overnight. The apparatus was flame dried and kept under an argon atmosphere while the solvent or solution was placed in vessel A, the alloy or metal was placed in vessel B, and high boiling liquids or solids, if any, were placed in vessel D. The solutions were degassed on a high-vacuum apparatus, the metal distilled from vessel B to vessel C, and the apparatus closed with a flame at the constriction. The solution was distilled from vessel A to vessel C and the apparatus closed with a flame at the constriction. Agitation with cooling produced the typical blue color. The saturated solution with a small excess of metal was poured into the optical cell and the apparatus closed with a flame at the constriction. Samples were stored under liquid nitrogen until just prior to the examination of their spectra.

Acknowledgment. The support of this work by a grant from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. (±)-**2**, 3539-39-7; (±)-**2** *p*-toluenesulfonate ester, 42274-61-3; (*S*)-**2**, 76946-21-9; (*S*)-**2** *p*-toluensulfonate ester, 42274-61-3; (±)-**3**, 76900-31-7; (*R*)-(−)-**3**, 76946-22-0; (*S*)-(+)-**3**, 76946-23-1; (2*S*,15*S*)-(+)-**4**, 76900-32-8; (2*S*,15*S*)-(+)-**4** bis(tetrahydropyran-2-yl) ether, 76900-33-9; (3*S*,16*S*)-(−)-**5**, 76915-09-8; (2*S*,2′*S*)-(+)-**6**, 61217-63-8; (2*S*,2′*S*)-(+)-**6** bis(tetrahydropyran-2-yl) ether, 76946-24-2; (2*S*,2′*S*)-(−)-**7**, 76900-34-0; (2*S*,6*S*)-(+)-**8**, 76900-35-1; (2*S*,5*S*,9*S*,12*S*)-(+)-**9**, 76900-36-2; (2*S*,5*S*,9*S*,12*S*)-(+)-**9** bis(tetrahydropyran-2-yl) ether, 76900-37-3; (2*S*,6*S*)-(+)-**10**, 76946-25-3; (3*S*,6*S*,10*S*,13*S*)-(−)-**11**, 76915-14-5; (2*S*,5*S*,9*S*,12*S*)-(+)-**12**, 76900-38-4; (±)-**13**, 76900-39-5; (±)-**13** bis(tetrahydropyran-2-yl) ether, 76900-40-8; (2*S*,12*S*)-(+)-**13**, 76946-26-4; (2*S*,12*S*)-(+)-**13** bis(tetrahydropyran-12-yl) ether, 76984-82-2; (3*S*,13*S*)-(−)-**14**, 76900-41-9; (3*S*,11*S*)-(+)-**15**, 76900-42-0; (±)-**20**, 76946-27-5; (*S*)-(+)-**20**, 63126-47-6; (±)-**21**, 13346-01-5; (*R*)-(−)-**21**, 7202-43-9; (*S*)-(+)-**21**, 7175-81-7; (*S*)-(+)-**21** (L)-(+)-tartrate, 33002-02-7; (2*S*,3*S*)-(−)-**22**, 26549-21-3; 2-hydroxyethyl ether, 111-46-6; 2,2′-oxybis[1-(*p*-toluenesulfonoxy)-ethane], 7460-82-4; 1,8-bis(*p*-toluenesulfonoxy)-3,6-dioxaoctane, 19249-03-7; (*S*)-(+)-1,2-propanediol, 4254-15-3; (*R*)-(−)-1,2-propanediol, 4254-14-2; 1,11-bis(*p*-toluenesulfonoxy)-3,6,9-trioxaundecane, 37860-51-8.

Kinetics of the Thermal Skeletal Inversion of Bicyclo[2.1.0]pentane and Methylbicyclo[2.1.0]pentanes

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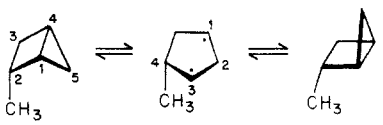
cis-exo-2,3-Dideuteriobicyclo[2.1.0]pentane, *cis-exo*-2,3-dideuterio-1-methylbicyclo[2.1.0]pentane, and the endo and exo isomers of 5-methylbicyclo[2.1.0]pentane have been prepared; rate constants for the gas-phase equilibrations between these substrates and the corresponding ring-inverted isomers have been determined between 153 and 208 °C. The parent hydrocarbon and 1-methylbicyclo[2.1.0]pentane have equal or nearly equal activation energies, 37.8 ± 0.1 and 38.0 ± 0.4 kcal/mol; the 2-methyl and 5-methyl systems have slightly higher E_a values, 38.7 to 39.2 kcal/mol. These data and related information from the literature are assessed in terms of electronic and steric substituent effects on ground-state bicyclopentanes and transition states leading to planar 1,3-cyclopentadiyl diradicals.

Thermal interconversion of *endo*- and *exo*-2-methylbicyclo[2.1.0]pentane (**1** ⇄ **3**) was observed by Chesick in 1962.[1] Tentative structural assignments for the isomers were suggested, and the activation parameters log A = 14.45 and E_a = 38.9 ± 0.8 kcal/mol for the gas-phase approach to equilibrium were determined. The reaction was presumed to involve incomplete cleavage of the C(1)–C(4) bond at the transition state and the planar cyclic diradical intermediate **2**. An analogy between this isomerization and the geometric isomerization of the 1,2-dideuteriocyclopropanes[2,3] was noted.



1 **2** **3**

The 2-methylbicyclo[2.1.0]pentane eluted first on a silicone oil or Carbowax GLC column has been shown to be the exo isomer,[4,5] as Chesick provisionally suggested.[1] Other bicyclo[2.1.0]pentanes undergo thermal stereomutations consistent with C(1)–C(4) bond cleavage and skeletal inversion but incompatible with alternative formulations involving C(2)–C(3) or C(1)–C(5) cleavage.[6-9]

Direct experimental observations on the 4-methyl-1,3-cyclopentadiyl diradical **2**, the parent diradical **5**, and several other representatives of this novel class of localized 1,3-diradicals have been reported.[10] Generation of these diradicals under matrix-isolation conditions at 5.5 K gave rise to strong ESR signals attributable to triplet diradicals. The barrier for formation of bicyclopentane **4** from the triplet diradical was estimated to be 2.3 ± 0.2 kcal/mol. In a revealing CIDNP experiment, triplet-sensitized photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene, precursor to

(1) J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962).
(2) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).
(3) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).
(4) K. B. Wiberg and K. C. Bishop, III, *Tetrahedron Lett.*, 2727 (1973).
(5) M. D. Harmony, C. S. Wang, K. B. Wiberg, and K. C. Bishop, III, *J. Chem. Phys.*, **63**, 3312 (1975).
(6) J. A. Berson, W. Bauer, and M. M. Campbell, *J. Am. Chem. Soc.*, **92**, 7515 (1970).
(7) J. P. Grosclaude, H. U. Gonzenbach, J. C. Perlberger, and K. Schaffner, *Chimia*, **29**, 528 (1975); *J. Am. Chem. Soc.*, **97**, 4147 (1975); *Helv. Chim. Acta*, **59**, 2919 (1976).
(8) K. Schaffner, *Tetrahedron*, **32**, 641 (1976).
(9) J. J. Tufariello, J. H. Chang, and A. C. Bayer, *J. Am. Chem. Soc.*, **101**, 3315 (1979).
(10) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975); *ibid.*, **101**, 4688 (1979).

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Table I. First-Order Rate Constants for Skeletal Inversions of Bicyclo[2.1.0]pentanes

system	reaction	temp, °C	$k_1 + k_{-1}$, s^{-1}
parent	7 ⇄ 8	180.0	$(8.80 \pm 0.24) \times 10^{-5}$
		188.8	$(1.93 \pm 0.17) \times 10^{-4}$
		199.2	$(4.80 \pm 0.46) \times 10^{-4}$
		208.4	$(1.00 \pm 0.05) \times 10^{-3}$
1-methyl	10 ⇄ 11	153.2	$(3.26 \pm 0.40) \times 10^{-5}$
		162.0	$(8.27 \pm 0.66) \times 10^{-5}$
		169.8	$(1.79 \pm 0.09) \times 10^{-4}$
		180.5	$(4.85 \pm 0.21) \times 10^{-4}$
5-methyl	14 ⇄ 15	162.4	$(3.03 \pm 0.15) \times 10^{-5}$
		171.0	$(7.24 \pm 0.32) \times 10^{-5}$
		183.0	$(2.34 \pm 0.09) \times 10^{-4}$

the intermediate diradical **5**, led to enhanced proton NMR absorptions in the spectrum of the bicyclopentane formed.

4 **5** **4**

Computations[11] using SCF theory and a double ζ basis set have led to a reasonable predicted geometry for the 1,3-cyclopentadiyl diradical, and a small calculated difference in energy between ground-state triplet and the singlet diradical, modeled with a two-configuration SCF treatment;[12] ΔE ($^3B_2$–$^1A_1$) = 0.9 ± 3 kcal. The coefficients of the singlet ...$2a_2^2$ and ...$3b_1^2$ configurations were nearly equal, and the singlet diradical was considered nearly perfectly diradical-like in character.

An interest in substituent effects on the skeletal ring inversion of bicyclo[2.1.0]pentanes led to the kinetic studies now being reported. The activation parameters for skeletal inversion of the parent hydrocarbon, for the C(1) and C(5) methyl derivatives, and for the C(2) methyl isomers studied by Chesick[1] provide some indication of the roles played by steric and electronic effects on ground and transition states.

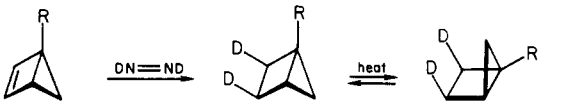
Results

Syntheses of Substrates. Reduction of bicyclo[2.1.0]pent-2-ene (**6**)[13-16] and 1-methylbicyclo[2.1.0]pent-2-ene (**9**)[17] with dideuteriodiimide[18] generated from potassium azodicarboxylate[19] and deuterioacetic acid in tetrahydrofuran gave, respectively, *cis-exo*-2,3-dideuteriobicyclo[2.1.0]pentane (**7**) and *cis-exo*-2,3-dideuterio-1-methylbicyclo[2.1.0]pentane (**10**).[20]

Table II. Activation Parameters and Relative Rate Constants for Skeletal Inversions of Bicyclo[2.1.0]pentanes

system	reaction	E_a, kcal/mol	log A	k_{rel}[a]
parent	7 → 8	37.8 ± 0.1	13.9	1
1-methyl	10 → 11	38.0 ± 0.4	14.7	5
exo-2-methyl[b]	1 → 3	38.65 ± 0.8	13.9	0.3
endo-2-methyl[b]	3 → 1	39.15 ± 0.8	14.4	0.7
exo-5-methyl	14 → 15	39.1 ± 0.1	14.6	1
endo-5-methyl	15 → 14	39.2 ± 0.1	15.0	3

[a] At 175 °C. [b] Reference 1.

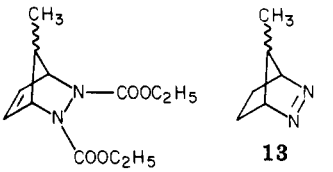


6, R = H
9, R = CH_3

7, R = H
10, R = CH_3

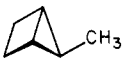
8, R = H
11, R = CH_3

To prepare the epimeric 5-methylbicyclo[2.1.0]pentanes, 5-methylcyclopentadiene[21] and diethyl azodicarboxylate were combined to form the Diels–Alder adducts **12**, which were hydrogenated over palladium-on-carbon, saponified, decarboxylated, and oxidized with cupric chloride. The resultant azo compounds **13** were pyrolyzed at 200–220 °C to give a mixture of **14** and **15**.[22]

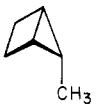


12

13



14



15

The epimers **14** and **15** were separated and identified through proton and carbon NMR spectroscopy.[23] The isomer of shorter retention time on both β,β'-oxydipropionitrile and dimethylsulfolane columns proved to be the exo compound **14**.

Kinetic Determinations.[24] Rate measurements were made by using a gas-phase reactor,[25] vacuum line, and either NMR spectroscopy or GLC as the analytical method. For the interconversions 7 ⇄ 8 and 10 ⇄ 11, the characteristic 0.8-ppm difference in chemical shift between C(2,3) endo and exo protons[25] provided a measure of the extent of reaction. For the 4 ⇄ 5 isomerization, GLC on a β,β'-oxydipropionitrile column was used to determine the mole fractions of each isomer for each kinetic sample. The first-order rate constants for approach to equilibrium as a function of temperature are listed in Table I.

(11) M. P. Conrad, R. M. Pitzer, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **101**, 2245 (1979). See also F. S. Collins, J. K. George, and C. Trindle, *ibid.*, **94**, 3732 (1972).
(12) For the relationship between configuration interaction wave functions and orbital symmetry constraints see: J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Acc. Chem. Res.*, **5**, 402 (1972); J. E. Baldwin in "Pericyclic Reactions", Vol. 2, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York 1977, p 273ff, and reference therein.
(13) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966).
(14) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).
(15) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, **93**, 6145 (1971).
(16) A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., *Org. Synth.*, **53**, 15 (1976).
(17) J. E. Baldwin and G. D. Andrews, *J. Am. Chem. Soc.*, **94**, 1775 (1972).
(18) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Am. Chem. Soc.*, **90**, 4746 (1968); *ibid.*, **91**, 1684 (1969).
(19) J. Thiele, *Justus Liebigs Ann. Chem.*, **271**, 127 (1892).
(20) Unlabeled 1-methylbicyclo[2.1.0]pentane has been synthesized photochemically from 2-methylpenta-1,4-diene: J. Meinwald and G. W. Smith, *J. Am. Chem. Soc.*, **89**, 4923 (1967); R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4932 (1967).
(21) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313 (1965).
(22) Compare P. Gassman and K. T. Mansfield, *Org. Synth.*, **49**, 1 (1969); L. A. Paquette and L. M. Leichter, *J. Org. Chem.*, **39**, 461 (1974).
(23) D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 7931 (1972).
(24) Preliminary report: J. E. Baldwin and J. Ollerenshaw, 166th National Meeting of the American Chemical Society, Chicago, IL, Aug 1973, Organic Abstract 40.
(25) J. E. Baldwin and R. H. Fleming, *J. Am. Chem. Soc.*, **95**, 5249 (1973).

The mole fraction of the *endo*-5-methyl isomer determined with samples heated for 15 half-lives at 171 °C was 0.286; this value was used to calculate ln ($[15]_e - [15]_t$) for the least-squares linear plots of kinetic runs starting with the exo isomer **14**.

Activation Parameters. For bicyclo[2.1.0]pentane and 1-methylbicyclopentane, the skeletal inversion equilibrium constant is 1. The variation in $k_1 = k_{-1}$ as a function of temperature gives identical or nearly identical E_a values for inversion for the two systems. Rate constants for the exo–endo interconversions of 2-methyl- and 5-methylbicyclopentanes may be calculated from the experimental values of $(k_1 + k_{-1})$ and K_{eq}; the derived quantities are given in Table II.

Experimental Errors. While the calculated "probable errors" for E_a values in Table II are small, the real uncertainties in E_a are larger; the standard deviations in the first-order rate constants summarized in Table I imply uncertainties in E_a values of around 2 kcal/mol, and in log A values of about 1.[26]

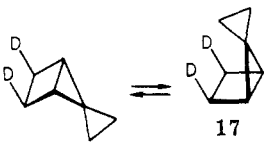
Discussion

Activation parameters and relative rate constants for ring inversions in bicyclo[2.1.0]pentane and the five methyl-substituted bicyclo[2.1.0]pentanes are very similar. The small apparent differences in E_a values suggest that bicyclo[2.1.0]pentane and 1-methylbicyclo[2.1.0]pentane have the same or almost the same activation energy for ring inversion, while the 2-methyl and 5-methyl systems have slightly higher E_a parameters.

The activation parameters for interconverting *cis-exo*- and *cis-endo*-2,3-dideuteriobicyclo[2.1.0]pentane, derived through a kinetic study based on microwave spectroscopic techniques,[27] $E_a = 38.5 \pm 1.4$ kcal/mol and log $A = 14.35 \pm 0.7$, agree within likely experimental uncertainties with the values in Table II.

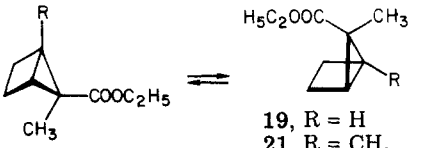
Since 1962, the kinetic data for ring inversion of the 2-methylbicyclo[2.1.0]pentanes[1] have been used together with estimations of heat of reaction for the parent hydrocarbon system (**4** → **5**) to calculate the depth of the local energy minimum corresponding to the planar intermediate: values ranging from 7 to 15 kcal have been deduced.[1,28-34] Using E_a for the reaction **7** ⇄ **8** in place of the value for the skeletal inversion of the 2-methyl isomers reduces the estimated depth of the well to 6–14 kcal. The discrepancy between this range and the energy barrier of 2.3 ± 0.2 kcal estimated experimentally[10] remains to be explained; it must stem from faulty appraisal of ΔH_f for 1,3-cyclopentadiyl.

The difference in activation energy for the parent bicyclopentane isomerization and the spiro system **16** ⇄ **17**, 8.8 kcal/mol, is now in exact agreement with the estimated ring-strain differences.[35,36]



16 **17**

Jorgenson and co-workers[37] used literature data to estimate that methyl in place of hydrogen would stabilize a diradical intermediate by 2.4 to 3.9 kcal/mol. The differences in activation energy for the interconversions **18** ⇄ **19** and **20** ⇄ **21**, 2–3 kcal/mol, were taken as support for this estimation. But in view of the small rate effect brought by methyl at C(1) in **10** ⇄ **11**, it seems likely that ground-state destabilization through steric interactions in **20** and **21** may be the major factor behind the lower E_a value for approach to equilibrium.



18, R = H
20, R = CH_3

19, R = H
21, R = CH_3

While 1-methylbicyclo[2.1.0]pentane appears to be the first C(1) monosubstituted bicyclopentane for which kinetic data on the thermal skeletal inversion have become available, several C(5) monosubstituted systems have been investigated. π donors at C(5), such as methoxy, facilitate the stereomutation dramatically,[38-41] but neither a σ donor such as methyl nor π acceptors such as methoxycarbonyl and cyano have much influence on the barrier to skeletal inversion. Theoretical models for substituent effects account for half of the experimental reality, the rate enhancing effect of π donors at C(5); they do not accommodate the insensitivity of stereomutation rates to π acceptors.[42-48]

Experimental Section

Proton and carbon NMR spectra were obtained with deuteriochloroform solutions on a Varian Associates XL-100-FT spectrometer. Preparative GLC separations were done with a Varian Aerograph 1520, while analytical work was performed on a Perkin-Elmer F-11, using flame-ionization detection and disk integration.

(26) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).
(27) S. N. Mathur and M. D. Harmony, *Anal. Chem.*, **48**, 1509 (1976).
(28) R. B. Turner, "Theoretical Orghanic Chemsitry: Kekulé Symposium", Butterworths, London, 1959, p 67.
(29) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962).
(30) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).
(31) K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 5272 (1966).
(32) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).
(33) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", National Bureau of Standards, Washington, D. C., 1970, p 326.
(34) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinetics*, **2**, 423 (1970).
(35) W. R. Roth and E. Enderer, *Justus Liebigs Ann. Chem.*, **730**, 82 (1969).
(36) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **7**, 397 (1966).
(37) M. J. Jorgenson, T. J. Clark, and J. Corn, *J. Am. Chem. Soc.*, **90**, 7020 (1968).
(38) K. Fellenberger, M. Schöllkopf, C. A. Bahn, and P. von R. Schleyer, *Tetrahedron Lett.*, 359 (1972).
(39) J. J. Tufariello, A. C. Bayer, and J. J. Spadero, Jr., *Tetrahedron Lett.*, 363 (1972); *J. Am. Chem. Soc.*, **101**, 3309 (1979).
(40) J. J. Tufariello and A. C. Bayer, *Tetrahedron Lett.*, 3551 (1972).
(41) J. J. Tufariello, J. H. Chang, and A. C. Bayer, *J. Am. Chem. Soc.*, **101**, 3315 (1979).
(42) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); *J. Am. Chem. Soc.*, **90**, 1475 (1968); *Tetrahedron Lett.*, 2907 (1970).
(43) H. Günther, *Tetrahedron Lett.*, 5173 (1970).
(44) J. C. Barborak, S. Chari, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **93**, 5275 (1971).
(45) R. Hoffmann and W. D. Stohrer, *J. Am. Chem. Soc.*, **93**, 6941 (1971).
(46) R. E. Penn and J. E. Boggs, *J. Chem. Soc., Chem. Commun.*, 666 (1972).
(47) D. B. Chesnut, S. Ferguson, L. D. Smith, and N. A. Porter, *Tetrahedron Lett.*, 3713 (1972).
(48) R. Hoffmann, H. Fujumoto, J. R. Swenson, and C. C. Wan, *J. Am. Chem. Soc.*, **95**, 7644 (1973).

***cis-exo*-2,3-Dideuteriobicyclo[2.1.0]pentane (7).** About 400 mL of an approximately 1% solution of bicyclo[2.1.0]pent-2-ene[16] in tetrahydrofuran was added to 20.0 g (0.118 mol) of potassium azodicarboxylate[19] in an ice bath cooled 1000-mL flask under nitrogen. The mixture was stirred and treated with 14 mL of CH_3COOD added dropwise over a 30-min period at 0 °C. The stirred reaction mixture was maintained at 0 °C another 2.5 h and then allowed to warm to room temperature. Two hours later, GLC analysis on a 3 mm × 5 m βββ TCEP column at 25 °C showed that no bicyclopentene remained. The mixture was filtered and concentrated by distillation, first using a 50-cm Vigreux column and then a 60-cm Teflon spinning-band column; the labeled bicyclopentane 6 (768 mg) was obtained in pure form by preparative GLC on a 6 mm × 5 m βββ TCEP column at 25 °C.

***cis-exo*-2,3-Dideuterio-1-methylbicyclo[2.1.0]pentane (10).** About 200 mL of an approximately 1% solution of methylbicyclo[2.1.0]pentenes[17] in tetrahydrofuran was combined with 5 g (0.03 mol) of potassium azodicarboxylate and then treated with 3.5 mL of CH_3COOD in a procedure analogous to that detailed above. When GLC analysis indicated that reduction by dideuteriodiimide was complete, the reaction mixture was filtered through coarse sintered glass at an aspirator; the filtrate was diluted with ice–water and extracted with pentane; the hydrocarbon phase was washed with 15 20-mL portions of water, and the labeled 1-methylbicyclo[2.1.0]pentane was obtained in pure form by preparative GLC on a 6 mm × 5 m βββ TCEP column, first at 50 °C and for the second and final chromatography at 25 °C.

Two preparations on this scale gave 322 mg of the deuterated product **10**.

***exo*- and *endo*-5-Methylbicyclo[2.1.0]pentane (14 and 15).** 5–Methylcyclopentadiene was prepared by the method of McLean and Haynes.[21] To about 1000 mL of diglyme which had been freshly distilled from sodium was added 82.5 g (1.25 mol) of cyclopentadiene, followed by 28.75 g (1.25 mol) of sodium. The mixture was heated to reflux for 18 h. The resulting purple solution was cooled and added dropwise to 255 g (2.0 mol) of dimethyl sulfate cooled to −10 °C in a 2-L flask equipped with a mechanical stirrer. The reaction mixture was stirred and kept below −10 °C throughout the addition, stirred at −10 °C for another hour after addition was complete, and then stored for 2 h at −20 °C. Distillation from the flask at −10 °C (0.8 mm) gave 8.5 mL of product, which was placed in a 50-mL two-necked round-bottom flask cooled in an ice–salt bath and fitted with an addition funnel containing 15.7 g (0.091 mol) of diethyl azodicarboxylate in 15 mL of ether.[22] The addition was done over a 5-h period with magnetic stirring in a −20 °C cold room. The reaction mixture was placed in a +4 °C cold room overnight and then allowed to warm to room temperature. Solvent was removed at aspirator pressure to leave 21.1 g of a yellow oil. The NMR spectrum of this material (e.g., methyl doublet at δ 0.08, J = 6 Hz) was consistent with anticipations for diethyl 2,3-diaza-7-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**12**).

The Diels–Alder adduct was dissolved in 25 mL of absolute ethanol and hydrogenated over 100 mg of 5% palladium-on-carbon in a Parr bottle. The customary workup led to 20.7 g of yellow oil, shown by NMR to be completely reduced.

Dry nitrogen was bubbled for 20 min through 120 mL of mildly warmed ethylene glycol in a 250-mL three-necked flask fitted with magnetic stirrer, condenser, and thermometer. Potassium hydroxide pellets (27.5 g, 0.042 mol) were added in two portions, and the solution was heated to 125 °C. The diazabicycloheptane derivatives **13** (20.7 g, 0.081 mol) were added quickly; the reaction mixture was stirred for 1 h at 125 °C, allowed to cool, and poured slowly into a mechanically stirred mixture of 100 g each of ice and water and 45 mL of concentrated hydrochloric acid. This hydrolysis mixture was warmed to 40 °C and neutralized with 5 N ammonium hydroxide. Six 6-mL portions of 2 N cupric chloride solution were added with stirring. After each of the six additions, enough 5 N ammonium hydroxide was added to bring the pH to 5–6. The brick-red precipitate was collected by filtration; the filtrate was treated again with cupric chloride and ammonium hydroxide solutions, and a second crop of product was thus obtained. The combined precipitate was washed with 100 mL of 20% aqueous ammonium chloride, 200 mL of 95% ethanol, and 200 mL of water. It was sucked as dry as possible on the funnel, then slurried with 40 mL of water, and treated with a slowly added solution prepared from 6 g of sodium hydroxide and 10 mL of water. The resulting orange-yellow suspension was continuously extracted with pentane for 48 h. The hydrocarbon solution was dried over potassium carbonate; filtration and concentration gave 3.45 g of a brown oil. Another 48-h extraction led to another 40 mg of material. The NMR of the 3.49 g of intermediate was consistent with the 2,3-diaza-7-methylbicyclo-[2.2.1]hept-2-ene structure **13** expected (yield 50.5% from reduced Diels–Alder adduct).

The azo compound (1.41 g) was placed in a 5-mL flask which was fitted with a 20-cm unpacked column connecting directly to a receiver cooled in a dry ice–acetone bath. The flask was kept at 200–220 °C by an oil bath for 9 h, giving 485 mg of colorless liquid in the receiver. Analytical GLC on a 3 mm × 2.4 m ββ ODPN column at 25 °C showed traces (<2%) of 1-methylbicyclopentane and bicyclopentane and two major products. These were collected by preparative GLC on a 6 mm × 5 m βββ TCEP column at 35 °C and identified through proton and carbon NMR spectra as *exo*-(shorter retention time) and *endo*-5-methylbicyclo[2.1.0]pentane in a 3.5:1 ratio.[23]

Kinetics of the gas-phase isomerizations were determined by using a well-seasoned 300-mL round-bottomed glass vessel with a length of 9-mm glass tubing connected through a "greaseless" Teflon stopcock to a vacuum line. The bath design and temperature control system have been described elsewhere.[25] After each run, hydrocarbons were condensed back in the vacuum line and analyzed either by NMR spectroscopy or GLC. The results are summarized in Table I.

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Registry No. **6**, 5164-35-2; **7**, 51794-28-6; **8**, 60426-74-6; **9**, 36112-14-8; **10**, 76847-16-0; **11**, 76898-64-1; **12**, 76847-17-1; **13**, 76847-18-2; **14**, 76898-65-2; **15**, 50338-79-9; 5-methylcyclopentadiene, 96-38-8; diethyl azodicarboxylate, 1972-28-7.

Resonance Energies of π Hydrocarbon Radicals. Radical Reactivities of Polycyclic Aromatic Hydrocarbons[1]

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Resonance energies for π hydrocarbon radicals can be calculated by using the empirical, parameterized, valence-bond method called structure-resonance theory. The calculations are in good agreement with kinetic data which experimentally model the difference in resonance energies between reactants and radical intermediates.

Quantitative aspects of aromatic hydrocarbon reactivities are well-described by structure-resonance theory calculations.[2] A recent example[3] involved kinetic studies of the Diels–Alder reactions of 46 polycyclic benzenoid

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