Thermal Equilibration of Substituted Bicyclo[2.1.0]pentanes[1]

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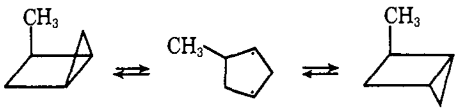
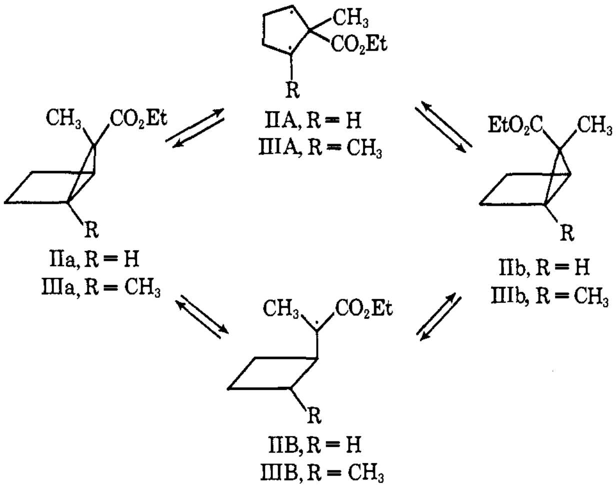
Abstract: The kinetics and position of equilibrium of the thermal isomerization IIa $\rightleftarrows$ IIb and IIIa $\rightleftarrows$ IIb were investigated in the temperature range of 140–160°. Substituents at C_5 accelerate the equilibration reaction by factors of 3–16 in II and III compared with I. The effect of the methyl bridgehead substituent in III amounts to a rate increase over that for II, by factors of 8 and 15 for the pairs IIIa–IIa and IIIb–IIb, respectively. Activation parameters for compounds I, II, and III are compared and mechanistic conjectures are made.

A comparison of the characteristics of the thermal reactions of bicyclo[2.1.0]pentane with those of the smallest and most highly strained member of the bicyclo[*n*.1.0]alkane series, bicyclo[1.1.0]butane[2,3] and those of higher homologs,[3b,4] affords insight into the fundamental properties of highly strained σ bonds. The thermal reactions taking place in the bicyclic series resemble those occurring in the common monocyclic parent cyclopropane; attention has been focused on this relationship.[3–5]

The simplest of these thermal reactions is the scission and reconstitution of the strained cyclopropane bond, a process which gives rise to geometrical isomerization. This phenomenon has been investigated in some detail in the *cis–trans* isomerization of cyclopropanes.[3b,6] In the bicyclic series, it has not as yet been detected for bicyclo[1.1.0]butanes[3a,7] but can be conveniently examined in bicyclo[2.1.0]pentanes. Only one case of this reaction, however, that of the thermal equilibration of the stereoisomeric 2-methylbicyclo[2.1.0]pentanes (Ia and Ib),[8] has been reported. The intervention of a diradical IA formed from the rupture of the internal bond can be justified on thermodynamic grounds;[4] cleavage of the external bond is more energetic. The possibility of preferential cleavage of the external bond in derivatives of bicyclo[2.1.0]pentane cannot be precluded, however. In the thermal equilibration of the derivatives II and III, the formation of intermediates IIB and IIIB *via* cleavage of the external bond could be electronically favored over IIA and IIIA, because of increased stabilization of one of the radical sites by the methyl and carbethoxy groups.[9] For this reason, despite the ring strain remaining in diradical B, the equilibration of II and III could take this mechanistic course.



Ia IA Ib



The thermal equilibration of II and III was studied in the hope of obtaining evidence for a discontinuity in the mechanistic pathway. A comparison of the reactivities of I, II, and III would also afford a semiquantitative appraisal of stereoelectronic effects which come into play during the course of these isomerizations and would thus further clarify the mechanistic features of these equilibrations.

Experimental Section

Preparation of Bicyclo[2.1.0]pentanes II and III. The formation of III from the photolysis of ethyl 2-methyl-3-cyclopropyl-2-butenoate has been reported by us previously.[10] Facile separation of III from the starting material and olefinic photoproducts could be readily accomplished by ozonolysis.[11] A fraction of the photolysis product mixture, enriched in III, was ozonized in hexane solution. After completion of the ozonolysis, the clear solution was decanted from the insoluble ozonides directly onto a column of Merck neutral alumina. Elution with benzene immediately yielded III. The recovery, based on an estimate of the amount of III pres-

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[1] Reactions of Bicyclo[2.1.0]pentanes. III. Paper I: M. J. Jorgenson and T. J. Clark, *J. Am. Chem. Soc.*, **90**, 2188 (1968). Paper II: M. J. Jorgenson, *Tetrahedron Letters*, 4577 (1968).

[2] (a) K. B. Wiberg and D. S. Conner, *J. Am. Chem. Soc.*, **88**, 4437 (1966); (b) K. B. Wiberg, G. M. Langman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2740 (1965).

[3] (a) K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 5272 (1966); (b) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 148 (1966).

[4] C. Steel, R. Zand, R. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).

[5] M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

[6] (a) B. S. Rabinowitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, 28, 504 (958); (b) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (London), 257A, 122 (1960).

[7] G. L. Closs and P. E. Pfeffer, *J. Am. Chem. Soc.*, **90**, 2452 (1968).

[8] J. P. Chesick, *ibid.*, **84**, 3250 (1962).

[9] In the thermal ring opening of methyl cyclobutanecarboxylate the carbomethoxy group is reported to stabilize the transition state relative to that for alkylcyclobutanes by approximately 5 kcal [M. Zupan and W. D. Walters, *J. Am. Chem. Soc.*, **86**, 173 (1964)]. In the thermal vinylcyclopropane rearrangement of 1,5-dicarbethoxybicyclo[3.1.0]hex-2-ene, the two carbethoxy substituents reduce the energy of activation for this reaction by 24 kcal [H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965)] compared to the unsubstituted parent [R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, *A*, 553 (1966)]. In addition, one of the radical sites in B is tertiary, compared to being secondary in A, contributing further to the stabilization of B.

[10] M. J. Jorgenson, *J. Am. Chem. Soc.*, **88**, 3463 (1966).

[11] W. G. Dauben and J. Wiseman, *ibid.*, **89**, 3545 (1967). We thank Professor Dauben for drawing attention to this convenient procedure.

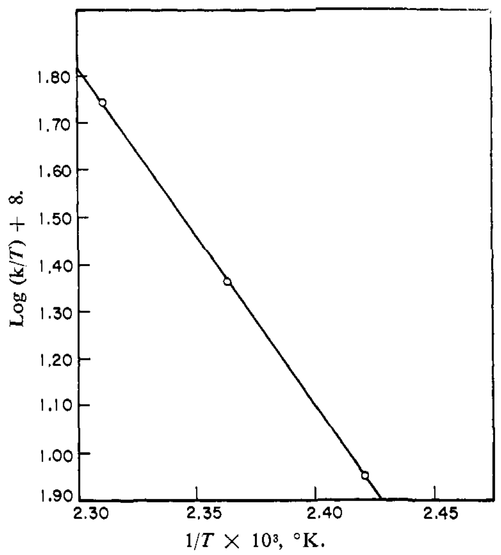

Figure 1. Enthalpy of activation plot for IIIa.

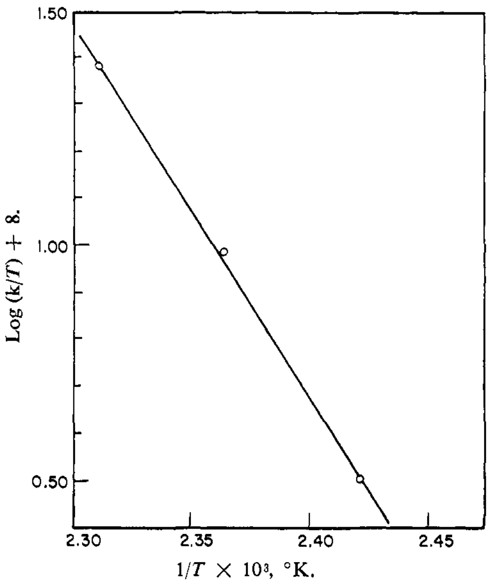

Figure 2. Enthalpy of activation plot for IIIb.

ent in the starting sample, after ozonolysis and chromatography was about 50%. The two isomers of III, which were present in a 40:60 ratio, were separated by gas chromatography by use of a 10 ft × 0.5 in. NPGS on Chromosorb W 60–20 column; the detector temperature was kept below 200° in order to avoid isomerization during the separation.

Photolysis of ethyl 2-methyl-3-cyclopropyl-2-propenoate furnished II.[12] The isolation and separation of the isomers, present in a 1:1 ratio after ozonolysis, was accomplished in a manner similar to that employed for III.

Kinetics. Isomerizations were carried out in sealed tubes of 3.0-ml capacity constructed from 9-mm Pyrex tubing. A 1-μl sample of compound was placed by means of a Hamilton syringe into a constricted tube, the tube was cooled in a Dry Ice–acetone bath, evacuated to 0.2 mm and sealed. The scale, pressure, and vessel size employed were such that the sample was entirely vaporized at the reaction temperatures, the gas pressure in the vessel being approximately 40 mm. At least eight tubes were used in a run; they were placed in an oil bath maintained to ±0.06°. Individual tubes were withdrawn at appropriate intervals, the lower third was cooled in liquid nitrogen, the tube above the cooled portion was broken, and 50 μl of benzene was added. The solution which resulted was analyzed on a 10 ft × 0.25 in. column of Carbowax 20M on 60–20 Chromosorb W. Retention times at a column temperature of 140° and a gas flow of 60 cc/min were 11.5 and 13.5 min for isomers IIIa and IIIb and 11 and 16 min for isomers IIa and IIb. Isomers IIIa and IIIb were not entirely separated under these conditions. The areas of the peaks were determined with a disk integrator, and the percentage composition of the mixture was derived from these areas. Three analyses were made on each solution and the results were averaged. The result of an individual analysis was usually within 1% of the average of the three. Two runs in which IIIb was the starting material and one run in which IIIa was the starting material were made at each of three temperatures. One run starting with IIa and one starting with IIb were carried out at each of two temperatures.

The reactions were followed through three half-lives. The data fit the expression

$$\ln \frac{X_e - X_t}{X_e - X_0} = \frac{-kt}{X_e}$$

where X_e, X_0, and X_t are the mole fraction at equilibrium, zero time, and time t of that isomer the concentration of which increases with time during the equilibration. A small variation in the value of X_e causes a large variation in the slope of the regression line of $\ln (X_e - X_t)$ on t. In order to make the data internally consistent, a pair of values of X_{ea} and X_{eb}, always within 1% of the determined values, was selected so that the slope of the regression line of $\ln (X_{ea} - X_{ta})$ on t was equal to the slope (or average slope) of $\ln (X_{eb} - X_{tb})$ on t. Reasonable estimates of the errors in rate constants were made and uncertainties in $\Delta H^{\ddagger}$ were estimated by the method of Morse.[13,14] Activation parameters were calculated by standard methods; enthalpy of activation plots for IIIa and IIIb are reproduced in Figures 1 and 2.

Results and Discussion

Stereochemistry and Position of Equilibrium of II and III. The difference in the chemical shift values of the C_5 methyl group in IIa and IIb permitted a stereochemical assignment to be made. One stereoisomer exhibited a methyl singlet at τ 8.9 while the other isomer displayed its methyl singlet at τ 8.6. Because of the greater shielding effects of the cyclobutane bonds[15,16] operative on the *endo* methyl, the isomer which possesses the more highly shielded methyl is assigned geometry IIa. This assignment to the isomer which is present in lesser amount at thermal equilibrium (Table I) also follows from an estimation of the differences in steric interactions present in IIa and IIb. Since the *cis* interactions of the *exo* substituent should be largely the

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[12] The exper imental details for the generation of II and III will be reported in detail in a full publication dealing with the photochemistry of cyclopropylacrylic esters.

[13] B. K. Morse, in "Investigation of Rates and Mechanisms of Reactions," Part I, S. L. Friess, E. S. Lewis, and M. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1961, p 506.

[14] Analysis of error by standard statistical methods did not yield meaningful results. These analyses suggested that rate constants determined for IIIa and IIIb had a probable error of less than 1% at 139.9 and 150.1° and those determined at 159.6° had a probable error of less than 3% and that enthalpies of activation for IIIa and IIIb had a probable error of 0.5 kcal. These errors are unrealistically small in view of the strong dependence of the slope of the regression line on the value of X_e selected and the fact that isomers IIIa and IIIb were not completely separated by the column. Moreover, semiquantitative analysis of mixtures heated to higher temperatures showed that the equilibrium composition of a mixture of the isomers of III changed more slowly and that of a mixture of isomers of II changed more rapidly with temperature than predicted by the obtained values of the enthalpies and entropies of activation.

[15] The diamagnetic anisotropy of carbon–carbon single bonds is an accepted phenomenon [*cf.* J. I. Musher, *J. Chem. Phys.*, 35, 1159 (1961)] and many examples of higher shielding for the proton which is *cis* compared to that which is *trans* to methyl or methylene groups exists. For example, Roth and Martin[16] have conclusively shown that the 5-*endo* hydrogen in bicyclo[2.1.0]pentane is located at higher field by 0.2 ppm than the 5-*exo* hydrogen.

[16] W. R. Roth and M. Martin, *Ann. Chem.*, 702, 1 (1967).

same in IIa and IIb,[17] one can attribute the ΔF measured at 150° for the equilibrium of II as being almost exclusively due to the interactions of the *endo* substituent with the dimethylene bridge. The steric relationship of the carbon–carbon bond of the *endo* group with the cyclobutane carbon–carbon bonds is between that of a *gauche* and an eclipsed interaction,[18] so that the steric demands of the C_5 substituent in the *endo* position should be somewhat larger than found for the same substituent in an axial position in cyclohexane, where such butane interactions are *gauche*. In accordance with this analysis, ΔF measured for the IIa $\rightleftarrows$ IIb equilibrium (1.2–1.3 kcal/mol) is larger than the value predicted from the conformational free energy values in cyclohexane, where acceptable values of 1.7 kcal/mol for methyl[19] and 1.2 kcal/mol for the carbethoxy group[20] lead to ΔF of about 0.5 kcal/mol. Because the steric requirement of a methyl group is larger than that of a carbethoxy group, IIa is the less stable isomer.

Table I. Equilibration of II

Isomer	T, °C	10^5k, sec^{-1}	Position of equilibrium[a] % IIa	% IIb	ΔF, kcal
a	150.1	1.22	18.4	81.6	−1.250
b	150.1	0.276			
a	159.6	3.17	18.9	81.1	−1.235
b	159.6	0.739			

[a] Value selected to make rate data internally consistent.

In the case of III the nmr spectra[10] of the two stereoisomers were inconclusive for assignment of geometry. The isomers of III possess an additional interaction, the vicinal *cis* interaction of the *exo*-cyclopropane substituents. However, these interactions should be less[18] than those which the *endo* substituent is subjected to *vis à vis* the dimethylene bridge. It follows from this reasoning that the isomer which predominates at thermal equilibrium is IIIb. The free energy difference between IIIa and IIIb at 150° is less than that for II (0.7 kcal/mol compared to 1.2 kcal/mol); this smaller value is expected because of the additional interactions present which cause the stabilities of the stereoisomers of III to be more alike than those of II.[21]

Substituent Effects on Equilibration Rates. Gas phase equilibration of the stereoisomers of II and III (Tables I and II) proceeded smoothly at moderate temperatures. At these temperatures no reaction other than equilibration was observed. Excellent linear plots were obtained for all runs when the kinetic expression presented in the Experimental Section was employed.

Table II. Equilibration of III

Isomer	T, °C	10^5k, sec^{-1}	Position of equilibrium[a] % IIIa	% IIIb	ΔF, kcal
a	139.9	3.72	26.2	73.8	−0.863
b	139.9	1.32			
a	150.1	10.1	28.7	71.3	−0.764
b	150.1	4.07			
a	159.6	24.1	30.1	69.9	−0.724
b	159.6	10.4			

[a] Values selected to make rate data internally consistent.

The kinetic data for II and III are most effectively evaluated in comparison with the reported data for I[8] which in the absence of data for the deuterated parent is taken as the reference system. The less strained *trans* isomer Ib[22] approximates best the strain present in the parent hydrocarbon, and its equilibration rate is therefore used as the reference rate in Table III. Since the substituent effects as represented by the enthalpy of activation may be considerably masked by experimental error,[23] a comparison of the relative rates at a common temperature is considered to be a more accurate index of stereoelectronic effects.

Table III. Comparison of Rates and Activation Parameters

Compd	Rel rate at 150°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg
Ia[c]	1.6	38.3	4.2[a]
Ib[c]	1.0	37.8	2.1[a]
IIa	16.2	35.8 ± 2.2	2.9 ± 5.2
IIb	3.6	37.0 ± 2.7	2.7 ± 6.1
IIIa	133	32.9 ± 1.4 (32.4[b])	0.1 ± 3.5 (3.9[b])
IIIb	53.5	36.4 ± 1.8 (34.6[b])	6.6 ± 4.2 (2.3[b])

[a] Calculated from rate data in ref 8. [b] Calculated from rate data at 150 and 160°C. [c] See ref 8.

Compared with Ib, the stereoisomers of II incorporate additional strain due to the presence of the crowding 5-*endo* substituent. A mechanism proceeding *via* a diradical (IIA or IIB) predicts relief of strain in the transition state and therefore a steric acceleration of the equilibration of II compared to I. Modest acceler-

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(17) The eclipsed H–H and CH_3–H interactions are similar, as measured from the rotational barrier in ethane and propane: E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 9, footnote 21.

(18) The exact nature of these interactions will depend to a large degree on the geometry of the bicyclo[2.1.0]pentane skeleton, in particular on the interplanar angle. An accurate determination of the bond angles and bond lengths has yet to be made.

(19) Reference 17, p 44.

(20) E. L. Eliel and M. C. Reese, *J. Am. Chem. Soc.*, **90**, 1560 (1968), and references therein.

(21) The difference in free energy differences between II and III ($\Delta\Delta F$) as calculated on this basis, is 0.5 kcal/mol. This value should represent closely the difference between the *cis*-cyclopropane 1,2 CH_3–CH_3 and 1,2 CH_3–CO_2Et interactions in the two isomers of III, since all other interactions either remain constant or are nearly the same between the two pairs of bicyclo[2.1.0]pentanes.[17] If the assignment to IIIa and IIIb were reversed, the $\Delta\Delta F$ value would be about 2 kcal/mol, a value which is unrealistically high. Because of the spreading of the angle which the substituent forms with the cyclopropane bonds, the two groups are farther apart than in an eclipsed butane conformation. Further, the two *cis*-1,2 interactions in III are likely to be considerably less eclipsing than in cyclopropane; the juncture to a cyclobutane ring causes the external angles at the bridgehead carbons to be considerably different from those at the bridge carbon.

(22) The chemical shift of the 2-methyl group in Ia and in Ib differ by 0.4 ppm. That isomer which has its methyl group in a more shielded environment is taken to be the *cis* isomer Ia. This assignment is also made by Roth and Martin.[16] These authors have shown that a *cis* substituent on C_2 is shielded by the cyclopropane; in the parent hydrocarbon the difference in shielding between the *cis* and *trans* C_2 protons amounts to 0.75 ppm.

(23) The apparently incongruous values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for IIIb may be due to experimental error. Since the position of equilibrium for III changes more slowly than predicted by the equilibration data and the ΔH and ΔS derived from them, it is apparent that there is an error in the determination of the equilibrium position at one or more temperatures. Visual inspection makes the value at 139.9° suspect. Calculation of the enthalpy of activation for IIIa and IIIb from the two temperatures (150 and 160°) employed in the study of II results in enthalpies of activation of 32.4 and 34.6 kcal/mol and entropies of activation of 3.9 and 2.3 cal/deg (Table III). These values are more in line with the activation parameters for the other compounds.

ations by factors of 3.6 and 16.2 for IIa and IIb, respectively, are in fact measured. Ester III differs from II in the presence of a bridgehead methyl substituent. Further destabilization of the ground state of IIIa and IIIb, compared to Ib, because of the presence of an *exo,cis* 1,2 interaction, and hence a faster rate should be the consequence. Formation of the diradical intermediate, IIIA or IIIB, is also facilitated for III compared to II or I, because of the increased stabilization in the transition state of one of the developing radical sites; this site will be tertiary in III, but will be secondary in I and II. Both of these effects predict a faster rate for IIIa compared to IIa and for IIIb compared to IIb. The measured effects are relatively modest, being factors of 8 and 15, respectively.[24a]

Reaction Mechanism. On the basis of the activation energy measured for the isomerization of I, Chesick[8] has implied that the transition state for this reaction does not closely resemble a diradical. Other investigators[4] find that value compatible with a diradical mechanism. No definitive evidence for or against the intervention of a diradical exists.

On the assumption that diradicals[25] intervene, two distinct mechanistic possibilities can be envisaged. The equilibration could be either a two-step reaction with the intervention of a common planar diradical, or a three-step mechanism with the intermediacy of two nonplanar interconverting diradicals. The energy profile in Figure 3 is the most probable one for a two-step mechanism. According to this scheme the energy barrier for the collapse of the diradical A to isomer a is larger than that for the collapse to isomer b. Other energy profiles in which $\Delta F^{\ddagger}_{\mathrm{A}\rightarrow\mathrm{a}}$ is equal to or less than $\Delta F^{\ddagger}_{\mathrm{A}\rightarrow\mathrm{b}}$ do not realistically take into account the nonbonded interactions developing in the transition state leading to isomers a and b. For I it has been estimated[4] that this barrier amounts to 8–9 kcal, from the measured energy of activation for the equilibration of I and from a calculated bond strength[26,26a] (30 kcal/mol) of the internal bond in bicyclo[2.1.0]pentane. For the isomerizations of II and III this barrier is surely larger and should be higher for the closure to the more highly strained isomer a than to the more stable isomer b.

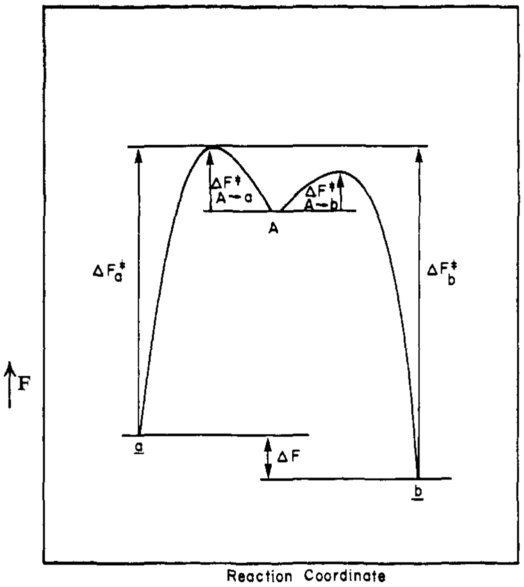

Figure 3. Two-step reaction profile for equilibration of stereoisomers a and b.

Various energy profiles can be devised for a mechanism proceeding *via* two interconverting diradicals. Allred and Smith[27] have invoked such diradicals as intermediates in the generation of 2-methoxybicyclo[2.1.0]pentanes from 5-methoxy-2,3-diazabicyclo[2.2.1]heptene. From the reported fractions of diradicals which interconvert before closing and which close to product without interconverting, a partial energy profile can be constructed which indicates that the barrier for the interconversion of the diradicals is higher than that for the collapse to the more stable but lower than that for the collapse to the less stable isomer of 2-methoxy bicyclo[2.1.0]pentane. In analogy, such an energy profile (Figure 4) suggests itself for the equilibration of II and III. Since the barrier to interconversion of the diradicals is appreciable, another scheme (Figure 5) is particularly attractive for systems in which the interconversion between diradicals A′ and A′′ is attended by considerable nonbonded interactions in the transition state (which should resemble a planar diradical). When substituents are present at the bridgehead carbons as in III, this process could require either more or less energy, depending on the geometry of the diradical and the transition state, than in II which lacks this substituent. Indeed, if the differences between the activation parameters for IIIa and IIIb are real, then this suggests as one possibility that the mechanistic details for the interconversion of III differ from those for II. One reaction might be characterized by the scheme in Figure 4, and the other by the profile in Figure 5.

The simplest possible mechanism, a one-step process, warrants consideration. While such a process is difficult to envisage for the isomerization of cyclopropanes, the equilibration reaction of bicyclo[2.1.0]pentanes could be conceived of as a continuous bond-stretching process, involving concomitant rehybridization and inversion of the cyclopropane ring.

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(24) (a) An indication of the effect of a methyl substituent on the ease of cleavage of the cyclopropane bond is afforded from the E_a values reported for the isomerization of *cis*-1,2-dideuteriocyclopropane (64.2 kcal/mol[6a]) and of *cis*-1,2-dimethylcyclopropane (59.4 kcal/mol[6b]). The difference in ground-state deactivation between these two is due primarily to the *cis*-1,2-methyl–methyl interaction, present in the 1,2-dimethylcyclopropane, since all other interactions are nearly the same.[17] The steric destabilization of IIIb compared to IIb is also due almost entirely to the presence of a similar interaction. The value of 2.4 kcal/mol per methyl for the stabilization in dimethylcyclopropane is in close agreement with the differences in the enthalpies between IIa and IIIa and IIb and IIIb, when the latter value is calculated from the rate data at 150 and 160°. However, from the thermal vinylcyclopropane rearrangement of *trans*-2-methyl-1-vinylcyclopropane [W. R. Roth and J. König, *Ann.*, **688**, 28 (1965)] and vinylcyclopropane [M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961)] the stabilizing effect of the diradical intermediate by a methyl is derived to be 3.9 kcal/mol.

(25) We do not specify here whether the diradicals are free diradicals with noninteracting electrons, or are "expanded ring" species, like those which have been invoked in the case of cyclopropanes.[3b]

(26) This value has been estimated by others to be 19[8] and 26 kcal.[3a] If the barriers to collapse of the diradicals in II and III are at least 10 kcal, then the corresponding bond strengths in these systems would range from 23 to 27 kcal and are probably lower.

(26) (a) NOTE ADDED IN PROOF. Recently, the energy change attending the conversion of I to Ia has been estimated to be at most 27.5 kcal/mol, so that the energy barrier to the collapse of IA to Ia or Ib is at least 11.4 kcal/mol [R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968)].

(27) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967).

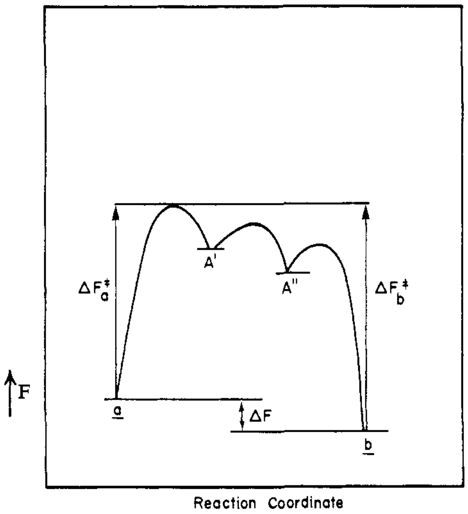


Figure 4. Reaction profile for equilibration with two interconverting diradicals.

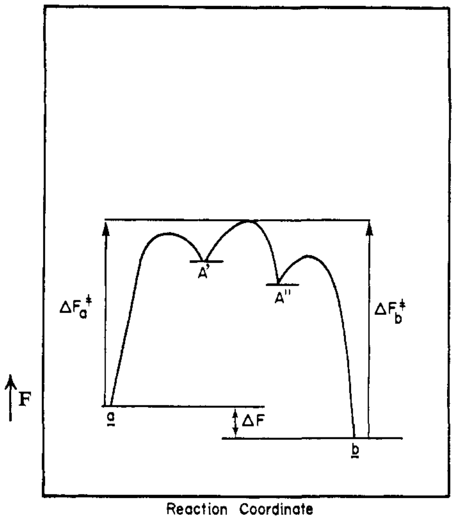
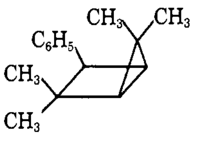


Figure 5. Reaction profile for equilibration with two interconverting diradicals.

No discreet diradical intervenes in this process. Electronic effects would be relatively unimportant in such a mechanism, and the modest accelerations noted by the bridgehead methyl in III is at least consonant with this proposal.

The activation parameters for I, II, and III[23] are much alike and for this reason consistent with the intervention of similar diradicals in the equilibration of these systems. No mechanistic discontinuity needs to be invoked, but the possibility that a diradical of type B intervenes in some favorable cases remains open. This question could be settled unambiguously from the study of 2-substituted derivatives of II and III. The stereochemical relationship of the cyclopropane bridge to the C_2 substituent after equilibration would distinguish between the two mechanisms.

Recently, Kristinsson and Hammond[28] have reported that the stereoisomeric bicyclo[2.1.0]pentanes IV do not interconvert. This observation is surprising since the data obtained for II and III indicate that steric acceleration is an imporant factor in these equilibrations. Compounds IVa and IVb incorporate strain far beyond that present in II or III, so that the rate of equilibration is expected to be faster than that for I, II, or III. One possible explanation of this anomaly is that the strain in IV is relieved not by cleavage of the internal bond, but by the cleavage of the external bond to give a diradical which is unproductive. The fact that acid is reported to cleave primarily the external bond in one of the isomers lends some support to this conjecture.[29]



IVa

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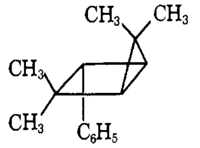

IVb

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(28) H. Kristinsson and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 5970 (1967).

(29) Acid cleavage in bicyclo[2.1.0]pentane is reported to occur exclusively at the internal bond [R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963)].