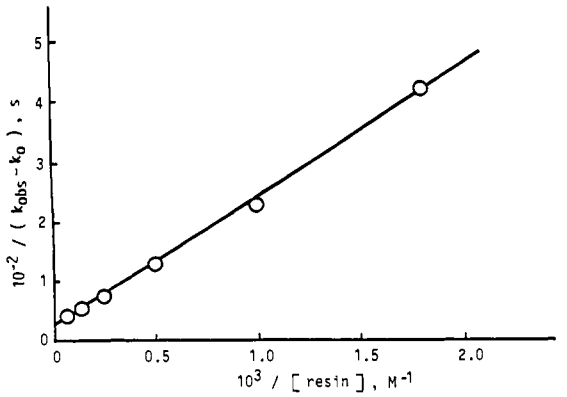


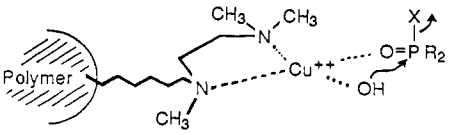
Figure 3. Lineweaver–Burk-type plot based on the data in Figure 2. The k_0 represents the rate of NPDPP hydrolysis in the absence of polymer catalyst.

phosphorus(V) functionalities.[8]

Although an outer hydrocarbon "coat" does not improve catalysis, a hydrocarbon chain between the polymer and metal site definitely does. For example, runs 3 and 6 show that introduction of a six-carbon spacer accelerates NPIPP hydrolysis 8-fold under our standard conditions. Runs 9 and 10 show a similar rate change with NPDPP. Spacer effects arise no doubt from steric factors; substrates have better access to catalytic sites if they are well separated from the polymer backbone.[9]

The rate constants for NPDPP hydrolysis catalyzed by various amounts of P-H_2-M(high) are listed in Table IV. Once again for simplicity we have taken the resin "concentration" as the concentration of Cu^{2+} that would exist in solution were the polymer water-soluble. A plot of k_{obs} vs [resin] curves downward (Figure 2), typical of a preassociation mechanism as found with enzymes. A Lineweaver–Burk-type double reciprocal plot (Figure 3) provided an apparent $K_{assoc} = 114\ M^{-1}$ for NPDPP/polymer binding and a $k_{lim} = 4 \times 10^{-2}\ s^{-1}$ corresponding to the rate of totally bound substrate. In all likelihood, both Cu^{2+}/phosphate interactions and hydrophobic attraction contribute to the overall substrate binding at the polymer surface.

Data in Table V show that hydrolysis rates are pH-insensitive near neutrality (varying only 2.5-fold over 2.5 pH units for NPIPP). Hydroxide ion cannot, therefore, represent the nucleophilic entity that attacks the phosphate or phosphinate ester. Instead, these substrates very likely have their *p*-nitrophenol leaving groups replaced by a metal-bound hydroxyl (drawn below). An identical mechanism was proposed and discussed in connection with metallomicelle-catalyzed hydrolyses.[2]



Catalysts must by definition display "turnover" where each catalyst molecule induces the destruction of multiple substrate units.[10] To test whether turnover is operative in our metallopolymer systems, we measured the yield of 4-nitrophenol when the substrate was in excess over the catalyst. As seen in Table VI, even a 10-fold excess of NPIPP over catalyst leads to a quantitative yield of 4-nitrophenol based on the *total* initial amount of substrate. Thus, reaction between substrate and polymer is not stoichiometric but catalytic in the true sense of the word.

B. Use of Metallopolymers in Organic Synthesis. Having demonstrated the efficacy of the copper-loaded polymers with nerve-agent simulants, we examined their utility in synthetically useful conversions. Six diverse reactions were selected for study (Table VII) including a Diels–Alder, an epoxide ring opening, and an aryl iodide hydrolysis. Exact literature procedures were repeated with both the prescribed soluble copper salt and a heterogeneous metallopolymer catalyst. The data in Table VII show that in all but one case (i.e. the final reaction in the table) copper-loaded polymers either improve the yield or lower the reaction time relative to conventional copper salts. This, plus the ease of metallopolymer removal by filtration, renders the metallopolymers an attractive alternative to current literature methods.

Acknowledgment. This work was supported by the Army Research Office.

Registry No. I, 80751-39-9; II, 10359-36-1; DHTEDA, 120743-24-0; $HN(Me)(CH_2)_2NH(Me)$, 110-70-3; $BrCH_2(CH_2)_8CH_3$, 112-71-0; $Me_2N(CH_2)_2NHMe$, 142-25-6; $CH_3(CH_2)_4CH(Br)OH$, 120743-25-1; $CH_2{=}C(Cl)CN$, 920-37-6; $PhCO(NH)_2H$, 613-94-5; PhCN, 100-47-0; PhSeCN, 2179-79-5; furan, 110-00-9; 5-chloro-5-cyano-7-oxabicyclo-[2.2.1]-2-heptene, 84752-04-5; benzoic acid, 65-85-0; 2,3-dihydroindeno[1,2-*b*]oxirene, 768-22-9; 2,3-dihydro-1,2-hydroxyindene, 4370-02-9; benzaldehyde, 100-52-7; 4-hydroxy-3-iodo-5-methoxybenzaldehyde, 5438-36-8; 3,4-dihydroxy-5-methoxybenzaldehyde, 3934-87-0; cyclohexene, 110-83-8; *trans*-1-methoxy-2-phenylselenenylcyclohexane, 51533-22-3.

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Fluorine- versus Methyl-Substituent Effects in the 6-Methylenebicyclo[3.2.0]hept-2-ene–5-Methylenebicyclo[2.2.1]hept-2-ene Thermal Rearrangement

William R. Dolbier, Jr.,* and Otto Phanstiel, IV

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. *Received September 19, 1988*

Abstract: It was observed in a study of the thermal rearrangement of the *exo*- and *endo*-7-fluoro-6-methylenebicyclo-[3.2.0]hept-2-enes that the fluorine substituent gave induced kinetic and stereochemical effects on the rearrangement which were virtually identical with those reported for a methyl substituent.

Ever since Berson observed the 1,3-sigmatropic rearrangement of *endo*-6-acetoxy-*exo*-7-deuteriobicyclo[3.2.0]hept-2-ene to *exo*-5-acetoxy-*exo*-6-deuteriobicyclo[2.2.1]hept-2-ene,[1] a process which occurs with complete inversion, the stereochemistry of

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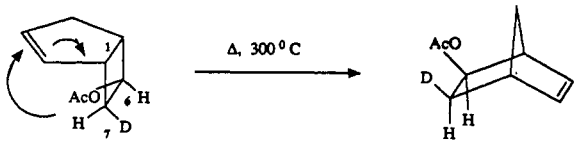
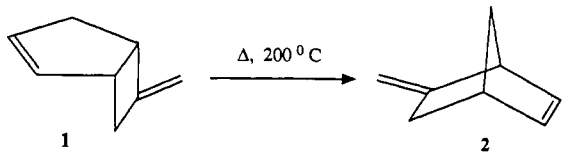


1,3-sigmatropic migrations of carbon has been the subject of considerable interest and much work by physical-organic chemists.[2-13]

It was found very early that steric effects appeared to play a significant role in determining the stereochemical and regiochemical outcome of such reactions and that rearrangement with even predominant inversion at the migrating center is the exception, not the rule.[2-13]

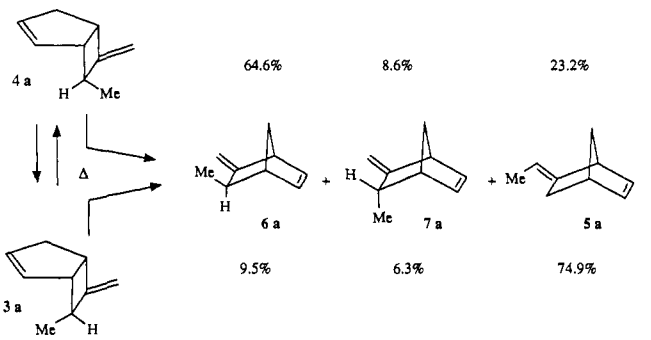
A system which has received considerable attention in this regard is the 6-methylenebicyclo[3.2.0]hept-2-ene (**1**), 5-methylenebicyclo[2.2.1]hept-2-ene (**2**) system, which has the great



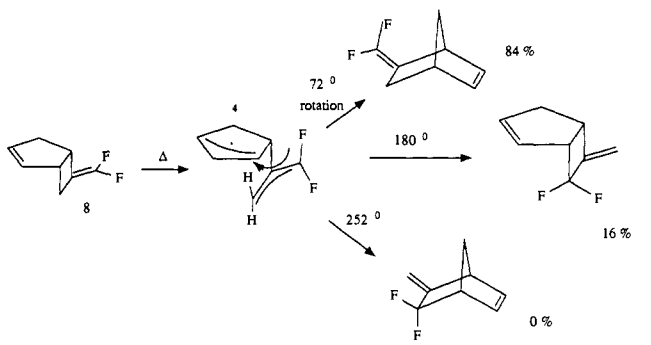
advantage over the non-methylene-substituted system of not having a predominant retro-[2 + 2]-cycloaddition to contend with. The energetics and stereochemistry of the rearrangement of 7-substituted derivatives of **1** have been examined elegantly by Hasselman in a series of papers.[14,15] Of particular importance was his study of the epimeric *endo*- and *exo*-7-methyl derivatives, **3a** and **4a**, the latter of which rearranged with predominant inversion at C7, while the first rearranged contrarily, largely via a formal, 3,3-sigmatropic process with the minor 1,3-pathway proceeding with little stereoselectivity (Scheme I).[15]

In recent years, we have, using the generally sterically insignificant but potentially electronically influential fluorine substituent as a probe, been looking at electrocyclic[16] and sigmatropic[17] systems where "steric" effects have been invoked as being dominant in determining the kinetic behavior and/or stereochemical outcome of orbital-symmetry-allowed reactions. In the case of the 6-methylenebicyclo[3.2.0]hept-2-ene system, which involves a 1,3-sigmatropic rearrangement of carbon, it is now generally accepted that this process is *not* concerted or orbital-symmetry controlled, but proceeds via a complicated mechanism involving nonequilibrated, conformationally related diradical intermediates, in accord

Scheme I



Scheme II



Scheme III

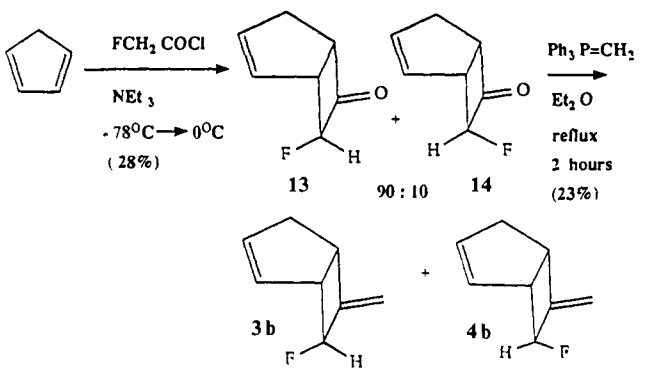


Table I. Rate Constants for the rearrangement of *endo*-7-Fluoro-6-methylenebicyclo[3.2.0]hept-2-ene

temp, °C	rate × 10^{-5}, s	SD	corr coeff
179.75	0.36	0.01	0.9996
199.75	2.28	0.06	0.9985
205.25	3.84	0.08	0.9984
213.50	9.54	0.21	0.9988
223.00	18.30	0.75	0.9966

Table II. Rate Constants for the rearrangement of *exo*-7-Fluoro-6-methylenebicyclo[3.2.0]hept-2-ene

temp, °C	rate × 10^{-5}, s	SD	corr coeff
172.25	0.56	0.02	0.9976
187.25	2.35	0.08	0.9969
194.00	4.30	0.11	0.9972
205.50	11.30	0.20	0.9994
213.50	22.20	0.80	0.9961

with the "continuous diradical" mechanistic picture proposed by Doering and Sachdev.[2,18]

In an earlier study of 6-(difluoromethylene)bicyclo[3.1.0]-hept-2-ene, where steric influences at C7 were not a factor, we were able to explain the product distribution from the thermolysis

(1) (a) Berson, J. A.; Nelson, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 5503. (b) Berson, J. A. *Acc. Chem. Res.* **1968**, *1*, 152.
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Scheme IV

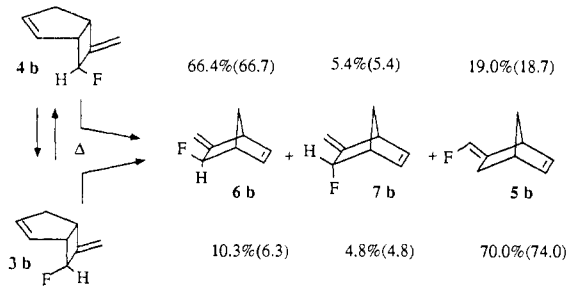

Table III. Arrhenius Parameters for *endo*- and *exo*-7-Fluoro-6-methylenebicyclo[3.2.0]hept-2-ene

k	log A	E_a[a]	ΔH^{+}[a,b]	ΔS^{+}[c]	ΔG^{+}[a,b]
k_{endo}	14.5 (± 0.5)	41.3 (± 1.2)	40.4	4.9	38.1
k_{exo}	13.6 (± 0.1)	38.4 (±0.2)	37.4	0.7	37.1

[a] Kilocalories/mole. [b] The mean temperatures for the endo and exo isomers were 204.05 and 194.30 °C, respectively. [c] Calories/degree.

of **8** via a least-motion argument wherein there was an assumed reluctance of the allyl methylene or CF_2 group to rotate through the C4 CH_2 group of the cyclopentane ring (Scheme II).[19]

It was the intention of the present work to substitute a fluorine substituent for the methyl substituents of **3a** and **4a** in order to (a) evaluate the importance of steric effects in the stereochemical outcome of the reaction and (b) to observe whether an "special" kinetic effect due to the fluorine substituent, similar to those observed in cyclobutene ring cleavage, might be observed in this homolytic, nonpericyclic process.

Synthesis. The 7-fluoro-6-methylenebicyclo[3.2.0]hept-2-enes, **3b** and **4b**, were synthesized by Wittig olefination of the corresponding 7-fluoro-6-methylenebicyclo[3.2.0]hept-2-en-6-ones, **12** and **13**. These in turn were synthesized from the reaction of monofluoroketene and cyclopentadiene[20] (Scheme III). The isomers (**3b** and **4b**) were readily distinguished due to the characteristic syn hydrogen–fluorine coupling present in the *exo*-fluoro compound (ϕ = −163.7, dd, J^2_{H-F} = 16.7 Hz) and *absent* in the endo isomer (ϕ = −178.8, d, J^2_{H-F} = 57 Hz).

Thermal Rearrangements—Results

The endo (**3b**) and exo (**4b**) isomers of 7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene underwent thermal rearrangement in the gas phase to give the rate constants found in Tables I and II, respectively. The product distributions are given in Scheme IV. The experimental product ratios were corrected (values in parentheses) for the partial contribution made to them by the observed interconversion of exo and endo isomers **4b** and **3b** under the pyrolysis conditions. Products **5b**, **6b**, and **7b** did *not* interconvert under the reaction conditions. The activation parameters for isomerization of the two isomers are found in Table III. (It should be noted that the k_{exo}/k_{endo} at 200 °C was 3.1.)

Four products were formed from the thermolysis of the *endo*-7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene (**3b**). The corrected ratios (at 15% conversion) of the four products were as follows: *E* isomer of 5-(fluoromethylene)bicyclo[2.2.1]hept-2-ene (**5b**) (74.0%), *exo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**6b**) (6.3%), *endo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**7b**) (4.8%), and *exo*-7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene (**4b**) (14.9%). The observed yield for the overall rearrangement after 1 half-life was 93% and, after 98% conversion, 88%.

These pyrolysis products were separated by GC and fully characterized by ^{1}H NMR, ^{19}F NMR, and low-resolution mass spectroscopy. The *E* (**5b**) (^{19}F NMR: ϕ = −138.8, dd, J^2_{H-F} = 87.0 Hz) and *Z* (**14**) (^{19}F NMR: ϕ = −136.8, dd, J^2_{H-F} = 87.0 Hz, J^4_{H-F} = 3.5 Hz) isomers of 5-fluoromethylenebicyclo-[2.2.1]hept-2-ene had been synthesized previously from cyclopentadiene and monofluoroallene. The exo (**6b**) (^{1}H NMR: δ 4.82, d, 1 H, J^2_{H-F} = 58.4 Hz, CHF. ^{19}F NMR: ϕ = −171.8, d, J^2_{H-F} = 58.3 Hz) and endo (**7b**) (^{1}H NMR: δ 5.41, d, 1 H, J^2_{H-F} = 57.8 Hz, CHF. ^{19}F NMR ϕ = −177.4, d, J^2_{H-F} = 58.0 Hz) isomers of 6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene were assigned according to the well-documented evidence for the shielding of endo substituents at C-6 in norbornene.

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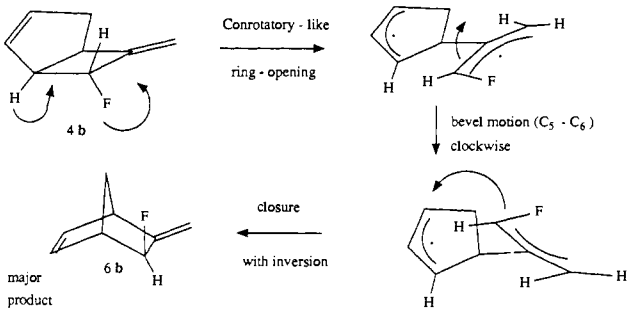
Scheme V



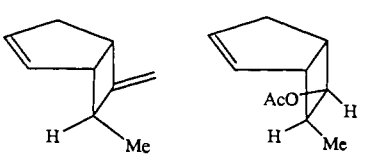
Pyrolysis of the *exo*-7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene (**4b**) also yielded four products. The kinetically formed (at 15% conversion) ratios of the products were (*E*)-5-(fluoromethylene)bicyclo[2.2.1]hept-2-ene (**5b**) (18.7%), *exo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**6b**) (66.7%), *endo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**7b**) (5.4%), and *endo*-7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene (**3b**) (9.2%). The amount of (*Z*)-5-(fluoromethylene)bicyclo[2.2.1]hept-2-ene (**14**) formed in the pyrolyses of either the endo or the exo isomers was not more than 1% (none was actually observed).

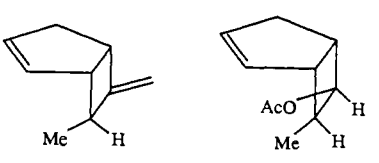
Thermal Rearrangements—Discussion

First, it can be seen that there were *no* dramatic kinetic or stereochemical effects, of the type seen in the cyclobutene ring opening, observed in this system as a result of the presence of the fluorine substituent. It was however clear that, in spite of its acknowledged small steric requirement, *exclusive* outward rotation of the fluorine was observed in the cleavage of the C7–C1 bond for *both* the endo and the exo isomers.

Another significant observation was that the exo isomer was noticeably more reactive than the endo isomer. If steric acceleration of C7–C1 bond cleavage were playing a role, the *endo* isomer would have been expected to be more reactive.[21]

Keeping these facts in mind, it is observed that the endo and the exo isomers rearrange to give radically different product mixtures. The exo isomer **4b**, for the most part, undergoes a highly stereoselective 1,3-sigmatropic shift, a result which is consistent with Hasselmann's and Berson's reported results for related endo-substituted bicyclo[3.2.0]hept-2-ene systems (**4b** and **15**).[15,3]

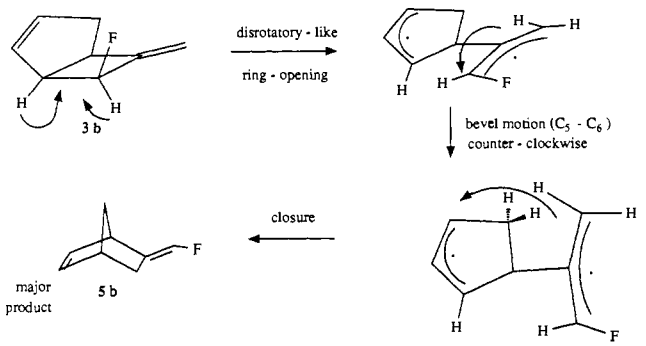




Also consistent with results for the thermal rearrangement of related endo systems (**3a** and **16**) were the results for endo isomer (**3b**) wherein *little* stereoselectivity was observed in its *minor* 1,3-sigmatropic rearrangement pathway.

(21) Similar retardations of endo relative to the exo isomer were reported for **3a** and **16**.[3,15]

Scheme VI



The kinetic and stereochemical results which were observed for our *exo*-and *endo*-fluoro systems could be rationalized in terms of a general mechanism for methylenecyclobutane rearrangements (and more specifically for 6-methylenebicyclo[3.2.0]hept-2-ene systems) which was proposed by Gajewski.[2,4] He proposed a process involving a highly stereoselective, conrotatorylike[22] C7–C1 bond cleavage which is proposed to take place synchronously with a specific beveling rotation of the C5–C6 bond. Schemes V and VI demonstrate the application of Gajewski's hypothesis to the rearrangements of **3b** and **4b**.

In Scheme V, it can be seen that the rotation of the fluorine substituent of **4b** outward, coupled with the bevel motion clockwise about C5–C6, brings C7 and C3 into close proximity, while it also points the back lobe of the newly formed p orbital at C7 toward the p orbital on C3. Thus, a scheme involving such outward rotation of the fluorine substituent coupled with a clockwise beveling motion about C5–C6 nicely rationalizes the formation of inverted *exo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene, **6b**, as the major product of the thermolysis.

In the case of the endo isomer **3b**, a motion similar to that observed for **4b** would rotate the fluorine substituent directly into the cyclopentane ring. Such a motion, on the basis of the results observed, obviously has been prohibited. This could be considered a "steric" prohibition, in which case the fluorine substituent is exerting a rarely observed steric effect. This steric effect is *not* derived from a steric strain in the ground state but merely from the *avoidance* of steric repulsions in the otherwise preferred transition state, thus causing the alternative transition state to become favored. In order for the fluorine substituent to thus rotate outward, the ring cleavage must occur in a disrotatorylike manner, coupled with rotation (or bevel) counter-clockwise about C5–C6 (Scheme VI). The net result of such motion would be to rotate the fluorine-bearing end of the allyl radical *away* from the cyclopentane ring, thus pushing the CH_2 end of this allyl radical past the CH_2 group at C4 and into a position to readily bond to C3, hence forming (*E*)-5-(fluoromethylene)bicyclo[2.2.1]hept-2-ene, **5b**, as the principle product. With the fluorine-substituted methylene not being in a position to form product in the proposed initially formed diradical intermediate, it is not surprising that little stereochemical preference is observed in the minor formation of the 6-fluoro-5-methylenebicyclo[2.2.1]hept-2-enes, **6b** and **7b**.

Hasselmann's studies of the 6-methylene-7,7-dideuteriobicyclo[3.2.0]hept-2-ene and 6-(dideuteriomethylene)bicyclo[3.2.0]hept-2-ene[14] systems gave clear evidence that there is an intrinsic preference, in the 6-methylenebicyclo[3.2.0]hept-2-ene system, for the type of coordinated cleavage and clockwise beveling motion depicted in Scheme V. The presence of the endo fluorine substituent in **3b** is apparently sufficient to inhibit such motion. The fact that the *endo*-fluorine substituent of **3b** forces the cleavage

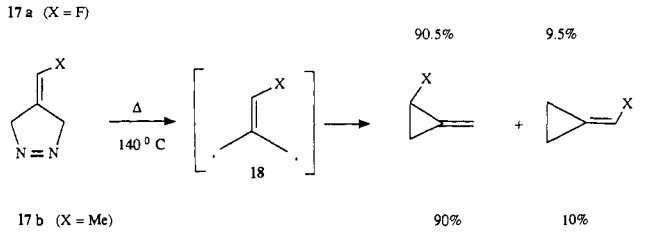
(22) The terms conrotatory*like* and disrotatory*like* refer only to rotational motions and not to concertedness in the Woodward–Hoffmann sense. They refer to the motion of the orbitals involved in the cleavage of the C7–C1 σ bond of **3** and **4**, recognizing that the substituent rotations that occur in these systems are not equivalent to those which take place in the classical monocyclic systems, but for the most part they involve *mono*rotation of the C7 substituent-bearing methylene group in conjunction with a rehybridization to sp^2 at C1.

Table IV. Comparison of the Product Ratios for Thermal Rearrangements of the *exo*- and *endo*-7-Fluoro- and -7-Methyl-6-methylenebicyclo[3.2.0]hept-2-enes

	% products				
reactants	**7**	**6**	**5**	**4**	**3**
exo					
X = Me,[a] **4a**	8.6	64.6	23.2		3.5
X = F, **4b**	5.4	66.7	18.7		9.2
endo					
X = Me,[a] **3a**	6.3	9.5	74.9	9.3	
X = F, **3b**	4.8	6.3	74.0	14.9	

[a] Normalized for the products listed. The amounts of (*E*)- and (*Z*)-6-ethylidenebicyclo[3.2.0]hept-2-ene were 3.0 and 0.1%, respectively, for the exo starting material and 5.4 and 0.2%, respectively, for the endo starting material. These products are not listed since they were not observed in the pyrolyses of the fluoro systems. The amount of (*Z*)-5-substituted-methylenebicyclo[2.2.1]hept-2-ene formed in the pyrolysis of both the methyl and fluoro systems not more than 1%.

Scheme VII



of the C7–C1 bond to proceed via an apparently less-favorable pathway in itself explains the observed lower reactivity of **3b** compared to its exo isomer. The observed 3 kcal/mol greater $\Delta H^{\ddagger}$, coupled with the 4 eu greater entropy associated with dissociation of **3b** versus **4b**, are consistent with a later transition state which requires more bond breaking.

The most striking aspect of these results derives from their comparison with those obtained by Hasselmann in his study of the analogous methyl-substituted molecules **3a** and **4a**.[15] This comparison is shown graphically in Table IV. It can be seen that the product ratios reported by Hasselmann for methyl analogues **3a** and **4a** resemble *very* closely our observed ratios for the fluorine-substituted species **3b** and **4b**.

Kinetically there is also not much to choose between the systems, with the *exo*- and *endo*-methyl species being more reactive than their respective fluoro-substituted analogues by only a factor of 2 at 189 °C.

This is not the first time that we have observed such a resemblance in kinetically controlled product formation behavior of methyl- and fluorine-substituted diradical species. In work published in 1984,[23] it was observed that in the deazetation of 4-(fluoromethylene)-1-pyrazoline, **17a**, the regiochemistry of cyclization of the proposed fluorotrimethylenemethane intermediate, **18a**, as shown in Scheme VII, was virtually identical with that observed earlier by Crawford in his investigation of the deazetation of methyl analogue **17b**.[24]

Such similarity in thermal behavior for methyl- and fluoro-substituted hydrocarbons has not by any means been a uniform observation. In the electrocyclic ring opening of 3-substituted cyclobutenes, for example, fluorine has been shown to exert a dramatically greater effect upon the kinetics and stereochemistry of the reaction than a methyl substituent.[16] Indeed, in *pericyclic* (i.e. one step, concerted) reactions, the *electronic* effect of substituents sometimes can be quite dramatic and, when so, will dominate more subtle influences. We believe, however, that in *nonconcerted*, homolytic processes involving formation or destruction of diradical species and when overt steric effects do not

(23) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Am. Chem. Soc.* **1984**, *106*, 2139.

(24) (a) Chang, M. H.; Crawford, R. J. *Can. J. Chem.* **1981**, *59*, 2556. (b) Crawford, R. J.; Chang, M. H. *Tetrahedron* **1982**, *38*, 837.

play a role in such systems, more subtle influences can and will be observable.

Until additional, more basic probes of such subtle effects may be carried out, it is not possible to provide definitive answers as to the source of the dynamic factors which give rise to the observed virtual identity of fluorine and methyl substituent effects observed in these two diradical processes. This similar behavior of fluorine and methyl substituents does not obviously seem to be deriving from either steric or electronic influences. At this point, one feels compelled to invoke the possibility of a dynamical effect related to their similar *mass* being involved. This effect is related to a hypothesis proposed by Carpenter[25] which suggests that when, in homolytic reactions, the reactant reaches the intermediate stage, "conservation of momentum" carries the diradical to the product that is closest to the straight-line path. Carpenter suggests that this phenomenon might well explain the observed stereochemistries observed in many sigmatropic-like thermal rearrangements.

Experimental Section

***endo*- and *exo*-7-Fluorobicyclo[3.2.0]hept-2-ene-6-one (12 and 13).**[20] Into a 3-necked 250-mL round-bottom flask equipped with a stirring bar, addition funnel, and a nitrogen inlet was placed a solution of triethylamine (11.0 g, 0.1089 mol), freshly distilled cyclopentadiene (26.0 g, 0.3939 mol), and 150 mL of dry diethyl ether. This solution was cooled to −78 °C and fluoroacetyl chloride (8.60 g, 0.0878 mol) in 50 mL of dry diethyl ether was added dropwise over 30 min. After the addition was complete, the flask was warmed to 0 °C and stirred for 48 h. The white precipitate was filtered off and vacuum distillation gave 3.70 g of a crude mixture. The endo and exo isomers were separated on a 20 ft × $^1/_8$ in. OV-210 column at 70 °C to yield 3.15 g (28%). The endo:exo ratio was 90:10.

***endo*-7-Fluorobicyclo[3.2.0]hept-2-en-6-one (12)**: ^{1}H NMR δ 5.95 (m, 1 H, olefinic), 5.71 (m, 1 H, olefinic), 5.60 (dddd, 1 H, J^2_{H-F} = 53.4 Hz (from ^{19}F NMR), J^3_{H-H} = 8.3 Hz, J^4_{H-H} = 0.8 Hz, CHF), 3.90 (br m, 1 H, CHCF), 3.51 (m, 1 H, CHC=O), 2.85–2.45 (complex m, 2 H, CH_2); ^{19}F NMR ϕ = −185.8 (d, J^2_{H-F} = 53.4 Hz); ^{13}C NMR δ 180.8 (s, C=O), 136.2 (s, =*C*HCH$_2$), 126.4 (d, J^3_{C-F} = 3.6 Hz, =*C*HCH), 96.8 (d, J^1_{C-F} = 239.5 Hz, CHF), 53.1 (d, J^3_{C-F} = 12.2 Hz, *C*HC=O), 46.2 (d, J^2_{C-F} = 18.9 Hz, *C*HCHF), 35.4 (s, CH_2).

***exo*-7-Fluorobicyclo[3.2.0]hept-2-en-6-one (13)**: ^{1}H NMR δ 5.90 (m, 2 H, olefinic, 4.96 (ddd, 1 H, J^2_{H-F} = 54.1 Hz, J^3_{H-H} = 2.85 Hz, J^4_{H-H} = 2.22 Hz, CHF), 4.05 (complex m, 1 H, C*H*C=O), 3.63 (complex m, 1 H, CHCF), 2.65 (m, 2 H, CH_2); ^{19}F NMR ϕ = −178.5 (dd, J^2_{H-F} = 54.6 Hz, J^3_{H-F} = 15.3 Hz); ^{13}C NMR δ 180.8 (s, C=O), 134.8 (d, J = 2.2 Hz, =*C*HCH$_2$), 127.9 (d, J = 5.9 Hz, =*C*HCH), 102.6 (d, J^1_{C-F} = 223.5 Hz, CF), 59.8 (d, J = 4.9 Hz, *C*HC=O), 47.1 (d, J = 20.9 Hz, *C*HCF), 35.5 (s, CH_2); mass spectrum, *m*/*z* (relative intensity) 127 (M^+ + 1, 0.16), 126 (M^+, 0.89), 125 (M^+ − 1, 7.96) 98 (50.47), 97 (100.0), 79 (45.36), 78 (17.21), 77 (27.67).

***endo*- and *exo*-6-Methylene-7-fluorobicyclo[3.2.0]hept-2-ene (3b and 4b).** A solution of 1.6 mL of *n*-butyllithium in hexane (2.5M) and 12 mL of dry ether was stirred under nitrogen and 1.42 g of methyltriphenylphosphonium bromide was added over 5 min with a solid addition funnel. Upon stirring of the mixture at room temperature for 4 h, a small amount of Wittig reagent precipitated. 7-Fluorobicyclo[3.2.0]hept-2-en-6-one (mixture of isomers) (0.500 g) in 5 mL of ether was added dropwise to this mixture and it was refluxed for 2 h and then allowed to stir at room temperature overnight. After filtration the ether solution was washed with water, dried with $MgSO_4$, filtered, concentrated, and purified by GC on a 20 ft × $^1/_4$ in. DNP Column at 100 °C (yield = 23%). The endo and exo isomers were separated with the above column, each >98% pure. The kinetics were done on these purified samples.

***endo*-6-Methylene-7-fluorobicyclo[3.2.0]hept-2-ene (3b)**: ^{1}H NMR δ 5.85 (m, 2 H, CH=CH), 5.45 (ddt, 1 H, J^2_{H-F} = 56.2 Hz, J^3_{H-H} = 7.4 Hz, J^4_{H-H} = 2.1 Hz, CHF), 5.20 (m, 2 H, =CH_2), 3.70 (br m, 1 H, C*H*CH$_2$), 3.05 (dd?, H, C*H*CF), 2.72–2.38 (complex m, 2 H, CH_2); ^{19}F NMR ϕ = −178.8 (d, J^2_{H-F} = 56.5 Hz); ^{13}C NMR δ 154.3 (d, J^2_{C-F} = 14.7 Hz, quarternary olefinic), 134.8 (s, =*C*HCH$_2$), 127.5 (d, J^3_{C-F} = 5.3 Hz, =*C*HCH), 109.4 (s, =CH_2), 89.6 (d, J^1_{C-F} = 220.4 Hz, CHF), 52.0 (d, J^2_{C-F} = 18.7 Hz, *C*HCF), 39.8 (d, J^4_{C-F} = 1.9 Hz, CH_2), 38.1 (d, J^3_{C-F} = 11.1 Hz, *C*HCH$_2$); high-resolution mass spectrum, mean of 10 scans was 124.0675 ± 0.00077 (6.3 ppm), calculated for $C_9H_9F_1$ was 124.0688, deviation = −0.00127 (−10.3 ppm).

***exo*-6-Methylene-7-fluorobicyclo[3.2.0]hept-2-ene (4b)**: ^{1}H NMR δ 5.78 (m, 2 H, CH=CH), 5.27 (complex m, 2 H, =CH_2), 4.92 (ddt, 1 H, J^2_{H-F} = 57.9 Hz, J^3_{H-H} = 3.2 Hz, J^4_{H-H} = 1.3 Hz, CHF) 3.68 (br m, 1 H, C*H*CH$_2$), 3.45 (complex m, 1 H, C*H*CF), 2.71–2.32 (complex m, 2 H, CH_2); ^{19}F NMR ϕ = −163.7 (dd, J^2_{H-F} = 57.9 Hz, J^3_{H-F} = 16.7 Hz); ^{13}C NMR (quarternary olefinic not visible) δ 134.0 (d, J^4_{C-F} = 2.2 Hz, =*C*HCH$_2$), 128.2 (d, J^3_{C-F} = 7.2 Hz, =*C*HCH), 114.4 (s, =CH_2), 94.0 (d, J^1_{C-F} = 205 Hz, CHF), 52.0 (d, J^2_{C-F} = 22.8 Hz, *C*HCF), 42.1 (d, J^3_{C-F} = 3.6 Hz, *C*HCH$_2$), 39.2 (s, CH_2); mass spectrum, *m*/*z* (relative intensity) 125 (M^+ + 1, 0.76), 124 (M^+, 8.88), 123 (M^+ − 1, 17.51), 109 (96.31), 103 (20.38), 91 (46.78), 78 (63.20), 77 (23.35), 66 (100.00).

***endo*- and *exo*-6-Fluoro-5-methylenebicyclo[2.2.1]hept-2-enes (7b and 6b).** These products were separated by GC after pyrolyses of the 7-fluoro-6-methylenebicyclo[3.2.0]hept-2-enes (3b and 4b).

***exo*-6-Fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (6b)**: ^{1}H NMR δ 6.30 (m, 1 H, olefinic), 6.01 (m, 1 H, olefinic), 5.13 (m, 2 H, =CH_2), 4.82 (d, 1 H, J^2_{H-F} = 58.4 Hz, CHF), 3.20 (s, 1 H, bridgehead), 3.06 (s, 1 H, bridgehead), 1.93 (m, 2 H, CH_2); ^{19}F NMR ϕ = −171.8 (d, J^2_{H-F} = 58.3 Hz); ^{13}C NMR δ 141.2 (s, olefinic 133.0 (d, J_{C-F} = 8.7 Hz, olefinic), 123.1 (s, olefinic), 108.1 (d, J_{C-F} = 4.7 Hz, olefinic), 93.3 (d, J^1_{C-F} = 189.4 Hz, CHF), 48.2 (s, bridgehead), 47.8 (d, J_{C-F} = 19.0 Hz, bridgehead), 47.1 (d, J_{C-F} = 3.1 Hz, CH_2; mass spectrum, *m*−*z* (relative intensity) 125 (M + 1, 1.75), 124 (M^+, 22.23), 123 (M − 1, 15.60), 109 (82.61), 91 (32.81), 78 (63.83), 77 (20.22), 66 (100.00).

***endo*-6-Fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (7b)**: (obtained as a 6% impurity in the *E* isomer of 5-(fluoromethylene)bicyclo[2.2.1]-hept-2-ene (5b) ^{1}H NMR δ 6.40 (m, 1 H, olefinic), 6.10 (m, 1 H, olefinic), 5.41 (d, 1 H, J_{H-F} = 58.0 Hz, CHF), 5.12 (m, 2 H, olefinic), (bridgehead resonances buried at 3.2 (s, 1 H) and 3.06 (s, 1 H)), 1.61 (m, 2 H, CH_2); ^{13}F NMR ϕ = −177.4 (d, J_{H-F} = 58.0 Hz); mass spectrum, *m*/*z* (relative intensity) 125 (M^+ + 1, 0.57), 124 (M^+, 17.40), 123 (M^+ − 1, 16.81), 109 (100.00), 103 (19.97), 91 (39.66), 78 (75.27), 77 (27.13), 66 (99.59), 65 (22.70).

***(E)*- and *(Z)*-5-(Fluoromethylene)bicyclo[2.2.1]hept-2-ene (5b and 14).** The *E* (**5b**) and *Z* (**14**) isomers of 5-(fluoromethylene)bicyclo-[2.2.1]hept-2-ene were synthesized by reacting monofluoroallene and cyclopentadiene at 0 °C.[24] In the ^{19}F NMR the *E* isomer had ϕ = −138.8 (d, J^2_{H-F} = 87.0 Hz) and the *Z* isomer had ϕ = −136.8 (dd, J^2_{H-F} = 87.0 Hz, J^4_{H-F} = 3.5 Hz).

Thermal Rearrangement of 6-Methylene-7-fluorobicyclo[3.2.0]hept-2-ene. *endo*-6-Methylene-7-fluorobicyclo[3.2.0]hept-2-ene (**3b**) (80 mm) was expanded into a well-conditioned pyrolysis bulb and pyrolyzed at five temperatures between 179.75 and 223.00 °C. The reaction was followed by GC with a J&W Scientific MEGABORE™ column at 25 °C. The rate constants and activation parameters are given in Tables I and III. The pyrolysis afforded four products, one of which was unstable. The kinetically formed (15% conversion) product ratios were determined by ^{19}F NMR integrations and found to be as follows: the *E* isomer of 5-(fluoromethylene)bicyclo[2.2.1]hept-2-ene (**5b**) (72.5%), *exo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**6b**) (8.9%), *endo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**7b**) (5.0%), and *exo*-7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene (**4b**) (13.6%). The endo product (**7b**) decomposes slowly. The yield after 1 half-life was 93%; however, after 98% conversion the yield was 88%.

exo-6-Methylene-7-fluorobicyclo[3.2.0]hept-3-ene (**4b**) (80 mm) was likewise expanded into the same vessel as above and pyrolyzed at five temperatures between 172.25 and 213.50 °C. The reaction was followed with the same column and the rate constants and activation parameters are given in Tables II and III. The kinetically formed (20% conversion) product ratios were determined by ^{19}F NMR integrations and found to be as follows: *exo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**6b**) (66.4%), *endo*-6-fluoro-5-methylenebicyclo[2.2.1]hept-2-ene (**7b**) (5.4%), *(E)*-5-fluoromethylenebicyclo[2.2.1]hept-2-ene (**5b**) (19%), and *endo*-6-fluoro-7-methylenebicyclo[3.2.0]hept-2-ene (**3b**) (9.2%). The yield at 89% conversion was 90%. The amount of *(Z)*-5-fluoro-methylene-bicyclo[2.2.1]hept-2-ene formed in both the pyrolyses of the endo and exo isomers was no more than 1%.

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