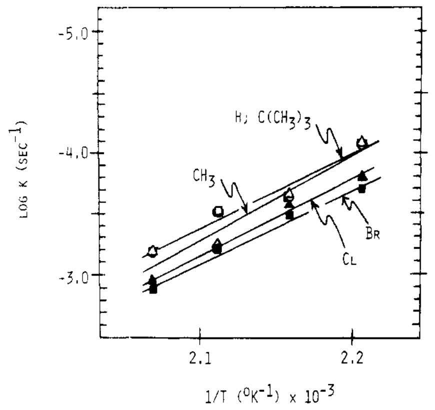

Figure 2. Variation of log k vs. $1/T$ over the temperature range 180.0 to 210.0 ± 0.2 °C for alcohols **2**: □ (R = C(CH$_3$)$_3$); △ (R = CH$_3$); ○ (R = H); ▲ (R = Cl); ■ (R = Br).

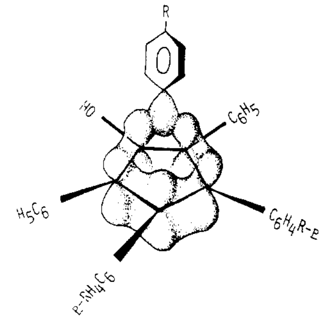

Figure 3. Transition state devoid of charge separation.

tropic *hydrogen* rearrangement, in a substituted isoindene system,[15] has afforded such a relationship.

A number of workers[16-20] have offered explanations for electronic effects observed in neutral sigmatropic reactions, but given the limited number of systems studied and the fact that only one has afforded a linear free-energy relationship, it appears to be premature to offer a comprehensive theory to account for such effects. Indeed, each system appears to be unique and given the situation that electronic effects have been observed in neutral sigmatropic rearrangements but have resisted a predictive theory, optimism suggests a spectrum of reactivity to account for the observed variability among neutral systems which rearrange by a sigmatropic mechanism. In this scheme, the rearrangement of the alcohols **1** and **2** should be placed at one end of the spectrum, where rearrangements occur by a *purely* concerted mechanism having a transition state devoid of charge separation (Figure 3).

The possibility certainly exists that the steric constraints of this system are so great that the individual members of the system are reduced to energetic equivalence.

Registry No. **1** (R = CF$_3$), 64706-20-3; **1** (R = Br), 19057-23-9; **1** (R = Cl), 15946-43-7; **1** (R = C$_6$H$_5$), 19209-97-3; **1** (R = H), 2137-74-8; **1** (R = CH$_3$), 64706-19-0; **1** (R = C(CH$_3$)$_3$), 64706-17-8; **1** (R = OCH$_3$), 64706-18-9; **2** (R = Br), 56549-00-9; **2** (R = Cl), 22926-90-5; **2** (R = CH$_3$), 19059-95-1; **2** (R = C(CH$_3$)$_3$), 64706-21-4.

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(15) K. K deFonseca, C. Manning, J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, **99**, 8257 (1977).

(16) F. Scheidt and W. Kirmse, *J. Chem. Soc., Chem. Commun*, 716 (1972).

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Polar Effect in Alkyl Radical Reactions. Carbon Kinetic Isotope Effects in Halogen Atom Transfer to Tin(III) and Chromium(II)

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Halogen atom transfer from organic halides is an important process in free-radical chemistry, and it can be effected by a variety of reagents, foremost of which are organometallic radicals and transition metal complexes, e.g., eq 1, where X = Cl, Br, and I.[1,2] Halogen atom

$$CH_3X + M^{n+} \rightarrow CH_3\cdot + XM^{n+1} \qquad (1)$$

transfer is accompanied by a change in the formal oxidation state of the metal center by one unit, as indicated by the superscripts in eq 1.

The transition state for halogen atom transfer may be qualitatively described in the context of the polar effects by involving various canonical forms, as in Figure 1.[3]

Indeed in a recent study,[4] Blackburn and Tanner reported that halogen atom transfer from a series of substituted benzyl chlorides, bromides, and iodides to tri-n-butyltin radicals, i.e., eq 2, showed excellent Hammett

$$ArCH_2X + n\text{-}Bu_3Sn^{III} \rightarrow ArCH_2\cdot + n\text{-}Bu_3Sn^{IV}X \qquad (2)$$

correlations. The variation in the postive ρ values and the use of σ^- substituent constants accorded with the importance of bond breaking and electron transfer in the transition state, as depicted by the contributions from the forms II and III, respectively, in Figure 1.

The relative reactivities of benzylic bromides to n-butyltin radicals in eq 2 compare favorably with those measured earlier for bromine atom transfer to the transition metal complexes of chromium(II),[5,6] i.e., eq 3. The

$$ArCH_2Br + Cr^{II} \rightarrow ArCH_2\cdot + BrCr^{III} \qquad (3)$$

latter was made in connection with a comparison of the polar effects in hydrogen atom and halogen atom transfers in the formation of benzylic radicals.[7]

In this report we present our initial efforts in the measurement of the kinetic isotope effects (KIE) as a complementary approach to ascertaining the extent of bond breaking and electron transfer in the transition state for halogen atom transfer. In particular, the availability of a sensitive isotope-ratio mass spectrometer capable of measuring $^{13}C/^{12}C$ to ±0.0005[8] allowed us to establish the carbon-13 KIE (in natural abundance) for chlorine, bromine, and iodine atom transfers in eq 1, using the tri-

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(1) Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: London, 1974; pp 296, 349ff.

(2) (a) Davies, A. G.; Roberts, B. P. *Free Radicals* **1973**, *1*, Chapter 10. (b) Poutsma, M. L. *Ibid.* **1973**, *2*, Chapter 14.

(3) For a general discussion of polar effects, see: Russell, G. A. in ref 2, Vol. 1, Chapter 7. To emphasize the negative charge on carbon in the electron-transfer canonical form III, it may be represented alternatively as [$CH_3{:}^-$ X· M^{n+1}].

(4) Blackburn, E. V.; Tanner, D. D. *J. Am. Chem. Soc.* **1980**, *102*, 692. (b) See also: Grady, G. L.; Danyliw, T. J.; Rabideux, P. *J. Organomet. Chem.* **1977**, *142*, 67.

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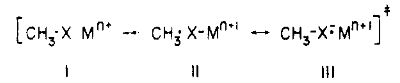
Table I. Carbon-13 Kinetic Isotope Effects in Bromine Atom Transfer from Methyl Bromide to Triphenyltin(III)[a]

CH_3Br, mmol	CH_4, μmol (%)[b]	δ $^{13}C_{PDB}$ CH_3Br	δ $^{13}C_{PDB}$ CH_4	$\frac{k_{12}}{k_{13}}$
1.116	15.9 (1.425)	−46.68 ± 0.09	−77.79 ± 0.08	1.0338
1.116	21.35 (1.913)	−46.93 ± 0.08	−78.44 ± 0.17	1.0347
1.116	22.45 (2.012)	−47.11 ± 0.07	−77.52 ± 0.11	1.0337
0.2741	16.12 (5.881)	−46.52 ± 0.06	−74.82 ± 0.09	1.0312
0.2741	19.86 (7.246)	−46.45 ± 0.07	−78.52 ± 0.08	1.0357
0.05917	17.51 (29.59)	−47.07 ± 0.04	−78.30 ± 0.02	1.0409

average δ $^{13}C_{PDB}$ CH_3Br = −46.81   average $\frac{k_{12}}{k_{13}} = 1.0350 \pm 0.0013$

[a] In 0.20 mL of 0.2 M Ph_3SnH in n-hexane at 0 °C. [b] Yield based on CH_3Br in parentheses.



$$\left[\underset{\text{I}}{CH_3{\cdot}X\ M^{n+}} \leftrightarrow \underset{\text{II}}{CH_3{:}X{-}M^{n+1}} \leftrightarrow \underset{\text{III}}{CH_3{-}X^{\overset{-}{\cdot}}M^{n+1}}\right]^{\ddagger}$$

Figure 1. Transition state for halogen atom transfer from methyl halides to metal complexes, including the contributions from homolytic bond breaking and electron transfer.

Table II. Carbon-13 Kinetic Isotope Effects for Halogen Atom Transfer from Methyl Iodide, Bromide, and Chloride to $Ph_3Sn(III)$ and $en_2Cr(II)$[a]

methyl halide	k_{12}/k_{13}	
	$en_2Cr(II)$	$Ph_3Sn(III)$
CH_3I	1.0433 ± 0.0009	1.0136 ± 0.0010 (Δ)[c] 1.0123 ± 0.0002 (hν)[b]
CH_3Br	1.0514 ± 0.0012	1.0350 ± 0.0013 (hν)[b]
CH_3Cl	1.0625 ± 0.0021	1.0475 ± 0.0014 (hν)[b]

[a] At 0 °C in n-hexane [$Ph_3Sn(III)$] or aqueous dimethylformamide [$en_2Cr(II)$]. [b] Reaction initiated photochemically. [c] Under thermal conditions in the dark.

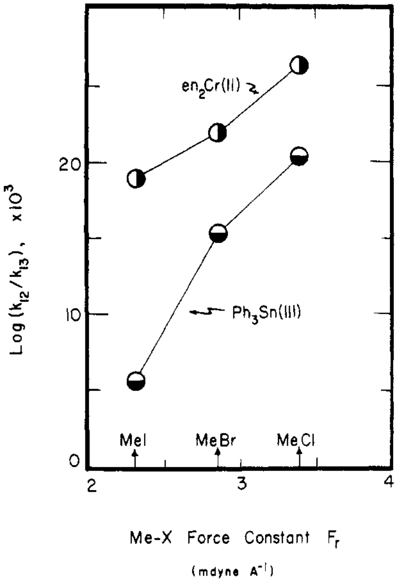


Figure 2. Variation of the kinetic isotope effect for halogen atom transfer from methyl chloride, bromide, and iodide to $en_2Cr(II)$ (◑) and $Ph_3Sn(III)$ (⊖) with the carbon–halogen stretching force constant F_r.

phenyltin radical $Ph_3Sn(III)$ and bis(ethylenediamine)chromous, $en_2Cr(II)$, as the halogen acceptors. In both systems, the methyl radical is known to be quantitatively converted to methane subsequent to the rate-limiting halogen transfer.[9-11]

Results

Measurement of the Isotope Effect. Experimental values of the isotopic fractionation accompanying the formation of methane were obtained at various conversions of the methyl halide, employed in excess. The consistency of results is shown in Table I for a typical example in which the reduction of methyl bromide by triphenyltin hydride was carried out in n-hexane solutions. The carbon isotopic composition of methane derived from the reduction is compared with that of the methyl bromide, and the isotopic compositions are reported in Table I in terms of δ $^{13}C_{PDB}$, which is $[R_{sample}/R_{PDB} - 1]10^3$, where $R = {}^{13}C/{}^{12}C$ and PDB indicates the PeeDee Belemnite isotopic standard, $R_{PDB} = 0.011\,237\,2$.[12] The units for δ are denoted by the symbol ‰, expressed as per mil. The tabulated isotope effects were calculated from the data by using eq 4, where

$$\left(\frac{k_{13}}{k_{12}} - 1\right)\log(1 - \alpha f) = \log\left[1 + \left(\frac{\delta_0 - \delta_p}{\delta_0 + 10^3}\right)\left(\frac{f}{1 - \alpha f}\right)\right] \quad (4)$$

f is the fractional degree of conversion (i.e., $0 \le f \le 1.0$), and δ_0 and δ_p represent the δ $^{13}C_{PDB}$ values for the starting methyl iodide and methane, respectively. The coefficient α is a correction factor taking into account the finite abundance of the "tracer" isotope (i.e., ^{13}C). Its value depends on the isotopic composition of the reactant, the pooled product, and the isotopic standard, and it is given in this case by $\alpha = (101124 + 1.124\delta_0)(101124\delta_p)$. Equation 4, originally derived by Bigeleisen and Wolfsberg,[12] has been recast in terms of δ and is exact for all values of δ and for $0 < f < 1$. The complete carbon kinetic isotope listings for the reactions of triphenyltin radical with methyl iodide and methyl chloride are included in the supplementary material.

The reactions of $en_2Cr(II)$ with methyl chloride, bromide, and iodide were carried out in aqueous dimethylformamide solutions, and the KIEs are summarized in Table II, together with those for the triphenyltin radical. The complete carbon kinetic isotope results for $en_2Cr(II)$ are also listed in the supplementary material.

Discussion

Several features are noteworthy about the results in Table II which summarizes the carbon-13 kinetic isotope effects for halogen atom transfer from methyl iodide, bromide, and chloride to $Ph_3Sn(III)$ and $en_2Cr(II)$ according to eq 1. Thus with both reagents, there is a

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(10) Davies, A. G. *Adv. Chem. Ser.* **1976**, *157*, 26. Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

(11) Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 137.

(12) Craig, H. *Geochim. Cosmochim. Acta.* **1957**, *12*, 133. Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1952**, *1*, 15.

(13) Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9002.

monotonic trend for k_{12}/k_{13} to increase in the order: $CH_3I < CH_3Br < CH_3Cl$. Next, for a given methyl halide, the magnitude of the isotope effect is always much larger for $en_2Cr(II)$ than for $Ph_3Sn(III)$. Furthermore, the magnitude of the difference $\Delta k_{12}/k_{13}$ [i.e., the KIE for $en_2Cr(II)$ minus that for $Ph_3Sn(III)$] measured for CH_3I ($\Delta k_{12}/k_{13} = 0.030$) is greater than that for either CH_3Br (0.016) or CH_3Cl (0.015). This important point is illustrated graphically in Figure 2, in which the kinetic isotope effect [log (k_{12}/k_{13})] is plotted against the force constant F_r for the principal carbon–halogen stretching mode in the methyl halides.[13] Such a comparison focuses on the inherent differences in the transition states for the transfer of various halogen atoms to $en_2Cr(II)$ and to $Ph_3Sn(III)$.

The kinetic isotope effect is expressed in eq 5 as a

$$\frac{k_{12}}{k_{13}} = \frac{\nu_{12L}}{\nu_{13L}}[\mathrm{ZPE}] \quad (5)$$

product of an imaginary frequency factor ν and a zero point energy (ZPE) term.[14] The maximum value of the zero point energy term is reflected in the equilibrium isotope effect (EIE) which has been calculated at 1.027 for CH_3I and 1.035 for CH_3Cl in the hypothetical equilibrium process[14] shown in eq 6. Values of the kinetic isotope effect

$$CH_3X \rightleftharpoons CH_3\cdot + X\cdot \quad (6)$$

larger than the equilibrium isotope effect reflect motion of the halogen along the reaction coordinate, generally signifying a late transition state.[16] Thus we qualitatively interpret the KIE for halogen atom transfer to $en_2Cr(II)$ in excess of the EIE to reflect extensive bond breaking, as in II in Figure 1. Furthermore, the more or less linear trend shown in Figure 2 suggests that a rather uniform mechanism pertains to iodine, bromine, and chlorine atom transfers to $en_2Cr(II)$. Indeed this trend also applies to bromine and chlorine transfer to $Ph_3Sn(III)$, as indicated by the same slope in Figure 2. However, it is noteworthy that the KIE for iodine transfer to $Ph_3Sn(III)$ is significantly less than the EIE. Moreover, there is a marked break in the slope of the curve in Figure 2, suggesting that iodine atom transfer to $Ph_3Sn(III)$ is not subject to all the same types of interactions as those enjoyed by CH_3Br and CH_3Cl.

Blackburn and Tanner[4] found iodine atom transfer to n-$Bu_3Sn(III)$ from a series of substituted benzyl iodides to exhibit anomalously high ρ values, compared to those for benzyl bromides and chlorides. Iodine atom transfer was also subject to increased sensitivity to solvent polarity, relative to bromine and chlorine atom transfers. Their conclusion of an increased contribution from electron transfer (as in III in Figure 1) is certainly consistent with the characteristic kinetic isotope effect for iodine atom transfer in Table II.[17] If the contribution from III is indeed considered to be the polar effect, the trend in the KIE for halogen atom transfers clearly shows that it is also dependent on the nature of the acceptor. As such, the driving force for electron transfer [i.e., E^0 for the couple $M^{n+} \rightleftharpoons M^{n+1} + e^-$] may be one important factor in assessing its importance.[18-21]

Although a quantitative description of the transition state for halogen atom transfer is premature on the basis of the limited data on hand, the KIE results obtained thus far clearly point out the importance of polar effects in halogen atom transfer. We hope that the examination of the KIE with a greater variety of halogen acceptors will provide the basis for a more quantitative description.[22]

Experimental Section

Materials. Methyl iodide from Matheson, Coleman and Bell Company was washed successively with aqueous sodium bisulfite, distilled water, aqueous sodium carbonate, and water. After being dried over calcium chloride, it was distilled from phosphorus pentoxide in the dark under an argon atmosphere and stored in a Schlenk flask over a copper wire at −30 °C until used. Methyl bromide and chloride were distilled as received from Matheson, Coleman and Bell Company. Spectranalyzed N,N-dimethylformamide was vacuum distilled from barium oxide in vacuo prior to use. n-Hexane and diethyl ether were reagent-grade materials, redistilled from benzophenone sodium ketyl. Ethylenediamine (Matheson, Coleman and Bell Co.) was redistilled from potassium hydroxide under argon.

Triphenyltin hydride was prepared from triphenyltin chloride (M. T. Chemicals Co.) and lithium aluminum hydride under an argon atmosphere in the dark.[9,23] Recrystallization from 90% (v/v) methanol–water yielded colorless crystals: mp 22.5–23.5 °C (lit. 26–28 °C); ^{1}H NMR (acetone-d_6) δ 7.3 (m, 15 H), 6.8 (s, 1 H).

Preparation of Chromium (II) Triflate. A Schlenk flask containing 20 mL of 1 M trifluoromethanesulfonic acid was deoxygenated by argon purging with the aid of a Teflon cannula. An excess of chromium metal (99.995%, Varlacoid Chemical Co.) was broken into small chips, one of which was activated by dipping into 70% perchloric acid until vigorous hydrogen evolution occurred. The chips were quickly rinsed with distilled water and added to the Schlenk flask. With the temperature maintained below 40 °C with external cooling, the complete reaction required approximately 24 h. The resulting bright blue solution gave no indication of the presence of chromium(III) species. [The solution exhibited a single spectral band at λ_{max} 710 nm, but no absorption at 580 nm. Chromium(III) was always present when the preparation was carried out with perchloric acid.]

Reduction of Methyl Halides (I, Br, Cl) with $en_2Cr(II)$. The reaction with methyl iodide was carried out in a 25-mL round-bottom flask equipped with a Teflon stirbar and a sidearm stopcock. A mixture of 3.5 mL of DMF and 0.5 mL of H_2O was added to the flask, and the solution was thoroughly deoxygenated via freeze–pump–thaw cycles. A 0.10-mL aliquot of the stock chromium(II) solution was added, followed by 15 μL of ethylenediamine. After the flask was equilibrated at 0 °C, the reaction was initiated by injecting 0.40 mL of deoxygenated MeI with the aid of a hypodermic syringe. [In several reactions, MeI was added to the aqueous DMF solution of Cr(II), and reaction was initiated by the addition of ethylenediamine, but the order of addition had no effect upon the isotopic results.] The reaction was stirred for 30 min at 0 °C, and 1 mL of deoxygenated aqueous 1 M $HClO_4$ was added to ensure complete cleavage of methylchromium(III).[11] The methane produced was transferred to a combustion vacuum line by means of a Toepler pump and completely converted to carbon dioxide, which was collected and analyzed by mass spectrometry.[24] In control experiments, a mixture of chromium(II) and methyl iodide in the absence of ethylenediamine

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[14] O'Leary, M. H. In "Isotope Effects on Enzyme-Catalyzed Reactions"; Cleland, W. W., O'Leary, M. H., and Northrup, D. B., Eds.; University Park Press: Baltimore, 1977.

[15] Vogler, E. A.; Stein, R. L.; Hayes, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3163.

[16] Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980.

[17] The discrete values of the KIE for iodine atom transfer to $Ph_3Sn(III)$, however reduced in magnitude, indicate that complete electron transfer has not been effected in the transition state.

[18] For example, bromine atom transfer from benzylic bromides to cobalt(II) complexes such as $Co(DMG)_2PPh_3$ shows a rather larger positive ρ value.[19]

[19] Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2.

[20] It also bears on the general question of oxidative addition of organic halides to metal complexes.[21]

[21] See: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 7. Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

[22] For example, see: Burton, G. W.; Sims, L. B.; Wilson, J. C.; Fry, J. *J. Am. Chem. Soc.* **1977**, *99*, 3371, and ref 14.

[23] van der Kerk, G. J. M.; Noltes, J. G.; Luitjten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.

[24] For details of the experimental procedure, see ref 15.

produced no detectable amounts of CH_4 after several days. Similarly, mixtures containing only methyl iodide and ethylenediamine produced no methane. The reactions with methyl bromide and methyl chloride were carried out in an analogous fashion, except that these gases were introduced into the reaction flask from calibrated Pyrex bulbs. The reaction times were extended to 24 h or longer in order to accommodate the lower reactivity of these halides.

Thermal Reaction of Triphenyltin Hydride with Methyl Iodide. A cylindrical reaction tube equipped with a Teflon covered stirrer was attached to a vacuum line and flame dried. A 0.20-mL aliquot of a 0.2 M hexane solution of Ph_3SnH was added to the cooled tube under a stream of argon. The contents of the reaction tube were deoxygenated by means of three freeze–pump–thaw cycles. A weighed amount of methyl iodide was distilled into the tube, and the flask was sealed under vacuum. The reaction mixture was stirred in the dark at 0 °C for 24 h. The flask was then attached to a combustion line and the methane was removed and converted to carbon dioxide for isotopic analysis.

Photochemical Reactions of Triphenyltin Hydride with MeX (X = I, Br, Cl). A cylindrical reaction tube equipped with a Teflon covered stirrer was attached to a vacuum line and flame dried. After the flask had cooled, 0.40 to 0.50 mL of a 7.0×10^{-2} M hexane solution of Ph_3SnH and 3.0 mL of hexane were added under a stream of argon. The contents was thoroughly deoxygenated by freeze–pump–thaw cycles. A weighed amount of methyl iodide was distilled into the flask, and the flask was sealed in vacuo. The flask was placed in a 0 °C bath contained within the photolysis chamber (Rayonet photochemical reactor, Southern N.E. Ultraviolet Co., Middletown, CT) and thermally equilibrated for 10 min. The rapidly stirred solution was irradiated for 60 s with lamps nominally emitting at 350 nm. The methane was transferred to a combustion vacuum line by means of a Toepler pump and analyzed in the usual manner. The reactions involving methyl bromide and methyl chloride were prepared in an analogous fashion, except these gases were introduced with the aid of calibrated Pyrex bulbs. The conditions for the photolysis of methyl bromide were similar to those employed for methyl iodide. However, the reactions of methyl chloride required more concentrated solutions and longer periods of irradiation. Photolysis of methyl iodide in the absence of Ph_3SnH produced less than 5.0×10^{-5} mmol of methane under these experimental conditions.

Acknowledgment. We thank Dr. John M. Hayes for his helpful interest, the National Institutes of Health (General Medical Sciences), the National Science Foundation, and the National Aeronautics and Space Administration for financial assistance.

Registry No. Methyl bromide, 74-83-9; methane, 74-82-8; methyl iodide, 74-88-4; methyl chloride, 74-87-3; chromium(II) triflate, 58164-61-7; triphenyltin hydride, 892-20-6; $en_2Cr(II)$, 15525-39-0; $Ph_3Sn(III)$, 14971-33-6.

Supplementary Material Available: A complete listing of kinetic isotope effects at various conversions of methyl iodide, bromide, and chloride with Ph_3SnH and $en_2Cr(II)$ (4 pages). Ordering information is given on any current masthead page.

Kinetics of the Cope Rearrangement of a 3,4-Diphenylhexa-1,5-diene

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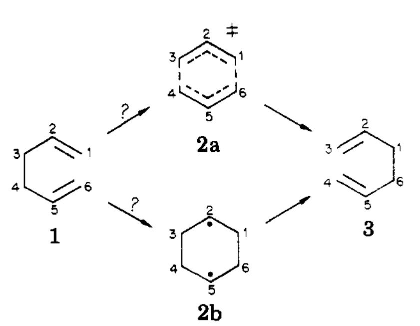
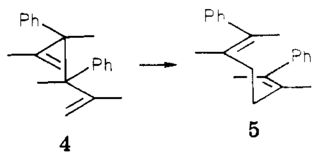
Received April 15, 1980

The mechanism of the thermal Cope rearrangement has generally been conceived as a concerted process (1 → 2a → 3), designated at one time as a "no mechanism" reaction, and later labeled as an allowed [3,3] sigmatropic shift.[1] However, the possible intervention of a cyclohexane-1,4-diyl intermediate (**2b**) was recognized early on[2] and recently received experimental support from the work of Dewar and Wade,[3] who established that phenyl substituents in the 2- or 2,5- positions, a substitution pattern which should promote stabilization of the radical centers of a species such as **2b**, did indeed lead to significant rate enhancement in the Cope rearrangement. Dewar and Wade determined kinetic parameters for the 2-phenyl-, 3-phenyl-, 2,4-diphenyl- and 2,5-diphenylhexa-1,5-dienes for comparison with the parent hexa-1,5-diene. In view of the significance of the phenyl-substituted substrates in defining the emerging picture of the Cope rearrangement mechanism, we complete the series by reporting our kinetic parameters for the Cope rearrangement of *dl*-3,4-diphenylhexa-1,5-diene (**4**),[4] a substrate with both phenyl groups positioned in such a way as to preclude participation in cyclohexane-1,4-diyl delocalization.



We had established earlier that 4 rearranges cleanly through a chair-like transition state, yielding exclusively *trans,trans*-1,6-diphenylhexa-1,5-diene (**5**) as the kinetically controlled product.[5] The pseudoequatorial disposition of phenyl groups in the transition state derived from 4 allows electronic interaction with the phenyl groups with minimal complications by steric effects.



4 5

First-order rate constants at three temperatures were determined in *n*-heptane, with product formation monitored by the increase in UV absorption. Values are summarized in Table I, along with Arrhenius activation parameters; these lead to $\Delta H^* = 24.0 \pm 0.2$ kcal/mol and $\Delta S^* = -12.4 \pm 0.6$ eu. Significant rate enhancement by the phenyl groups in this system can be seen by comparison with the parent hexa-1,5-diene, where $E = 34.3$ kcal/mol, $\log A = 10.36$, $\Delta H^* = 33.5$ kcal/mol, and $\Delta S^* = -13.8$ eu.[2c] Activation by unsaturated substituents in the 3 and/or 4 positions is typical for Cope rearrangements and is usually interpreted as stabilization of a transition state resembling a pair of weakly interacting allyl radicals (**2a**). Rate enhancement in 4 is roughly equivalent to that observed for

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(1) For a recent review, see S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 1 (1975).

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