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Activation Parameters for the Additions of Arylhalocarbenes to Alkenes

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Abstract: By use of nanosecond laser flash photolytic methods, absolute rate constants have been obtained for the additions of *p*-(trifluoromethyl)phenylbromocarbene ($CF_3C_6H_4CBr$), phenylbromocarbene (PhCBr), phenylchlorocarbene (PhCCl), phenylfluorocarbene (PhCF), and *p*-methoxyphenylfluorocarbene ($CH_3OC_6H_4CF$) to tetramethylethylene (TME) and 1-hexene. The rate constants ranged from 1.7×10^9 ($CF_3C_6H_4CBr$/TME) to 5.0×10^4 L/(M·s) ($CH_3OC_6H_4CF$/1-hexene); classical structure/reactivity relations were obeyed. Determination of the rate constants at temperatures between 315 and 200 K gave E_a, log A, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for the 10 reactions. All of the reactions were dominated by $\Delta S^{\ddagger}$. $\Delta G^{\ddagger}$ ranged from 5.0 to 11 kcal/mol for the fastest and slowest reactions. Negative values of E_a were observed for some of the faster reactions at higher temperatures. These results are analyzed in terms of single-step addition reactions where $\Delta G^{\ddagger}$ is dominated by $\Delta S^{\ddagger}$ and, alternatively, in terms of a two-step mechanism proceeding through a carbene–alkene complex.

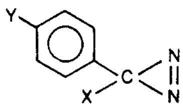
Nearly 20 years ago, Skell and Cholod used variable-temperature relative rate measurements to dissect the contributions of differential activation entropies and enthalpies in the additions of CCl_2 to alkenes.[1] Although $\Delta\Delta G^{\ddagger}$ varied with alkene structure in an understandable way, it was the entropic term, rather than the enthalpic term, that usually paralleled the rates and was the dominant contributor to $\Delta\Delta G^{\ddagger}$; only with the less reactive 1-alkenes did enthalpy dominate. Application of the Hammond postulate led to suggestions that more reactive carbenes and alkenes traversed earlier, looser, entropy-dominated transition states, whereas less reactive carbenes and alkenes reacted via later, tighter, enthalpy-controlled transition states.[1,2]

More recently, the experiments of Giese[3] and the theoretical studies of Houk[4] have strongly emphasized the role of entropy in carbene/alkene addition reactions. The applicability of nanosecond laser flash photolysis to the determination of *absolute* rate constants for (singlet) arylhalocarbene/alkene addition reactions[5] now provides an opportunity to *directly* examine Skell's suggestions,[1] as well as certain of Houk's predictions.[4]

At present, sensitivity considerations have restricted laser flash photolytic studies to carbenes that contain an aromatic chromophore.[6] Within that restriction, and on the basis of our previous research,[5] it was clear that the widest reactivity range of readily available singlet carbenes would be afforded by *p*-(trifluoromethyl)phenylbromocarbene[7] (*p*-$CF_3C_6H_4CBr$) and *p*-methoxyphenylfluorocarbene (*p*-$CH_3OC_6H_4CF$), representing (relatively) reactive and unreactive arylhalocarbenes, respectively. In order to provide continuity in the reactivity spectrum, phenylfluorocarbene (PhCF),[5d,e] phenylchlorocarbene (PhCCl),[5a,b,e] and phenylbromocarbene (PhCBr)[5d,e] were also included in our study. Kinetic results for these latter three carbenes were available from previous work.[5e] Tetramethylethylene and 1-hexene were chosen as (relatively) reactive and unreactive substrates, respectively. It was our objective to determine the absolute rate constants and activation parameters for all of the carbene/alkene addition reactions with this set of reactants and substrates.

Results

Precursors. Each of the five carbenes was generated by photolysis of the appropriate 3-aryl-3-halodiazirine, **1–5**. Bromodiazirines **4** and **5** and chlorodiazirine **3** were prepared directly by hypobromite or hypochlorite Graham oxidation of the appropriate benzamidine.[8,9] The fluorodiazirines, **1** and **2**, were derived from the corresponding bromodiazirines (available from Graham oxidations) by fluoride/bromide exchange reactions with molten, nearly anhydrous tetra-*n*-butylammonium fluoride.[9] Full experimental details and characterizations have been provided for these precursors.[8,9]



1, Y = CH_3O, X = F
2, Y = H, X = F
3, Y = H, X = Cl
4, Y = H, X = Br
5, Y = CF_3, X = Br

Flash Photolytic Studies. Flash photolytic studies were carried out using the procedures and apparatus previously described in detail for PhCF, PhCCl, and PhCBr.[5e] Thus, the excitation wavelength was 351 nm, and a ~15-ns, 35-mJ pulse of laser light

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(1) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

(2) A remarkable possibility was that the changeover from $\Delta\Delta S^{\ddagger}$- to $\Delta\Delta H^{\ddagger}$-dominated reactions might occur with compensation that maintained good structure/reactivity correlations based on $\Delta\Delta G^{\ddagger}$.[1]

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(6) Scaiano, J. C. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z., Ed.; CRC: Boca Raton, FL, in press. We thank Dr. Scaiano for a preprint.

(7) (a) We considered the possibility that $F_3CPhCBr$ might have a readily accessible triplet state, but this seems unlikely on the basis of the Houk–Liebman relation (vide infra, ref 6b) which gives $E(T) - E(S) \sim 12$ kcal/mol for PhCBr itself. Additionally, ESR studies show no signals for matrix-isolated $F_3CPhCBr$ nor is this carbene's UV spectrum quenched in O_2-saturated fluorocarbon solvents. (b) Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5049.

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(9) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K.-J. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

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Table I. Absolute Rate Constants for Carbene/Alkene Additions[a]

	k_{abs}	
carbene	TME	1-hexene
p-$CF_3C_6H_4CBr$[b]	1.7 ± 0.05 × 10^9	2.4 ± 0.1 × 10^7
PhCBr[c]	3.8 ± 0.3 × 10^8	4.0 ± 0.4 × 10^6
PhCCl[c]	2.8 ± 0.2 × 10^8	2.2 ± 0.2 × 10^6
PhCF[c]	1.6 ± 0.2 × 10^8	9.3 ± 0.5 × 10^5
p-$CH_3OC_6H_4CF$[b]	1.1 ± 0.04 × 10^7	5.0 ± 0.3 × 10^4

[a] Rate constants were measured at 23–25 °C. Units are $M^{-1}\ s^{-1}$. [b] This work. [c] Data from ref 5d and 5e.

Table II. Arrhenius Parameters for Carbene Additions[a]

	tetramethylethylene				1-hexene	
carbene	E_a[b]	log A[b]	E_a[c]	log A[c]	E_a[e]	log A[e]
p-$CF_3C_6H_4CBr$	−1.0	8.5	1.3	10.5	0.4	7.7
PhCBr	−1.5	7.7	1.3	10.5	1.1	7.4
PhCCl	−1.7	7.2	0.8	9.7	1.1	7.4
PhCF	−1.7	7.0	0.1[d]	8.9[d]	1.3	6.9
p-$CH_3OC_6H_4CF$	0.2[e]	7.2[e]			3.1	6.9

[a] Units are E_a in kcal/mol and log A in $M^{-1}\ s^{-1}$. [b] Negative activation energies refer to 310 K < T < 263 K; see text. [c] These activation parameters pertain to 250 K < T < 200 K. [d] In this case, 210 K < T < 180 K. [e] log k_{abs} vs. $1/T$ was linear and normal.

was employed. Diazirine solutions were made up in isooctane to give optical densities of ~0.4 at 351 nm, corresponding to concentrations of ~1 × 10^{-3} M.

A transient absorption spectrum from the photolysis of **1** showed maxima at 305 and 290 nm, with product absorptions at ~320 nm and an isosbestic point at ~316 nm. The 305-nm absorption was taken as representative of p-$CH_3OC_6H_4CF$ by analogy with earlier assignments in the ArCX series[5e] and on the basis of the alkene quenching experiments (see below). In the absence of alkene, the carbene decayed by pseudo-first-order reaction with an unknown quencher; its lifetime was ~20 μs at 25 °C.

Similar preliminary experiments with diazirine **5** gave a transient absorption spectrum with maxima at ~296 and 330 nm; a product absorbed strongly at ~280 nm. The 330-nm absorption was assigned to p-$CF_3C_6H_4CBr$, again on the basis of earlier studies[5e] and subsequent quenching experiments. The carbene's lifetime in isooctane was ~5 μs.

To determine the absolute rate constants for the alkene additions, diazirine solutions in spectrograde isooctane were diluted with varying quantities of (spinning-band distilled) tetramethylethylene (TME) or 1-hexene. The diazirine concentrations were fixed at ~2 × 10^{-3} M, and the solutions were laser irradiated at 351 nm (see above). The decays of p-$CH_3OC_6H_4CF$ and p-$CF_3C_6H_4CBr$ were monitored at 305 and 325 nm, respectively.

At sufficiently high alkene quencher concentrations, the decay of the carbene spectra was pseudo first order and linearly dependent on the quencher concentration. A plot of the rate constant for decay vs. [alkene] then gave the bimolecular quenching rate constant (i.e., k_{abs} for carbene/alkene addition) as the slope.[5] The rate constant for the reaction of p-$CH_3OC_6H_4CF$ with 1-hexene was the smallest that we have yet measured; to obtain this value, the carbene decay rate constants were determined in solutions of 20%, 40%, 60%, and 80% 1-hexene is isooctane. The rate constants for the carbene–alkene additions are collected in Table I.

In order to obtain activation parameters for these reactions, we determined the absolute rate constants at various temperatures between ~315 and 200 K. With the TME substrate, all of the carbenes except p-$CH_3OC_6H_4CF$ gave *curved* Arrhenius plots of the type that we encountered previously.[5b,e] As an example, we reproduce the temperature dependence of k_{abs} for the p-$CF_3C_6H_4CBr$/TME reaction in Figure 1. These Arrhenius relations led to negative E_a's at higher temperatures (~310–263 K) and small (0.2–1.3 kcal/mol) "normal" E_a's at lower temperatures. With p-$CH_3OC_6H_4CF$/TME and 1-hexene (for all carbenes studied), normal Arrhenius behavior was observed. The activation parameters, E_a and log A, are collected in Table II. We estimate the errors in the activation parameters to be ±0.5 kcal/mol in E_a and ±0.5 unit in log A (Table II).

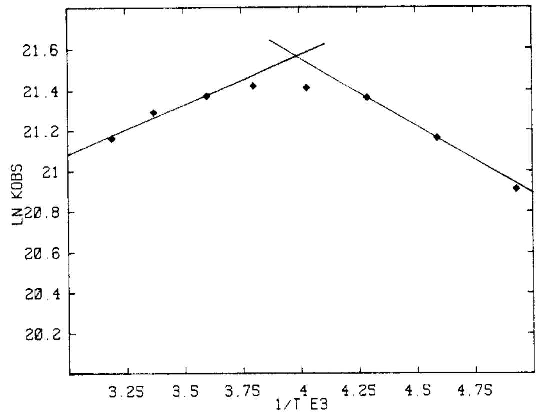

Figure 1. ln k_{obsd} (s^{-1}) vs. $1/T$ (K^{-1} × 1000) for the addition of p-$CF_3C_6H_4CBr$ to tetramethylethylene. The left-hand portion of the correlation (312–263 K) leads to E_a = −1 kcal/mol. The right-hand correlation (232–203 K) leads to E_a = 1.3 kcal/mol. See text for discussion.

Steady-State Photolytic Studies. Simple cyclopropane adducts of PhCCl, PhCBr, and PhCF have been long known and well characterized. More importantly, they are obtainable by photolysis in alkenes of the diazirines **2–4**.[10] In the present study, the cyclopropane adducts of the new carbenes (p-$CH_3OC_6H_4CF$ and p-$CF_3C_6H_4CBr$) with TME and 1-hexene were isolated from steady-state photolyses (λ > 300 nm) of diazirines **1** and **5** in these alkenes. The products were purified by chromatography (SiO_2/pentane) and characterized by NMR and exact mass spectroscopy or elemental analysis.

As a check on the absolute kinetic data (Table I), we determined the product-based, *relative* rate constants, $k_{TME}/k_{1\text{-hex}}$, by the standard alkene competition method.[11] The relative rate constants were 185 for p-$CH_3OC_6H_4CF$ and 69.3 for p-$CF_3C_6H_4CBr$, which agree reasonably well (within experimental error) with the corresponding *ratios* of the absolute rate constants (220 and 70, respectively) from Table I.

Discussion

Structure/Reactivity Dependence. The substitution of the p-methoxy substituent on phenylfluorocarbene is seen from Table I to be worth k_{abs} *decreases* of ~14- and 19-fold with TME and 1-hexene substrates, respectively. Conversely, p-trifluoromethyl substitution on phenylbromocarbene engenders k_{abs} *increases* of 4.5–6. Comparison of the fastest (p-$CF_3C_6H_4CBr$/TME) and slowest (p-$CH_3OC_6H_4CF$/1-hexene) addition reactions affords a k_{abs} ratio of 3400, the largest differential carbenic reactivity yet reported for singlet carbene/alkene additions. These substituents therefore extend the kinetic range of our experiments by an additional factor of ~75.

Considering the entire data matrix of Table I, the carbenic reactivity order with either alkene is p-$CF_3C_6H_4CBr$ > PhCBr > PhCCl > PhCF > p-$CH_3OC_6H_4CF$, in accord with classical ideas about carbene structure/stability/reactivity relationships.[11,12] Similarly clear is the effect of alkene structure, where TME > 1-hexene by ~70 with p-$CF_3C_6H_4CBr$ and ~220 with p-$CH_3OC_6H_4CF$. Note, too, that the less reactive 1-hexene "spreads" the rate constants of the five carbenes over a wider range (480) than does the more reactive TME (154). These observations comprise normal reactivity/selectivity behavior.[12,13]

Activation Parameters and Reaction Models. There are currently two ways of dealing with the negative activation energies

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(12) (a) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58. (b) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(13) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461. Klumpp, G. W. *Reactivity in Organic Chemistry*; Wiley: New York, 1982; pp 219–222, 352–372.

Table III. Differential Activation Parameters for Carbene Reactions[a]

carbene	tetramethylethylene $\Delta\Delta H^{\ddagger}$	tetramethylethylene $\Delta\Delta S^{\ddagger}$	tetramethylethylene $\Delta\Delta G^{\ddagger}$	1-hexene $\Delta\Delta H^{\ddagger}$	1-hexene $\Delta\Delta S^{\ddagger}$	1-hexene $\Delta\Delta G^{\ddagger}$
p-$CF_3C_6H_4CBr$	−3.5	−15	1.1[b]	−2.1	−19	3.7
PhCBr	−4.7	−22	2.0	−1.4	−21	4.7
PhCCl	−4.4	−23	2.2	−1.5	−21	5.1
PhCF	−4.4	−24	2.5	−1.2	−23	5.6
p-$CH_3OC_6H_4CF$	−2.2	−21	4.2	0.6	−23	7.5

[a] Units are kcal/mol for $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta G^{\ddagger}$ and cal/(deg·mol) for $\Delta\Delta S^{\ddagger}$. The solvent is isooctane, and the reference temperature is 298 K. See text for a discussion of the derivation and meaning of these values. [b] This entry is slightly less accurate due to a slight curvature in the plot of log (k_{-1}/k_2) vs. $1/T$.

encountered in the higher temperature regime for the more reactive carbene/alkene combinations (cf. Table I and Figure 1). These alternative treatments are keyed to two different mechanistic models for the carbene/alkene addition reaction. In the model of Houk et al.,[4] the carbene adds to the olefin in a single step, no intermediates intervene, and the activation free energy is dominated by a large, positive $-T\Delta S^{\ddagger}$ term that increases sharply as the carbene approaches the olefin. In this model, $\Delta H^{\ddagger}$ decreases (i.e., is negative) as the reaction proceeds for such reactive carbenes as CBr_2. Noting that $\Delta H^{\ddagger} = E_a - RT$, this is the case that corresponds to those reactions with $E_a < 0$ in Table I. It is entropic control, engendered by the reaction energy surface, that is responsible for the activation barrier in the Houk carbene addition model.[4] A second way of interpreting the data is to postulate that a reversibly formed carbene/alkene complex is an intermediate in the reaction; cf. eq 1 and 2. Here, C is the carbene, A is the

$$C + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C/A \qquad (1)$$

$$C/A \xrightarrow{k_2} \text{cyclopropane} \qquad (2)$$

alkene, and C/A is the complex. This scheme has previously been used to interpret other examples of carbene additions with negative activation energies.[5b,e] and it is related to analogous mechanisms for other examples of fast bimolecular reactions.[5e] We have shown[5b,e] that the mechanism of eq 1 and 2 gives rise to eq 3, where

$$k_{-1}/k_2 = (k_1 - k_{\text{obsd}})/k_{\text{obsd}} \qquad (3)$$

k_{abs} (or k_{obsd}) is not a single rate constant but is related to the other rate constants as indicated. Equating k_1 in eq 1 with the rate constant for *diffusion* in isooctane (k_{diff}), we can calculate the temperature dependence of k_{diff}, and hence of k_1, from the temperature dependence of solvent viscosity.[14] From eq 3, the ratio k_{-1}/k_2 (i.e., the ratio of the rate constant for dissociation of the carbene/alkene complex to that for completion of the cyclopropanation) can be estimated at any temperature by computing the quantity $(k_{\text{diff}} - k_{\text{obsd}})/k_{\text{obsd}}$.

In contrast to the behavior of log k_{abs} with temperature, plots of log (k_{-1}/k_2) vs. $1/T$ are linear,[5b,e] and from their slopes one can obtain *differential* activation parameters, e.g., $\Delta\Delta G^{\ddagger}$, in which the $\Delta\Delta$ represents the value for k_2 (complex cyclopropanation) less the value for k_{-1} (complex dissociation). The results of applying this model to the temperature-dependent kinetic data for the reactions of Table I are shown in Table III.

We can also convert[15] the Arrhenius data of Table II into *absolute* values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ suitable for discussion of the Houk reaction model. This is done in Table IV. It is conceivable that diffusion control becomes significant or dominant with the fast reactions at lower temperatures (<250 K), leading to curvature of the k_{abs}/T^{-1} correlations, positive values of E_a and $\Delta H^{\ddagger}$, and "subversion" of the entropic control[4] manifested at higher temperatures (320–260 K). Put another way, solvent viscosity and diffusion may generate the "stickiness" necessary for the intervention of carbene/alkene complexes in the low-temperature regions. These considerations lead us to include only the high-temperature data for the first three TME reactions in Table IV.

Table IV. Activation Parameters for Carbene/Alkene Additions[a]

carbene	tetramethylethylene $\Delta H^{\ddagger}$	tetramethylethylene $\Delta S^{\ddagger}$	tetramethylethylene $-T\Delta S^{\ddagger}$	tetramethylethylene $\Delta G^{\ddagger}$	1-hexene $\Delta H^{\ddagger}$	1-hexene $\Delta S^{\ddagger}$	1-hexene $-T\Delta S^{\ddagger}$	1-hexene $\Delta G^{\ddagger}$
p-CF_3–C_6H_4CBr	−1.6	−22	6.6	5.0	−0.19	−25	7.4	7.2
PhCBr	−2.1	−25	7.4	5.3	0.40	−26	7.7	8.1
PhCCl	−2.3	−28	8.3	6.0	0.51	−27	8.0	8.5
PhCF	−2.3	−28	8.3	6.0	0.71	−29	8.6	9.3
p-CH_3–OC_6H_4CF	−0.4	−27	8.0	7.6	2.5	−29	8.6	11.

[a] Data are calculated from the entries in Table II at 298 K. Units are kcal/mol for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $-T\Delta S^{\ddagger}$ and cal/(deg·mol) for $\Delta S^{\ddagger}$.

Comparison of Reaction Models. We cannot yet distinguish between entropic control of carbene additions by the reaction energy surface[4] or carbene/alkene reversible complexation[5b,e] in these reactions. Each model has particular advantages in analysis of the experimental data.

The carbene complex mechanism has become very popular as an aid to the rationalization of complex kinetic data for competitive carbene reactions.[16] However, carbene/alkene complexes have yet to be directly *observed*, and we cannot take kinetic fitting as conclusive evidence for their existence. Indeed, the kinetic data can often be explained in ways that do not involve a carbene/alkene complex.[17] In sum, the principal advantages of the carbene complex model are that it leads naturally to a rationalization of the negative activation energies often observed in carbene/alkene additions and that it has precedent in mechanisms applied to other reactive intermediates.[5e] On the other hand, it complicates an understanding of the vast body of relative rate data for carbene additions obtained by classical alkene competition reactions.[11] The complication is not fatal, however,[18] and mechanistically useful structure/reactivity correlations can be made in terms of the complex model (see below and ref 5b, 5c, and 5e).

There are also advantages to the Houk model,[4] which is better suited to discussions of either the transition-state parameters of Table IV or Skell's predictions.[1] This model also allows discussion of the classical relative rate data[11] in straightforward terms without the necessity of invoking the intermediacy of a complex. In the remainder of this Discussion section, we will briefly analyze the temperature-dependent kinetic data according to each of the reaction models. Our concern will be to highlight, wherever we can, common ground *shared* by the two mechanistic models.

In terms of the Houk model, we focus on the observation that comparisons of $-T\Delta S^{\ddagger}$ with $\Delta G^{\ddagger}$ (Table IV) show that all of these reactions are entropy controlled;[19] even in the "slow" *p*-$CH_3OC_6H_4CF$/1-hexene reaction, $-T\Delta S^{\ddagger}$ is 78% of $\Delta G^{\ddagger}$. This general entropic control and $\Delta H^{\ddagger} < 0$ observed for the TME additions (as well as *p*-$CF_3C_6H_4CBr$/1-hexene) are consonant with Skell's findings for CCl_2[1] and Houk's analysis for the alkene additions of "reactive" carbenes such as CBr_2[4] or *p*-$CF_3C_6H_4CBr$.[20]

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(14) Riddick, J. A.; Bunger, W. *Tech. Chem.* (*N. Y.*) **1970**, *2*, 95. We used the relation $k_{\text{diff}} = 2 \times 10^5 T/\eta$ between k_{diff}, temperature, and viscosity. Note that the approximation of k_1 by k_{diff} may be poorer in the least reactive systems such as *p*-$CH_3OC_6H_4CF$/1-hexene. However, the differential activation parameters that result (Table III) appear reasonable.

(15) Gordon, A. J.; Ford, R. A. *The Chemists Companion*; Wiley: New York, 1972; p 136.

(16) See, for example: Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 982. Liu, M. T. H.; Subramanian, R. *Tetrahedron Lett.* **1985**, *26*, 3071. Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. *J. Am. Chem. Soc.* **1984**, *106*, 454. Liu, M. T. H.; Subramanian, R. *J. Chem. Soc., Chem. Commun.* **1984**, 1062.

(17) Warner, P. M. *Tetrahedron Lett.* **1984**, *25*, 4211.

(18) Platz, M. S. *Tetrahedron Lett.* **1983**, *24*, 4763.

(19) This conclusion is common to the carbene complex model as well; see below.

(20) Our data show *p*-$CF_3C_6H_4CBr$ to be a good "model" for CBr_2, so that entropic control is anticipated. However, *p*-$CH_3OC_6H_4CF$ is not a good model for the "stabilized"[12] CF_2; the enthalpic dominance predicted[1,4] for this species is not realized with *p*-$CH_3OC_6H_4CF$. From the latter's probable m_{CXY} index[12a] (~1.1, where $m_{\text{PhCF}} = 0.89$[12a]), *p*-$CH_3OC_6H_4CF$ should be compared to CCl_2, $m = 1.0$,[12a] for which entropic control[1] and $\Delta H^{\ddagger} < 0$ are expected with reactive alkenes.[4b,c]

k_{abs} has not yet been measured for a carbene as stabilized[12b] as CF_2, and we can now appreciate that this order of stability is *unreachable* in the arylhalocarbene series, where even p-$CH_3OC_6H_4CF$ is only comparable with CCl_2.[20]

Therefore, we cannot yet provide a total demonstration of Skell's predictions,[1] which would require a reactivity spectrum broad enough to encompass the *transition* from $\Delta S^{\ddagger}$ to $\Delta H^{\ddagger}$ control. As one moves from the most to the least reactive carbene/alkene pair of Table IV, allowing for the imprecision (±0.5 kcal/mol) in the data, there is a gradual increase in $\Delta H^{\ddagger}$. However, $-T\Delta S^{\ddagger}$ also increases, so that the overall $\Delta G^{\ddagger}$ increase of 6 kcal/mol consists of ~4 kcal/mol in $\Delta H^{\ddagger}$ and ~2 kcal/mol in $-T\Delta S^{\ddagger}$. Transition from $\Delta S^{\ddagger}$ to $\Delta H^{\ddagger}$ control is still not attained.

A most important question is how much further we must go in order to reach the enthalpy-dominated regime. Qualitative extrapolation of the foregoing trends suggests that more stabilized[12b] carbenes, such as CF_2 or FCOMe, might afford enthalpy-dominated reactions and that k_{abs} for these additions should fall in the 10–10^3 L/(M·s) range. A simple preparation of 3-fluoro-3-methoxydiazirine has now been accomplished,[21] so that a test of these predictions for FCOMe may soon be possible. We note that these extrapolations and predictions should be *independent* of the model chosen to discuss the data.

Application of the carbene complex model to the kinetic data generates the differential activation parameters that appear in Table III. Again, we observe that the entropy terms are dominant; $-T\Delta\Delta S^{\ddagger}$ is ~6 kcal/mol in all cases (except for the reaction of p-$CF_3C_6H_4CBr$ with TME, where it is ~4.5 kcal/mol), so that the principal component of $\Delta\Delta G^{\ddagger}$, for any selected reaction, is entropic. Nevertheless, as we found earlier,[5b,e] the differential entropies of activation are, with the exception just noted, all very similar. Therefore, in any comparison of the reactivities of alkene *pairs*, relative rate constants (i.e., rate constant ratios) will depend upon the differences in $\Delta\Delta H^{\ddagger}$ that ultimately appear in $\Delta\Delta G^{\ddagger}$. That is, with $\Delta\Delta S^{\ddagger}$ nearly constant, the relative enthalpies for cyclopropanation vs. dissociation of the carbene complexes determine the observed $\Delta\Delta G^{\ddagger}$'s and rate constants.[22]

We have termed this effect "de facto enthalpic control",[5b] and its practical expression is the larger k_{abs} values observed for cyclopropanations of the more highly substituted alkenes; e.g., TME > 1-hexene, in accord with the classical structure/reactivity analysis of the carbene/alkene addition reaction.[11] Thus, although $\Delta\Delta S^{\ddagger}$ is usually the same for reactions of ArCX with either TME or 1-hexene (Table III), $\Delta\Delta H^{\ddagger}$ is always more favorable (i.e., more negative) for the TME reaction. This means that $\Delta H^{\ddagger}$ for completing the cyclopropanation, *from the complex*, is enthalpically better than dissociation of the complex, to a greater extent, when the alkene is TME than when it is 1-hexene. This is consistent with the increased electron-donating ability of the more highly substituted alkene and the resultant increased stabilization of the transition state for cyclopropane formation.

We close by noting that the Houk and carbene complex models for addition will approach each other as the carbene increases in stability. For a stabilized, relatively unreactive carbene, $\Delta G^{\ddagger}$ should be dominated by enthalpy. The energy surface for the alkene addition of this species will resemble those commonly encountered for other cycloadditions (e.g., the Diels–Alder reaction), and both $\Delta H^{\ddagger}$ (or E_a) and $\Delta S^{\ddagger}$ will be of appropriate sign and magnitude. However, in such a "well-behaved" carbene/alkene addition, cyclopropanation will be attended by a large activation barrier that will dwarf the barrier into or out of any prior carbene/alkene complex. Accordingly, the formation or dissociation of such a complex will be kinetically unimportant in either reactivity or selectivity considerations.

It is only when a carbene is highly reactive, and the activation barrier to cyclopropanation is very low, that a weakly bound carbene/alkene complex, perhaps best regarded as an encounter pair in a solvent cage, can play any role in the kinetics. This is also the setting where, in the absence of a sizeable enthalpic barrier to cyclopropanation, a barrier arising primarily in the loss of translational entropy can dominate the overall reactivity.[4]

Experimental Section

Diazirines. The carbene precursors, diazirines **1–5**, have been fully characterized, and preparative details have been furnished.[8,9]

Cyclopropanes. Adducts of PhCBr, PhCCl, and PhCF to TME and 1-hexene were obtained by photolysis ($\lambda > 300$ nm) of diazirines **2–4** in these alkenes as described in the literature.[10] The new adducts of p-$CH_3OC_6H_4CF$ and p-$CF_3C_6H_4CBr$ to TME and 1-hexene were prepared similarly, according to the following procedure illustrated for the adduct of p-$CF_3C_6H_4CBr$ and 1-hexene.

Diazirine **5** (0.30 g, 1.1 mmol) was mixed with 0.72 g (8.6 mmol) of 1-hexene and photolyzed for 5 h in a Pyrex tube with the light from a 200-W, focused Osram XE mercury lamp. The reaction temperature was maintained at 25 °C by a water bath, and the reaction mixture was stirred magnetically. Excess hexene was removed by simple distillation, and the residual oil was purified by chromatography on silica gel with pentane elution. We thus obtained 23.6 mg (0.074 mmol, 7%) of pure 1-bromo-1-(p-(trifluoromethyl)phenyl)-2-n-butylcyclopropane: ^{1}H NMR (CCl_4) δ 0.63–1.93 (m, 12 H, alkyl + cyclopropyl), 7.56 (d, 4 H, aryl).[23] Anal. Calcd for $C_{14}H_{16}BrF_3$: C, 52.34; H, 5.02. Found: C, 52.57; H, 5.14.

1-Bromo-1-(p-(trifluoromethyl)phenyl)-2,2,3,3-tetramethylcyclopropane was obtained from p-$CF_3C_6H_4CBr$ and TME in 11% isolated yield: NMR δ 1.07 (s, 6 H, Me's), 1.47 (s, 6 H, Me's), 7.30–7.77 (q, 4 H, aryl). Anal. Calcd for $C_{14}H_{16}BrF_3$: C, 52.34; H, 5.02. Found: C, 52.17; H, 4.96.

1-Fluoro-1-(p-methoxyphenyl)-2-n-butylcyclopropane was obtained from p-$MeOC_6H_4CF$ and 1-hexene in 8% isolated yield: NMR δ 0.50–1.83 (m, 12 H, alkyl + cyclopropyl), 3.77 (s, 3 H, OMe), 6.63–7.47 (m, 4 H, aryl);[23] mass spectrum, m/z calcd for $C_{14}H_{19}FO$ [M^+] 222.141 99, found 222.141 43.

1-Fluoro-1-(p-methoxyphenyl)-2,2,3,3-tetramethylcyclopropane was obtained from p-$MeOC_6H_4CF$ and TME in 10% isolated yield: NMR δ 0.90 (d, 6 H, Me's),[24] 1.20 (d, 6 H, Me's),[24] 3.73 (s, 3 H, OMe), 6.67–7.40 (q, 4 H, aryl); mass spectrum, m/z calcd for $C_{14}H_{19}FO$ [M^+] 222.141 99, found 222.141 21.

Competition Reactions. Product-based relative reactivities were determined in the standard manner.[11] A small quantity of diazirine **1** or **5** (~0.7 mmol) was photolyzed in a binary mixture of TME and 1-hexene. Each alkene was present in at least 6-fold molar excess over the diazirine. Photolysis (with the Osram lamp described above) was carried out for 6 h, on a magnetically stirred solution contained in a jacketed Pyrex vessel that was kept at 25 °C by circulating 2-propanol from a Haake F3 constant-temperature bath. After photolysis, the product mixtures were evaluated by capillary GC,[25] and relative reactivities were calculated from the molar ratios of initial alkenes and product cyclopropanes according to the expression $k_1/k_2 = (O_2/O_1)(P_1/P_2)$, where O_i represents alkene and P_i represents cyclopropane.[11] For $k_{\mathrm{TME}}/k_{1\text{-hex}}$ we found 69.3 ± 2.2 (with p-$CF_3C_6H_4CBr$) and 185 ± 8 (with p-$CH_3OC_6H_4CF$), for three competitions in each case.

Absolute Rate Constants. The laser flash photolytic system and the methods used to obtain the absolute rate constants for the carbene/alkene additions of PhCF, PhCCl, and PhCBr have been described in detail in previous publications.[5a,e] Briefly, the transient absorption apparatus consisted of a 300-W Varian Eimac xenon arc lamp, with an ISA H-10 monochromator and a RCA 4840 photomultiplier tube as the monitoring system. Samples were photolyzed in 1-cm^2 cuvettes by a Model EMG-101 Lambda Physik excimer laser. The PMT output terminated in a

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[21] Moss, R. A.; Fedorynski, M.; Terpinski, J.; Denney, D. Z. *Tetrahedron Lett.* **1986**, *27*, 419.

[22] That $\Delta\Delta S^{\ddagger}$ is nearly independent of carbene and alkene reactants is in keeping with Houk's representation of $\Delta S^{\ddagger}$ for carbene/alkene additions as a single, reactant-independent function of reactant separation, the largest component of which is due to the decrease in translational entropy.[4] In terms of the carbene complex model, Houk's $\Delta S^{\ddagger}$ would correspond to $\Delta S^{\ddagger}$ for cyclopropanation from the complex. However, $\Delta S^{\ddagger}$ for complex *formation* is governed by a wide and "unselective" pass[5e] that should also be nearly reactant independent. Therefore, $\Delta\Delta S^{\ddagger}$ would be nearly constant, regardless of carbene and alkene identity.

[23] This adduct was a mixture of syn and anti isomers that were separable by capillary GC (see note 25 for conditions). The isomer distributions were 1.0–1.2 with p-$CF_3C_6H_4CBr$ and 1.0–1.3 with p-$CH_3OC_6H_4CF$.

[24] About 1 Hz of long-range HF coupling was visible in both pairs of methyl groups.

[25] Quantitative GC analyses employed a Varian Model 3700 instrument interfaced to a Varian Model 4270 electronic integrator. All separations were carried out with a 12-m, 0.22-mm (internal diameter) Varian bonded-phase, vitreous silica BP 1 (equivalent to SE-30) column, operated at 170 °C. Injector and detector temperatures were 250 and 300 °C, respectively, and N_2 carrier gas was supplied at 14 psig. The flame ionization detector was calibrated with pure adducts.

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50-Ω load resistor and was analyzed by using a Tektonix 7912 AD transient digitizer liked to a Tektronix WP2252 signal processing system. All alkenes were distilled before use, and spectrograde solvents were employed. Further details appear above (see Discussion section), where particulars of the studies with *p*-$CF_3C_6H_4CBr$ and *p*-$CH_3OC_6H_4CF$ are described.

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Registry No. 1, 95911-65-2; **2**, 87282-19-7; **3**, 4460-46-2; **4**, 4222-25-7; **5**, 95911-64-1; TME, 563-79-1; *p*-$F_3CC_6H_4CBr$, 104197-52-6; PhCBr, 14541-26-5; PhCCl, 19807-41-1; PhCF, 17825-75-1; *p*-$MeOC_6H_4CF$, 104197-53-7; 1-hexene, 592-41-6; 1-bromo-1-(*p*-trifluoromethyl)-phenyl)-2-*n*-butylcyclopropane, 104197-48-0; 1-fluoro-1-(*p*-methoxyphenyl)-2-*n*-butylcyclopropane, 104197-49-1; 1-fluoro-1-(*p*-methoxyphenyl)-2,2,3,3-tetramethylcyclopropane, 104197-50-4; 1-bromo-1-(*p*-(trifluoromethyl)phenyl)-2,2,3,3-tetramethylcyclopropane, 104197-51-5.

Electronic Structure of Cyclic Bicalicenes

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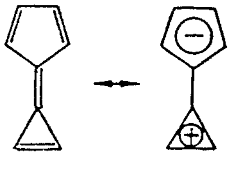
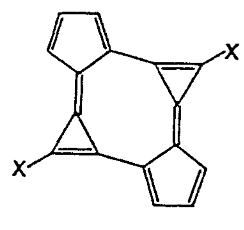
Abstract: The novel π-electron system, pentacyclo[11.3.0.0^{2,4}.0^{5,9}.0^{10,12}]hexadeca-1,3,5,7,9,11,13,15-octaene ("cyclic bicalicene") has been prepared, in which two calicene units are joined in a head-to-tail manner. The X-ray crystallographic analysis indicates that the cyclic bicalicene skeleton is completely planar; i.e., the molecule has D_{2h} symmetry. Cyclic bicalicene is shown to have a characteristic absorption band at around 500 nm, which is interpreted as an intramoleculer charge-transfer band by a SCF-CI MO method. From the ^1H NMR spectra, the paramagnetic ring current due to peripheral 16π conjugation is not observed. The ^1H and ^{13}C NMR chemical shifts suggest that a considerably large polarization of each calicene unit occurs in the cyclic system. The alternating polarization in cyclic bicalicene is also supported by the graph-theoretical and SCF MO calculations.

Cyclopropenylidenecyclopentadienide (calicene) (**1**) is a cross-conjugated π system, whose synthesis and characterization have been of keen interest.[1] Thus far, the parent calicene has not been isolated. However, a number of calicene derivatives substituted with strong electron-donating and/or electron-withdrawing groups at the cyclopropenyl and/or cyclopentadienyl rings have been isolated as stable compounds. From the investigation of their electronic character, it has been shown that a polar structure (**1B**) contributes significantly to the ground state.[2]



(**1A**) (**1B**)

Recently, we have succeeded in the isolation of the 3,11-bis(*tert*-butylthio) derivative **2a** as a stable crystalline compound.[3] This compound contrasts in stability to 5,6-bis(*tert*-butylthio)calicene,[11] which is unstable even at −78 °C and which evidences a large contribution of covalent structure (**1A**) based on NMR and IR spectral data. Furthermore, the parent system **2b** has been isolated as stable crystals by the reductive desulfurization of **2a**.[3] As we briefly reported before, since **2b** is an unprecedented "aromatic" system with a 16π-electron periphery, we have investigated its electronic structure and π-conjugatin mode based on ^1H and ^{13}C NMR spectral data, X-ray structural analysis, and graph-theoretical and a modified Pariser-Parr-Pople-type SCF MO methods ("the variable integrals method I") and elucidated the cause of stabilization. In addition, acyclic bicalicene has been synthesized as a reference π system for cyclic bicalicene. Since the electronic spectrum of cyclic bicalicene is very characteristic, the character of electronic transition is interpreted by using the



(**2a**): X=SBu^t

(**2b**): X=H

(**2c**): X=SnBu$^n_3$

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