

prepared by reaction of the glycols with PBr_3 and pyridine. Workup with water- CCl_4 followed by removal of the solvent gave the pure (TLC) dibromides in 50–56% yield.

Nonaethylene Glycol Dibromide. Excess triethylene glycol and triethylene glycol dichloride were reacted in the presence of NaOH according to Krespan.¹⁷ Distillation of the reaction mixture gave crude nonaethylene glycol, bp ca. 240 °C (0.4 mmHg). Treatment of the latter with PBr_3 -pyridine as above, followed by column chromatography on silica gel with AcOEt, gave pure nonaethylene glycol dibromide in 12.7% overall yield.

Pentadecaethylene Glycol Dibromide. Pentadecaethylene glycol was prepared as above from pentaethylene glycol, pentaethylene glycol dibromide, and NaOH. After removal under vacuum of excess pentaethylene glycol, the residue was treated with PBr_3 and pyridine in the usual way. Chromatography of the crude material on alumina with AcOEt-benzene 1:1 followed by AcOEt gave pure (TLC) pentadecaethylene glycol dibromide in 8.3% yield. All the dibromides gave ^1H NMR spectra consistent with the expected structure.

***o*-Hydroxyphenyl ω -Bromopoly(oxaalkyl) Ethers.** The preparation of *o*-hydroxyphenyl 3,6,9,12-tetraoxa-14-bromotetradecyl ether ($1, x = 4$) has been reported in a previous paper.^{9a} The other compounds were prepared in a similar way from the proper poly(ethylene glycol) dibromide, catechol, and KOH in the molar ratio of 1:4:1. Purification of the crude products was carried out by column chromatography. Details of the chromatographic conditions and yields of isolated pure products are as follows: *o*-Hydroxyphenyl 3-oxa-5-bromopentyl ether ($1, x = 1$): silica gel, CHCl_3 , 8% yield. *o*-Hydroxyphenyl 3,6-dioxa-8-bromooctyl ether ($1, x = 2$): silica gel, CHCl_3 -MeOH 49:1, 16% yield. *o*-Hydroxyphenyl 3,6,9-trioxa-11-bromoundecyl ether ($1, x = 3$): silica gel, CHCl_3 -MeOH 49:1, 18% yield. *o*-Hydroxyphenyl 3,6,9,12,15-penta-oxa-17-bromohexadecyl ether ($1, x = 5$): silica gel, benzene-AcOEt 1:1,

20% yield. *o*-Hydroxyphenyl 3,6,9,12,15,18,21,24-octa-oxa-26-bromohexacosyl ether ($1, x = 8$): alumina, benzene-AcOEt 1:3, 31% yield. *o*-Hydroxyphenyl 3,6,9,12,15,18,21,24,27,30,33,36,39,42-tetradeca-oxa-44-bromotetradecyl ether ($1, x = 14$): alumina AcOEt-EtOH 20:1, 16% yield.

All compounds were liquids at room temperature and gave the expected ^1H NMR spectra. Bromine content was -0.5% for compound 1, $x = 14$, and within $\pm 0.3\%$ of theory in the other cases.

Benzo-30-crown-10 ($3, x = 8$) was prepared by cyclization of 1, $x = 8$, in Me_2SO solution in the presence of Me_4NOH . The reaction was run under nitrogen in a 250-mL, three-necked flask charged with Me_2SO (70 mL). The reagents were added separately and simultaneously to the well-stirred solvent, heated at 40 °C, by means of two motor-driven syringes. One syringe was charged with 1 mmol of 1, $x = 8$, in 10 mL of Me_2SO , and the other with 1.1 mmol of Me_4NOH in 10 mL of Me_2SO - H_2O 9:1. When the addition was over (4 h), ice-cold water was added, and the mixture was continuously extracted with diethyl ether for several hours. After removal of the solvent, the residue was freed from a small amount of Me_2SO by distillation under vacuum and then was chromatographed on silica gel with AcOEt-MeOH 25:1 to give the desired product in 81% yield, mp 37–38 °C, from heptane. ^1H NMR was as expected; $M^+ m/e$ 488. Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{O}_{10}$: C, 59.00; H, 8.25. Found: C, 59.61; H, 8.44.

Kinetics. Rate measurements were carried out in 99% Me_2SO by following the disappearance of the phenoxide absorption at 314 nm. The reactions were started by adding by a microsyringe a calculated amount of Me_4NOH stock solution (2×10^{-2} M in 98% Me_2SO) into a 10-mm quartz cuvette containing a very dilute (ca. 1×10^{-4} M) substrate solution in 99% Me_2SO . Clean first-order kinetics were observed up to high conversions. In all cases the infinity spectra showed a residual phenoxide absorption.⁷ Yields of cyclic products in the kinetic runs were calculated as the fraction of phenoxide absorption disappeared in the course of the reaction. The intermolecular model reaction was studied under pseudo-first-order conditions in the presence of a 50- to 200-fold excess of $\text{EtOCH}_2\text{CH}_2\text{Br}$.

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(17) Krespan, C. G. *J. Org. Chem.* 1974, 39, 2351.

Degenerate Thermal Rearrangement of 1,3-Dimethylenecyclopentane. Evidence for Partially Stereospecific Biradical Formation and Closure in a 1,3 Shift¹

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Abstract: Pyrolysis of 1,3-bis(dideuteriomethylene)cyclopentane at 370 °C resulted in a first-order degenerate rearrangement in which the 1,3- and 3,3-shift products were formed in a 2:1 ratio, respectively, indicating the intermediacy of an effectively orthogonal 2,2'-bis(allylmethane) biradical. Pyrolysis of *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentane (T and C) gave 1,3- and 3,3-shift products with stereochemistry consistent with predominant conrotatory-bevel ring opening to produce the orthogonal diradical directly. Pyrolysis of optically active T gave the 1,3-shift products with 20.8% inversion of configuration of the migrating carbon indicative of partial stereospecific closure of the biradical. Comparative pyrolysis of optically active T and its bis(dideuteriomethylene) derivative revealed no secondary kinetic deuterium isotope effect, but an alteration in the extent of racemization of starting material and amounts of 1,3- and 3,3-shift products indicates a product-determining isotope effect. These data provide further evidence for an intermediate.

Because of their simplicity, unimolecular thermal isomerization reactions raise significant questions to experimentalists and theorists. Unaffected by polar solvents and catalysts, these reactions may be among the few in which questions about structure and

energy of transition states and intermediates can be focused solely on the molecule of interest and not solvents etc. Nonetheless there is controversy about the mechanism for these reactions since the Benson diradical hypothesis² and quantum chemical calculation³

(1) This work was reported in preliminary form. Gajewski, J. J.; Salazar, J. *J. Am. Chem. Soc.* 1979, 101, 2739, 2740.

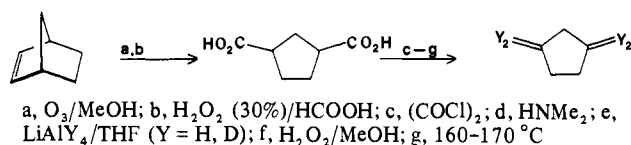
(2) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. For the original paper in the area see: Benson, S. W. *J. Chem. Phys.* 1961, 34, 521.

Table I. Deuterium Distribution of the Products of Pyrolysis of 1,3-Bis(dideuteriomethylene)cyclopentane (DMCP- d_4) at 370.2 °C

reaction time, h	% of exchangeable protium on <i>exo</i> -methylenes ($^1\text{H NMR}$) ^a	<i>m/e</i> 56:58:60	SA- d_0 , SA- d_2 , SA- d_4	% of exchangeable protium on <i>exo</i> -methylenes (mass spectrum) ^b	SA- d_2 /SA- d_4
24.0	13.5	85.3:14.7:7.1	80.1, 13.2, 6.7	13.3	1.97
48.0	22.4	99.8:35.4:16.9	65.6, 23.3, 11.1	22.8	2.10

^a [*exo*-Methylene protium/(*exo*-methylene protium + protium on C-4 and C-5)] \times 100. ^b (SA- d_2 /2 + SA- d_4) \times 100.

Scheme I



often disagree. Furthermore Woodward–Hoffmann⁴ “allowed” stereochemistry is often observed in 1,3 shifts⁵ which are, by the diradical hypothesis, predicted to be nonconcerted processes because of their relatively high activation energies. It is the purpose of this paper to suggest that with modification the diradical hypothesis can serve to accommodate the experimental results in 1,3 shifts of 1,3-dimethylenecyclopentane and possibly those of other 1,3 shifts heretofore presumed to be concerted reactions.

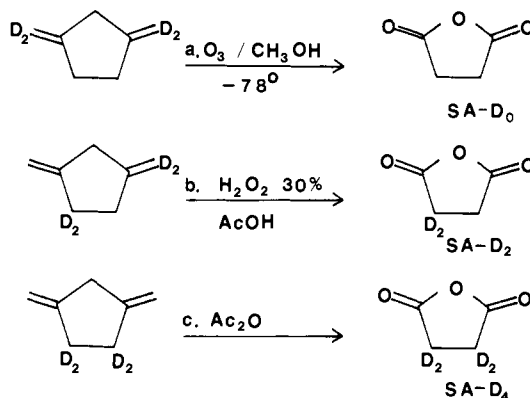
Four separate experiments are described: (1) pyrolysis of 1,3-bis(dideuteriomethylene)cyclopentane which demonstrates that a degenerate thermal rearrangement occurs via 1,3 and 3,3 shifts in a 2:1 relative rate ratio which suggests a biradical intermediate; (2) pyrolysis of *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentane results in different double-bond geometries in the product, suggesting conrotatory ring opening; (3) pyrolysis of optically active *trans*-4,5-dimethyl-1,3-dimethylenecyclopentane which gives 20.8% inverted 1,3-shift product; (4) pyrolysis of protio and bis(dideuteriomethylene) materials under identical conditions results in no kinetic isotope effect but in greater racemization of starting material and less 1,3- and 3,3-shift products from the d_4 material.

Results

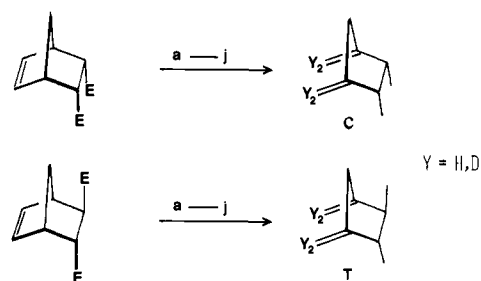
Synthesis and Pyrolysis. The synthetic sequence for the preparation of 1,3-bis(dideuteriomethylene)cyclopentane (DMCP- d_4) is shown in Scheme I. This material was prepared from 1,3-cyclopentanedicarboxylic acid, which was obtained by ozonolysis and further oxidation of norbornene.⁶ This acid was treated with oxalyl chloride and then with dimethylamine to give the corresponding bisamide which was reduced with lithium aluminum deuteride; oxidation of the amine followed by pyrolysis of the amine oxide afforded the olefin, which by NMR analysis had 97.3% tetradeuteration and 2.7% trideuteration assuming that only d_4 and d_3 species were present.

Pyrolysis of DMCP- d_4 . In a 2-L Pyrex vessel pretreated successively with dichlorodimethylsilane and with pyrrolidine, DMCP- d_4 was pyrolyzed in the vapor phase (\sim 3 torr) at 370.2 °C for 24–48 h. The recovered pyrolysate from each run was analyzed by $^1\text{H NMR}$ (220 MHz). Rearrangement was evidenced by the appearance of the vinylic $^1\text{H NMR}$ signals at 4.80 ppm and a decrease in the allylic signal at 2.45 ppm. For determination of the distribution of the deuterium scrambling, the recovered pyrolysate from each run was converted by ozonolysis and further oxidation into a mixture of deuterated and undeuterated succinic acids. This mixture was treated with acetic anhydride giving succinic anhydride (Scheme II), which was analyzed by mass

Scheme II



Scheme III



a, $\text{LiAlH}_4/\text{THF}$; b, MsCl/Py ; c, LiAlH_4 , LiH/THF ; d, TsCl/py ; e, $\text{O}_3/\text{CH}_3\text{OH}$, H_2O_2 (30%)/ HCOOH ; f, $(\text{COCl})_2$; g, $\text{HNMe}_2/\text{ether}$; h, LiAlY_4 (Y = H, D)/ THF ; i, H_2O_2 (30%)/ MeOH ; j, 160–170 °C

spectroscopy (25 eV). The molecular ion in the spectrum of succinic anhydride could not be used for evaluation of its deuterium content because of the propensity for this ion to capture one or two hydrogens (or deuterium). However, the ($M - 44$) ion, i.e., $(\text{CH}_2\text{CH}_2\text{CO})^+$, is suitable for evaluation of the deuterium-labeling extent of this material. Undeuterated succinic anhydride, SA- d_0 , served as standard to correct for a small amount (2%) of hydrogen loss from the ($M - 44$) ion.

In a control experiment in the mass spectral analysis, a 50:50 mol % mixture of SA- d_0 and SA- d_4 was prepared and its mass spectrum examined. No appreciable intermolecular hydrogen (or deuterium) scrambling was found. The products SA- d_0 , SA- d_2 , and SA- d_4 from a number of pyrolyses, at different lengths of time, had the deuterium distribution shown in Table I. Not only are the formal 1,3- and 3,3-shift products formed in a 2:1 ratio but also the data yield a first-order rate constant for approach to equilibrium of $(3.42 \pm 0.06) \times 10^{-6}/\text{s}$ at 370.2 °C [$\ln((A - 0.5)/(0.993 - 0.5)) = -k_{\text{eq}}t$].

Thermal Rearrangement of *cis*- and *trans*-4,5-Dimethyl-1,3-dimethylenecyclopentane (C and T). Synthesis and Pyrolysis. For investigation of the stereochemistry in the ring opening of 1,3-dimethylenecyclopentane, the synthesis and pyrolysis of *cis*- and *trans*-4,5-dimethyl-1,3-dimethylenecyclopentane (C and T) was undertaken.

The synthetic route of these compounds is shown in Scheme III. Diels–Alder products from cyclopentadiene and the appropriate dienophile served as starting materials for the preparation of the intermediate compounds, namely, *endo-cis*- and *trans*-5,6-dimethyl-2-norbornene, by a similar sequence used by H.

(3) For examples see: Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. Horsely, J. A.; Sean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *Ibid.* **1972**, *94*, 279. Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *Ibid.* **1972**, *94*, 638.

(4) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(5) (a) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406. (b) Berson, J. A.; Dervan, P. B.; Malherbe, P.; Jenkins, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5937. (c) Roth, W. R.; Fridrich, A. *Tetrahedron Lett.* **1969**, 2607.

(6) Perry, R. H., Jr. *J. Org. Chem.* **1959**, *24*, 829.

Table II. Experimental^a and Calculated Relative Concentrations in the Pyrolysis^b of T and C at 358.3 °C

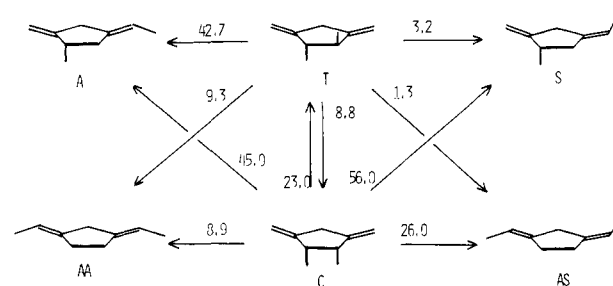
time, s	C		T		S		A		AS		AA	
	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
	T											
21 600	0.015	0.014	0.869	0.873	0.007	0.006	0.087	0.088	0.003	0.000	0.019	0.018
28 800	0.018	0.020	0.829	0.831	0.010	0.010	0.113	0.114	0.004	0.000	0.025	0.025
36 000	0.021	0.022	0.791	0.786	0.013	0.014	0.139	0.141	0.005	0.006	0.030	0.030
43 200	0.024	0.025	0.755	0.754	0.015	0.015	0.163	0.167	0.006	0.006	0.035	0.035
57 600	0.027	0.026	0.688	0.690	0.021	0.020	0.209	0.202	0.009	0.009	0.045	0.052
	C											
18 000	0.751	0.747	0.034	0.034	0.087	0.089	0.072	0.070	0.041	0.041	0.014	0.014
21 600	0.710	0.705	0.039	0.046	0.102	0.099	0.084	0.085	0.047	0.047	0.017	0.017
28 800	0.634	0.643	0.048	0.048	0.129	0.126	0.107	0.105	0.060	0.057	0.021	0.020
36 000	0.565	0.557	0.055	0.054	0.154	0.155	0.128	0.131	0.071	0.073	0.025	0.026
43 200	0.504	0.504	0.061	0.058	0.175	0.181	0.147	0.146	0.081	0.082	0.029	0.028
50 400	0.452	0.452	0.066	0.061	0.195	0.194	0.165	0.159	0.090	0.090	0.033	0.032

^a All analyses have a standard deviation of $\pm 1\%$ or less of the mole fraction provided that the mole fraction is above 0.05. The analysis of starting material has a standard deviation of $\pm 0.3\%$. ^b Each experimental time represents a separate pyrolysis experiment, and each analysis was conducted at least three times by capillary analytical GC under conditions where all compounds were separated to base line and integrated with a VIDAR AUTOLAB electronic integrator. Detector response was assumed to be identical for these isomeric hydrocarbons.

Miller.⁷ Starting with the corresponding *cis* and *trans* diesters, each was treated successively with lithium aluminum hydride, methanesulfonyl chloride, or *p*-toluenesulfonyl chloride in pyridine and then lithium aluminum hydride to give the dimethylnorbornene derivative. These hydrocarbons were ozonized and oxidatively degraded into the respective *cis*- and *trans*-dimethylnorcamphoric acids. Each one of these was treated successively with oxalyl chloride, dimethylamine, lithium aluminum hydride (or deuteride), and hydrogen peroxide. Pyrolysis of the corresponding bis(amine oxide) afforded C and T in ~ 25 –40% yield from the respective norcamphoric acids.

Pyrolysis of samples of GC purified *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentane, >99% pure, were carried out in the vapor phase (~ 2 torr and 100 torr in N_2) at 358–360 °C. T gave primarily *anti*-1-ethylidene-3-methylene-4-methylcyclopentane (A) and *anti,anti*-1,3-diethylidenecyclopentane (AA) along with small amounts of C as well as *syn*-1-ethylidene-3-methylenecyclopentane (S) and *anti,syn*-1,3-diethylidenecyclopentane (AS). On the other hand, C gave roughly equal amounts of A and S along with more AS than AA as well as some T. The product distribution varied slightly with time as indicated in Table II. However, the product stereochemistry from T and C could not be established rigorously. From its NMR AS as the only 1,3-diethylidenecyclopentane without a symmetry element could be assigned with high confidence. The major 1,3-diethylidenecyclopentane isomer from T could be either AA or its *syn,syn* isomer, SS, from the symmetry of its NMR spectrum; however, judging by the dominance of one 1,3-shift product over the other from T and the near equivalence of both 1,3-shift products from C in a pattern so reminiscent of that from the 3,4-dimethyl-1,2-dimethylenecyclobutanes,⁸ we assumed the major 3,3-shift isomer from T to be AA and the major 1,3-shift isomer from T to be A. Indeed, this is the most consistent stereochemical assignment that fits a simple rational pattern given the spectra data. While confirmatory evidence is desirable (low-temperature X-ray crystallography of A was unsuccessful due to randomly oriented molecules in the crystal), the likelihood of incorrect assignment which could negate the conclusions seems remote. It is clear that partial stereospecificity accompanies the reaction and that it fits a previously observed pattern in a similar system⁸ in terms of not only relative amounts but also stereochemistry where it is possible to identify the material, e.g., AS from C and a symmetrical 3,3-shift product from T. In the next most logical scenario of stereochemistries given the data, T would give SS as the major 3,3-shift isomer, implying that the 1,3-shift product is S. While this is a consistent pattern given the data, it requires a sterically unlikely inward conrotation of the methyls relative to the sterically

Scheme IV

First-order rate Constants in units of $10^{-7}/s$ at 358.3 °C

good outward conrotation that gives AA and A as major products (see Discussion).

Pyrolysis of A (separated by VPC) at 358.3 °C for 12 h showed only a slight conversion to other products. These results are consistent with the assumption of irreversibility in the formation of A, S, AA, and AS at low conversion. Because of the slow geometrical isomerization of C and T under the reaction conditions, the rates of disappearance of each isomer are nearly, but not exactly, first order. Therefore, the observed product distribution does not correspond exactly to the true reactivity of a given starting material since part of a given product may arise via the other geometrical isomer. For the rate constants to be obtained for the direct conversions, the differential equations for the kinetic scheme were integrated numerically by the Runge-Kutta method using rate constants that gave calculated concentrations that mimicked the experimental values. Starting in each case from C or T at low conversion, we obtained rough values of the individual rate constants. These values served as input data to calculate the starting material and product distribution as a function of time. The refined values for the ten rate constants that define the system are shown in Scheme IV. Table II gives the experimental and calculated fractions from C and T.

It is necessary to note that each time point represents a separate pyrolytic experiment in a dichlorodimethylsilane treated vessel. The good first-order behavior as indicated by the fit to the data of Table II and the fact that the same conditioning method prevented conversion of ester enols to esters at 370 °C⁹ suggests that the surface of the vessel is "well conditioned". However, the concentration of reactants had to be less than 10 torr or recovery was poor presumably because of bimolecular reactions which were not investigated.

The standard deviation in the analyses of each component was $\pm 1\%$ of the mole fraction if it was greater than 0.05 except with that of starting material where the standard deviation was $\pm 0.3\%$

(7) Miller, H., Ph.D. Dissertation, The Ohio State University, 1959.

(8) Gajewski, J. J.; Shih, C. N. *J. Am. Chem. Soc.* **1969**, *91*, 5900; *Ibid.* **1972**, *94*, 1675; Gajewski, J. J. *Ibid.* **1975**, *97*, 3457.

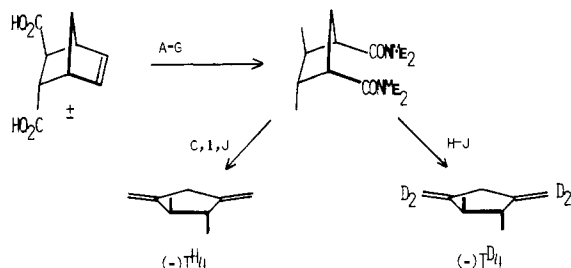
(9) Gajewski, J. J.; Weber, R. J.; Braun, R.; Manion, M. L.; Hymen, B.; *J. Am. Chem. Soc.* **1977**, *99*, 816.

Table III. Experimental^a and Calculated Relative Concentrations in the Pyrolysis^b of T^{H4}, T^{D4}, C^{H4}, and C^{D4} at 360.4 °C for 24 h

	C		T		S		A		AS		AA	
	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
T ^{H4}	0.0245	0.0237	0.5240	0.5239	0.0244	0.0247	0.3140	0.3142	0.0155	0.0157	0.0975	0.0977
T ^{D4}	0.0253	0.0246	0.5365	0.5369	0.0229	0.0233	0.3113	0.3108	0.0140	0.0142	0.0900	0.0900
C ^{H4}	0.2103	0.2119	0.0659	0.0655	0.2739	0.2737	0.2328	0.2325	0.1518	0.1512	0.0652	0.0652
C ^{D4}	0.2252	0.2291	0.0718	0.0718	0.2685	0.2676	0.2305	0.2297	0.1431	0.1410	0.0608	0.0605

^a All analyses have a standard deviation of $\pm 1\%$ or less of the mole fraction provided that the mole fraction is above 0.01. The analysis of starting material has a standard deviation of $\pm 0.3\%$. ^b Each run was conducted at least twice. The analyses are the average values for the runs.

Scheme V



a, cinchonine/acetone, water; b, MeOH/H⁺; c, LiAlH₄; d, TsCl/py; e, O₃/MeOH, H₂O₂/HCOOH; f, (COCl)₂; g, HNMe₂/ether; h, LiAlD₄; i, H₂O₂/MeOH, Pd/C; j, 160–170 °C

and with those of the 3,3-shift products where the standard deviation occasionally rose to $\pm 10\%$.

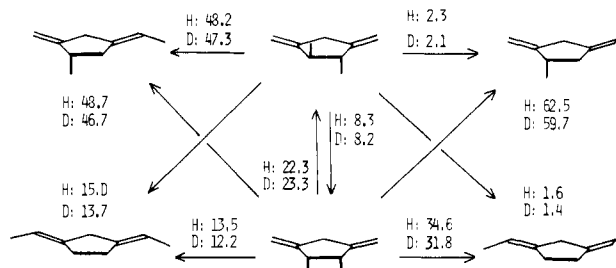
The precision in the derived rate constants is difficult to estimate because of the empirical curve fitting required for the integrations. However, since the reversible geometric isomerization is only a 10% component of this reaction, the errors in the mole fraction determinations probably translate into errors in rate constants as in parallel first-order reactions. Thus the average deviations in calculated and experimental mole fractions of starting material, typically $\pm 5\%$, suggest approximately an error of $\pm 2\%$ in the rate constant for global loss of starting material from T and from C. The error in the individual rate constants is then the accumulation of errors in the global rate constant and the fraction of the total product that the particular product represents. There must be a large error in the smaller rate constants, perhaps as much as 20% with the forming AS and 10% with that forming C and AA from T and 10% in that forming T and AA from C. However, those rate constants for formation of the major products are probably good to $\pm 1-5\%$. Further, in altering rate constants for the best computer fit a change of any rate constant of greater than 3% substantially degraded the fit.

Thermal Rearrangement of (-)-(4R,5R)-trans-4,5-Dimethyl-1,3-dimethylenecyclopentane [(-)-T^{H4}]. For the determination of the configuration of the migrating carbon in the 1,3-shift product, a study of optically active labeled T provides a test of whether the migration occurs with retention or inversion of configuration. The synthesis of optically active T started with the resolution of *trans*-2,3-norbornenedicarboxylic acid;¹⁰ its (+)-enantiomer was converted to (-)-T^{H4} by a route similar to that used in the synthesis of racemic T. Optically active (-)-T^{D4} was prepared from the same sample of the resolved norbornenedicarboxylic acid used in the preparation of the protio compound (Scheme V).

Two samples of optically pure (-)-(4R,5R)-*trans*-4,5-dimethyl-1,3-dimethylenecyclopentane, T^{H4}, were pyrolyzed in the vapor phase at 360.4 °C for 24.00 h in the standard 2-L vessel. Two samples of C^{H4} were also pyrolyzed under the same conditions. The relative concentrations of starting material and products from these runs are given in Table III, and the rate constants were derived as described previously (Scheme VI).

The optical rotations of T^{H4} and of the 1,3-shift product from them after the 24.00-h pyrolyses are given in Table IV where the

Scheme VI



First-order rate constants in units of $10^{-7}/s$ that give the calculated mole fractions of Table III.

Table IV. Absolute Configurations and Rotatory Power of T^{H4act} and T^{D4act} and the 1,3-Shift Products A^{H4act} and A^{D4act}

compd	$[\alpha]_D$, deg	$[\alpha]_{546}$, deg	$[\alpha]_{365}$, deg
Unpyrolyzed			
(-)-(4R,5R)-T ^{H4}	-102.6	-122.4	-381.1
(-)-(4R,5R)-T ^{D4}	-98.9	-118.4	-374.4
After Pyrolysis (24.0 h at 360.4 °C) ^a			
(-)-(4R,5R)-T ^{H4} ^b	-89.3 ± 1.0	-106.4 ± 1.2	-331.1 ± 3.5
(-)-(4R,5R)-T ^{D4} ^b	-82.9 ± 1.0	-100.2 ± 1.0	-310.4 ± 3.0
(+)-A ^{H4} ^c			$+43.1 \pm 1.3$
(+)-A ^{D4} ^c			$+37.0 \pm 1.3$

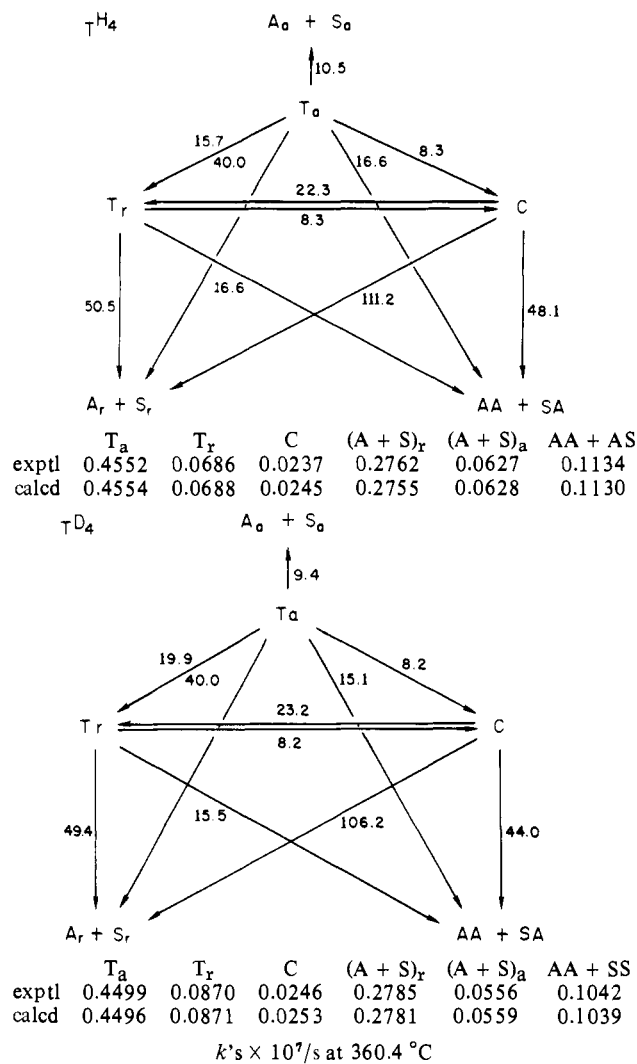
^a Error limits are the average deviation in two separate runs.

^b Correction was made for the presence of the *cis* isomer. ^c 7% of the *S* isomer is an inseparable contaminant.

average of two runs each are reported. To summarize, (-)-T^{H4} racemized to the extent of $13.1 \pm 1\%$ and the preparative *gc* inseparable 93:7 mixture of A and S of $[\alpha]_{365} = +41.1 \pm 1.3$ (CCl₄) was degraded to (-)-(*S*)-2-methylsuccinic anhydride which was 18.5% optically pure. With the assumption that A and S are formed with comparable stereospecificities, the 1,3-shift of T^{H4} occurs with partial inversion of configuration. However, the optical purity of the 1,3-shift product is a minimum value for the inversion since the starting material racemizes to a small extent and since racemic 1,3-shift product is also formed via the *cis* isomer which is also formed to a small extent. The magnitude of the correction for these extra racemizing processes should be small, but a direct calculation of the actual fraction of inversion is possible, recognizing that this fraction is the ratio of the rate constants for formation of inverted 1,3-shift product to the sum of the rate constants for formation of inverted 1,3-shift product and formation of the racemic 1,3-shift product. These rate constants can be determined by the numerical integration approach since the rate constants for reaction of T and for reaction of C under the conditions of the optical activity experiment were determined (Scheme VI). The kinetic scheme that embodies the appropriate transformations is given in Scheme VII where the mole fractions of A and S are combined and then separated into racemic and inverted portions which is known from the optical activity data. It is also convenient to combine the 3,3-shift products since they are of no importance in the question of stereochemistry of the 1,3-shift. The data of Tables III and IV combined and separated as described are given in Scheme VII along with the rate constants that provide the best fit to the data. Most of the rate constants

(10) Pincock, R. E.; Tong, M. M.; Wilson, K. R. *J. Am. Chem. Soc.* 1971, 93, 1669.

Scheme VII



are necessarily those of Scheme VI, the only rate constants that were allowed to vary to obtain a fit were those for conversion of T_a and T_r and those for conversion of T_a and $A_a + S_a$ and $A_r + S_r$. In the latter case the sum of these two rate constants must necessarily be that for conversion of T to $A + S$ of Scheme VI. Examination of the rate constants of Scheme VII reveals that the percent net inversion in the 1,3-shift of $(-)-T^H_4$ is $(10.5/10.5 + 40.0) \times 100 = 20.8\%$ (79.2% racemization).

The editor has expressed concern that the rate constants of Schemes VI and VII deviate in some cases significantly from those of Scheme IV even after a reasonable correction for the $2^\circ C$ temperature difference. Specifically, multiplication of all of the k 's of Scheme IV by 1.15 gives a rate constant for conversion of $T \rightarrow A$ that is only 2% higher than that of Scheme VI but the corrected $T \rightarrow C$ rate constant is 22% higher and that for $T \rightarrow AA$ is 29% lower. The smaller rate constants deviate more significantly: that for $T \rightarrow S$ is 65% higher although that for $T \rightarrow AS$ is only 6% lower. The origin of the differences is not obvious although the relative magnitudes of the differences are in the relative proportions of the rate constants and may simply reflect the experimental error in each rate constant. However, the two data sets (Tables II and III) were taken 1 year apart, and valuable experience in operating the capillary GC and electronic integrator as reflected by lower error limits on the integrations of Table III suggests that the rate constants of Scheme IV have a large systematic error and that the rate constants of Schemes VI and VII are more reliable, and it was these latter rate constants that were used to analyze the optical data which was taken at the same point in time as the data of Table III. Concern that the percent inversion in the 1,3-shift product may be sensitive to errors in the rate

constants led to a recalculation of the fraction of inversion by using Scheme VII and the rate constants of Scheme IV corrected for temperature and by varying the appropriate rate constants as described above to obtain the best fit to the optical data. This gave a calculated percent inversion of 21.2%. However, the fit was not as good as with the rate constants of Scheme VII. The calculated mole fractions of $A_a + S_a$ and $A_r + S_r$ were both 4% higher than the experimental values; the calculated mole fractions of $AA + AS$ were 26% lower (0.084 compared to 0.113). Nonetheless, it does appear to be true that this percent inversion is not very sensitive to changes in the rate constants for conversion of T to C .

Thermal Rearrangement of $(-)-4R,5R$ -*trans*-4,5-Dimethyl-1,3-bis(dideuteriomethylene)cyclopentane $[(-)-T^D_4]$. At the same time that the samples of optically active *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentane were being pyrolyzed, multiple samples of each of the corresponding bis(dideuteriomethylene) isomers $(-)-T^D_4$ (of the same optical purity as $(-)-T^H_4$) and C^D_4 were pyrolyzed in the same vessel for 24.00 h at $360.4^\circ C$. The data are included in Tables III and IV, and the derived rate constants are given in Schemes VI and VII. The percent net inversion from $(-)-T^D_4$ is $(9.4/9.4 + 40.0) \times 100 = 19.0\%$ (81% racemization) and T^D_4 racemized to the extent of $16.2 \pm 1.0\%$. The error limits for the rate constants of Schemes VI and VII are again difficult to estimate, but examination of the mole fraction data for T^H_4 and T^D_4 indicates differences outside of experimental error which suggests that kinetic isotope effects are responsible for the differences.

Absolute Configurations and Optical Purities. $(-)-4,5$ -Dimethyl-1,3-dimethylenecyclopentane $(-)-T$, was prepared from $(+)-trans$ -2,3-norbornene-5-dicarboxylic acid whose optical rotation was the same as the highest reported rotation,¹⁰ and the two resolutions used different resolving agents. This suggests that the diacid was optically pure. Further confirmation comes from degradation of $(-)-T$ to $(+)-2,3$ -dimethylsuccinic anhydride whose rotation was identical with the highest reported rotation which was obtained by two different resolving agents.¹¹ Further, $(+)-2,3$ -dimethylsuccinic anhydride has been converted to $(+)-(R)$ -2-methyl-2-butanol,^{11c} establishing that $(-)-T$ is the $4R,5R$ enantiomer as indicated in Schemes V and VI.

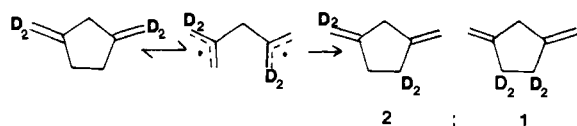
The absolute configuration of the 1,3-shift product, A (93%) and S (7%), $[\alpha]_{365} = +41.1^\circ$ (CCl_4), was determined by degradation to $(-)-(S)$ -2-methylsuccinic anhydride $[\alpha]_D = -6.1^\circ$ (EtOH). The absolute configuration of $(+)-2$ -methylsuccinic acid was determined by conversion to $(+)-(R)$ -2-methyl-1-butanol.^{11d} In that sequence $(+)-2$ -methylsuccinic acid, $[\alpha]_D = +13.11^\circ$ (EtOH), was converted $(+)-2$ -methyl-1,4-butanol which was 76.7% optically pure. With use of Berner and Leonardsen's data,^{11a} optically pure $(-)-(S)$ -2-methylsuccinic anhydride has $[\alpha]_D = -32.97^\circ$ (EtOH).

Discussion

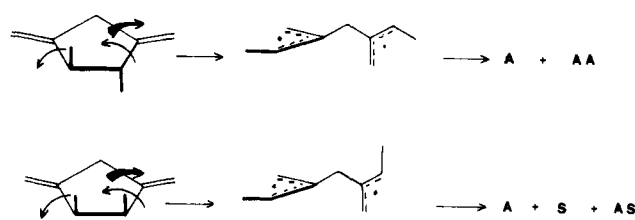
1,3-Bis(dideuteriomethylene)cyclopentane. The data of Table I clearly indicate a reversible first-order equilibration of C-4,C-5 ring and exomethylene hydrogens in 1,3-dimethylenecyclopentane at low pressure in the gas phase at $370^\circ C$. That this equilibration involves carbon shifts and not hydrogen shifts follows from degradation to succinic acid having only even numbers of deuteria. Reversible hydrogen-deuterium shifts should also have given succinic- d_1 and $-d_3$ acids. The degradations also indicate that a simple 3,3 shift (Cope rearrangement) is not solely involved nor is a 1,3 shift solely responsible for the equilibration. Indeed the most economical interpretation of the data would have C-4,C-5 ring opening to an effectively orthogonal 2,2'-bis(allylmethane) biradical which may reclose with equivalent rates in four different ways producing twice as much formal 1,3-shift product as 3,3-shift product due to statistics (Scheme VII). There is potential for an isotope effect here as is clear from subsequent work, but the

(11) (a) Berner, E.; Leonardsen, R. *Justus Liebigs Ann. Chem.* **1939**, 538, 1. (b) Carnmalm, B. *Arkiv. Kemi* **1960**, 215. (c) Jonsson, E. *Acta Chem. Scand.* **1965**, 19, 2247. (d) Rossi, R.; Diversi, P.; Ingrosso, G. *Gazz. Chim. Ital.* **1968**, 1391. Naps, M.; Jones, I. B. *J. Am. Chem. Soc.* **1940**, 62, 2450.

Scheme VIII



Scheme IX



limited precision of the mass spectral analyses precludes its observation.

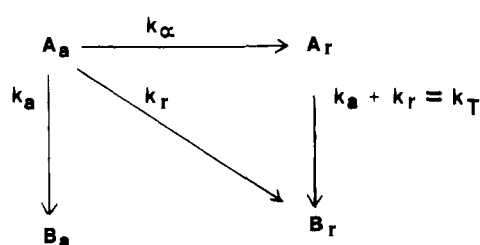
It is significant that the rate constant for equilibration indicates a ΔG^\ddagger of ~ 55 kcal/mol which is equal to or higher than the anticipated ΔG for cleavage of the C-4,C-5 bond. With use of 1,5-hexadiene for a starting point, the ΔG^\ddagger for its cleavage to two allyl radicals is 56 kcal/mol at 370 °C,¹² and with DMCP this value should be less due to relief of up to 5 kcal/mol of ring strain, assuming noninteracting biradicals. Thus, the proposed biradical intermediate of Scheme VIII is not inconsistent with the energetic demands of the reaction.

Stereochemistry of Ring Opening. Pyrolysis of *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentane, T and C, respectively, lead to different relative amounts of the stereoisomers of the 1,3- and 3,3-shift products. Moreover, T and C slowly interconvert under the reaction conditions. For determination of the stereospecificity in the reaction, the rate constants for all interconversions are required. Scheme IV is the simplest array of first-order interconversions which could satisfy the observations, and indeed numerical integration of the differential equations appropriate to this scheme allowed determination of rate constants that mimicked the experimental mole fraction of products from both T and C over roughly the first half-life. Despite the fact that ten rate constants are being determined, the irreversibility of almost all the reactions and the fact that both equilibrating compounds are examined separately strongly suggest that the rate constants are unique.

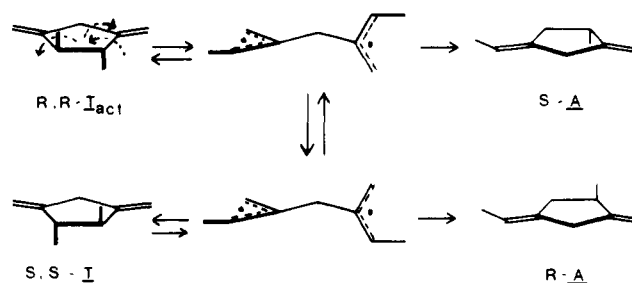
The rate constants of Scheme IV reveal that conrotatory ring opening of both T and C occurs. Judging by the rate constants to the 3,3-shift products, AA and AS, the preference for *con* over *dis* from T is 7.2 and 2.9 from C. Judging by the 1,3-shift products from T, the preference is 13.3. Just as in the case of 1,2-dimethylenecyclobutane, DMCB,⁸ conrotatory opening leads to stereochemistry distinct 2,2'-bis(methyl)methane biradicals from T and C, and closure of these with preservation of the stereochemistry of the allyl radicals can accommodate the product distribution: T should give AA and A and C should give AS, A, and S (Scheme IX). The less than complete stereospecificity probably results from incursion of some disrotatory ring opening and not isomerization about allyl radicals.

The fact that the reactions are partially stereospecific is remarkable and suggests that partially stereospecific formation of 1,5-biradicals like that of 1,4-biradicals⁸ should become a tenet of the biradical hypothesis. Further suggestion for the intermediacy of biradicals is provided in a subsequent section. Again as in the pyrolysis of DMCB a suggestion as to the origin of this phenomena arises from comparison of the overall rates of reaction of T and C. C reacts roughly twice as fast as T despite the preference for conrotation which should have resulted in a substantially slower rate of reaction of C relative to T is the ring

Scheme X



Scheme XI



opening led to planar biradicals since a methyl in C would be forced to turn inward into the molecular system.¹⁴ Apparently there is twisting about the C-1,C-2 and C-2,C-3 bonds to relieve this potential destabilizing interaction. These motions, termed conrotatory bevel in the case of DMCB,⁸ are depicted in Scheme IX.

It would appear that the origin of this specificity is steric. Moreover, if there is anything to the notion that bond cleavage should be a process of minimal destruction of overlap along the path to the biradical intermediate, the motions observed mesh with this idea.^{14,15} There may be some electronic reason for the conrotatory-bevel opening,¹⁴ but it would have to be a second-order effect due to the methylene "insulator" between the two developing allyl radicals.

Stereochemistry of Ring Closure. For detection of stereospecificity in the ring closure of the biradical, optically active T was prepared and pyrolyzed for 1 half-life. Under the reaction conditions T was racemized to the extent of 13.1% and the 1,3-shift products were formed with 18.5% net inversion. After determination of the rate constants as indicated in Scheme VII, the preference for inversion over racemization of the migrating carbon in the 1,3 shift is 20.8%.

As an aside here, the question of the effective optical purity of a racemizing starting material in the determination of the stereospecificity of a reaction is an old one in chemistry, and there are a number of schemes to make the calculation.¹⁶ None of them apparently recognize that the question of stereospecificity is the question of the rate constant ratio $k_a/(k_a + k_r)$ where k_a is the rate constant to optically pure product and k_r is the rate constant for formation of racemic product. The ratio can be determined easily and rigorously from experimental data at a single point by the equation: fraction stereospecificity, $k_a/(k_a + k_r) = (1 + k_a/k_T)B_a/(1 - A_a)$ where the terms are defined in Scheme X. The derivation follows easily from the definitions and the integrated rate expressions. However, this equation cannot be rigorously applied to the dimethyl-1,3-dimethylenecyclopentanes since the racemic material is also being formed to a small extent from another isomer, namely, C; therefore, the numerical integration approach was used as described in the results section.

That the 1,3-shift products from T are formed with partial inversion suggests that the diradical formed from T by conrota-

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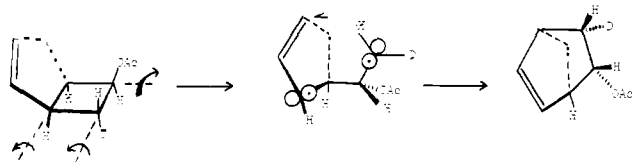
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(14) Criegee, R.; Seebach, D.; Winter, R. E.; Borretzen, B.; Brune, H. A. *Chem. Ber.* **1965**, *98*, 2339.

(15) Gajewski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 5254.

(16) For leading references see: Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705.

Scheme XII



tory-bevel motions closes by a least motion path competitive with the rotations that racemize the intermediate (Scheme XI).

The overall 1,3-shift pathway described occurs with suprafacial inversion stereochemistry, the Woodward-Hoffmann "allowed" pathway, although on the basis of just the stereochemical relationship between (-)-T and (+)-A the reaction could also be of overall antarafacial inversion stereochemistry. The crucial point though is that all the data are consistent with a biradical being formed with partial stereospecificity and closing with partial stereospecificity in a 1,3 shift, giving stereochemistry that could be interpreted as resulting from a W-H allowed concerted path. Further evidence for a biradical intermediate is discussed below.

Evidence for Biradicals. Besides the fact that 1,3-bis(di-deuteriomethylene)cyclopentane gives a 2:1 ratio of 1,3- and 3,3-shift products which is consistent with a random or orthogonal 2,2'-bis(allylmethane) biradical (Scheme VIII), other evidence for a biradical intermediate is suggested by comparison of the pyrolyses of (-)-T^{H₄} and (-)-T^{D₄}.

The data of Scheme VII reveal that the overall loss of (-)-T^{H₄} and (-)-T^{D₄} is within experimental error of one another (0.98 ± 0.03) but that (-)-T^{D₄} racemizes to a greater extent than (-)-T^{H₄} at the expense of the 1,3- and 3,3-shift products by a substantial factor (28 ± 16% increases in racemization of T^{D₄}). Moreover, even the 1,3-shift product from (-)-T^{D₄} is racemized to a greater extent than that from (-)-T^{H₄} by 10%, assuming no isotope effect on the maximum rotation of the product relative to protio material.

The indication that there is little or no kinetic isotope effect but a substantial isotope effect in the product distribution suggests that there is an intermediate in the reaction. Indeed the direction of the product determining IE is identical with that observed by Dolbier and ourselves in allyl radical ring closure reactions.¹⁷

Comparison to Other 1,3 Shifts. The thermal degenerate rearrangement of 1,3-dimethylenecyclopentane (DMCP), most closely resembles that of 1,2-dimethylenecyclobutane (DMCB) with one important difference: the 1,3-shift product from *trans*-4,5-dimethyl-1,3-dimethylenecyclopentane is partially inverted while that from *trans*-3,4-dimethyl-1,3-dimethylenecyclobutane is totally racemized. This difference can be rationalized nicely by the biradical hypothesis. If both materials ring open to an orthogonal chiral biradical, ring closure of the 1,4-biradical from the DMCB derivative should be slower than closure of the 1,5-biradical from the DMCP derivative. Apparently, ring closure in the 1,5-biradical competes effectively with rotation about central bonds which racemize the intermediate, but ring closure of the 1,4-biradical is substantially slower than central bond rotation.

The overall stereochemistry of the nonconcerted DMCP rearrangement is similar to that observed in a number of other 1,3-shifts which have been interpreted in terms of a concerted or parallel concerted reaction(s).⁵ This is not to say that the previously studied rearrangements are not concerted but that the biradical hypothesis, modified as indicated above, can also rationalize the data where the reactions are of the vinylcyclobutane type such that the intermediate biradical cyclizes to a larger ring. For example, the classic Berson-Nelson demonstration of suprafacial conversion stereochemistry in the rearrangement of bicyclo[3.2.0]hept-2-enes to bicyclo[2.2.1]hept-5-enes^{5a} might proceed by conrotatory-bevel ring opening to a biradical which

by least motion closure gives the observed stereochemistry (Scheme XII). The same interpretation can rationalize observations in similar systems.¹⁹

A second case where parallel concerted reactions have been invoked to explain the stereochemistry of a 1,3 shift is the conversion of *trans*-1,2-divinylcyclobutane to 4-vinylcyclohexene.^{5b} The elegant work of Berson and Dervan clearly rules out a randomized biradical intermediate but requires that a suprafacial retention pathway compete with a Woodward-Hoffmann "allowed" suprafacial inversion pathway. Concert in the former pathway has been attributed to subjacent orbital control.²⁰ However, the stereochemistry can be rationalized by a nonrandomized biradical formed via a conrotatory-bevel path which closes to 1,3-shift products via the least motion path a and near least motion path b competitive with bond rotation (Scheme XIII). Again it is important to emphasize that the data cannot be uniquely interpreted in terms of concerted or nonconcerted-nonrandomized biradical paths. The distinction between these two mechanistic alternatives is subtle but not meaningless. Experiments of the sort described for the DMCP rearrangement inspired by Dolbier¹⁷ can implicate a nonconcerted pathway.

A final example for a vinylcyclobutane rearrangement that occurs with suprafacial inversion stereochemistry is one in which a three-membered ring is generated in the closure, namely, the isomerization of bicyclo[2.1.1]hexene to bicyclo[3.1.0]hex-2-ene.^{5c} Again conrotatory-bevel ring opening to biradical followed by rapid least motion closure might give the observed product (Scheme XIV). It should be noted that there is developing evidence that closure of 1,3-biradicals is fast compared with bond rotation.²¹

Experimental Section

General Data. NMR spectra were recorded on Varian HR-220, EM-360, and T-60 spectrometers, and the chemical shifts were reported in parts per million downfield from tetramethylsilane. Infrared spectra were determined on a Perkin-Elmer 437 infrared spectrometer. High-resolution mass spectral analyses were made with an AEI Model MS-9. Low-resolution mass spectra were recorded with a Varian-MAT CH7. All melting points are uncorrected. Purification and separation of mixtures were accomplished on a Varian Aerograph Model A-90-P3 gas chromatograph, equipped with a thermal conductivity detector and helium as carrier gas, using the indicated columns. Quantitative analysis of mixtures was effected with a Varian Aerograph Model 1220-2 gas chromatograph with a flame ionization detector, using a 200 ft capillary DBTCP column. Relative areas were determined with a Vidar autolab integrator. Optical rotations were determined on a Rudolph Research Model 26202 automatic polarimeter. Rotations were obtained in a one decimeter tube on solutions in spectrograde solvents. Each rotation was measured five times for each solution, and the rotations reported for each compound are an average of these readings. Most reagent grade chemicals were used without further purification.

Vapor-Phase Pyrolyses. Apparatus. The pyrolysis reactor was a 2-L Pyrex round-bottomed flask conditioned with dimethylchlorosilane and then treated with diethylamine. The flask was immersed in a molten potassium nitrate/sodium nitrate (10:7) bath and heated by a 500-W Vycor immersion heater, and the temperature control was accomplished with a Bayley Controller Model 76-8 in connection with a 125-W stainless-steel knife type heater. The temperature was measured with a copper-constant thermocouple, and readout was performed with a Leeds and Northrup type K-3 potentiometer and a galvanometer. The vertical temperature gradient across the flask was approximately 0.5 °C, and the temperature reported was taken at the midpoint of the reactor, and this temperature was constant to ±0.1 °C.

Syntheses. *cis*-1,3-Cyclopentanedicarboxylic Acid. This acid was prepared by the method of Perry and was the general procedure used for other norbornene derivatives.⁷ A 20-g (0.21 mol) sample of norbornene in 250 mL of anhydrous methanol, in a 500-mL round-bottomed flask equipped with a fritted-glass inlet tube, was ozonized (ozone was generated by a Welsback Model T-408 Ozonator, operating at 110 V, 8 psi in dioxygen, and 0.72 mmol/min). A light blue color was indicative of the end point. The solvent was subsequently removed in vacuo leaving

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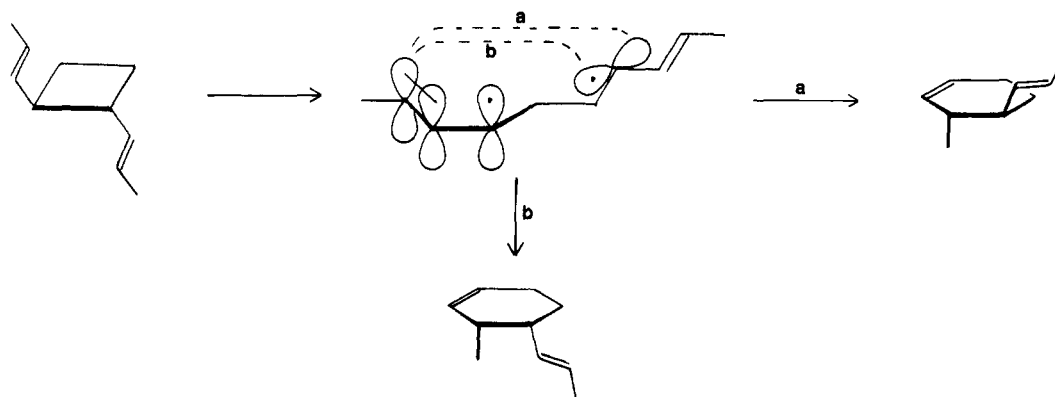
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(19) Hasselmann, D. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 257.

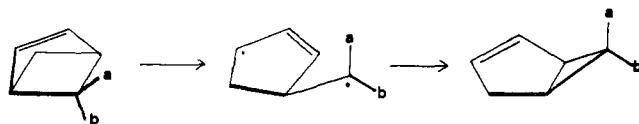
(20) Berson, J. A.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 8917.

(21) (a) Berson, J. A.; Willcott, M. R. *J. Am. Chem. Soc.* **1965**, *87*, 2571, 2756; **1966**, *88*, 2494. (b) Klärner, F.-G.; Brassel, B. *Ibid.* **1980**, *102*, 2439 and references contained therein.

Scheme XIII



Scheme XIV



a syrup as the nonvolatile product. This material was dissolved in 175 mL of 90% formic acid and 77.4 mL of 30% hydrogen peroxide. The solution was warmed to 55 °C, and a strongly exothermic reaction ensued causing refluxing. Excess of peroxide was destroyed by heating at 70 °C for 6 h. The solution was evaporated to dryness leaving a white solid which was recrystallized from water, giving 24 g (70%) of diacid: mp 116–119 °C (lit.⁷ 120–121 °C); IR (KBr) 3–4 (br), 5.8 (s), 10.5 (s) μm ; NMR (60 MHz, D_2O) δ 2.00–2.20 (m, 6 H), 3.0 (m, 2 H), 4.9 (HDO).

1,3-Bis(methylene)cyclopentane (DMCP). To 9.0 g (58 mmol) of *cis*-1,3-cyclopentanedicarboxylic acid, mp 116–119 °C,⁶ was added dropwise 22.0 g (173 mmol) of oxalyl chloride. The reaction mixture was stirred overnight at room temperature, and the excess of oxalyl chloride was removed in vacuo, giving 9.5 g of a pale brown liquid. A 9.0-g sample of this liquid was dissolved in 30 mL of anhydrous ether, and this solution was added dropwise to a solution of 25 mL of anhydrous dimethylamine in 100 mL of ether at 0 °C and was stirred at 0 °C overnight. The mixture was filtered and the solid washed with boiling ethyl acetate. Removal of the solvent in vacuo afforded 8.8 g of a pale yellow solid which was recrystallized from ethyl acetate; mp 72–74 °C. An 8.0-g portion of this solid was dissolved in 30 mL of dry THF, and this mixture was added dropwise to 2.9 g (75 mmol) of lithium aluminum hydride in 60 mL of THF. The gray mixture was refluxed and stirred for 24 h, then cooled at 0 °C, and hydrolyzed with a freshly prepared saturated aqueous solution of sodium sulfate. The solvent was removed in vacuo, giving 5.5 g of a pale yellow liquid. A 5.0-g portion of this liquid was dissolved in 10 mL of methanol, and to this solution was added dropwise 34.5 mL of 30% hydrogen peroxide. The mixture was stirred until a negative phenolphthalein test was obtained. The excess of peroxide was destroyed by addition of a small amount of 10% Pd on charcoal until the reaction mixture gave a negative test to a KI solution. The mixture was filtered and the solvent evaporated in vacuo at 50 °C, affording 4.0 g of a very viscous liquid, which was placed in a flask fitted with a short vigreux column and a collector tube immersed in a dry ice/acetone bath. The flask was heated at 110–120 °C and the system evacuated at ca. 10 torr; when the content of the flask was resolidified, the temperature was raised to 160–170 °C and maintained constant within this range during the pyrolysis. The organic layer from the pyrolysate was separated and washed with water and 5% HCl, giving 1.8 g of a pale yellow liquid. Separation of purification by preparative gas chromatography (25 ft \times 0.25 in, 25% LAC/benzene, 80 °C) afforded 1.5 g (60%) of diolefin: NMR (220 MHz, CCl_4) δ 2.45 (sharp s, 4 H), 3.00 (br s, 2 H), 4.77–4.81 (nearly equivalent, $J = 6$ Hz, 4 H); IR (neat) 3.2 (m), 6.0 (s), 11.4 (s) μm ; mass spectrum, m/e (M^+) 94.

1,3-Bis(dideuteriomethylene)cyclopentane (DMCP- d_4). This compound was prepared by a procedure similar to that used for DMCP, except that lithium aluminum deuteride (Merck Sharp and Dome) was the reducing agent (NMR showed no olefin proton signal at high signal amplitude): NMR (220 MHz, CCl_4) δ 2.45 (sharp s, 4 H), 3.00 (sharp s, 2 H); IR (neat) 4.3 (m), 4.5 (w), 14.2 (s) μm ; mass spectrum, m/e (M^+) 98.

Succinic- d_4 Anhydride (SA- d_4). Succinic- d_4 anhydride was prepared according to a procedure by A. T. Blomquist.²² A 3.3-g (50-mmol)

sample of potassium hydroxide and 7.6 g (50 mmol) of monopotassium acetylenedicarboxylate (Aldrich Chemical Co.) were dissolved in 30 mL of water. The solution was allowed to evaporate at room temperature for 2 days. The residue was washed with acetone and dried in vacuo over P_2O_5 for 36 h. The salt was crushed and dried in vacuo at 100 °C for 1 day, yielding 8 g of a white solid. A 0.9-g portion of this solid dissolved in 4 mL of D_2O was added dropwise to 25 g of freshly prepared 2% sodium amalgam. The reaction mixture was stirred for 1 h, giving a suspension which was separated from the mercury. Addition of 2 mL of D_2O dissolved the solid in suspension; then 3.5 mL of 48% of solution hydrobromic acid was added in one portion and the solution stirred for ~ 10 min. Following, the solution was evaporated to dryness and the solid continuously extracted with ether for 36 h. Removal of solvent afforded a white solid which was treated with 1.5 mL of acetic anhydride at 50 °C for 1 h. Evaporation of the solution to dryness in vacuo and sublimation (90 °C, 2 torr) of the residue afforded 200 mg of colorless crystals: mp 118–120 °C; mass spectrum, m/e 59 and 60 (6.5% d_3 and 93.5% d_4).

Degradation of DMCP to Succinic Anhydride. This oxidative degradation was carried out by a procedure similar to that used in the preparation of norcamphoric acid,⁶ except that ethyl acetate and acetic acid were the solvents. A typical procedure is described. After ozonolysis of DMCP followed by decomposition of the ozonide, the crude diacid was treated with 1 mL of acetic anhydride and this mixture heated at 60 °C for 2 h. The solvent evaporated and the crude product was sublimed at 80–90 °C (2 torr). The IR and NMR spectrum of this material were identical with those for commercial succinic anhydride: mp 115–117 °C; IR (KBr) 5.35 (m), 5.60 (s), 9.50 (s) μm ; mass spectrum, m/e (relative intensity) 56 (77.80), 28 (100.00).

Control Experiment. An equal mixture of succinic- d_0 and - d_3 acids was treated with acetic anhydride, and the resulting mixture, after purification by sublimation, was analyzed by mass spectrometry. The mass spectrum of this mixture was examined in the region of m/e 55–61, indicating that appreciable scrambling of hydrogen or deuterium between the anhydrides had not occurred: succinic- d_0 anhydride, m/e (relative intensity) 55 (1.82), 56 (85.30), 57 (2.80); succinic- d_4 anhydride, m/e (relative intensity) 59 (7.69), 60 (100.00), 61 (3.15); equimolar mixture of SA- d_0 and SA- d_4 , m/e (relative intensity) 55 (0.51), 56 (96.69), 59 (7.17), 60 (90.18), 61 (2.12).

Pyrolysis of 1,3-Bis(dideuteriomethylene)cyclopentane (exo-DMCP- d_4) at 370.2 °C. In a typical vapor-phase pyrolysis, 30–40 μL of the diolefin was transferred into an evacuated 2-L well-conditioned bulb. After pyrolysis for the stated time intervals, the pyrolysate was collected by evacuating the system through a spiral trap cooled with liquid nitrogen, and then the pyrolysate was vacuum transferred to a collection tube. The recovered pyrolysate was diluted in 500 μL of ethyl acetate or anhydrous methanol and ozonized at -78 °C until a light blue color persisted (~ 10 min). Excess of ozone was removed by bubbling dry nitrogen through the solution. Removal of solvent left a slurry, which was treated with 500 μL of acetic acid and 450 μL of 30% hydrogen peroxide. This mixture was heated at 60–70 °C for 12 h. After evaporation of solvent to dryness, a white solid was obtained; this material was treated with 500 μL of redistilled acetic anhydride and heated at 60 °C for 2 h. Removal of solvent left a solid which was sublimed at 80–90 °C (2 torr). This sublimed material was subjected to mass spectral analysis (Varian MAT. CH-7, 25 eV). Mass spectra in the $M - 44$ region for several runs revealed a succinic- d_2 -/ d_4 anhydride ratio of $\sim 2:1$. The results at dif-

(22) Blomquist, A. T.; Hiscock, B. F.; Harpp, D. N. *J. Org. Chem.* **1966**, *31*, 4121.

ferent time intervals and the comparison with their ^1H NMR analyses are given in Table I.

endo-cis-5,6-Dimethyl-2-norbornene. This compound was prepared by a similar procedure by H. Miller,⁷ except that a different LiH/LiAlH₄ ratio was used as the reducing mixture. To 15.0 g (390 mmol) of lithium aluminum hydride in 250 mL of dry THF was added dropwise a solution of 40.0 g (250 mmol) of *endo-cis*-5-norbornene-2,3-dicarboxylic anhydride. After refluxing with stirring for 48 h and normal workup, 28 g (76%) of a white solid was obtained. A 12.0-g portion of this solid was dissolved in 50 mL of pyridine and cooled at 0 °C. To this cooled solution was added in several portions 33 g of TscI. Normal workup afforded 30 g of a white fine solid, mp 100–102 °C (lit. 103–104 °C). The white solid was dissolved in 250 mL of dry THF, and the mixture added dropwise to a suspension of 6.0 g (158 mmol) of LiAlH₄ and 1.9 g (237 mmol) of LiH in 100 mL of THF. The reaction mixture was stirred and refluxed for 30 h, and after workup 4.0 g (50%) of the hydrocarbon was obtained in ~95% purity by VPC: NMR (60 MHz, CCl₄) δ 6.10 (s, 2 H), 2.60 (s, 2 H), 2.10 (apparent q, 2 H), 1.30 (apparent d, 2 H), 0.75 (d, $J = 6$ Hz, 6 H); IR (neat) 3.27 (s), 6.75 (s), 14.0 (s) μm .

cis-4,5-Dimethyl-1,3-dimethylenecyclopentane (C). Ozonolysis of 7.0 g (57 mmol) of *cis-endo*-4,5-dimethyl-2-norbornene, using the equipment and techniques described for the preparation of *cis*-1,3-cyclopentanedicarboxylic acid,⁶ afforded 4.5 g (42%) of the corresponding diacid. A 3.7-g portion of diacid when treated with 10.1 g (79 mmol) of oxalyl chloride and worked up gave 4.0 g of pale brown oily liquid, which was dissolved in 30 mL of anhydrous ether and added dropwise to a solution of 15 mL of dimethylamine in 30 mL of anhydrous ether. Following the corresponding workup the diamide was obtained in 64% yield. Reduction of the diamide followed by oxidation and pyrolysis of the corresponding amine oxide gave 800 mg (23%) of C after purification by VPC (6 ft \times 0.25 in., 20% DBTCP, 110 °C): NMR (220 MHz, CCl₄) δ 4.75 (s, 4 H), 3.00 (s, 2 H), 2.54 (complex m, 2 H), 0.90 (d, $J = 6$ Hz, 6 H); IR (neat) 3.25 (m), 6.04 (s), 11.42 (vs) μm ; mass spectrum, m/e calcd 122.1090, found 122.1086.

cis-4,5-Dimethyl-1,3-bis(dideuteriomethylene)cyclopentane (C^{D4}). This compound was synthesized by a procedure similar to that used for C, except that lithium aluminum deuteride was the reducing agent: NMR (220 MHz, CCl₄) δ 3.00 (s, 2 H), 2.54 (complex m, 2 H), 0.90 (d, $J = 6$ Hz, 6 H); IR (neat) 3.35–3.50 (s), 4.30 (m), 4.50 (w), 6.20 (s), 13.00 (s), 14.00 (s)- μm ; mass spectrum, m/e calcd 126.1346, found 126.1343.

rac-trans-5,6-Dimethyl-2-norbornene. This compound was prepared according to a method by Mehta and Pandey.²³ To 7.5 g of *trans*-5-norbornene-2,3-dimethanol (obtained from the reduction of the corresponding dimethyl ester) was added 16.7 mL (144 mmol) of mesyl chloride dropwise, maintaining the reaction mixture at 0 °C and stirring for 8 h; then the mixture was poured into ice/water and extracted with CH₂Cl₂ (2 \times 100 mL). The extract was washed successively with 5% HCl (3 \times 100 mL), 5% sodium bicarbonate (2 \times 100 mL), and brine. After workup 13.0 g (88%) of a pale yellow solid was obtained; mp 62–65 °C. The mesylate was reduced by a LiH/LiAlH₄ reducing mixture in a 1:3:3 ratio in THF, giving 2.7 g (57%) of the hydrocarbon: NMR (220 MHz, CCl₄) δ 6.09 (asymmetrical q, $J = 3$ Hz, 1 H), 5.82 (asymmetrical q, $J = 3$ Hz, 1 H), 2.52 (s, 1 H), 2.27 (s, 1 H), 1.36–1.47 (m, 2 H), 1.02 (d, $J = 6$ Hz, 3 H), 0.80 (d, $J = 6$ Hz, 6 H).

rac-trans-4,5-Dimethyl-1,3-dimethylenecyclopentane (T). This olefin was prepared by a procedure similar to that used in the synthesis of C. Starting with 2.2 g of the corresponding diacid derived from the ozonolysis of *rac-trans*-5,6-dimethyl-2-norbornene, the olefin was obtained in a (24%) (350 mg) overall yield from the diacid. Purification was carried out in the same conditions as those for C: NMR (220 MHz, CCl₄) δ 4.77 (singlet, 4 H), 3.04 (s, 2 H), 1.91 (br s, 2 H), 1.10 (d, $J = 6$ Hz, 6 H); IR (neat) 3.20 (m), 6.00 (s), 11.40 (vs) μm ; mass spectrum, m/e calcd 122.1096, found 122.1088.

Resolution of rac-trans-2,3-Norbornene-5-dicarboxylic Acid. The racemic acid was prepared by the Diels–Alder reaction of cyclopentadiene and fumaric acid in a mixture of acetone/water, according to H. Koch.²⁴ In a typical resolution, 86 g (470 mmol) of diacid was dissolved in 1100 mL of 2:1 acetone/water mixture and this solution heated to boiling; then 140 g (470 mmol) of cinchonine was added in several portions until complete dissolution. The mixture was allowed to reach room temperature, giving 68 g of colorless crystals. The recrystallization was repeated twice, and 32 g of the monosalt was obtained. The acid was liberated by dissolving the salt in 250 mL of 5% HBr and extracting with ether (7 \times 100 mL). After workup 12.0 g (28%) of recrystallized (from water) optically active acid was obtained: mp

175–177 °C (lit.¹⁰ 177–179 °C); $[\alpha]_D + 148^\circ$ (acetone), $[\alpha]_{365} = +449^\circ$ (lit.¹⁰ $[\alpha]_D + 147^\circ$).

(+)-**trans-5,6-Dimethyl-2-norbornene.** This hydrocarbon was prepared by the method used in the preparation of *endo-cis*-5,6-dimethyl-2-norbornene. Esterification of 29.0 g of the optical active norbornene acid gave 28 g of the corresponding dimethyl ester. Reduction of 27 g of this ester by LiAlH₄ in THF afforded 18 g of the diol which was treated with mesyl chloride in pyridine, and the mesylate was reduced by a mixture of LiAlH₄ and LiH in THF, giving 5.8 g of the optically active norbornene hydrocarbon; $[\alpha]_D + 95.3^\circ$, $[\alpha]_{365} + 301^\circ$ (CCl₄). NMR and IR spectra were identical with those for the racemic hydrocarbon.

(-)-**(4R,5R)-trans-4,5-Dimethyl-1,3-dimethylenecyclopentane [(--)-T^{H4}].** This olefin was prepared by a procedure similar to that used in the preparation of T_{rac} and C. Starting with 2.5 g of the corresponding optically active norcamphoric acid derived from the ozonolysis of (+)-*trans*-5,6-dimethyl-2-norbornene, the optically active olefin was obtained in 34% yield from the diacid. Separation and purification by VPC was carried out under the same conditions as those for C: $[\alpha]_D - 103^\circ$, $[\alpha]_{365} - 381^\circ$ (in CCl₄); NMR (220 MHz, CCl₄) δ 4.77 (s, 4 H), 3.04 (s, 2 H), 1.91 (br, s, 2 H), 1.10 (d, 6 H); mass spectrum, m/e calcd 122.1096, found 122.1088.

(-)-**(4R,5R)-trans-4,5-Dimethyl-1,3-bis(dideuteriomethylene)cyclopentane [(--)-T^{D4}].** This compound was prepared by a procedure similar to that used for the preparation of T^{H4}_{act}, except that lithium aluminum deuteride was the reducing agent. Starting with 3.0 g of the optically active diamide used for the synthesis of (–)-T^{H4}, the olefin was obtained in 32% yield overall: $[\alpha]_D - 98.9^\circ$, $[\alpha]_{365} - 374^\circ$ (in CCl₄); NMR (220 MHz, CCl₄) δ 3.03 (s, 2 H), 1.89 (br s, 2 H), 1.08 (d, 6 H); IR (CCl₄) 3.38 (s), 3.43 (m), 3.50 (m), 3.52 (m), 4.33 (w), 4.51 (vw), 6.15 (m), 14.00 (vs) μm ; mass spectrum, m/e calcd 126.1347, found 126.1343.

Degradation of (–)-T^{H4} to (+)-(2R,3R)-2,3-Dimethylsuccinic Anhydride. This conversion was carried out starting with the ozonolysis of 18.5 mg (0.15 mmol) of (–)-T^{H4} $[\alpha]_{365} - 381^\circ$ (CCl₄) in 300 μL of anhydrous methanol at –78 °C for 15 min. The excess of ozone was eliminated by bubbling dinitrogen through the reaction mixture. Evaporation of solvent left a slurry, which was treated with 2 mL of 30% hydrogen peroxide and 2 mL of acetic acid, at 55 °C for 24 h to assure complete oxidative degradation. After evaporation of solvent to dryness, 14.4 mg of a white solid was obtained (mp 120–124 °C; IR spectrum superimposable with the spectrum of the racemic one). This solid was dissolved in 2 mL of anhydrous ether, and to this solution was added 18 mg of DCC. The mixture was stirred at room temperature for 2 h. A white precipitate was formed during the course of the reaction. After filtration the solvent was evaporated, leaving 12 mg of a white solid, which was sublimed at 80–100 °C (2–4 torr): mp 99–101 °C (lit.¹⁷ 103–105 °C); $[\alpha]_D + 117^\circ$, $[\alpha]_{365} + 319^\circ$ in benzene (lit.¹¹ $[\alpha]_D + 116.3^\circ$); IR (KBr) 5.40 (m), 5.65 (s) μm .

Preparative Pyrolysis of T and C. For identification and characterization of the rearrangement products in the pyrolysis of T and C, samples of ~40 μL for each compound were pyrolyzed at 358.4 °C for 24 h. The recovered pyrolysate from T was separated by VPC (6 ft \times 0.25 in., 20% DBTCP, 90 °C), collecting the fractions of four peaks in order of elution.

Fraction No. 1. Retention time, IR, and NMR were identical with those of starting material T. Contamination with C was detected by NMR and analytical capillary GC.

Fraction No. 2. This fraction was actually two overlapping peaks in the ratio ~1:10: the major peak was assigned to *anti*-1-ethylidene-3-methylene-4-methylcyclopentane (A): IR (CCl₄) 3.25–3.50 (s), 6.10 (w), 14.05 (s); NMR (CCl₄, 220 MHz) δ 5.14 (m, 1 H), 4.70 (s, 2 H), 2.93 (s, 2 H), 2.46 (s, 2 H), 1.95 (m, 1 H), 1.54 (d, $J = 6$ Hz, 3 H), 1.08 (d, $J = 6$ Hz, 3 H), mass spectrum, m/e (M⁺) 122.

Fraction No. 3. This fraction was assigned to *anti,syn*-1,3-diethylidenecyclopentane (AS): NMR (CCl₄, 220 MHz) 5.22 (br s, 2 H), 2.84 (br s, 2 H), 2.27 (br s, 4 H), 1.56 (t, $J = 6$ Hz, 6 H); IR (CCl₄) 3.28 (w), 3.35–3.55 (s), 6.0 (vw) μm , mass spectrum, m/e (M⁺) 122.

Fraction No. 4. This material was assigned to *anti,anti*-1,3-diethylidenecyclopentane (AA): NMR (CCl₄, 220 MHz) δ 5.20 (quintuplet, $J = 7$ Hz, 1 H), 2.86 (s, 2 H), 2.30 (s, 4 H), 1.55 (d, 6 H); IR (CCl₄) 3.25 (w), 3.30–3.50 (s), 5.95 (vw) μm ; mass spectrum, m/e (M⁺) 122.

In a similar fashion the recovered pyrolysate, from the pyrolysis of C, was separated by VPC (same conditions as for T). Four fractions were collected.

Fraction No. 1. Retention time, IR, and NMR were identical with those of C. This fraction was contaminated with T.

Fraction No. 2. This fraction was actually two overlapping peaks in ~1:1 ratio. The first eluant was assigned to *syn*-1-ethylidene-3-methylene-4-methylcyclopentane (S) and the second one to *anti*-1-ethylidene-3-methylene-4-methylcyclopentane (A). Since the separation of these two compounds was not possible, the reported NMR spectral properties are the corresponding ones to the mixture of A and S: NMR

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(CCl₄, 220 MHz) δ 5.15–5.24 (m, 1 H), 4.70–4.75 (br s, 2 H), 2.93–3.00 (br s, 2 H), 2.42 (m, 1 H), 1.82–1.95 (m, 2 H), 1.54 (d, $J = 6$ Hz, 3 H), 1.08 (d, $J = 6$ Hz, 3 H); mass spectrum, m/e (M^+) 122.

Fraction No. 3. The peak corresponding to this fraction had identical retention time and NMR spectrum as those reported for AS.

Fraction No. 4. The peak corresponding to this fraction had identical retention time and NMR spectrum as those reported for AA.

Kinetics. The pyrolysis apparatus for the kinetic study of C and T was the same used in the pyrolysis of DMCP-*d*₄. For a typical pyrolysis run, 8 μ L of pure sample was transferred into an evacuated 2-L well-conditioned bulb, timing being started when the bulb's valve was closed. After pyrolysis at the stated time interval, the pyrolysate was collected in a spiral coil trap at the temperature of liquid nitrogen and then vacuum transferred into a collector. The recovered pyrolysate was diluted with ~ 25 μ L of pentane and analyzed on a 200 ft \times 0.1 in. i.d. stainless-steel capillary column packed with DBTCP which separated all components to base line. Each run was analyzed from three to five times, and the average of these values for each time interval is reported. Since there is interconversion of C \rightleftharpoons T and the two reactants yield the same 1,3- and 3,3-shift products, the kinetics are not strictly first order. In order to account for this interconversion, we solved the kinetic scheme by using a numerical integration Runge-Kutta program. Table II shows the experimental and calculated mole fractions as a function of time, using the refined ten rate constants which define the system.

Pyrolysis of (-)-(4*R*,5*R*)-trans-4,5-Dimethyl-1,3-dimethylenecyclopentane and -1,3-Bis(dideuteriomethylene)cyclopentane [(-)-T^H and (-)-T^D]. In a typical pyrolysis run ~ 25 – 35 μ L of each compound was pyrolyzed at 360.4 °C for 24 h. The recovered pyrolysate was separated by VPC (6 ft \times 0.25 in., 20% DBTCP, 90 °C). Because of difficulties found in the separation of C and T and S from A, the collected fractions

are mixtures of the corresponding isomers. Quantitative analysis of the recovered pyrolysate was done in the same conditions as for T and C. The values of the optical activity for the recovered starting materials (-)-T^H and (-)-T^D are the average of two experiments at the respective wavelengths, (Table IV).

Degradation of (+)-(+*S*)-anti-1-ethylidene-3-methylene-4-methylcyclopentane [(+)-A] to (-)-(S)-Methylsuccinic Anhydride. The collected fraction of (+)-A ($\sim 7\%$ contaminated with S) from the pyrolysis of (-)-T^H was ozonized and oxidatively degraded under the same conditions as described for the degradation of DMCP to succinic acid; however the conversion of methylsuccinic acid to its anhydride was modified. Treatment of the crude product from the degradation with a 20:1 mixture of acetyl chloride/thionyl chloride at 45 °C for 1.5 h gave a semisolid after purification by vacuum distillation (70–90 °C (1 torr)). This semisolid showed IR and MS spectral characteristics identical with those for synthetic methylsuccinic anhydride. The optical purity of this material was determined by comparing its optical rotatory power value ($[\alpha]_D -6.1^\circ \pm 0.2$, $[\alpha]_{365} -16.2 \pm 0.4$ (c 6.8 mg/mL in ethanol)) with the highest value reported ($[\alpha]_D +32.97$).^{11,25}

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(25) The initial report of this work¹ used a value for the highest rotation reported which was shown to be incorrect.^{11d}

Laser Flash Photolysis Study of the Reactions of Carbonyl Triplets with Phenols and Photochemistry of *p*-Hydroxypropiofenone

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Abstract: The quenching of aromatic carbonyl triplets by phenols is a very fast process for both n,π^* and π,π^* states. Representative rate constants for benzophenone triplets in benzene are 1.3×10^9 (phenol) and 8.1×10^8 (*m*-fluorophenol) $M^{-1} s^{-1}$, while for *p*-methoxypropiofenone the values are 4.9×10^9 and $5.0 \times 10^9 M^{-1} s^{-1}$ for the same pair of substrates; 18 different phenols were examined. The rate constants are smaller in wet acetonitrile as a result of hydrogen bonding; for example for the benzophenone-phenol system we measured $8.0 \times 10^7 M^{-1} s^{-1}$. Isotope effects are larger for *p*-methoxypropiofenone than for benzophenone: for example in the case of phenol the values of k_H/k_D are 3.9 and 1.2, respectively (in wet acetonitrile). The quenching reaction leads to the efficient, but not quantitative, formation of phenoxy and ketyl radicals, with the only exception of *p*-nitrophenol where the process involves electronic energy transfer. The temperature dependence of a few representative systems, as well as the quenching by methyl ethers of similar structure, has also been examined. The photochemistry of *p*-hydroxypropiofenone is characterized by efficient self-quenching involving a head-to-tail hydrogen-transfer reaction.

Carbonyl triplets abstract hydrogen atoms from a variety of substrates,³ including hydrocarbons, alcohols and amines; these reactions have been proposed to occur by either an atom-transfer or an electron-transfer mechanism. In the latter case, the reaction is usually followed by proton transfer. Although there have been numerous studies regarding intermolecular and intramolecular hydrogen abstraction reactions³⁻⁵ of carbonyl triplets, the photo-

chemistry of carbonyl compounds in the presence of phenols has received only limited attention. In particular, Turro et al.^{6,7} have examined the photochemistry of biacetyl in the presence of phenols and observed that efficient triplet quenching was not accompanied by product formation. It was suggested that the

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