The Mechanism of the Reaction between Silyl Radicals and Chloroethylenes: A Case Study of the Et_3Si–C_2Cl_4 Reaction

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Abstract: The photolysis and radiolysis of C_2Cl_4 solutions in Et_3SiH were studied at 298 K. The main products, Et_3SiCl and C_2Cl_3H, are formed in equal yields and via a free radical chain mechanism, as indicated by the high quantum yields ($\sim$500) and *G* values ($\sim$1600). The reactions $C_2Cl_3 + Et_3SiH \rightarrow C_2Cl_3H + Et_3Si$ (3) and $Et_3Si + C_2Cl_4 \rightarrow Et_3SiCl + C_2Cl_3$ (4) constitute the chain propagation step. Competitive studies yield k_4/k_{11} of 018 ± 0.01 (2σ) where $Et_3Si + t$-BuCl $\rightarrow Et_3SiCl + t$-Bu (11). The mechanistic implications and consequences of the observation that the reaction of Et_3Si radicals with C_2Cl_4 results almost exclusively in Cl transfer rather than addition are discussed, and the conclusions are generalized for similar reactions of other chloroethylenes.

The addition of silanes to carbon–carbon double bonds has been extensively studied mainly because of its importance in the synthesis of organosilicon compounds.[1] However, the kinetic rate data on the free radical reactions that lead to the formation of these compounds are still rather limited. In the gas phase the room temperature rate constant for the addition of D_3SiSiD_2 radicals was determined by Strausz et al.[2] Dohmaru and co-workers determined the relative gas-phase Arrhenius parameters for the addition of trichlorosilyl radicals to ethylene,[3] 1-olefins,[4] and 2-olefins.[5] In the liquid phase Choo and Gaspar[6] utilized the kinetic EPR method to estimate the rate of addition of Me_3Si radicals to ethylene. More recently an extensive study of the liquid-phase addition reactions of Et_3Si radicals has been carried out by Chatgilialoglu, Ingold, and Scaiano[7] whose method of absolute rate constant determination is based on the monitoring of the growth of the (triethylsilyl)benzil adduct radical formed in the laser flash photolysis of di-*tert*-butyl peroxide–triethylsilane solvent.

The technique used by Chatgilialoglu et al. is a rather powerful tool whose applicability has been demonstrated in the determination of rate data of a large variety of Et_3Si radical reactions such as halogen atom transfer[8] and addition to carbonyl,[9] olefinic,[7] and aromatic[7] double bonds. However, when not accompanied by product analysis, this method has some shortcomings. It yields overall rate constants and therefore it cannot distinguish between different parallel reaction channels of the Et_3Si radical nor does it yield information on the exact site of reaction.

Recently Chatgilialoglu and co-workers reported the measurement of the rate constants for the reaction between Et_3Si radicals and chloro-substituted ethylenes.[7] They postulated that the evaluated rate constants were those of the addition to the C=C bond. This assumption is at odds with an earlier work from this laboratory in which it was shown that, in their reaction with

trichloroethylene, Et_3Si radicals undergo addition as well as Cl-transfer reactions and that at 65 °C these reactions proceed at almost equal rates.[10] In that study we utilized γ radiation as the means of initiation of the free radical reactions. This method has been employed by us in kinetic studies of a large number of radical liquid-phase reactions.[11]

The present photolytic and radiolytic study of the free radical reaction in the Et_3SiH–C_2Cl_4 system was undertaken in order to resolve the apparent descrepancy between our results and those of Chatgilialoglu and co-workers[7] and in order to gain further insight into the factors governing the mechanism of the reactions of silyl radicals.

Experimental Section

Cyclohexane and *n*-pentane (Phillips research grade), C_2Cl_4 (Eastman spectrograde) and *t*-BuCl (Fluka, puris) were used as received. Et_3SiH (PCR) was purified by trap-to-trap distillation. The middle fraction was retained and found by GC to be free of detectable impurities.

Thoroughly degassed samples were sealed in Pyrex ampules. In the photolytic experiments 1-mL samples were irradiated in square Pyrex cells with a total volume of 1.5-mL while in the radiolytic runs 0.1-mL samples were used and placed in ampules with a 0.2-mL total volume. The full arc of a 200W high-pressure mercury lamp (Osram HBO 200) was used for photolysis. The intensity of the incident and transmitted collimated light was monitored with a photodiode (RCA 935) mounted at the back of the cell, and the intensity was attenuated with neutral density filters. C_2Cl_4 solutions in *n*-pentane were used for actinometry, assuming that in this system C_2Cl_3H is formed as a result of direct photolysis only. This assumption is based on earlier studies of C_2Cl_4 photolysis[12] and radiolysis[13] in alkanes. Radiolysis was carried out in a γ source (Gamma Cell 200, Atomic Energy of Canada) for which the dosimetry was determined with cyclohexane, taking $G(H_2) = 5.65$.[14] The radiolysis and photolysis were carried out at 298 K.

A gas chromatograph equipped with a FI detector (HP 7620A) served for product analysis. C_2Cl_3H, *n*-C_5H_{12}, Et_3SiH, and C_2Cl_4 were separated on a 10% silicon oil DC200 stainless steel 12 ft × 1/8 in. column held at 60 °C. For the determination of Et_3SiCl the temperature of this column was raised to 100 °C. A 6 ft × 1/8 in. stainless steel column filled with Porapak Q and held at 80 °C was used for the determination of BuH.

Results and Discussion

Photolysis. In the earlier radiolytic study of the Et_3SiH–C_2Cl_3H system the chain formation of dichloroethylenes and $Et_3SiCH=CCl_2$ was ascribed to free radical reactions. Ions are formed in the initial stages of the interaction of γ radiation with matter.

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Table I. Photolysis of C_2Cl_4 in n-C_5H_{12}–Et_3SiH Solutions at 298 K[a]

[n-C_5H_{12}], mM	[Et_3SiH], mM	irradiation time, min	[C_2Cl_3H], mM	[$-\Delta C_2Cl_4$], mM	[Et_3SiCl], mM	$\Phi_{C_2Cl_3H}$	[C_2Cl_3H]/[Et_3SiCl]
7.75	0.63	6	30.6		29.7	109	1.030
6.89	1.26	6	52.8	55.1	49.9	188	1.058
6.02	1.89	6	74.6	62.3	74.5	265	1.001
4.30	3.14	4	73.9	81.0	69.5	394	1.063
2.15	4.71	3	68.5	56.2	66.4	487	1.031
	6.28	3	77.2	76.4	81.1	549	0.952
							av = 1.023 ± 0.08

[a] Initial concentration of C_2Cl_4 in all runs at 445 mM, $I_0 = 2.82 \times 10^{16}$ quanta/min cell.

Table II. Formation of Main Products in the Radiolysis of Tetrachloroethylene Solutions in Triethylsilane at 298 K[a]

[C_2Cl_4], mM	irradiation time, min	[C_2Cl_3H], mM	[Et_3SiCl], mM	[C_2Cl_3H]/[Et_3SiCl]	$G(C_2Cl_3H)$, molecules/100 eV
56	9	1.59	1.45	1.097	452
111	9	3.18	3.32	0.958	895
223[b]	45	25.8	26.9	0.959	1432
445[b]	45	29.8	29.7	1.003	1614
890[b]	45	31.8	31.2	1.019	1636
1780[b]	45	34.9	33.0	1.058	1640
				av = 1.016 ± 0.118	

[a] Dose rate in pure $Et_3SiH = 2.35 \times 10^{16}$ eV mL⁻¹ min⁻¹. [b] Dose rate corrected for the difference in electron density between Et_3SiH and C_2Cl_4.
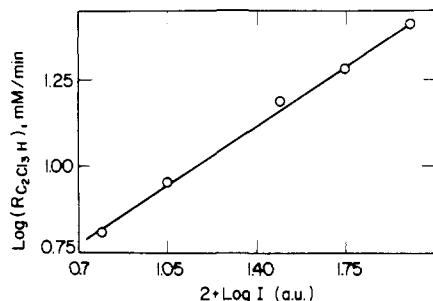
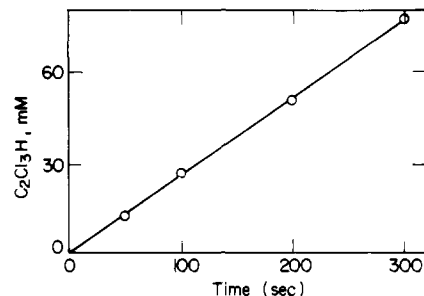**Figure 1.** The effect of light intensity on the rate of formation of C_2Cl_3H.

Figure 2. The variation of C_2Cl_3H formation with time in the photolysis of a 445 mM C_2Cl_4 solution in Et_3SiH.

Therefore the unlikely possibility that the observed products in the Et_3SiH–C_2Cl_3H system were formed in ionic reactions cannot be completely ruled out. The photolytic experiments were thus carried out in order to unequivocally establish the free radical nature of the reactions between Et_3SiH and chloroethylenes.

Table I summarizes the results obtained in the photolysis of C_2Cl_4 solutions in mixtures of Et_3SiH and n-pentane while Figures 1 and 2 show the effect of intensity and irradiation time, respectively, on product formation. It can be seen that the main products are Et_3SiCl and C_2Cl_3H and that, within the experimental error, these products are formed and C_2Cl_4 is consumed with equal rates. The high quantum yields clearly indicate that Et_3SiCl and C_2Cl_3H are formed by a chain mechanism. This chain is terminated by "radical–radical" reactions as evidenced by the fact that the least-squares calculated slope of the line shown in Figure 1 equals 0.49 ± 0.03 (2σ). Finally the linear variation of C_2Cl_3H formation with time, shown in Figure 2, points to the absence of secondary reactions in the system studied.

The experimental observations can be rationalized in terms of the following reaction scheme

$$C_2Cl_4 + h\nu \rightarrow C_2Cl_3 + Cl \tag{1}$$

$$Cl + Et_3SiH \rightarrow HCl + Et_3Si \tag{2}$$

$$C_2Cl_3 + Et_3SiH \rightarrow C_2Cl_3H + Et_3Si \tag{3}$$

$$Et_3Si + C_2Cl_4 \rightarrow Et_3SiCl + C_2Cl_3 \tag{4}$$

$$Et_3Si + Et_3Si \rightarrow Et_3SiSiEt_3 \tag{5}$$

$$C_2Cl_3 + C_2Cl_3 \rightarrow C_4Cl_6 \tag{6}$$

$$Et_3Si + C_2Cl_3 \rightarrow Et_3SiC_2Cl_3 \tag{7}$$
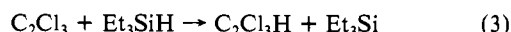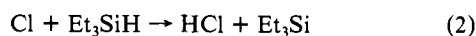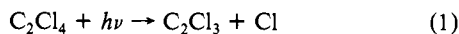
When n-pentane is added to the Et_3SiH–C_2Cl_4 system only the

initiation step will be slightly altered because of the occurrence of the hydrogen abstraction reaction

$$Cl + n\text{-}C_5H_{12} \rightarrow HCl + n\text{-}C_5H_{11} \tag{8}$$
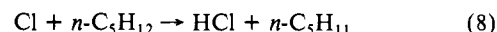
Reaction of n-pentyl radicals with C_2Cl_4 leads to the formation of n-$C_5H_{11}CCl=Cl_2$.[12] Its absence among the products shows that pentyl radicals are rapidly converted into Et_3Si radicals via reaction 9 and therefore, even if reaction 8 does take place, it is

$$n\text{-}C_5H_{11} + Et_3SiH \rightarrow n\text{-}C_5H_{12} + Et_3Si \tag{9}$$
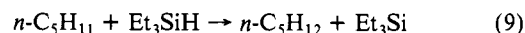
insignificant inasmuch as the overall chain reaction is considered. On the basis of observation that Cl_3C radicals react much faster with Et_3SiH than with cyclohexane[15] we can assume that in our system the trichlorovinyl radicals do not abstract hydrogen from n-pentane. In any case, even if this reaction takes place to some extent, the pentyl radicals would again be rapidly converted into Et_3Si radicals via reaction 9.

Radiolysis. The radiolytic experiments are summarized in Table II. Again Et_3SiCl and C_2Cl_3H are formed in equal yields and by a chain mechanism. The only difference between the radiolytic and photolytic systems is in the initiation step and in the reaction chain length. The initiation in this case can be schematically represented[11] by reaction 10. The difference in the chain length

$$2Et_3SiH \rightarrow 2Et_3Si + H_2 \tag{10}$$
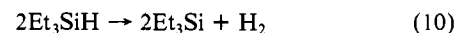
between the photolytic and radiolytic experiments reflects the effect of intensity, i.e., the effect of the rate of initiation. The photodecomposition of C_2Cl_4 leads to the formation of two radicals per

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Table III. Main Radiolytic Products in Solutions of *t*-BuCl and C_2Cl_4 in Triethylsilane at 298 K[a]

[C_2Cl_4], mM	[*t*-BuH], mM	[C_2Cl_3H], mM	[Et_3SiCl], mM	[*t*-BuH + C_2Cl_3H]/ [Et_3SiCl]
116	11.9	8.51	19.2	1.063
174	10.8	11.1	20.9	1.048
231	9.30	13.5	21.8	1.045
345	7.63	15.5	23.5	0.984
462	6.85	18.4	26.5	0.953
696	6.12	26.1	31.1	1.036

[a] In all experiments [*t*-BuCl] = 0.840 mM, dose rate = 2.31 × 10^{16} eV mL^{-1} min^1, irradiation time 65 min.
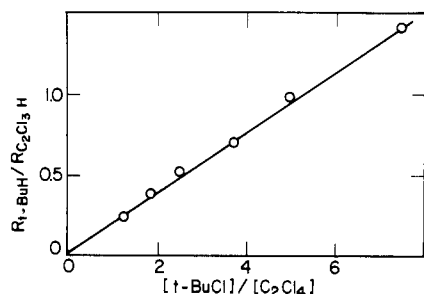
Figure 3. The effect of *t*-BuCl on the formation of C_2Cl_3H in the radiolysis of *t*-BuCl–C_2Cl_4 solutions in Et_3SiH.

every quanta of absorbed light while in the case of radiolysis G(radicals) ~ 5–10. It can be shown then that the effective initiation rate in the photolysis of 446 mM solutions was about 24 times higher than that in the radiolysis of the same solutions. We would then expect the G values to be higher by a factor of about 5 than the quantum yields. The observed $G(C_2Cl_3H)/\Phi_{C_2Cl_3H}$ for the 446 mM solutions, namely 4.10(1614/394), is in good agreement with this prediction. This observation renders further support to the mechanism suggested.

Competitive Experiments. The competitive radiolytic experiments in solution of *t*-BuCl and C_2Cl_4 in Et_3SiH are summarized in Table III. The additional reactions in this system are

$$Et_3Si + \textit{t-BuCl} \rightarrow Et_3SiCl + \textit{t-Bu} \qquad (11)$$

$$\textit{t-Bu} + Et_3SiH \rightarrow \textit{t-BuH} + Et_3Si \qquad (12)$$

In terms of the suggested mechanism the product ratio *t*-BuCl/C_2Cl_3H is then given by expresion 13. A plot of the data

$$\frac{[\textit{t-BuH}]}{[C_2Cl_3H]} = \frac{k_{11}[\textit{t-BuCl}]_{av}}{k_4[C_2Cl_4]_{av}} \qquad (13)$$

according to this expression is shown in Figure 3. The corresponding least-squares calculated k_{11}/k_4 value is 0.18 ± 0.01 (2σ). This result is in good accord with k_{11}/k_4 = 0.25 obtained from the directly determined[7,8] rate constants (1.0 ± 0.2) × 10^7 and (2.5 ± 0.2) × 10^6 M^{-1} s^{-1} for C_2Cl_4 and *t*-BuCl, respectively.

The observed good agreement between the k_{11}/k_4 value obtained in the present study and the value derived for this ratio using the absolute method of Chatgilialoglu et al.[7] points to the reliability of the competitive radiolytic method employed in our laboratory. Incidentally, this is not the only example of the good match between the kinetic data derived by these two methods. In an earlier study Chatgilialoglu and co-workers[8] have shown that their method and ours[16,17] yield almost identical relative rate constants for the Cl-transfer reactions of Et_3Si radical with a series of

Table IV. Relative Rate Constants for the Addition of Various Radicals to *cis*- and *trans*-Dichloroethylene
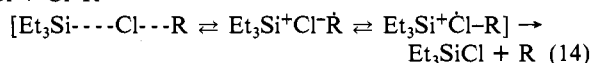
radical	k(trans)/k(cis)	T, K	ref
CCl_3	2.7 (l)	300	19
CF_3	2.5 (g)	300	20
vinyl acetyl	6.0 (l)	333	21
styryl	5.8 (l)	333	21

chloromethanes and chloroethanes.

The Mechanism of Et_3Si Reaction with Chloroethylenes. The findings of the present study do not completely rule out the possibility that a small fraction of the Et_3Si radicals adds to C_2Cl_4. The accuracy of the GC method employed leads us to an estimate that no more than 5% of the Et_3Si radicals may react via this route. Even in this case, the observation that C_2Cl_4 almost exclusively undergoes a Cl-transfer reaction sheds a new light on the course and mechanism of the reaction of Et_3Si radicals with chloroethylenes. Consequently the earlier data and interpretations which were based on the assumption that addition is the sole reaction channel in these systems have to be reexamined.

Chatgilialoglu and co-workers suggested that the electron-withdrawing properties were the main factor governing the reactivity of chloroethylenes.[7] As a typical example these authors cited the example of C_2Cl_4 which, even though sterically hindered, reacts with Et_3Si almost as readily as it reacts with ethylene. Since the method used by Chatgilialoglu et al. is very precise and reliable, their results, combined with the present findings, seem to point to the contrary, namely that steric factors have a major effect on the reactivity of chloroethylenes in their addition reactions with Et_3Si. This conclusion is further supported by the fact that in the case of the less sterically hindered trichloroethylene, addition and Cl transfer proceed with almost equal rates.[10]

In view of the strength of the SiCl bond (113 kcal mol^{-1} in Me_3SiCl^{18}), the ability of chloroethylenes to undergo the very exothermic Cl-transfer reaction with Et_3Si is not surprising. On the other hand, the fact that steric effects appear to play a major role in determining the course of reaction, i.e., addition or Cl transfer, requires clarification. It appears that the ability of silicon to expand its 3d orbitals and the resulting $(p \rightarrow d)_\pi$ bond formation in Et_3SiCl have a strong effect on the interaction between the Et_3Si radicals and chloroethylenes while the transition state is being formed. It is quite possible that not only a polar transition state is involved in the Cl transfer (reaction 14) as has been suggested by Jackson[1] but also that the polar effect of the approaching Et_3Si

$$Et_3Si + Cl\text{-}R \rightarrow$$
$$[Et_3Si\text{-}\text{-}\text{-}\text{-}Cl\text{-}\text{-}\text{-}R \rightleftarrows Et_3Si^+Cl^-\dot{R} \rightleftarrows Et_3Si^+\dot{C}l\text{-}R] \rightarrow$$
$$Et_3SiCl + R \qquad (14)$$

radical is such that it results in a relatively long-range interaction with the Cl atom and in partial polarization of the chloroethylene. Indeed, evidence for the formation of a "loose" transition state can be deduced from the findings of Aloni et al.[16,17] and of Chatgilialoglu and co-workers,[8] who have shown that in the Cl-transfer reactions between chloromethanes and chloroethanes and Et_3Si the reactivity trends, to a large extent, are determined by the abnormally high Arrhenius preexponential factors. Chatgilialoglu and co-workers[8] further pointed out that the polar interactions probably relax the restriction on the colinearity of the Si, Cl, and C atoms in the transition state of Cl-transfer reaction.

In terms of this picture the reactivity trends in the addition reactions of chloroethylenes with Et_3Si radicals which are caused by steric effects to a large extent reflect the screening effect of the polar interactions in the competing Cl-transfer reactions. Support for this idea is provided by the rate data for the reaction of Et_3Si with the cis and trans isomers of dichloroethylene.

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Chatgilialoglu et al.[7] have found that at 300 K the cis isomer is 2.4 times more reactive than the trans isomer, the respective absolute k values being 2.1×10^7 and 8.9×10^6 M^{-1} s^{-1}. Table IV lists relative addition rate data for the reaction of these two compounds with various radicals. It can be seen that in all the reactions the trans isomer is more reactive than the cis isomer. The observation that this order of reactivity is reversed in the

reactions with triethylsilyl radicals can be rationalized if it is assumed that the cis isomer reacts mainly by Cl transfer and that in this reaction it is much more reactive than the trans isomer of dichloroethylene.

Registry No. C_2Cl_4, 127-18-4; Et$_3$SiH, 617-86-7; Et$_3$SiCl, 994-30-9; C_2Cl_3H, 79-01-6; *t*-BuCl, 507-20-0; *t*-BuH, 1320-76-9.

Pyramidalization of Carbonyl Carbons in Asymmetric Environments: Carboxylates, Amides, and Amino Acids

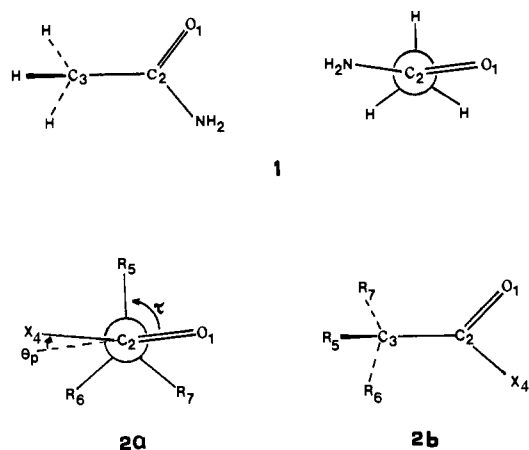G. A. Jeffrey,*[1a] K. N. Houk,*[1b] Michael N. Paddon-Row,*[1b,c] Nelson G. Rondan,*[1b] and J. Mitra[1a]

Contribution from the Departments of Crystallography and Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received May 16, 1984

Abstract: Ab initio molecular orbital calculations, in some cases using unusually stringent convergence criteria for both SCF and geometry optimizations, predict that pyramidalization of the sp^2 carbon atoms will occur in the asymmetric conformers of acetamide, acetic acid, acetaldehyde, propionaldehyde, and the acetate anion. This pyramidalization is small, $\approx 2°$, such that the displacement of the apex of the pyramid is anti to the direction of the bond on the adjacent carbon atom which is most nearly normal to the mean plane of the sp^2 C bonds. This produces partial staggering about the bond to the carbonyl carbon. A survey of 49 neutron diffraction crystal structure analyses of amino acids and dipeptides provides experimental evidence in qualitative support of these theoretical predictions.

Theoretical studies of a variety of alkenes[2–4] and acetaldehyde[2b] led to the prediction that doubly bonded carbon atoms will pyramidalize toward a staggered geometry when the local molecular environment is asymmetrical with respect to the formal plane of the sp^2-hybridized orbitals of the alkene carbons. Dramatic examples of pyramidalization have been found in X-ray crystal structures of polycyclic alkenes.[5,7] These distortions are also obtained in molecular mechanics (force-field) calculations and have been interpreted to be the consequence of torsional strain.[4,6,7]

We now report a systematic study of pyramidalization in carboxylates, amides, and amino acids, based on theoretical ab initio calculations and a survey of some relevant crystal structural data. This work was prompted by the observation of pyramidalization in the molecule of acetamide in its rhombohedral crystalline form.[8] Although acetamide has C_s symmetry in the gas phase and solution, in the trigonal form of crystalline acetamide, the molecules have the asymmetric conformation, **1**, in

Chart I

1

2a

2b

3

X = H, NH$_2$, O$^\ominus$
R = H, CH$_3$

4

X = NH$_2$, NHR, O$^\ominus$
R$_1$–R$_3$ = H, R
R = alkyl or amino acid residue

an asymmetric crystal structure, space group $R3c$. One of the three methyl C–H bonds is almost normal to the molecular plane of the non-hydrogen atoms, as in **1**. This alteration of conformation about the C–C(O) bond of amides and peptides is well-

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(2) (a) Mazzochi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436.

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