The above discussion can be extended to the expulsion step whose TS geometries and barriers derive from the crossing requirements of Figure 2 (compare **6A** vs. **6B** above). A link can thus be drawn between barriers, TS geometries, and the distortion efforts required to shift a single electron in both the addition and elimination steps of NVS reactions.

Concluding Remarks

The state correlation diagram model[13,14] provides a methodology for piecing up a reaction profile from its component building blocks. For NVS reactions, the model is shown to lead to a unified understanding of the factors controlling the mechanistic choice of a given reactant pair ($N:^-$/olefin), the variation of the reaction barriers, and the geometries of the transition state. The addition and elimination steps of NVS (eq 1) are shown to consist of trends that project the nature of these steps as processes that involve single electron shifts synchronized with bond interchange.

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Registry No. $H_2C{=}CH_2$, 74-85-1; $H_2C{=}CHF$, 75-02-5; $H_2C{=}CF_2$, 75-38-7; $FHC{=}CHF$, 1691-13-0; $H_2C{=}CHCl$, 75-01-4; $H_2C{=}\dot{C}H_2^-$, 34527-91-8; $H_2C{=}\dot{C}HF^-$, 80009-98-9; $H_2C{=}\dot{C}F_2^-$, 77845-44-4; $HFC{=}\dot{C}H^-$, 80009-96-7; H, 12184-88-2.

Supplementary Material Available: Four tables containing DZ//4-31G energies and geometries of olefins and A_1 and A_2 carbanions. Included also are outlines for calculating W_1 indices of radical anions, A_{CX} and $G(A_2^*)$ values (6 pages). Ordering information is given on any current masthead page.

Acceptor, Donor, and Captodative Stabilization in Transition States of 5-Hexen-1-yl Radical Cyclizations

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Abstract: Rate constants and activation parameters for cyclization of the 6-substituted hex-5-en-1-yl radicals (6-cyano (**1b**), 6-methoxy (**1c**), and 6-cyano-6-methoxy (**1d**)) have been determined. At 50 °C, the rate constants for cyclization to the corresponding cyclopentylmethyl radicals are 1.65×10^8, 1.45×10^6, and 2.49×10^8 s^{-1}, respectively. The rate accelerations for the cyclizations of **1b–d** relative to that of the parent radical, hex-5-en-1-yl (**1a**), are discussed in terms of the substituents' perturbations of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) of the alkene moiety. The large rate accelerations of **1b** and **1d** (275-fold and 415-fold, respectively, at 50 °C) result primarily from increased interaction of the semioccupied molecular orbital (SOMO) with the alkene LUMO, whereas the small rate acceleration of **1c** results from increased SOMO–HOMO interaction. Radicals **1b** and **1d** were found to have looser, hence earlier, transition states for cyclization than do **1a** and **1c**. Comparison of the E_a's for **1b–d** relative to that for **1a** indicates that there is a slight extra stabilization (captodative effect) in the transition state for cyclization of **1d**.

The cyclization of 5-hexen-1-yl radicals, especially that of the parent radical **1a**, have been studied in some detail. Radical **1a** cyclizes predominantly to cyclopentylmethyl (**2a**) with a rate constant of 2.5×10^5 s^{-1} at 25 °C;[3] the regioselectivity results primarily from stereoelectronic effects favoring the transition state which leads to **2a** over that leading to the more thermodynamically stable radical, cyclohexyl.[4] The cyclizations of **1a** and its ana-

a, R = R' = H; b, R, R' = H, CN; c, R, R' = H, OCH_3; d, R, R' = CN, OCH_3

logues have been used extensively in mechanistic studies, both as qualitative probes to implicate free radicals as intermediates in reaction sequences and as quantitative "radical clocks",[4] and recently there has been an increasing interest in synthetic applications of hexenyl-radical cyclizations.[5]

A variety of alkyl-substituted, bicyclic, and heteroatom-containing analogues of **1a** have been studied,[4] but little is known about the effects on cyclization of radical-stabilizing groups on the terminus of the alkene moiety in **1a**. This is unlike the case for intermolecular radical additions to substituted olefins where several systems have been studied, and the results have been collected in a succinct review by Giese.[6] In this paper, we report the effects on the cyclization rates of incorporating acceptor and donor groups at the incipient radical center in **1a** (radicals **1b–d**). Radicals are stabilized by acceptors and donors, and when both are present in the same system, increased stabilization over that of the sum of the individual components (known as captodative stabilization, mero stabilization, or push-pull stabilization) is

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(5) Many examples are given in ref 4. For recent representative examples, see: (a) Hart, D. J. *Science (Washington, D.C.)* **1984**, *223*, 883–887. (b) Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448–1449. (c) Stork, G.; Kahn, M. *Ibid.* **1985**, *107*, 500–501. (d) Burnett, D. A.; Choi, J.-K.; Hart, D. J.; Tsai, Y.-M. *Ibid.* **1984**, *106*, 8201–8209. (e) Hart, D. J.; Tsai, Y.-M. *Ibid.* **1984**, *106*, 8209–8217. (f) Ladlow, M.; Pattenden, G. *Tetrahedron Lett.* **1984**, *25*, 4317–4320. (g) Clive, D. L. J.; Beaulieu, P. L.; Set, L. *J. Org. Chem.* **1984**, *49*, 1313–1314. (h) Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *Ibid.* **1984**, *49*, 2298–2300. (i) Beckwith, A. L. J.; O'Shea, D. M.; Roberts, D. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1445–1446. (j) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564–5566.
(6) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753–764.

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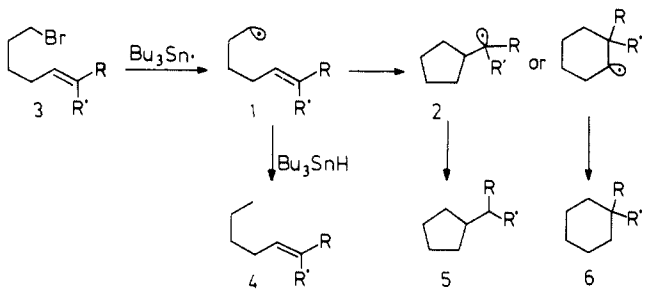
Table I. Rate Constants and Activation Parameters for Cyclizations of Radicals 1[a]

	radical			
	1a[b]	1b	1c	1d
$10^{-6}k_c$, s^{-1}[c]	0.60 ± 0.29	165 ± 9	1.45 ± 0.07	249 ± 15
$\Delta G^{\ddagger}$, kcal/mol[c]	10.41 ± 0.31	6.81 ± 0.04	9.84 ± 0.03	6.54 ± 0.04
E_a, kcal/mol[d]	6.85 ± 0.21	5.81 ± 0.07	6.56 ± 0.22	5.12 ± 0.51
log A[d]	10.42 ± 0.16	12.09 ± 0.05	10.43 ± 1.48	11.76 ± 0.35
$\Delta H^{\ddagger}$, kcal/mol[c]	6.21 ± 0.21	5.17 ± 0.07	5.92 ± 0.22	4.48 ± 0.51
$\Delta S^{\ddagger}$, cal/(mol- K)[c]	-13.0 ± 1.2	-5.1 ± 0.2	-12.1 ± 0.7	-6.4 ± 1.6

[a] Error limits are one standard deviation. [b] All parameters for **1a** are calculated from the Arrhenius function in ref 3. [c] At 50 °C. [d] Temperature range for **1b–d**: 25–75 °C.

Scheme I



possible. Different theoretical approaches predict that such an effect will[7a–c] or will not[7d,e] be found, but experimental studies generally have found only small captodative effects.[8] Intermolecular radical additions to 1,1-diarylethenes show a slight captodative stabilization in the transition states for addition,[8d] but intermolecular additions of carbon radicals to substituted ethylenes containing acceptor and donor groups bonded directly to the incipient radical center generally exhibit a rate retardation in comparison to additions to the analogous alkene containing only acceptor groups.[6] We expected to find stabilization in the transition states for cyclization of **1b** and **1d** compared to **1a**, and the objectives of this work were to seek exceptionally fast radical cyclization probes for mechanistic studies and to attempt to quantify any captodative stabilization afforded in the cyclization of **1d**.

Results

The bromide precursors **3b–d** for radicals **1** were prepared from Wittig-type reactions using 5-bromopentanal. Mixtures of double bond isomers were obtained in each case. These isomers were resolved by capillary GC, and in principle, pure isomers could have been obtained by preparative GC. However, our kinetic studies indicated that for radicals **1b–d**, the *E* and *Z* isomers cyclized at the same rates in each case (vide infra); thus, we did not attempt to isolate the isomers. The *E* and *Z* isomers of **3b** and **3c** could be identified by ^{1}H NMR spectroscopy which showed the expected *cis*- and *trans*-vinyl coupling constants.

Reduction of bromides **3** in radical-chain processes can lead to acycles **4** or cyclic products **5** or **6** (Scheme I). The bromide reacts with the tributyltin radical to give radical **1** which can cyclize or be trapped by *n*-Bu_3SnH. The cyclized radicals are also trapped by *n*-Bu_3SnH. To identify the products arising from **1b–d**, we prepared or purchased authentic products **4**, **5**, and **6** with the exception of potential product **6d**. In the case of acycles **4**, Wittig-type reactions with pentanal again gave mixtures of *E* and *Z* isomers which were resolved by capillary GC and which, for **4b** and **4c**, could be identified by ^{1}H NMR spectroscopy.

The reaction mixtures from *n*-Bu_3SnH reductions of **3b–d** in benzene were analyzed by capillary GC and by GC–mass spectrometry. Product identities were established by coelution of the products with authentic samples and by the identities of the mass spectra of the radical-derived products and the authentic materials. Depending on the concentration of *n*-Bu_3SnH, varying yields of products **4** and **5** were formed from **3**. No (<0.1%) endocyclic product **6b** or **6c** was formed in reactions of **3b** and **3c**, respectively, and no unidentified peak in the appropriate region of the GC trace for **6d** was present in the analysis of the products from **3d**. The mass balance of products **4** and **5** was typically 80–100% by GC.

The rates of cyclization of radicals **1b–d** to radicals **2b–d** were measured by the competitive tin hydride method. Benzene solutions of bromides **3b–d**[9a] and excess *n*-Bu_3SnH with 1–2 mol % 2,2′-azobis[2-methylpropanenitrile] (AIBN) for initiation were allowed to react to high consumption of **3**. In Scheme I, the unimolecular cyclization of **1** to **2** competes with the bimolecular reaction of **1** with *n*-Bu_3SnH. It should be noted that for kinetic analyses, only the rates of cyclization and trapping of **1** are important; the rate of trapping of **2** is not important.[10] The second-order rate constants for the intermolecular trapping reactions of **1** can be estimated with confidence since the reactions of the primary carbon radicals ethyl and butyl with *n*-Bu_3SnH are nearly identical.[3] One can predict that the primary radicals **1** will react with *n*-Bu_3SnH with the same rate constant, that being the average of the ethyl and butyl rate constants. Indeed, this assumption has been applied in the determination of the rate constant for cyclization of **1a** to **2a**.[3]

The rate constant for cyclization of **1** (k_c) could be calculated from eq 1. In this approach, we have assumed that the bimolecular reaction of **1** with *n*-Bu_3SnH can be treated as a pseudo-first-order reaction, and eq 1 is an approximation which is more accurate at high hydride-to-halide ratios where the hydride concentration changed only slightly during the course of the reaction. In eq

$$k_c = k_H[Bu_3SnH]_m\mathbf{5/4} \quad (1)$$

1, k_H is the calculated second-order rate constant for reaction of a primary radical with *n*-Bu_3SnH,[3] $[Bu_3SnH]_m$ is the mean concentration of tin hydride during the reaction, and **5/4** is the observed product ratio. The mean concentration of tin hydride was determined experimentally for each run; it is the average of

(7) (a) Crans, D.; Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1980**, *21*, 3681–3684. (b) Klessinger, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 908–909. (c) Leroy, G. "Advances in Quantum Chemistry"; Academic Press: Orlando, FL, 1985; Vol. 17; pp 1–95 (see Table XXXIII). (d) Leroy, G.; Peeters, D. *THEOCHEM* **1981**, *2*, 133–152. (e) Leroy, G.; Peeters, D.; Wilante, C. *Ibid.* **1982**, *5*, 217–233.

(8) For leading references, see: (a) Korth, H. G.; Lommes, P.; Sustmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 663–668. (b) Louw, R.; Bunk, J. J. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 119–120. (c) Zamkanei, M.; Kaiser, J. H.; Birkhofer, H.; Beckhaus, H.-D., Rüchardt, C. *Chem. Ber.* **1983**, *116*, 3216–3234. (d) Lahousse, F.; Merényi, R.; Desmurs, J. R.; Allaime, H.; Borghese, A.; Viehe, H. G. *Tetrahedron Lett.* **1984**, *25*, 3823–3826. (e) Himmelsbach, R. J.; Barone, A. D. Kleyer, D. L.; Koch, T. H. *J. Org. Chem.* **1983**, *48*, 2989–2994. (f) Viehe, H. G.; Merényi, R.; Stella, L., Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917–932.

(9) (a) The samples used were >98% pure by GC and had the following isomeric compositions: 51:49 (*E*/*Z*) for **3b**, 80:20 (*E*/*Z*) for **3c**, 54:46 (stereochemistry not assigned) for **3d**. (b) Average ratios of products **4**: 53:47 (*E*/*Z*) for **4b**, 78:22 (*E*/*Z*) for **4c**, 56:44 (stereochemistry not assigned) for **4d**.

(10) To clarify this point, we would like to emphasize that radical **2** will not ring open to radical **1**.[3] Thus, the rate at which **2** reacts with *n*-Bu_3SnH is of no consequence. The competition is only between cyclization of **1** and trapping of **1**. All radicals **1** are primary radicals which differ from one another only in substitution at a carbon atom five atoms removed from the radical center, three atoms of which are saturated. If one could show that the rates of reactions of the various radicals **1** with *n*-Bu_3SnH in fact differed by a significant amount, then one would have uncovered a fact of profound importance to those studying the rates of radical reactions and a fact contradictory to all evidence now available.[3] Since k_H for all radicals **1** will be the same, the differences in the product ratios (**5/4**) originate only from differences in the cyclization rate constants, k_c.

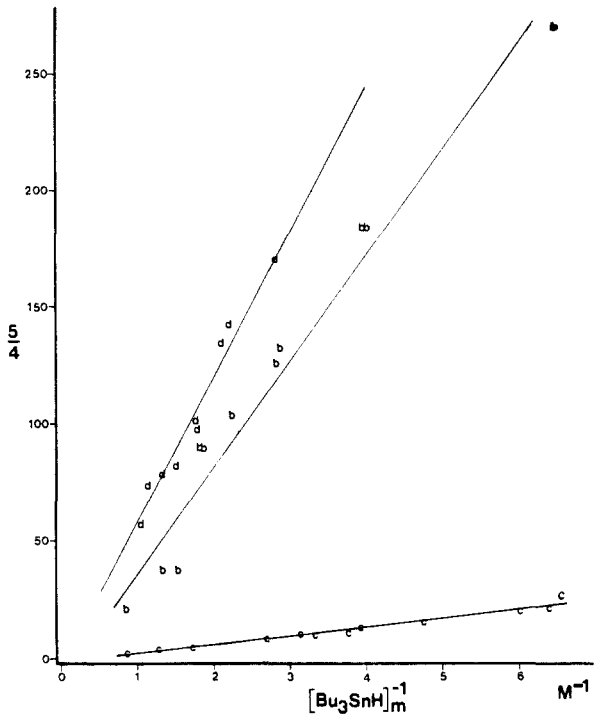


Figure 1. Observed ratio of products **5** to **4** as a function of the reciprocal of the mean concentration of Bu_3SnH at 50 °C. The letters correspond to the substitution of radicals **1**. For **1c**, the ratio plotted is 10 × **5**/**4**.

the initial concentration of *n*-Bu_3SnH and the final concentration of *n*-Bu_3SnH which was found by determining the percentage of halide reduced in each run and subtracting the millimoles of consumed halide from the millimoles of initial hydride. Equation 1, with the same definitions, was used in the graphical form discussed below.

To determine a precise k_c, we measured the **5**/**4** ratios for reactions of bromides **3b–d** with *n*-Bu_3SnH at several concentrations at 50 °C and plotted the ratios against the reciprocal of $[Bu_3SnH]_m$; Figure 1 shows the results. From the slopes, we calculated the first-order rate constants at 50 °C given in Table I. For comparison, the calculated rate constant for cyclization of **1a** at 50 °C is also given. The *E* and *Z* isomers of bromides **3b–d** reacted at comparable rates as expected. We found it somewhat surprising that the rate constants for cyclization of the *E* and *Z* isomers of each radical were also identical; the ratios of the *E* and *Z* isomers of acycles **4** were similar to those in the halide precursors **3**.[9b] The rate accelerations for **1b** and **1d** are 275-fold and 415-fold, respectively, in comparison to **1a**, and these reactions are among the fastest radical skeletal rearrangements to have been reported.[4a,11]

A series of control reactions were conducted at 50 °C to determine the product stabilities under the reaction conditions. For example, when reactions of **3c** were stopped short of complete consumption of bromide, the ratio of **4c**/**5c** was unchanged. Further, the ratio of the *Z* and *E* isomers of **4c** was constant.

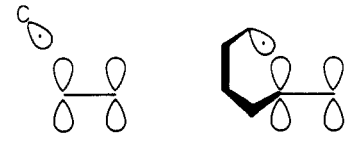
Temperature-dependent functions for the rearrangements were also determined. We measured one-point rate constants for the cyclizations of **3b–d** at four temperatures between 25 and 75 °C using eq 1 and used these values with the 50 °C rate constants to calculate Arrhenius functions. The precision of a single one-point rate constant can be questioned, but the good kinetic behavior we observed in the 9–12-point kinetic measurements at 50 °C and the reasonably low standard deviations we found for the Arrhenius functions (see Table I) suggest that our method was adequate. With the precise rate constants at 50 °C and the E_a's, we calculated $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ at 50 °C. These values are included in Table I; the error limits are propagated by standard methods.[12]

(11) The cyclopropylcarbinyl ring opening at 50 °C has a rate constant of 3–9 × 10^8 s^{-1}; see: Maillard, R.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7034–7026.

Discussion

Substituents on the olefin moiety in radicals **1** might exert steric as well as electronic effects in the transition states for cyclization. However, the substituents we studied (CN and OCH_3) are small groups and were expected to show only minor steric effects which, if present, should further favor the formation of five-membered ring products. That there were virtually no steric effects from these substituents is indicated by the observation that the *E* and *Z* isomer pairs of radicals **1b**, **1c**, and **1d** had the same rates of cyclization. Thus, the kinetic effects we found originated almost entirely in the substituents' electronic perturbations of the olefin.

Theoretical treatments of radical additions to alkenes predict an early, unsymmetrical transition state (A),[6] and the observed cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical rather than to the thermodynamically favored cyclohexyl radical is readily explained by the unsymmetrical transition state (B). Giese[6] has convincingly argued that, since the transition



A B

states are early in the highly exothermic additions of radicals to alkenes, rationalization of substituents' kinetic influences should be sought in the perturbation of the frontier orbitals of the reducing moieties. Briefly, the semioccupied molecular orbital (SOMO) of the radical will interact with the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) of the alkene, and both interactions will be stabilizing. An electron-withdrawing group (CN) on the alkene will lower the HOMO and LUMO energies of the alkene leading to increased SOMO–LUMO interaction, and an electron-donating group (OCH_3) will have the opposite effect on the alkenes' HOMO and LUMO leading to increased SOMO–HOMO interaction. In addition, in both cases, the coefficient of the carbon atom which will be attacked by the radical (C-1) in the MO of increasing interaction (LUMO for CN, HOMO for OCH_3) is larger than in the unperturbed alkene's corresponding MO.[13,14] These effects were summarized in a pioneering work by Houk et al.[13] and presented graphically by them in a figure which does not need to be reproduced here. For comparisons of our cyclizations, we need to note (1) that the effect of the two substituents in **1d** will be a composite of the effects of the individual groups[13] wherein the cyano group is dominant[15] and (2) that alkyl substitution on the olefin terminus perturbs the MO's in the same direction but to a smaller extent than does methoxy.[13]

In the context of the qualitative MO picture outlined above, the kinetic effects of the substituents we studied may be rationalized. If we assume that the constraints of the five-membered ring formation require that all the cyclizations follow the same trajectory, then the lower LUMO energies and larger C-1 coefficients of **1b** and **1d** relative to **1a** lead to stronger SOMO–LUMO interaction and are the dominant features leading to increased rates of cyclization. The methoxy substituent leads to a small rate acceleration in **1c** over that of **1a** (2.4-fold at 50 °C) because of an increased SOMO–HOMO interaction. In agreement with the expectation that the methoxy group in **1d** will have little effect on the acrylonitrile LUMO and a slight effect on the HOMO,[15]

(12) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969.

(13) Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287–7301.

(14) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976.

(15) Simple HMO theory[16] indicates that methoxy substitution at C-2 of acrylonitrile perturbs mainly ψ_1 of acrylonitrile; the HOMO orbital of acrylonitrile is slightly destabilized, the LUMO is virtually unaffected, and the coefficients at C-1 in each are perturbed by ca. 10%. Similar results are seen in more sophisticated calculations of methoxy perturbation of butadiene's MO's.[13]

a rate acceleration of 1.5-fold at 50 °C is seen in comparing **1d** with **1b**.[17] The previously reported relative rates of cyclization of *trans*-5-heptenyl (**1**: R = H, R′ = CH_3, $k_{c(X)}/k_{c(1a)} = 1$)[18a] and 6-methyl-5-heptenyl (**1**: R = R′ = CH_3, $k_{c(X)}/k_{c(1a)} = 2.4$)[18b] are also consistent with the MO explanation where the increased SOMO–HOMO interaction is offset by a decreased SOMO–LUMO in the former case and where increased SOMO–HOMO interaction dominates in the latter case.

The activation parameters for cyclizations of **1a–1d** also can be compared. The cyano group stabilizes a radical center more than a methoxy group,[7d,7e,19] and even though the early transition states for the cyclizations will most resemble the reactants, the stabilities of the products **2b** and **2d** are expected to be reflected in lower energy and even earlier transition states for **1b** and **1d** relative to **1a** and **1c**. The activation parameters at 50 °C are in accord with these expectations. Not only are the $\Delta H^{\ddagger}$'s for **1b** and **1d** lowered, but the $\Delta S^{\ddagger}$'s for these radicals are less negative that those for **1a** and **1c**, suggesting looser, hence earlier, transition states for cyclization.

Whether or not the captodative system **2d** displays unusual stability which is reflected in the transition state for cyclization of **1d** depends on one's definition of a captodative effect. It appears that large captodative stabilizations will not be found experimentally,[8] but Sustmann has noted that radical stabilization by multiple substitution of the same nature is usually *less* than the sum of the individual substituents' stabilizing effects and that additivity in radical stabilization by an acceptor and donor substituent might appropriately be termed a special captodative effect.[8a] In the context of that definition, there is a slight captodative stabilization in the transition state for cyclization of **1d** since the ΔE_a for **1d** relative to **1a** is greater than the sum of the ΔE_a's for **1b** and **1c** relative to **1a**.[20]

The kinetic effects in the intramolecular reactions we studied can be compared to kinetic effects in intermolecular additions of carbon radicals to substituted olefins. In intermolecular reactions,[6] replacement of hydrogen on the alkene by cyano generally leads to larger kinetic accelerations than we observed in **1b**, whereas replacement of hydrogen on the alkene by an alkoxy group generally leads to nearly an order of magnitude rate depression. The attentuated effect of cyano substitution in **1b** and the inverted effect of methoxy substitution in **1c** relative to the analogous intermolecular radical additions suggest that there is less of the expected[21] negative charge development at C-2 in the cyclizations than in the intermolecular additions, but we have no rationalization for the origin of such an effect.

Regardless of the explanation, the fact that the methoxy-substituted radical **1b** cyclizes faster than unsubstituted **1a** may be important in syntheses. Radical cyclizations have been incorporated into synthetic sequences,[5] but we are aware of only one report of radical cyclizations onto vinyl ethers, and these cyclizations were sterically directed to attack at the α center of the vinyl ethers.[5f] Those who wish to use radical cyclizations onto the β center of vinyl ethers should note that intermolecular radical additions to alkoxy-substituted olefins may be poor models for predicting the kinetics of the cyclizations.

Conclusions

The relative rates of cyclization of hexenyl radicals **1** to give the acceptor, donor, and captodative stabilized radicals **2b–d** can be rationalized qualitatively in terms of interactions of the semioccupied MO of the radical center with the HOMO and LUMO orbitals of the alkene moieties; there are virtually no steric effects for the substituents we studied. From an analysis of the activation parameters for the cyclizations, we conclude that the stabilization in the transition state for the cyclization of captodative-substituted **1d** is slightly greater than the sum of stabilization afforded by the individual substituents and, thus, that a special "captodative effect" exists. Since the cyclizations of radicals **1b** and **1d** are especially fast, the bromides **3b** and **3d** may be useful as mechanistic probes, and since all three systems studied cyclize faster than the unsubstituted parent 5-hexenyl radical, the incorporation of cyano and methoxy groups onto the alkene moiety in synthetic applications of radical cyclizations should be possible with current methodology.

Experimental Section

General. All reactions were performed in oven-dried flasks under nitrogen. Syringe transfers were performed by using standard techniques. Nitrogen was dried by passing it through a Drierite tower. Tri-*n*-butylstannane was supplied by Alfa Products and was used without further purification, and other chemicals were supplied by Aldrich Chemical Co. Benzene was dried by distillation from lithium aluminum hydride. In kinetic runs, temperatures were controlled by using a Thermo-O-Watch L7-1100B/24T supplied by Instruments for Research and Industry. ^1H NMR spectra were obtained on a Varian EM-390 spectrometer at 90 MHz; chemical shifts were measured relative to the signal of tetramethylsilane as an internal standard. GC analysis were performed on a Hewlett-Packard (HP) 5790A series gas chromatograph equipped with a capillary injector and a flame ionization detector using a 25-m BP-1 (Scientific Glass Engineering) fused silica column; signal integration was achieved by using an HP 3390A integrator. GC–Mass spectral data were obtained by using an HP 5790A series gas chromatograph (25-m cross-linked 5% phenylmethylsilicone capillary column) with an HP 5970A series mass-selective detector; signal integration was obtained by using an HP 9825B computer and an HP 2671G recorder. IR spectra were performed by using a Perkin-Elmer spectrophotometer, Model 297.

5-Bromopentan-1-ol was prepared by the method of Kulkarni and Patel.[22] The product was pure by ^1H NMR spectroscopy, and it was used for the next step without further purification.

5-Bromopentanal was prepared by a modificiation of the method of Ratcliffe and Rodehorst[23] using 5-bromopentan-1-ol as the starting material in 69% yield; bp 53–55 °C (1.2 torr) [lit.[23] bp 87–89 °C (12 torr)].

7-Bromo-2-heptenenitrile (3b). To a solution containing 25 mL of 1.6 N *n*-BuLi in hexane and 30 mL of tetrahydrofuran (THF) was added dropwise a solution of 7.08 g (0.04 mol) of diethyl cyanomethylphosphonate[24] in 40 mL of THF at 0 °C under N_2. The ice bath was removed, and the mixture was stirred at 25 °C for 1 h. A solution of 3.91 g (0.024 mol) of 5-bromopentanal in 10 mL of THF was added dropwise at 25 °C, and the mixture was stirred for 1 h. The reaction mixture was treated with saturated NH_4Cl solution. After a conventional workup, column chromatography (silica gel, petroleum ether) followed by distillation gave 2.65 g (59%) of a mixture of **3b** isomers: bp 69–80 °C (0.1 torr); ^1H NMR ($CDCl_3$) (*E* isomer) δ 6.65 (1 H, d of t, J = 6, 15 Hz), 5.33 (1 H, d of t, J = 1, 15 Hz), 3.38 (2 H, t, J = 6 Hz), 2.25 (2 H, m), 1.05–2.05 (4 H, m); GC–mass spectrum, *m/e* (rel intensity) 189 (5), 187 (5), 108 (60), 107 (16), 41 (100); IR (film) 2220 cm^{-1}; high-resolution mass spectrum calcd 188.997 69 (^{81}Br), found 188.997 02.

6-Bromo-1-methoxy-1-hexene (3c). To a solution of 8.04 g (0.023 mol) of (methoxymethyl)triphenylphosphonium chloride in 100 mL of ether was added over 0.5 h 9.78 mL of 2.4 N phenyllithium in cyclohexane/ether at 0 °C under N_2. The resulting red solution was stirred for 0.25 h at 0 °C and for 0.5 h at 25 °C and was then cooled to 0 °C. A solution of 3.87 g (0.024 mol) of 5-bromopentanal in 20 mL of ether was added over 0.1 h. After stirring at 0 °C for 1 h, the reaction mixture was treated with saturated aqueous NH_4Cl solution. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated aqueous NaCl solution, dried over $MgSO_4$, and filtered. Ether was distilled in vacuo, and the resulting residue was treated with petroleum ether and cooled to −78 °C to pre-

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(20) The E_a's for the cyclizations of the series **1a–d** studied in this work show a striking parallel to the E_a's found in Sustmann's study of substituent effects on allyl radical rotations;[8a] for each case the ΔE_a for cyclization of **1b–d** relative to that of **1a** is about 20% of the ΔE_a found in the rotational barriers of the similarly substituted allyl radicals.

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cipitate byproducts. Following filtration, the solvent was distilled in vacuo, and the resulting residue was purified by column chromatography (silica gel, 1:1 benzene/petroleum ether) and then distillation to give a 1.6 g (35%) yield of a mixture of isomers of **3c**; bp 58–59 °C (1.1 torr); ^{1}H NMR ($CDCl_3$) (*E* isomer) δ 6.27 (1 H, d, J = 12 Hz), 4.70 (1 H, d of t, J = 7, 12 Hz), 3.57 (3 H, s), 3.40 (2 H, t, J = 7 Hz), 1.3–2.2 (6 H, m); (*Z* isomer) δ 5.85 (1 H, d, J = 7 Hz), 4.30 (1 H, q, J = 7 Hz), 3.47 (3 H, s), 3.40 (2 H, t, J = 7 Hz), 1.3–2.2 (6 H, m); GC–mass spectrum, *m/e* (rel intensity) 194 (4), 192 (5), 81 (21), 71 (100), 41 (52); IR (film) 1650, 1205, 1125 cm^{-1}; high-resolution mass spectrum calcd 192.014 69 (^{79}Br), found 192.014 66.

7-Bromo-2-methoxy-2-heptenenitrile (3d). To a suspension of 1.96 g (0.047 mol) of NaH (57% dispersion in oil) in 100 mL of THF at 25 °C under N_2 was added dropwise a solution of 9.61 g (0.047 mol) of diethyl cyano(methoxymethyl)phosphonate[25] in 50 mL of THF. After H_2 evolution ceased, a solution of 5.11 g (0.031 mol) of 5-bromopentanal in 50 mL of THF was added dropwise, and the resulting mixture was heated at 65 °C for 3 h. The mixture was treated with saturated aqueous NH_4Cl solution. Following a conventional extractive workup, the products were purified by column chromatography (silica gel, 99:1 hexanes/ethyl acetate) and distillation to give 5.12 g (76%) of a mixture of isomers of **3d**; bp 61–63 °C (0.03 torr); ^{1}H NMR ($CDCl_3$) (isomer A) δ 5.45 (1 H, t, J = 7.5 Hz), 3.70 (3 H, s), 3.40 (2 H, t, J = 6 Hz), 2.2 (2 H, m) 1.4–2.0 (4 H, m); (isomer B) δ 5.45 (1 H, t, J = 7.5 Hz), 3.60 (3 H, s), 3.40 (2 H, t, J = 6 Hz), 2.2 (2 H, m), 1.4–2.0 (4 H, m); GC–mass spectrum, *m/e* (rel intensity) 219 (7), 217 (6), 138 (13), 96 (100); IR (film) 2210, 2230 cm^{-1}; high-resolution mass spectrum calcd 219.008 24 (^{81}Br), found 219.008 59.

2-Heptenenitrile (4b) was prepared in 55% yield from the reaction of pentanal and diethyl cyanomethylphosphonate using the procedure given above for the preparation of **3b**: bp 25 °C (0.4 torr) [lit.[26] bp 71–74 °C (22 torr)]. GC and ^{1}H NMR analyses showed a 1:3 (*Z*/*E*) ratio of isomers.

1-Methoxy-1-hexene (4c) was prepared in 36% yield from the reaction of pentanal and (methoxymethyl)triphenylphosphonium chloride using the procedure given above for the preparation of **3c**; bp 48–50 °C (27 torr) [lit.[27] bp 110–118 °C (760 torr)]. GC analysis showed a 1:1 ratio of isomers.

2-Methoxy-2-heptenenitrile (4d) was prepared in 65% from the reaction of pentanal and diethyl cyano(methoxymethyl)phosphonate using the procedure given above for the preparation of **3d**: bp 28 °C (0.25 torr). GC analysis showed a 3:2 mixture of isomers: ^{1}H NMR ($CDCl_3$) δ 5.50 (1 H, J = 7.5 Hz), 3.70 and 3.60 (3 H, two s's), 2.1–2.4 (2 H, m), 1.1–1.6 (4 H, m), 0.9 (3 H, br t); GC–mass spectrum, *m/e* (rel intensity) 139 (19), 124 (35), 96 (100), 56 (63); IR (film) 2230 cm^{-1}.

Cyclopentylideneacetonitrile was obtained in 77% yield from the reaction of cyclopentanone and diethyl cyanomethylphosphonate using the procedure given above for the preparation of **3b**; bp 116 °C (57 torr); ^{1}H NMR ($CDCl_3$) δ 5.17 (1 H, m), 2.3–2.7 (4 H, m), 1.6–1.9 (4 H, m); GC–mass spectrum, *m/e* (rel intensity) 107 (59), 106 (34), 79 (51), 41 (100); IR (film) 2210 cm^{-1}.

Cyclopentaneacetonitrile (5b) was prepared by hydrogenation of 0.4 g (4 mmol) of cyclopentylideneacetonitrile in the presence of 50 mg of Pd on charcoal at 25 °C under H_2 (1 atm). Filtration of the reaction mixture and distillation gave 0.22 g (54%) of **5b**; bp 91 °C (20 torr) [lit.[28] bp 76–78 °C (15 torr)].

(Methoxymethyl)cyclopentane (5c). To a slurry of potassium hydride (1.3 g, 1.1 equiv, 35% in oil) in 30 mL of THF was added a solution of cyclopentyl methyl alcohol (1.0 g, 0.01 mol) dropwise at room temperature under nitrogen. After completion of hydrogen evolution, the reaction mixture was heated to 50 °C for 1 h. After cooling to room temperature, a solution of methyl iodide (2.77 g, 1.9 equiv) in 10 mL of THF was added. The reaction mixture was heated to 50 °C for 5 h. After a standard workup, distillation gave 0.4 g of product (35% yield): bp 59 °C (45 torr) [lit.[29] bp ca. 25 °C (0.2 torr)]; ^{1}H NMR ($CDCl_3$) δ 3.65 (3 H, s), 3.57 (2 H, d, J = 6.8 Hz), 2.3–1.0 (9 H, m); GC–mass spectrum; *m/e* (rel intensity) 114 (1), 82 (33), 68 (58), 45 (100), 41 (67); IR (film) 1120, 1100 cm^{-1}.

Methoxycyclopentylideneacetonitrile was prepared in 66% yield from the reaction of the cyclopentanone and diethyl cyano(methoxymethyl)-phosphonate by the method given above for the preparation of **3d**. The product was isolated from the reaction mixture via silica gel column chromatography (1% ethyl acetate in hexanes) and was pure by ^{1}H NMR. No further purification was attempted: ^{1} NMR ($CDCl_3$) δ 3.63 (3 H, s), 2.45 (4 H, m), 1.7 (4 H, m); GC–mass spectrum, *m/e* (rel intensity), 137 (23), 96 (100); IR (film) 2210 cm^{-1}.

Methoxycyclopentaneacetonitrile (5d). Methoxycyclopentylideneacetonitrile (120 mg, 0.88 mmol) was hydrogenated in the presence of Pd on $BaSO_4$ (50 mg) in ethanol at room temperature under H_2 at atmospheric pressure. A standard workup followed by preparative TLC (silica gel, petroleum ether) gave 43 mg of product (35% yield): ^{1}H NMR ($CDCl_3$) δ 3.85 (1 H, d, J = 7 Hz), 3.47 (3 H, s), 2.3 (1 H, m), 2.0–1.2 (8 H, m); GC–mass spectrum, *m/e* (rel intensity) 107 (2), 71 (100), 41 (45); IR (film) 2230 cm^{-1}.

Cyclohexanecarbonitrile (6b) was purchased from Aldrich Chemical Co.

Methoxycyclohexane (6c). To a slurry of sodium hydride (0.86 g, 1.1 equiv, 60% in oil) in 30 mL of THF was added a solution of cyclohexanol (2.00 g, 0.02 mol) dropwise at 40 °C under nitrogen. After completion of hydrogen evolution, the reaction mixture was heated to 50 °C for 1 h. After cooling to room temperature, a solution of methyl iodide (4.26 g, 1.5 equiv) in 20 mL of THF was added. The reaction mixture was heated to 50 °C for 2.5 h. After a standard workup, silica gel column chromatography (pentanes) gave 1.1 g of product (48.2% yield) after distillation of the solvents. The product was pure by ^{1}H NMR,[30] and no further purification was attempted.

Attempted Preparation of 1-Cyano-1-methoxycyclohexane (6d). The attempted synthesis of **6d** by the methylation of cyclohexanone cyanohydrin with methyl iodide in the presence of bases such as NaH, KH, and triethylamine, even at low temperature, or by the insertion of carbene from diazomethane under neutral conditions failed to give the desired product.

Reactions of Substituted Hexenyl Bromides with Tri-*n*-butylstannane. The substrate concentration was fixed at 0.1 M, and the tri-*n*-butylstannane concentration was varied from 0.2 to 1.2 M. At 12 h, the reaction was quenched by cooling the reaction mixture to −78 °C. The mixture was treated with saturated aqueous potassium fluoride solution and analyzed by GC. In all cases, control reactions containing no tri-*n*-butylstannane did not give either the open-chain or the cyclized product.

The following procedure is representative. The stock solution of substrate **3d** was prepared by dissolving **3d** (0.3045 g, 1.401 mmol), AIBN (3.1 mg) as an initiator, and dodecane (19.5 mg) as an internal standard in 5.6 mL of benzene. To five 0.4-mL portions of substrate solutions in 1.0-mL volumetric flasks were added 0.20, 0.25, 0.30, 0.35, and 0.40 mL, respectively, of 2.0 M tri-*n*-butylstannane solution. Benzene was added to the mark. Each flask was evacuated and filled up with nitrogen. The reactions were conducted at 50 °C in the dark. After 12 h, the reaction mixture was quenched and analyzed by GC.

Time-Dependent Experiments of 3c with Tri-*n*-butylstannane. A stock solution of **3c** was prepared by dissolving **3c** (30.2 mg, 0.1565 mmol), AIBN (2.5 mg), and dodecane (7.2 mg) in 0.175 mL of benzene. A stock solution of tri-*n*-butylstannane was prepared by dissolving 1.4568 g of tri-*n*-butylstannane in 5.0 mL of benzene. A mixture of 0.11 mL of the **3c** solution and 0.85 mL of the tri-*n*-butylstannane solution was diluted with benzene to 1.0 mL. The reaction was conducted at 50 °C and monitored by taking aliquots at 10, 20, 30, 60, 240, and 720 min which were treated and analyzed as described above.

Temperature-Dependent Experiments of 3b–d with Tri-*n*-butylstannane. The reactions of substrates **3b–d** with tri-*n*-butylstannane were performed at four different temperatures (25–75 °C). In all cases, the substrates concentrations were fixed at 0.1 M. The tri-*n*-butylstannane concentration was fixed at 0.6 M in the reaction of **3d** and at 0.4 M in the reactions of **3b** and **3c**. The reactions were conducted and analyzed as described above.

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