Investigation of the Early Stages of Electrophilic Addition of Br₂ to Olefins. Kinetic Evidence for a Reversibly Formed Bromonium Ion in the Reaction of Br₂ with Tetraisobutylethylene

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Abstract: The early stages of electrophilic bromination of a hindered olefin, tetraisobutylethylene (TIBE, **2**), have been investigated with an aim to determining the formation constant (K_f) for the 1:1 charge-transfer complex and information about the reversible formation of the corresponding bromonium ion. In dichloroethane and acetic acid at 25 °C, the respective K_f values are 9.71 (0.19) and 1.72 (0.2) M^{-1}, while in methanol, the value can be no larger than ~2.5 M^{-1}. On the basis of the values of K_f in dichloroethane at 6, 25, and 50 °C, the thermodynamic parameters for CTC formation from TIBE + Br₂ are $\Delta H = -4.07$ (0.35) kcal/mol and $\Delta S = -9.20$ (0.11) eu. TIBE reacts with bromine in acetic acid to form a double bond rearranged allylic bromide. The reaction is not consistent with a free radical process and is more consistent with one proceeding via an ionic bromonium ion intermediate. The kinetics of bromination in acetic acid at 25 °C of TIBE (**2-H8**) and d_8-TIBE (**2-D8**), in which the eight allylic positions are deuterated, reveal a substantial kinetic isotope effect (KIE) of 2.3 (0.1). This value is too large for any imaginable β-secondary KIE on the bromonium ion formation and is most consistent with a primary effect in which a CH or CD (CL) bond is removed in a rate limiting or partially rate limiting step. This step is suggested to be deprotonation of the bromonium ion which leads to formation of double-bond rearranged allylic bromide. The KIE data provide the first kinetic isotope evidence for the reversible formation of a bromonium ion.

Introduction

The generally accepted mechanism for addition of Br₂ to olefins is given in eq 1.[1,2] In protic solvents at low [Br₂], the reaction

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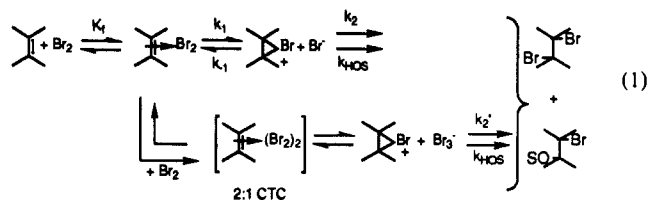
is first order in [Br₂], and proceeds via a 1:1 charge-transfer complex (CTC). In low-polarity solvents, terms second order in [Br₂] are observed and interpreted in terms of a Br₂-assisted ionization of the 1:1 CTC (perhaps via a 2:1 CTC) to produce a bromonium ion tribromide. For most olefins, the bromonium ions proceed to products very rapidly so that the early stages of the reaction yielding the CTC's and ion are not easily amenable to study. Although they are seldom considered in bromination structure/reactivity relationships, the early stages leading to reversibly formed CTC's[3] and ions[2] have a profound influence on the kinetics since the former species lie on the reaction pathway.
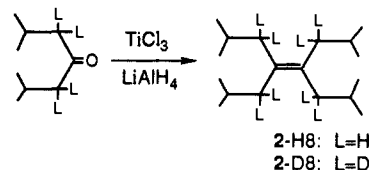
To investigate the early stages of electrophilic bromination, we have chosen to study sterically demanding olefins whose structure retards the backside attack of the counterion or solvent on the ion, thereby allowing the establishment of the CTC and ionic equilibria. One such olefin that we have investigated is adamantylideneadamantane (Ad=Ad, **1**) which, in the presence of Br₂, precipitates from solution as a bromonium ion tribromide salt[4a] that is characterized by X-ray crystallography.[4b]

However, the Ad=Ad:Br₂ system, when investigated in dichloroethane solution, exists as an instantaneously formed equilibrium mixture of **1–1b** and the corresponding bromonium ion pentabromide (**1c**).[5] Of note is the value of K_f in this system (289 M^{-1}) which, when compared with that for cyclohexene (0.47
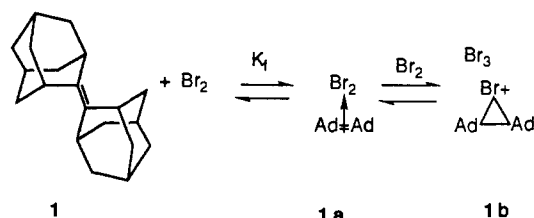
M^{-1}),[3] indicates that there is a considerable structural influence on the stability of the olefin:Br₂ CTC. Admittedly, Ad=Ad is a unique olefin whose structure absolutely impedes product formation, so it would be desirable to obtain information from other sterically demanding olefins that do react with Br₂, albeit at a rate that is reduced from those of unencumbered alkenes.

Tetraisobutylethylene (**2**, TIBE)[6] appeared to us to be a reasonable candidate, and it can be synthesized in modest yield via

2-H8: L=H
2-D8: L=D

the McMurry[7] coupling of two diisobutyl ketone units. As will

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be shown, the first product of the bromination of **2** is a double bond rearranged allylic bromide so that the reaction is not one of simple Br_2 addition. This leaves open the possibility that the rate-limiting step might occur after the formation of CTC and the bromonium ion and be kinetically probed by a suitably iso-topically enriched olefin, namely **2-D8**. Herein we report several observations pertaining to K_f and the reaction rate constants in various solvents, as well as the reaction products in acetic acid. The kinetics of **2-H8** and **2-D8** in acetic acid yield a kinetic isotope effect of 2.3 at 25 °C, which is best interpreted in terms of a mechanism proceeding through a reversibly formed bromonium ion.

Experimental Section

Materials. Tetraisobutylethylene (**2-H8**) was prepared by reductive coupling[7] of diisobutyl ketone. It was purified first by vacuum distillation (0.1 Torr, 65 °C) and then by preparative GLC (16 ft × $^3/_8$ in. 20% DEGS on Chromosorb W, 200 mesh, T = 185 °C, flow rate = 43 mL of He/min), with a final microdistillation; yield after purification, 20%. ^1H NMR (CDCl$_3$) δ 1.925 (8 H, d, J = 7.5 Hz), 1.717 (4 H, sept (br), $J \sim$ 7 Hz), 0.860 (24 H, d, J = 6.5 Hz); ^{13}C NMR (CDCl$_3$) δ 133.69 (C=C), 40.65 (CH$_2$), 27.69 (CH), 22.74 (CH$_3$).

Tetraisobutylethylene-d_8 (**2-D8**) was prepared and purified analo-gously, except that the starting diisobutyl ketone was tetradeuterated at the α positions as follows. Into a solution consisting of 50 mL of 1 N DCl in D$_2$O containing 10% EtOD (for solubility) was placed 13 g (0.092 mol) of diisobutyl ketone and the resulting mixture was heated at reflux overnight. The cooled mixture was extracted with CH$_2$Cl$_2$, and the combined extracts were dried (MgSO$_4$), filtered, stripped of solvent, and then distilled (100 °C, 4 Torr). ^1H NMR indicated ~95% replacement of the α-hydrogens with D. This material was then used for the McMurry coupling.[7] After GLC purification (as above), **2-D8** was obtained. ^1H NMR analysis indicated the presence of ~7% H at the allylic positions. Exact mass calcd for C$_{18}$H$_{28}$D$_8$: 260.3319. Found: 260.3311.

K_f and k_{obsd} **Measurements.** Purified ClCH$_2$CH$_2$Cl,[8] HOAc,[9] and MeOH[10] were employed for all equilibrium and rate measurements. For K_f measurements, solutions containing solvent plus various concentrations of **2** were rapidly mixed (HiTech SFA-11 Rapid Mixing Accessory) with those of the same solvent and variable [Br$_2$] and the UV-visible spectrum immediately (50 ms dead time) recorded from 250 to 500 nm with a HP 8451 A diode array spectrophotometer. In cases of the highest [Br$_2$] and [TIBE] (>0.11 M), the absorbances were measured at selected wave-lengths at time zero with a Durrum stopped-flow spectrophotometer, and the A_0 values so obtained were compared with those obtained with the HiTech/Hewlett Packard system. At least three separate determinations were made at each concentration of **2** + Br$_2$. The composite data for all runs in a given solvent were fit by a nonlinear least-squares procedure[5,11] (described in more detail in the Results and Discussion section) that yielded both K_f and the spectrum at the measured λ's for the CTC.

The kinetics of bromination in the two solvents (acetic acid and methanol) were extensively studied under a variety of conditions of excess **2** at 25 °C at 480 nm with use of a Cary 210 UV–visible spectropho-tometer. The absorbance vs time data were fit to a standard exponential model to yield pseudo-first-order rate constants (k_{obsd}). Second-order rate constants for bromination (k_{Br_2}) were evaluated as $k_{obsd}/[2]$ (for acetic acid) or the slope of a plot of k_{obsd} vs [2] (in MeOH). The respective values are 0.77 (0.1) and 0.37 (0.1) M^{-1} s^{-1} for **2-H8** and **2-D8** in acetic acid and 7.0 (0.2) M^{-1} s^{-1} for **2-H8** in MeOH.

Product Studies. The products of the addition of Br$_2$ to **2** were de-termined after reacting 2 × 10^{-4} mol of **2** with 2.1 equiv of Br$_2$ in 15 mL of acetic acid at room temperature for 10 min. The yellow reaction mixture was poured into ice water that was immediately extracted with 2 × 10 mL of CH$_2$Cl$_2$. The combined extracts were dried (MgSO$_4$), filtered, and stripped of solvent under reduced pressure to give a yellow, viscous oil. This was dissolved in 1 mL of pentane that was then cooled to –78 °C for 12 h after which time a precipitate had formed. The liquid was decanted, and the precipitate was dried with a stream of Ar. ^1H

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Table I. Initial Absorbances at 260 nm of Rapidly Mixed 1,2-Dichloroethane Solutions Containing TIBE (**2-H8**) and Br$_2$ (25 °C)

run no.	[Br$_2$],[a] 10^{3}M	2-H8, M	path length, cm	A_0[b]
1	3.23	3.15 × 10^{-3}	1	0.92
2	5.02	5.0 × 10^{-3}	1	1.78
3	1.90	1.71 × 10^{-2}	1	1.45
4	1.87	2.5 × 10^{-2}	0.2	0.416
5	1.52	4.0 × 10^{-2}	0.2	0.405
6	1.635	6.02 × 10^{-2}	0.2	0.617
7	1.44	7.87 × 10^{-2}	0.2	0.665
8	1.83	9.63 × 10^{-2}	0.2	0.887
9	1.05	1.99 × 10^{-1}	0.2	0.80

[a] At 260 nm, Br$_2$ has an ϵ of 148 M^{-1} cm^{-1}. [b] Absorbances obtained within 50 ms of mixing equal volumes of Br$_2$ and **2-H8** solutions ith a HiTech SFA-11 rapid mixing accessory and recorded with a Hewlett-Packard 8451 A diode array spectrophotometer. The small absorptiv-ity of **2** at 260 nm (6 M^{-1} cm^{-1}) is removed.
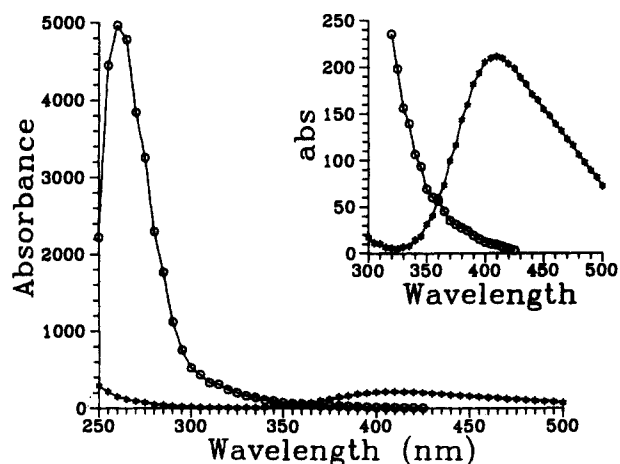

Figure 1. A plot of the computed best fit UV–visible spectrum of the 1:1 TIBE:Br$_2$ charge-transfer complex (○) along with that of Br$_2$ (*) at 25 °C in 1,2-dichloroethane.

NMR analysis (CD$_2$Cl$_2$, 400 MHz) and chemical ionization ms (iso-butane) showed the material to be comprised of two species, an allylic bromide (C$_{18}$H$_{35}$Br), and a diene allylic bromide (C$_{18}$H$_{33}$Br). Unfortu-nately neither material could be produced independently in pure form since further purification led to decomposition. However, repeats of the same procedure as above with the only variation being reaction times from 5 to 15 min yielded products with four low-field ^1H NMR doublets: three of equal intensity, and a fourth of varying intensity. The three, non-mutually coupled doublets at δ 5.5 (J = 10.5 Hz), 5.02 (J = 10 Hz), and 4.30 (J = 7.5 Hz) were each coupled to an isopropyl CH<, (~δ 2.1) and were attributed to the diene allylic bromide. The fourth doublet at δ 4.81 (J = 11 Hz) is also coupled to an isopropyl CH< at δ 2.15 and is attributable to the first formed allylic bromide.

Results and Discussion

Charge-Transfer Formation Constants for TIBE (2-H8) and Br$_2$. When TIBE (**2-H8**) was mixed with Br$_2$ in each of the above solvents, and the UV–visible spectrum monitored within 50 ms, an instantaneous decrease in the free [Br$_2$] was observed followed by a slower kinetic event that was tied to the loss of [Br$_2$].

Spectra of the reaction mixtures obtained immediately after mixing 1,2-dichloroethane (DCE) solutions of 3 × 10^{-3}–0.2 M **2-H8** with 1.05 × 10^{-3}–5.03 × 10^{-3} M Br$_2$ were recorded from 250 to 500 nm. The initial absorbances obtained at 260 nm, which is the λ$_{max}$ of the **2**:Br$_2$ CTC, are reported in Table I.

The Scott equation[12] for 1:1 complexes was used to fit the data, ignoring the small contribution to the initial absorbance (A_0) attributable to free [Br$_2$]. A satisfactory fit (r = 0.96) was obtained, yielding K_f and ϵ_{260} values for the CTC of 11.4 M^{-1} and 5081 M^{-1} cm^{-1}, respectively. These estimates were then used as starting parameters for the non-linear least-squares (NLLSQ) fitting procedure[5] with use of the entire set of absorbancies and

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Table II. Solvent and Temperature Dependence of the Formation Parameters of the TIBE (2-H8)-Br$_2$ CTC

solvent	T, °C	no. of data	fitting range[a]	K_f, M^{-1}	rms residuals, abs units
DCE	25	678	250–500	9.71 (0.19)[b]	0.026
DCE	50	155	350–500	5.80 (0.24)[b]	0.017
DCE	6	120	350–500	16.07 (1.05)[b]	0.025
acetic acid	25	216	270–500	1.72 (0.20)	0.058
methanol	25	5	400	~2.5	

[a] Data taken at 5-nm intervals. [b] 984 data fit using 6, 25, and 50 °C data and fitting ranges for DCE to give ΔH = −4.07 (0.35) kcal/mol and ΔS = −9.20 (0.11) eu (rms of the residuals = 0.030 abs units).

the contributions of free [Br$_2$] to A_0. This yielded a final K_f of 9.71 (0.19) M^{-1} (Table II). Illustrated in Figure 1 is the UV–visible best-fit calculated spectrum of the CTC from which ϵ_{max} and λ_{max} values of 4963 (19) M^{-1} cm^{-1} and 260 (2) nm could be obtained. The root-mean-square (rms) residual of the fit was 0.030.

Equal volumes of 2-H8 and Br$_2$ solutions in DCE were also mixed in a stopped-flow spectrophotometer and the reaction monitored in both the UV and visible regions in order to exclude significant contributions to the A_0 values from the first-formed products of the kinetic event. The substitution reaction produces a decrease in the free [Br$_2$] monitored at 400–500 nm and a small increase in absorbance in the UV region. This does not significantly affect the initial A_0 measured in the first 100–200 ms of the reaction provided the [2] is <0.2 M. Also, small amounts of HBr (that are produced during the substitution reaction) do not affect the A_0 values. Indeed, HBr gas bubbled through Br$_2$ solutions in dry DCE fails to produce HBr$_3$. Apparently the high value of the formation constant for the Br$^-$ + Br$_2$ ⇌ Br$_3^-$ equilibrium[5,11] in this solvent is conditional upon the presence of a more charged dispersed countercation.

The HiTech/Hewlett Packard system was used to register the A_0 data in acetic acid. Here, limited olefin solubility prevented using concentrations of 2 in excess of 0.11 M. Small traces of acetic anhydride in the solvent (used during the purification to remove H$_2$O) were found to contribute to the absorption in the UV region, so a more limited spectral range of 270–500 nm was used. TIBE and Br$_2$ solutions varying from 4 × 10^{-2}–0.11 M and 1.2 × 10^{-3}–4 × 10^{-3}M, respectively, were mixed, and a total of 216 experimental data were recorded and fit by the NLLSQ procedure to give K_f = 1.72 (0.20) M^{-1}, ϵ_{max} = 5633 (53) M^{-1} cm^{-1}, and λ_{max} = 275 (2) nm. As a check that subsequent reaction products were not altering the A_0 values in acetic acid, stopped-flow experiments were also conducted in the range of concentrations used to determine K_f. No interference was detected and the initial A_0 values obtained matched with those from the HiTech/Hewlett Packard measurements.

When the interaction of 2 and Br$_2$ in MeOH was monitored by stopped-flow techniques, a very fast formation of a highly absorbing species was observed in the UV region. This is probably due to the formation of Br$_3^-$[13] arising from the complexation of free Br$_2$ by the HBr produced by the substitution reaction. Therefore, the stopped-flow apparatus was used to monitor the initial absorbances at 400 nm of solutions containing up to 0.1 M 2. These were found to be up to ~25% less than expected for free [Br$_2$] alone, and on this basis and the assumption that the absorbance decrease is entirely due to the formation of the 2:Br$_2$ CTC, an upper limit for its K_f of 2.5 M^{-1} in MeOH can be inferred. Higher concentrations than 0.1 M (which would lead to more complexation) had to be avoided since the initial reaction became too fast even for the stopped-flow technique.

In dichloroethane, the CTC K_f was also determined at 6 and 50 °C over a 250–500-nm range in order to obtain the thermodynamic parameters for the CTC formation. However, at these two temperatures the absorbancies in the UV region were larger
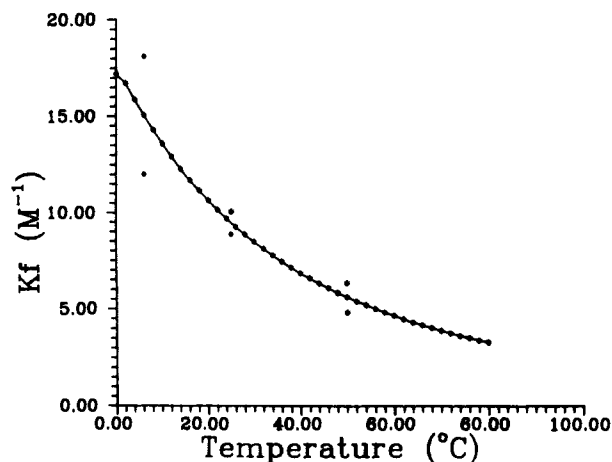

Figure 2. The K_f values for the 1:1 TIBE:Br$_2$ charge-transfer complex computed from the ΔH and ΔS values as a function of temperature in 1,2-dichloroethane. Vertical error bars encompassing 3 times the standard deviation (95% confidence level) are shown at 6, 25, and 50 °C.

than expected, which pointed to the presence of a highly absorbing contaminant. This was most likely Br$_3^-$, produced from trace H$_2$O contamination of the solution by leakage of the thermostating fluid into the UV cell. The presence of Br$_3^-$ in dichloroethane–Br$_2$ solutions has earlier been shown[2] to be markedly affected by trace H$_2$O. In view of this problem, data in the 350–500-nm range were used for the subsequent fittings. The results at 6, 25, and 50 °C are given in Table II.

The original NLLSQ Fortran program[3,5,11] was modified to allow simultaneous fitting of data taken at different wavelengths and temperatures. The modified program optionally takes as fitting parameters the formation enthalpy and entropy and computes the K_f values at each temperature from these parameters when it is required for deriving the equilibrium concentrations. The molar extinction coefficients of the CTC at each wavelength were also considered as temperature-independent fitting parameters. The fit of 984 data taken in the 250–500-nm range at 25 °C and in the 350–500-nm range for 6 and 50 °C yielded ΔH = −4.07 (0.34) kcal/mol and ΔS = −9.20 (0.11) eu. The correlation coefficient between the formation enthalpy and entropy was large (0.99995) as expected, because of the necessarily limited number of temperatures over which the measurements were feasible. As a consequence, the values of the thermodynamic formation parameters must be considered together. Shown in Figure 2 is the temperature dependence of the formation constant computed from the above ΔH and ΔS. The K_f values obtained by independent fittings at each measured temperature are also reported, with the corresponding confidence level (3 times standard deviation) indicating a satisfactory consistency of the computational procedure.

From the limited data in Table II, it can be concluded that there is a modest, but real influence of the K_f for the CTC on the nature of the solvent. It has been reasonably assumed[14,15] that such solvent effects on Br$_2$–olefin CTC formation are negligible compared with those on the ionization step, and the results for TIBE in the three solvents investigated here seem to corroborate that assumption. On first inspection, this may appear surprising since if charge is separated in the CTC relative to free olefin + Br$_2$, solvents that support charge might be expected to increase K_f. However, for such weak donor acceptor (π–σ) complexes, the equilibrium depends upon a complex mixture of specific solvent interactions with all constituents of the complex-forming reaction,[16] and these may vary with solvent changes in an unpredictable way.

(13) In MeOH, the equilibrium constant for Br$^-$ + Br$_2$ ⇌ Br$_3^-$ is 177 M^{-1} while in acetic acid it is 90 M^{-1}. Dubois, J. E.; Herzog, H. *Bull. Soc. Chim.* **1963**, 57.

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In addition, it is of importance that there are now three olefins for which accurate K_f values are known in dichloroethane (25 °C), namely Ad=Ad (289 M^{-1}),[5] TIBE (9.7 M^{-1}), and cyclohexene (0.47 M^{-1}).[3a] Thus, in contrast to a previous assumption,[17] K_f markedly depends upon olefin structure. For weak $\pi-\sigma$ and $n-\sigma$ donor-acceptor (DA) complexes, a linear correlation is observed between some of the parameters of the DA complex (such as $h\nu_{CTC}$ and $-\Delta H_f$) and the donor ionization potential (I_p) provided that the DA interaction is not made more difficult by steric interactions.[18] In a given comparison series, with a common acceptor, the composite effect on $-\Delta H$ relates to how good the electron donation is (how low is the I_p) and how close the acceptor may approach before the steric buttressing becomes dominant. For example, the relatively strong amine:I_2 complexes exhibit increasingly negative ΔH and ΔG values in passing from $NH_3 \rightarrow H_2NCH_3 \rightarrow HN(CH_3)_2 \rightarrow N(CH_3)_3$[19] commensurate with a decreasing I_p. However, in the pyridine, 2-methylpyridine, and 2,6-dimethylpyridine:I_2 series, the ΔH values are irregular at -7.5, -8.0, and -4.2 kcal/mol, respectively.[20]

The structural dependence of K_f is presumably a complex mixture of steric and electronic effects, and these are known to have a stronger bearing on the global rate constant (k_{Br_2}) for electrophilic bromination. For example, k_{Br_2} generally increases with the electron donor ability of the olefin as measured by its ionization potential.[21] Olefin ionization potential decreases with increasing alkylation,[22] but heavily substituted olefins (which should have low I_p's) often exhibit diminished kinetic reactivity[6,23] or even inertness[24] toward bromination.

Although we have shown above that there are modest solvent and more pronounced structural effects on the formation of the olefin:Br_2 CT complex, the perturbation of K_f relates to the global rate constant for electrophilic bromination in only an indirect way. In accordance with transition-state (TS) theory, the k_{Br_2} is determined by the energy separation between the ground state and transition state for the step that limits the rate. For bromination of olefins the rate-limiting step is generally assumed to occur after the CT complexation, for example bromonium ion formation or perhaps some later stage. Although the CTC is an obligatory intermediate along the reaction coordinate,[2] within a series of olefins changes in the pre-equilibrium K_f alone do not enhance k_{Br_2} unless the rate-limiting TS energy is brought down. Even if K_f is $\gg 1$, so that the energy of the CTC lies below that of the free olefin + Br_2, the rate acceleration can only occur if the structural change reduces the TS barrier even more than it enhances K_f. K_f and k_{Br_2} are both influenced by donor ionization potential and steric changes in the same direction, but the sensitivity of K_f is attenuated because there is considerably less charge development on the olefin carbons in the CTC than in the ion forming transition state. It is of note that Schmid and Gordon[25] have concluded that the sensitivity of K_f for a series of olefins reacting with ICl (as measured by a linear free energy ρ) is 24% of that of the reaction rate.

Rate Constants for the Reaction of 2-H8 and 2-D8 with Br_2. An earlier reported attempt at determining the bromination rate of TIBE[6] met with difficulty since the solutions became colored

Table III. Observed Pseudo-First-Order (k_{obs}) and Second-Order (k_{Br_2}) Rate Constants for the Reaction of Br_2 and 2-H8 or 2-D8 in Acetic Acid (T = 25 °C, λ = 480 nm)

run no.	[2-H8] 10^2M	[Br₂], 10^3M	[NaOAc], M	[LiClO₄], M	k_{obs},[a] $10^2 s^{-1}$	k_{Br_2},[b] $M^{-1}s^{-1}$
1	2.70	2.2			2.05 (0.03)	0.76
2	1.35	1.1			1.04 (0.02)	0.77
3	2.70	2.2	0.005[c]	0.095	3.42 (0.09)	1.26
4	2.70	2.2	0.005[c]	0.095	3.39 (0.08)	1.25
5	2.70	2.2	0.1		2.68 (0.03)	0.99
6	2.70	2.2	0.19		2.98 (0.02)	1.10
7	2.70	2.2	0.3		3.75 (0.04)	1.38
8	2.70	2.2	0.4		4.27 (0.05)	1.58
9	2.70	2.2	0.5		4.80 (0.07)	1.78

run no.	[2-D8] 10^2M	[Br₂], 10^3M	[NaOAc], M	[LiClO₄], M	k_{obs},[a] $10^3 s^{-1}$	k_{Br_2},[b] $M^{-1}s^{-1}$
10	1.17	1.1			4.21 (0.02)	0.36
11	2.6	2.2			10.1 (0.1)	0.38
12	1.17	1.1	0.05		5.31 (0.03)	0.45
13	2.2	2.2	0.005[c]	0.095	13.9 (0.3)	0.63
14	1.17	1.1	0.1		6.26 (0.03)	0.54
15	1.36	1.1	0.1		7.35 (0.07)	0.54
16	2.2	2.2	0.15		13.5 (0.1)	0.61
17	1.36	1.1	0.2		9.05 (0.05)	0.67
18	2.2	2.2	0.2		15.1 (0.01)	0.68
19	2.2	2.2	0.3		19.2 (0.2)	0.87
20	2.2	2.2	0.4		23.8 (0.3)	1.08
21	2.2	2.2	0.5		27.2 (0.5)	1.23

[a] Averages of duplicate runs. [b] k_{Br_2} = k_{obs}/[TIBE]. [c] 5 mM NaOAc added as buffer to scavenge H^+ produced.

due to product decomposition. We have corroborated these observations with TIBE when the solutions are allowed to stand for some time. However, in carefully purified acetic acid and methanol at T = 25 °C, the disappearance of Br_2 can be monitored at 480 nm under pseudo-first-order conditions of excess TIBE. The conditions were chosen to minimize higher order terms in [Br_2][26] and to avoid contributions to the absorbance produced by Br_3^-. The latter arises because the products are those of substitution, not addition, so that a competing $Br^- + Br_2 \rightleftharpoons Br_3^-$ equilibrium occurs to some extent. Under the conditions chosen, clean first-order kinetics are observed up to at least 90% reaction. In methanol, the observed second-order rate constant (k_{Br_2}) for 2-H8 is 7.0 (0.2) M^{-1} s^{-1} at 25 °C. Given in Table III are various rate constants for the bromination of 2-H8 and 2-D8 in acetic acid at 25 °C. The most striking observation from these data is a large observed kinetic isotope effect (KIE) of $k_H/k_D = 2.1$ (0.1) for the bromination in the absence of added salts. Since the sample of 2-D8 used contained ~7% H (based on ^1H NMR integrated intensities), the true KIE for the 100% isotopically pure material would be somewhat larger. If we are allowed simply to correct the observed value on the basis of the mole fraction of H in 2-D8, the calculated value is 2.3 (0.1).[27] In what follows, we will attempt to analyze this KIE in terms of a mechanism in which the rate-limiting step occurs after a reversible bromonium ion formation.

On several grounds, the kinetics of disappearance of Br_2 are not attributable to any radical-based process. First, the kinetic behavior is not capricious and shows a clear overall second-order behavior—first order in each of [Br_2] and [TIBE]. No indication

(17) For a discussion relating to the assumption that structural effects on olefin–halogen complex stabilities are small see ref 19 in: Ruasse, M.-F.; Dubois, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 3230–3234.

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(27) The integrated ^1H NMR intensities of 2-D8 indicate 7% residual H at the allylic positions, which implies that the sample contains ~43% D_8 and ~56% D_7, H, TIBE. We favor a mechanistic scenario where the free species, CTC, and bromonium ion of 2 exist in a preequilibrium, which is followed by a rate limiting or partially rate limiting conversion of the ion into a double bond rearranged allylic bromide. If this latter step is entirely rate limiting, then a simple statistical correction of the observed KIE for the mole fraction of H is justified in obtaining a true KIE of 2.3. If that step is only partially rate limiting, then the true KIE must be somewhat higher, since the reaction would preferentially select for elimination of H, rather than D, because now the balance of partitioning of the ion between reversion back to CTC and product formation has changed. We cannot say which of the two cases holds with any certainty. However, some evidence against the latter can be gained from the reaction of equimolar 2-D8 and Br_2 in HOAc, under ^2H NMR conditions, where the initial products show, within experimental error, an allylic D and DBr in a 1:1 intensity.

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of an induction period is seen. When the kinetics are determined in carefully degassed (5 freeze–thaw cycles) HOAc, the second-order rate constant for bromination of 2-H8 is, within experimental error, the same as determined in nondegassed media. The reaction is also not photoinitiated during the kinetic measurement at 480 nm. Thus, kinetics measured with the cells constantly exposed to the 480 nm light beam are the same as those observed when the cell is alternatively cycled in and out of the light beam. Finally, the salt effects seen with added NaOAc or LiClO$_4$ (Table III) are not easily explained by a radical process and are more consistent with an ionic mechanism.

In the great bulk of electrophilic bromination kinetic studies, the ionic intermediates have generally been considered to be irreversibly produced, so that $k_{Br_2} = K_f k_1$.[28] Reversible formation of ions has been invoked only rarely[29] in the addition of Br$_2$ to olefins. However, it has been shown that Br$_2$ can be scavenged both from bromonium ions produced from the solvolysis of *trans* bromohydrin brosylates in the presence of Br$^-$[2a] and from bromonium ion–bromide ion pairs generated by reacting bromo-hydrins with HBr gas.[2b,c] This and the *cis*- and *trans*-stilbene isomerization observed during the bromination of the former olefin[2b,30] indicate that the reverse step (k_{-1} in eq 1) cannot generally be neglected.

It has been pointed out[2b] that the reversible or irreversible formation of the bromonium ion cannot be revealed by simple kinetic measurements of the rates of Br$_2$ reaction with olefins unless particular features make the reverse step detectable. Normally, the putative reversibility would be masked, since re-formed Br$_2$ ultimately reacts to produce addition products. Kinetically, the partitioning of the bromonium ion simply is reflected in a complex constant that is incorporated into the global second-order rate constant for Br$_2$ disappearance. On the other hand, the fact that bromination of TIBE yields substituted products allows one to apply a kinetic test to see if there is a kinetic isotope effect on the rate. From the data in Table III, the KIE of 2.3 is in line with a primary effect in which an allylic CL bond is broken in a rate limiting or partially rate limiting step.[31] We believe that step to be deprotonation of one of the allylic CL bonds in converting the bromonium ion to an allylic bromide, so that the KIE consists of a primary isotope effect superimposed on a smaller secondary α-effect.

One must first consider a possibility that this KIE results from secondary β-effects of the eight allylic CL bonds on a possibly rate limiting bromonium ion formation. These are generally anticipated to be small for a given CL bond, but they could be dramatically enhanced when more than one β-CL is present.[32] For our purposes, the analysis of β-secondary KIE's can be broken down into three anticipated components: steric, inductive, and hyperconjugative. Secondary β steric and inductive effects are expected to be inverse since a C–D bond is shorter than a C–H bond.[33] Thus, if inductive effects and/or steric compressions dominate in the rate limiting TS for bromination of TIBE, and that is ion formation, then one anticipates $k_H/k_D < 1$. However, it is also known that in S$_N$1 reactions, where the rate limiting step involves placement of substantial charge on the α carbon (e.g., (CL$_3$)$_3$C–Cl → (CL$_3$)$_3$C$^+$), the KIE's are large and normal, being
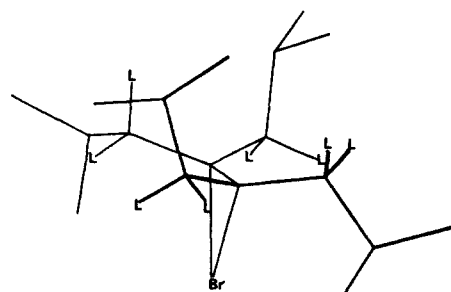

Figure 3. The structure of the MMX minimized bromonium ion of TIBE showing the heavy atoms and orientation of the β-CL bonds. The C–Br bond lengths and central bond angles are set at the experimental geometry found by X-ray crystallography for the bromonium ion of adaman-tylideneadamantane.[4b]

generally $k_H/k_D = 1.10 (0.05)/\beta$-CD.[34] The origin of this effect is hyperconjugation of the β-CL bond into the adjacent deficient orbital,[35] and this is known to be dependent upon the amount of (+) charge and the interorbital dihedral angle of the developing electron-deficient pseudo-π orbital and adjacent CL σ-bond.[35] We have considered the geometric situation expected in the TIBE bromonium ion by MMX calculation[36] of the energy minimized structure which is shown in Figure 3. This ion structure is presumably close to the TS for its production from the CTC. The C–Br bond lengths and bromonium ring angles were input to the calculation at the values found experimentally for the X-ray crystal structure of 1b.[4b] The calculated minimum structure possesses an approximate C$_2$ rotational axis through the Br perpendicular to the central C–C bond. The gross disposition of the four isobutyl substituents in the ion is similar to that calculated for TIBE,[6] which also possesses an approximate C$_2$ axis perpendicular to the central >C=C< plane. From Figure 3, it is evident that only two of the allylic C–L bonds are disposed appropriately for a favorable hyperconjugative interaction (dihedral angle ∼160–167°) while the other six are twisted from optimal alignment by 40, 47, 53, 66, 72, and 87°.

The question as to how much charge density is present on each of the two central carbons at the bromonium ion forming TS cannot be answered without recourse to sophisticated calculations, but since the (+) is distributed over at least three heavy atoms, the charge on C is certainly a fraction of what would be the situation in a carbocation-forming S$_N$1 reaction. To our knowledge, no pertinent β-secondary isotope effect data exist for a bromination reaction, but perhaps the most appropriate extant comparison would be for the solvolysis in eq 2 which proceeds via

$$(2)$$
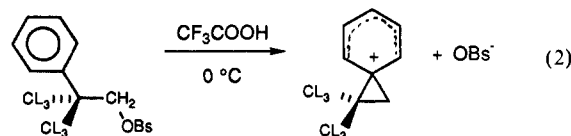
a phenonium ion with an observed total $k_H/k_D = 0.916$.[37] In sum, the above considerations suggest that the anticipated β-secondary KIE for a rate-limiting bromonium ion formation in the reaction of Br$_2$ + TIBE would be small (0.9–1.2), and certainly not large enough to account for the observed value of 2.1 (corrected to 2.3 for 100% D in 2-D8).

Salt Effects on k_{Br_2}. A linear least-squares treatment of the k_{Br_2} vs [NaOAc] data in Table III gives slopes of 2.03 (0.05) and 1.73 (0.04) M^{-2} s^{-1} respectively for 2-H8 and 2-D8. The accelerating affect of LiClO$_4$ on each reaction is larger, the slopes of the two point (0, 0.095 M) lines being 5.2 and 2.7 M^{-2} s^{-1}

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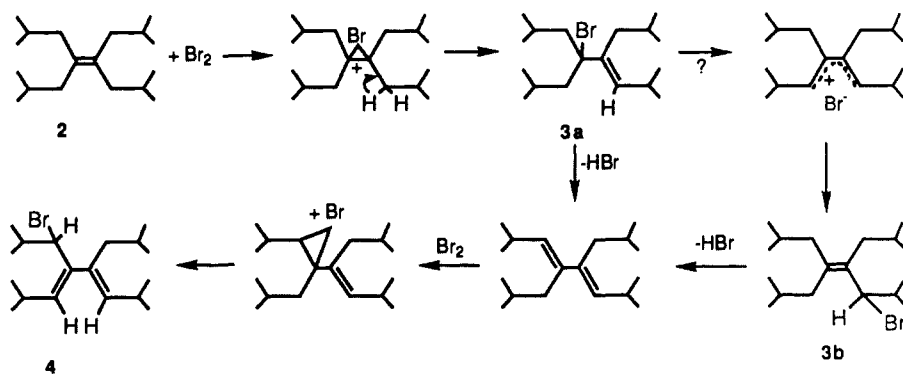
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Scheme I

respectively for 2-H8 and 2-D8. We have determined that $LiClO_4$ also accelerates the reaction of cyclohexene and cyclopentene with Br_2 in HOAc, $T = 25$ °C, the observed slopes of the k_{Br_2} vs $[LiClO_4]$ plots (0–0.1 M) being 1.3×10^4 M^{-2} s^{-1} (intercept 3.9 $\times 10^2$ M^{-1} s^{-1}) and 9.3×10^4 M^{-2} s^{-1} (intercept 8.9×10^3 M^{-1} s^{-1}), respectively.[38] We assume that perchlorate contributes a normal salt effect in accelerating these reactions, and the difference in the slopes for the H8 and D8 materials is due to some charge differences between the virtual transition states. If acetate were participating in the reaction as a general base in assisting deprotonation of the bromonium ion or CTC (the latter process leading directly to the allylic product completely bypassing the ion), one anticipates that its accelerating effect would be more prominent than that of ClO_4^-. Also, either process would require a primary isotope effect on the k_{Br_2} vs [NaOAc] slopes, which is anticipated to be larger than the 2.03/1.73 = 1.17 (0.04) observed. These expectations make it unlikely that acetate is acting as a base in the reaction, so that the observed linearity in the plot in each case is ascribed to normal salt effects as was the case with ClO_4^-. Since acetate is incapable of acting as a base, we tentatively propose that in HOAc the product is formed via an intimate bromonium ion/bromide ion pair with the intimate Br^- acting as an internal base.

As adumbrated above, the observed KIE of 2.1 (corrected to 2.3 for 100% D in 2-D8) seems most consistent with a process involving allylic CL removal in a rate limiting or partially rate limiting step, and this could involve direct deprotonation of either the CTC or bromonium ion. The kinetics cannot unambiguously rule out one of these, but chemical intuition leads us to favor deprotonation of the ion. We have demonstrated here that there is an observable $TIBE:Br_2$ CTC. Previously, for the hindered special olefin Ad=Ad (1) we have demonstrated that in dichloroethane solution there is an instantaneous attainment of equilibrium consisting of 1 + Br_2, CTC 1a, ion 1b, and the bromonium ion pentabromide.[5] In that system, the bromonium ions are observable and instantly formed, but they are prevented from producing product. The question of relevance to the $TIBE:Br_2$ system would be why in this system a similarly instantaneous formation of bromonium ion would not be allowed since the ion is likely not appreciably different in steric crowding from its CTC predecessor.

The KIE for bromination of TIBE is at the low end of the values expected for a primary effect (2–7). This is possibly because the TS for the ion decomposition is early, or that the isotope-sensitive TS is only partially rate limiting because that barrier is similar in energy to the one that leads from the ion back to the CTC. In either case, the observation of such a large KIE requires that all steps preceding the rate-limiting one(s) must have lower activation energies. This in turn suggests that the bromonium ion intermediate must be reversibly formed. We believe this to be the first kinetic isotope evidence for the reversible formation of a bromonium ion.

Products. ^1H NMR analysis of solutions of 1.0×10^{-2} mmol each of TIBE (2-H8) and Br_2 in d_4-acetic acid indicated the

disappearance of only 50% of the TIBE and the appearance of a vinyl doublet at δ 4.75 ($J = 11$ Hz), which was coupled to an isopropyl CH< at δ 2.10. The rest of the Br_2 appeared as Br_3^-, indicating that the first-formed product was one of substitution, not addition. Apparently Br_3^- was not particularly reactive toward TIBE, but its color was immediately removed by the addition of cyclohexene, to which Br_3^- is known to add rapidly. In a second ^1H NMR experiment conducted as the first, when the solution was allowed to stand overnight, the vinyl doublet at δ 4.75 disappeared and was replaced by several low-field vinyl H's and the solution became deep purple (consistent with the report of Andersen et al.[6]), reminiscent of a highly conjugated polyene.

The first experiment was repeated with equimolar 2-D8 and Br_2 in HOAc, and the ^2H NMR spectrum was monitored. Prior to the addition of Br_2, the allylic D's appeared as a single peak at δ 1.94: after the addition of Br_2, two new equal intensity peaks are seen at δ 4.75 and 11.55 ppm. These were attributed to the first-formed allylic bromide and equimolar DBr that was released to the solvent.[27]

A series of three preparative experiments was conducted with 50.4 mg of TIBE (2-H8) in 10 mL of acetic acid to which was added 25 μL of Br_2 (2.0 equiv) in 1 mL of acetic acid. The solutions were allowed to stand for 5, 10, and 15 min, respectively after which they were separately diluted with ice water and extracted with CH_2Cl_2. Following the workup described in the Experimental Section, a white solid was isolated and subjected to ^1H NMR analysis ($CDCl_3$). The three experiments each yielded similar product mixtures, but the relative peak intensities in the vinyl region (δ 4–6) indicated that there were two main products, an allylic bromide (identical with that produced in the d_4-acetic acid ^1H NMR experiment above) and a second one that contributed 3 non mutually coupled doublets that we tentatively ascribe to a diene bromide. Exact mass analyses of the products from one such determination yielded peaks at m/z (% intensity) 331.1817 (9.50), 330.1779 (5.77), 329.1838 (9.84), and 328.1759 (4.36) corresponding to $C_{18}H_{33}^{79,81}Br$ and $C_{18}H_{34}^{79,81}Br$ as well as peaks at 250.2643, 249.2586, and 248.2508 corresponding to $C_{18}H_{34}$, $C_{18}H_{33}$, and $C_{18}H_{32}$. Finally, a UV spectrum of 0.13 mg of the solid in 3.0 mL of hexane gave an intense band at 247 nm, $A = 1.193$ corresponding to an ϵ of 9051 M^{-1} cm^{-1} assuming a MW of 329. This band is probably attributable to a conjugated diene.

On the basis of this evidence, the two substituted products above are probably those formed by the process given in Scheme I, where the first-formed product is the allylic bromide 3a (olefin geometry unknown) and the tentative diene bromide is 4 (geometry unknown). The process is mechanistically similar to that reported Wynberg et al.[39] wherein NCS, NBS, or *tert*-butyl hypochlorite can react rapidly with tetraalkylethylenes to yield allylic halides with the double bond shifted relative to the starting olefin. The bromination of two sterically demanding olefins, octamethylcyclopentene[40] and (E)-2,3-di-*tert*-butyl-2-butene,[41] with Br_2 has

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also been reported to yield rearranged allylic bromides and dienes.

Conclusions

1. TIBE reacts with Br_2 instantly to form a charge-transfer complex that ultimately evolves into a double bond shifted allylic bromide. The reaction with Br_2 is slow enough that information about the CTC and its formation constant can be obtained. The CTC formation constant is shown to have a small sensitivity to the nature of the solvent: K_f(solvent), 9.71 M^{-1} (CH_2ClCH_2Cl), ≤ 2.5 M^{-1} (methanol), 1.72 M^{-1} (acetic acid). Also, from the K_f values at 25 °C for cyclohexene, Ad=Ad, and TIBE in CH_2-$ClCH_2Cl$ of 0.47, 289, and 9.71 M^{-1}, respectively, it can be concluded that there are sizable structural effects on the CTC formation constants.

2. Kinetic studies of the reaction of 2-H8 and 2-D8 with Br_2 in acetic acid, 25 °C, gives evidence of a large kinetic isotope effect of 2.3 (0.1). This is too large for any β secondary KIE on a process where the rate limiting step is formation of a bromonium ion. The observed KIE is more consistent with a primary effect (superimposed on a secondary α effect of the remaining CL) in which a CL bond is breaking in a rate limiting or partially rate limiting step. Added acetate accelerates the reaction, not as a general base, but rather as a normal salt.

3. The best explanation for the KIE attributes the effect to deprotonation of the bromonium ion. That the KIE of 2.3 is at the low end of the values expected for a primary effect (2–7) is possibly because the TS for the ion decomposition is early, or that the isotope sensitive TS is only partially rate limiting because that barrier is similar in energy to the one that leads from the ion back to the CTC. In either case, the observation of the KIE requires that all steps preceding the rate limiting one(s) must have lower

activation energies, which would suggest that the ionic intermediates (bromonium ion) must be reversibly formed.

4. Specially engineered olefins such as Ad=Ad or TIBE allow one to probe the reversible nature of bromonium ion formation. This results from raising the barriers for the product-forming steps to prevent production formation (as in the case of Ad=Ad) or deflecting the course of the reaction from addition into double bond rearranged substituted products as in the case of TIBE. In the absence of special features, the partitioning of a given bromonium ion between reversal and product formation is difficult to evaluate, but it is generally controlled by the relative barrier heights. One can envision a spectrum of situations ranging from exclusive ion reversal (Ad=Ad) to a progressively irreversible ion formation if the product-forming barrier is substantially lower than the reverse barrier. These relative barrier heights are expected to be sensitive functions of the structure, solvent, and nature of the ionic intermediates with respect to intimate ion pairs or solvent-separated ions. We do not claim bromonium ion reversal to be extant in all cases. However, what we have shown here, and in earlier reports,[2] is that the bromonium ions of TIBE and Ad=Ad (produced during bromination of the olefins in HOAc and DCE, respectively) and those of cis-stilbene, cyclohexene, and cyclopentene (formed solvolytically in DCE or HOAc) can reverse in accordance with the mechanism given in eq 1. This leaves open the possibility that ion reversal may be more prevalent than has been generally considered.

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Cyclopentannulation Reactions with Organoiron Reagents, Facile Construction of Functionalized Hydroazulenes

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Abstract: Troponeiron tricarbonyl, 2-methyltroponeiron tricarbonyl, and 4-methyltroponeiron tricarbonyl are converted to fluxional tropyliumiron tricarbonyl salts by treatment with either trimethylsilyl or di-n-butylboron triflate. These pentadienyliron cations react with (η^1-allyl)-, (η^1-propargyl)-, and (η^1-allenyl)Fp complexes [Fp = $C_5H_5Fe(CO)_2$] to give ketohydroazulene cycloadducts derived, in each reaction, from a single tautomeric tropylium cation. The further reaction of two such cycloadducts 14 and 22b with lithium dimethyl cuprate gave tricyclic ketones 25a and b, through a sequence depicted as involving initial formation of an anionic acyliron complex, followed by migratory insertion and an intramolecular aldol condensation.

Although no single cycloaddition reaction, comparable to the Diels–Alder reaction in its breadth of synthetic power, is available for the construction of five-membered carbocycles, a number of [3 + 2] cycloaddition reactions of more limited scope have been devised. These include reactions in which the three-carbon unit is variously an allenylsilane,[1] a cyclopropylphosphonium salt,[2] a (bromoacetylmethylene)triphenylphosphorane,[3] a cyclopropenone ketal,[4] an α,α'-dibromoketone,[5] a 1,3-diyl diradical,[6] a tri-

methylenemethane–palladium complex,[7] an acryloyl chloride,[8] or 3-iodo-2-[(trimethylsilyl)methyl]propene.[9]

Some time ago we showed that the (η^1-allyl)Fe complex 1 (Fp = CpFe(CO)$_2$) and the congeneric (η^1-allenyl)-, (η^1-propargyl)-, and (cyclopropyl)Fp complexes react as 1,3-dipole equivalents with either carbon or heteroatomic electrophiles in a highly regio- and stereospecific, two-step cycloaddition process to give five-membered carbocyclic and heterocyclic rings.[10]

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