilibration.

TABLE 4. ABSORBANCES OF CALIBRATION MIXTURES[a]

% *cis*[b]	A_{920} cm^{-1}	A_{820} cm^{-1}
95·0	0·603	0·028
90·0	0·568	0·072
86·0	0·545	0·108
81·5	0·531	0·155
77·0	0·495	0·191
72·5	0·473	0·236
68·0	0·442	0·277
63·5	0·414	0·324
59·0	0·397	0·364
54·5	0·360	0·407
50·0	0·342	0·445

[a] Spectra were obtained using a 0·1 mm cell.
[b] Estimated to be correct to ±0·5%.

Beer's Law. Since it would have been difficult to prepare solns of known concentrations from mixtures of I and II obtained in the kinetic runs (*vide infra*), a calibration curve was obtained by plotting the ratio A_{920}/A_{820} *versus* percentage *cis*-isomer. The absorbances used in constructing the graph are given in Table 4.

c. *Kinetics.* Samples of approximately 30 μl. of *cis*-1,2-dideuteriospiropentane were transferred by standard vacuum techniques into degassed Pyrex ampoules having volumes of about 50 ml. For kinetic runs, the ampoule was preheated in an oven to 100° and then immediately transferred to an apparatus containing refluxing liquid.* The time at which thermal equilibration of the ampoule had been attained, as determined by temperature measurement at the extremes of the ampoule using a chromel–alumel thermocouple, was taken as t_0 for purposes of calculating rate constants. The time required for equilibration was less than 1% of the total time for the kinetic run except for runs 3 and 6 (Table 1), in which the percentages were 1·5 and 3·0, respectively. The rate constants obtained over a range of 304·6–336·0° are recorded in Table 1.

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* The apparatus is described in Ref. 2.