Table III. Activation Parameters Derived from k_1 and k_2 Rate Constants[8]

solvent	$E_{act}^{a,b}$	$\Delta H^{\ddagger\,b}$	$\Delta S^{\ddagger\,c}$	$\Delta G^{\ddagger\,b}$
	a. From k_1 Rate Constants			
DMSO	17.9 ± 0.5	17.3 ± 0.5	-22.5 ± 1.5	24.0 ± 1.6
DMF	12.4 ± 0.5	11.8 ± 0.5	-47.3 ± 1.4	25.9 ± 1.5
bromobenzene	10.5 ± 0.7	9.9 ± 0.7	-53.5 ± 2.0	25.9 ± 2.1
1,1,2,2-tetra-chloroethane	14.0 ± 0.7	13.4 ± 0.7	-45.4 ± 2.0	26.9 ± 2.1
toluene	16.4 ± 0.7	15.8 ± 0.7	-37.6 ± 2.0	27.0 ± 2.1
o-dichlorobenzene	19.0 ± 0.8	18.4 ± 0.8	-29.7 ± 2.1	27.3 ± 2.2
p-xylene	17.1 ± 0.7	16.5 ± 0.7	-36.2 ± 2.0	27.3 ± 2.1
1:1 decalin/toluene	16.7 ± 0.7	16.2 ± 0.7	-37.4 ± 2.1	27.3 ± 2.2
decalin	21.7 ± 0.7	21.1 ± 0.7	-21.9 ± 1.9	27.7 ± 2.0
m-xylene	20.9 ± 0.8	20.3 ± 0.7	-25.4 ± 2.4	27.8 ± 2.5
1,2,4-trimethyl-benzene	15.3 ± 0.9	14.7 ± 0.9	-45.2 ± 2.4	28.2 ± 2.6
o-xylene	21.9 ± 0.7	21.3 ± 0.7	-23.9 ± 2.0	28.5 ± 2.1
	b. From k_2 rate Constants			
DMF	12.7 ± 1.2	12.1 ± 1.2	-39.1 ± 3.8	23.7 ± 4.0
decalin	13.4 ± 0.7	12.8 ± 0.7	-38.3 ± 1.9	24.2 ± 2.0
DMSO	11.6 ± 0.5	11.0 ± 0.5	-47.2 ± 1.3	25.0 ± 1.4
bromobenzene	7.4 ± 0.7	6.8 ± 0.7	-60.8 ± 2.0	25.0 ± 2.1
1,1,2,2-tetra-chloroethane	8.8 ± 0.7	8.2 ± 0.7	-57.0 ± 1.9	25.2 ± 2.0
p-xylene	11.4 ± 0.7	10.8 ± 0.7	-52.4 ± 2.1	26.4 ± 2.2
m-xylene	12.9 ± 0.8	12.3 ± 0.8	-48.0 ± 2.2	26.6 ± 2.3
o-dichlorobenzene	17.8 ± 0.7	17.2 ± 0.7	-33.5 ± 2.1	27.2 ± 2.2
toluene	17.8 ± 0.8	17.2 ± 0.8	-33.4 ± 2.3	27.2 ± 2.4
1:1 decalin/toluene	21.8 ± 0.7	21.2 ± 0.7	-22.7 ± 2.1	28.0 ± 2.2
1,2,4-trimethyl-benzene	20.9 ± 0.8	20.3 ± 0.8	-27.0 ± 2.2	28.4 ± 2.3
o-xylene	27.1 ± 0.7	26.5 ± 0.7	-10.4 ± 2.1	29.6 ± 2.2

[a] Activation parameters derived from rate constants. [b] In kcal mol^{-1}. [c] cal mol^{-1} K^{-1}.

The reaction follows a unimolecular, first-order process in each solvent at low concentration of episulfide, but at higher concentrations, a bimolecular pathway becomes more important. Thus, in toluene, over a 400-fold increase in the rate of desulfurization is observed when the concentration is increased 38-fold, thus reflecting the contribution of the bimolecular term. At low concentration levels (ca. 0.10–0.15 mM) the nearly exclusive pathway is a unimolecular decomposition, while at higher concentrations (ca. 2.0 mM), the bimolecular path is actually followed by ca. 4:1. The bimolecular term predominates at higher concentrations in the majority of the solvents. In the case of DMF, at low concentrations, the exclusive pathway is unimolecular and at higher concentrations the unimolecular pathway is favored by ca. 2:1.

Arrhenius Parameters. The thermal decomposition of episulfide 2 was conducted at four temperatures for all solvents used in the study. Duplicate (sometimes triplicate) runs were made for each temperature point; points were reproducible over time and over different batches of episulfide. The values of the activation parameters E_{act}, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$ are included in Table IIIa and b in order of increasing $\Delta G^{\ddagger}$.

Relatively few articles in the literature have *thoroughly* dealt with the overall effect of changing the medium upon the activation energy (or enthalpy) and entropy. The variations in these kinetic activation parameters are frequently so unpredictable that no generalizations can be easily made.[10] In some ionization studies, certain regularities in the activation parameters do exist, and these data are consistent with the theory of absolute reaction rates.[11] DMF, a strong solvating agent, would experience little desolvation in the transition state and consequently

have a lower $\Delta H^{\ddagger}$, albeit we do not observe quite the same behavior in DMSO.

The somewhat large negative values of the entropy of activation suggest highly ordered transition states in which the solvent plays a strong stabilizing role. The ground state would have less ordering of solvent molecules. This further strengthens our proposed mechanism involving ionized intermediates. Ionization reactions usually accompany a large negative $\Delta S^{\ddagger}$ because of the loss of entropy of the solvent when going to the transition state. Large negative entropies have been observed in the unimolecular thermolysis reaction of α-chloroalkyl ethers in aprotic solvents.[12] For the majority of the solvents, the molecules are somewhat unordered in the ground state but on solvation in the transition state they experience a reduction in the number of degrees of freedom available to them and, therefore, suffer from a greater loss in entropy. Solvents which are already ordered in the ground state will suffer a smaller loss in entropy upon solvation in the transition state.

It is interesting to note that numerical values for $\Delta S^{\ddagger}$ of the bimolecular term are generally more negative than the $\Delta S^{\ddagger}$ in the unimolecular term. This is consistent with the fact that a bimolecular reaction usually involves more ordering of solute and solvent molecules as two reacting species must come together for reaction to occur. The fact that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are inconsistent within a series of solvents of similar structure or polarity (i.e., xylenes, haloaromatic solvents, polar/nonpolar solvents) implies solvent interactions, in both the ground and transition states, are too complicated for simple interpretation. The values of $\Delta G^{\ddagger}$ are all relatively constant which is consistent with the usually observed compensating effect of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Isokinetic Relationship. An interesting feature in our study is an observed isokinetic relationship. This phenomenon was first recognized by Leffler[13] who discussed its scope and significance. Enthalpy–entropy relationships are well-precedented in the literature.[14] In simple terms, it states that at the isokinetic temperature, β, all the reactions in a given series have identical rates, or that $\Delta\Delta G^{\ddagger} = 0$ (eq 2). The isokinetic plots for both unimo-

$$\Delta\Delta H^{\ddagger} = \beta\Delta\Delta S^{\ddagger} \qquad (2)$$

lecular and bimolecular terms are shown in Figure 2a and b, respectively, using the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from Table IIIa and b; the $\Delta G^{\ddagger}$ values do not range widely. The isokinetic temperatures are 40 and 112 °C, respectively, for the first- and second-order terms with good correlations of 0.94 and 0.98, respectively. The linearity of the isokinetic plots provides an indication that the reaction series in these solvents proceed with the same mechanism. Although it has been debated that the apparent isokinetic relationship is a result of indiscriminate experimental

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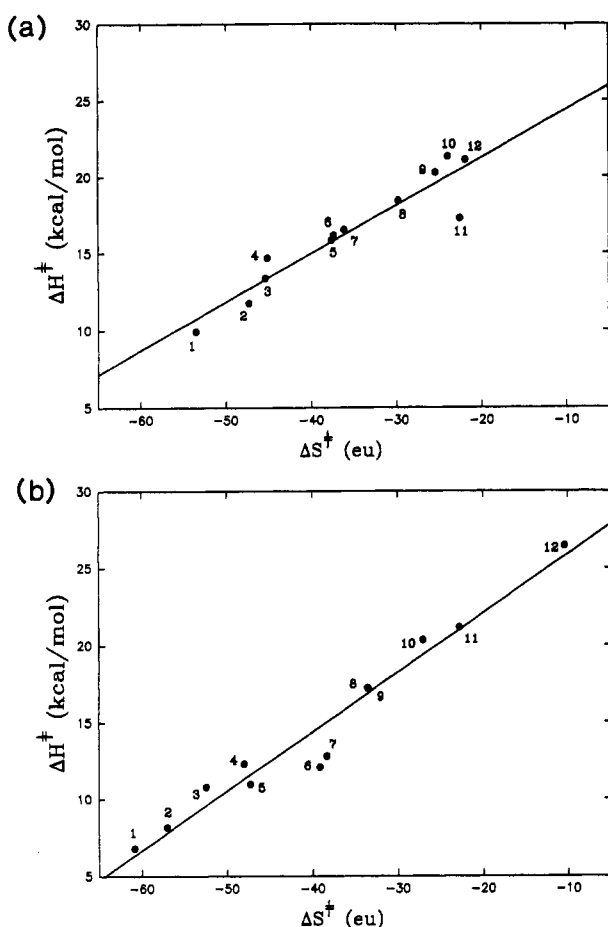
(a)

(b)

Scheme II

Figure 2. (a) Isokinetic plot from activation parameters derived from k_1 values. Isokinetic temperature = 40 °C (r = 0.94). Key: 1. bromobenzene; 2. DMF; 3. 1,1,2,2-tetrachloroethane; 4. 1,2,4-trimethylbenzene; 5. toluene; 6. 1:1 decalin/toluene; 7. p-xylene; 8. o-dichlorobenzene; 9. m-xylene; 10. o-xylene; 11. DMSO; 12. decalin. (b) Isokinetic plot from activation parameters derived from k_2 values. Isokinetic temperature = 112 °C (r = 0.98). Key: 1. bromobenzene; 2. 1,1,2,2-tetrachloroethane; 3. p-xylene; 4. m-xylene; 5. DMSO; 6. DMF; 7. decalin; 8. o-dichlorobenzene; 9. toluene; 10. 1,2,4-trimethylbenzene; 11. 1:1 decalin/toluene; 12. o-xylene.

error,[15] the range of ca. 15 kcal in $\Delta H^{\ddagger}$ and ca. 45 eu in $\Delta S^{\ddagger}$ in our data argue for the authenticity of our relationship.

Plausible Mechanism of Sulfur Extrusion. From the desulfurization kinetics of episulfide **2**, the following mechanism is proposed to account for the observations. At low concentrations, thermal ionization of the C–S bond in **2** (Scheme II) likely occurs as the first and rate-determining step. Such an intermediate has been suggested, as in the reaction between 9-diazoxanthene and coumarin-2-thione.[16] Cleavage of the C–S bond of **2** at the carbon bearing the two chlorines would be unfavorable due to their electron-withdrawing effect. The positive charge on the carbon bearing the fluorenyl substituent would be stabilized by resonance.[5b] The fast step would involve the subsequent attack of the sulfur anion species **7** on another molecule of episulfide **2**, giving intermediate **8**. This species would acquire sulfur atoms sequentially until an S_8 cycle is formed along with **3**.
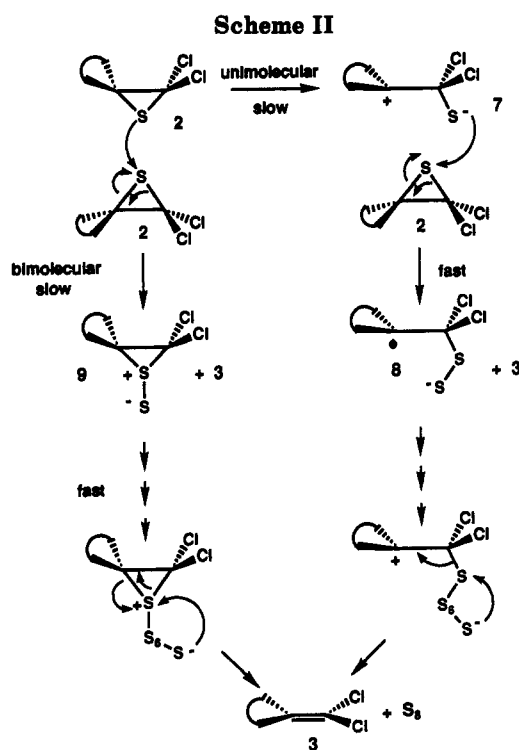
As the concentration of episulfide **2** increases, the second term in the rate equation becomes more important and a competing bimolecular mechanism is followed (Scheme II). The sulfur atom from one episulfide molecule abstracts the sulfur atom from another in the rate-determining step, giving intermediate **9**.[5b] The fast step is the subsequent concatenation of more sulfur atoms until S_8 is formed. At even higher concentration levels in 12 solvents, the bimolecular route actually becomes the rate-determining step.

Attempt To Correlate Reaction Rate with Solvent Polarity. Strong correlations between experimental rates and solvent properties are well documented;[17] the same holds for empirical solvent polarity scales.[18] Despite the observation that single empirical parameters serve as good approximations of solvent polarity, many solvent-sensitive processes do not correlate well with these parameters; our work appears to fall into this category. Plots of either log k_1 or log k_2 vs several polarity scales including dipole moment, Hildebrand's solubility parameter, Dimroth's E_T values, and refractive index, showed no apparent correlation. Log k_1 (or log k_2) against Grunwald's Y values were not plotted because of unavailable Y parameters for the solvents used in our study.

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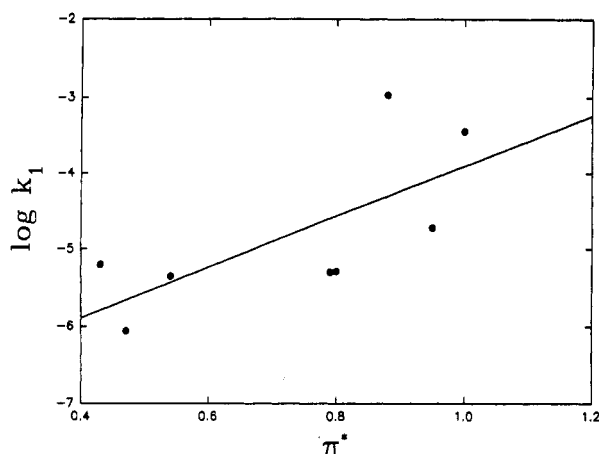
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Figure 3. Plot of $\log k_1$ vs π^* solvent polarity parameter showing a general increase in rate with π^*. The k_1 values were taken from Table I and have a π^* value that was measured ($r = 0.70$).

An enticing characteristic is found when $\log k_1$ or $\log k_2$ is plotted against $(D_c - 1)/(2D_c + 1)$,[19] where D_c is the dielectric constant. The quantitative correlation ($r = 0.72$ and 0.61, respectively) is not ideal, but with the exception of a few irregular data points, an increase in rate with dielectric constant is shown. This is reasonable evidence for the existence of an ionized transition state in agreement with our proposals. Several cases in the literature have shown $\log k$ vs $f(D_c)$ plots with a few scattered points, but a general increase in rate with dielectric constant (positive slope) is observed[19] thus supporting the existence of ionized transition states. We emphasize that no single physical parameter can effectively be used as a measure of solvent polarity in our system perhaps due to the multitude and complex nature of solute/solvent processes. There are many different kinds of interaction mechanisms between solute and solvent molecules which may act simultaneously.

Our attempt to correlate π^* values of Kamlet and Taft[20] with $\log k_1$ or $\log k_2$ was met with some success ($r = 0.70$). We observe a prevailing increase in rate ($\log k_1$) with the π^* solvent polarity parameter which is indicative of a dipolar mechanism (Figure 3). The lack of high correlation[21] of $\log k_1$ or $\log k_2$ with π^* can be attributed to the fact that these parameters stem from a particular effect the solvent polarity has on a certain model (reference) chemical process of a certain compound. These model processes do not bear much resemblance to our decomposition reaction, and hence the parameters do not correlate ideally with our reaction rates.

Similarly, the rate of reaction correlates reasonably well with the nonspecific parameters of Koppel and Palm.[22] Multiple regression provides eqs 3 and 4 where $f(D_c) = (D_c - 1)/(2D_c + 1)$ and $f(n^2) = (n^2 - 1)/(n^2 + 2)$. We see that the dielectric term plays a dominant role and the refractive index term plays a negative role in the overall reaction rate. If we increase the polarity of the solvent (i.e.,

$$\log k_1 = 1.85 + 5.75 f(D_c) - 29.43 f(n^2) \qquad (3)$$

$$\log k_2 = 0.31 + 6.59 f(D_c) - 24.49 f(n^2) \qquad (4)$$

dielectric constant) the rate increases, which is in agreement with our proposed ionic mechanism.

We should also note that in the Koppel and Palm approach we use the dielectric constants which are ground-state properties of the bulk solvent, and in the Kamlet and Taft illustration we use π^* values which are derived from probing the cybotactic region.[23] Overall, this suggests that, although the rates of reactions are mainly influenced by the cybotactic region more than the bulk solvent, the bulk solvent is meaningful in our system.

Evidence of proton transfer within this system was attained by the addition of acetic acid. The rate profile shown in Figure 4 was obtained starting with an initial concentration of episulfide 2 of 1.0 mM and varying the concentration of acetic acid. As the concentration of acetic acid is increased, the rate of formation of alkene in toluene at 80 °C is reduced dramatically. A 6-fold decrease in rate is observed when the concentration of acetic acid is increased by 1.5 times. This is compatible with the protonation of thiolate intermediates which would inhibit further decomposition.

Effect of Radical Inhibitor. We extended our mechanistic efforts by studying the effect of radical inhibitors on the decomposition of episulfide 2. If the rate is slowed, then we could conclude that the reaction possibly follows a radical-type mechanism. Rates were determined by ^{1}H NMR by following the increase in the appearance of alkene 3 in toluene-d_8 at 80 °C with and without addition of a radical inhibitor. The bimolecular rate constants were used for comparison of reaction rates and are shown in Table IV for two different radical inhibitors, acetanilide and styrene. The addition of either inhibitor, even at 2.2–2.7 times more concentrated than 2, showed no significant change in the rate, thus demonstrating that a radical mechanism is unlikely.

Experimental Section

General Methods. Melting points (mp) were determined using a Gallenkamp melting point apparatus using open-end capillaries and are uncorrected. Low-resolution electron impact (EI) mass spectra were obtained on a Kratos MS25RFA mass spectrometer equipped with a 70-eV ionizing energy source and used in direct-inlet mode. ^{1}H NMR spectra were recorded on either the Varian XL200 or the Varian XL300 spectrometer using deuteriochloroform as the reference solvent. ^{13}C NMR spectra were obtained at 75.4 MHz using the Varian XL300 spectrometer. Raman spectra were recorded on a S. A. Ramonor spectrometer equipped with a U-1000 double monochromator and a Spectra-Physics Argon ion laser at 514.5 nm and are reported in wavenumbers.

Materials. Hexanes was distilled over 7% by volume concentrated sulfuric acid and passed through an alumina column before use. Toluene and o-dichlorobenzene were purified by distillation from calcium hydride and stored over 4-Å molecular sieves prior to use. All other solvents and reagents were used as purchased from Aldrich Chemical Co. without further treatment. DMF and DMSO were stored over 4-Å molecular sieves. o-Xylene, m-xylene, and p-xylene were HPLC-grade quality.

UV Rate Measurements. The rates of decomposition were measured by following the increase in UV absorption of olefin

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(21) The lack of good correlation has also been observed in the plot of $\log k$ vs E_T ($r = 0.79$) and $\log k$ vs $\delta_H^2/100$ ($r = 0.76$); see ref 17f.

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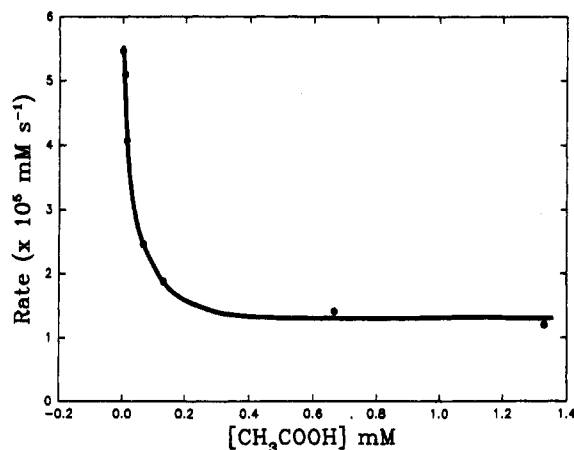
Figure 4. Effect of adding acetic acid in the decomposition of **2**.

Table IV. Second-Order Rate Constants Obtained from Appearance of 3 in Toluene-d_8 at 80 °C with and without Addition of Radical Inhibitor

	k_2 ($\times 10^5$ mM^{-1} s^{-1})
no inhibitor	0.38 ± 0.09
acetanilide	0.34 ± 0.07
styrene	0.33 ± 0.07

3 and were recorded on a Phillips Pye Unicam PU8800 UV/vis spectrophotometer equipped with an Accuron PSX 876 Series 2 temperature program controller. Quartz UV cells (Hellma Canada Ltd.) containing the solvent were allowed to equilibrate for 10–15 min at controlled temperatures (30–100 °C) prior to injection of the samples. The samples were injected via Hamilton syringes, and the cells were capped, shaken, and placed in the cell compartments. The absorbances were measured at various time intervals at $\lambda = 325$ nm and at a bandwidth of 2 nm. The method of initial rates was used in calculating observed rate constants. Extinction coefficients for each solvent were obtained from the slopes of the plots of absorbance ($\lambda = 325$ nm) vs concentration of olefin **3** which was obtained by heating a solution of **2** (0.15 g, 0.53 mmol) in 8 mL of toluene at reflux for 2.5 h and isolated by silica gel chromatography (hexanes eluent): mp 128–130 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.31 (dt, 2 H, $J_1 = 7.5$ Hz, $J_2 = 1.4$ Hz), 7.39 (dt, 2 H, $J_1 = 7.5$ Hz, $J_2 = 1.4$ Hz), 7.70 (dd, 2 H, $J_1 = 7.5$ Hz, $J_2 = 1.4$ Hz), 8.32 (dd, 2 H, $J_1 = 7.5$ Hz, $J_2 = 1.4$ Hz); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 119.6, 122.3, 125.8, 127.5, 129.1, 134.2, 136.5, 140.2; MS m/z (rel intensity) 250 (11), 248 (64), 246 (M$^{\cdot+}$, 100), 176 (M$^{\cdot+}$ – 2 × Cl, 70.9), 123 (16), 105 (15), 88 (33); UV λ_{max} (decalin) 308, 320 ($\epsilon = 4918, 5450$).

Rate Measurements: Radical Inhibitor Study. Rates were measured on a Varian XL300 spectrometer using toluene-d_8 as the reference solvent. A 5-mm (diameter) NMR tube containing the inhibitor dissolved in toluene-d_8 was allowed to equilibrate at 80 °C for 5–10 min in the sample probe prior to adding episulfide **2**. The episulfide was injected and the tube sealed and immediately placed in the sample probe. ^{1}H NMR spectra were acquired at various intervals over a period of 12–16 h. All spectra were obtained by acquiring 64 transients. The rates were calculated first by calculating the ratio of the peak heights measured at 8.3 ppm (in cm) and the peak height of toluene (methyl signal). Assuming the episulfide was completely converted to the olefin, the ratio of peak heights of the final spectrum would equal the initial concentration of episulfide. By plotting the concentration vs time, the second-order rate constant, k_2, can be calculated using the initial rate method. The first-order rate constant was assumed to be negligible since the initial concentration of the episulfide ranged from ca. 6 to 16 mM.

Preparation of 3′,3′-Dichlorospiro[fluorene-9,2′-thiirane] (2). The title compound was synthesized according to the procedure described by Staudinger and Siegwart.[24] To 2.5 g (13 mmol) of 9-diazofluorene suspended in 50 mL petroleum ether was added 1 mL (13 mmol) of thiophosgene in 5 mL of petroleum ether dropwise with the reaction being kept at 0 °C. The red suspension turned orange upon slow addition of the thiophosgene, and the evolution of nitrogen was apparent. After a few minutes, straw yellow needles began to appear. After the solution was allowed to warm to room temperature for 1 h, the mixture was collected yielding 2.2 g (61%) of the episulfide. No impurities were observed in the ^{1}H NMR and MS of **2**: mp 89–91 °C (lit.[24] mp 97 °C); ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.29 (dt, 2 H, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz), 7.45 (dt, 2 H, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz), 7.54 (dd, 2 H, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz), 7.75 (dd, 2 H, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz); ^{13}C NMR (75.4 MHz, CD$_2$Cl$_2$) δ 60.3, 77.3, 120.6, 126.6, 127.3, 130.2, 140.7, 142.3; MS m/z (rel intensity) 278 (M$^{\cdot+}$, 2), 246 (M$^{\cdot+}$ – S, 100), 208 (95); Raman 652 cm^{-1}.

Supplementary Material Available: NMR spectra for compounds 2 and 3 (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Regiospecific *Syn* Addition of (Polyfluoroaryl)copper Reagents to Fluorinated Acetylenes: Preparation and Subsequent Functionalization of Internal Vinylcopper Reagents[1]

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(Pentafluorophenyl)copper (C_6F_5Cu) can be prepared from a metathesis reaction between C_6F_5CdX (X = Br or C_6F_5) and CuY (Y = Cl or Br). The arylcopper reagent undergoes a stereo- and regiospecific *syn* addition to fluorinated alkynes, which results in the corresponding internal alkenylcopper intermediate. This vinylcopper reagent can be subsequently functionalized with a variety of electrophiles, including aryl, alkyl, allyl, and acyl halides, to afford tetrasubstituted fluoroalkenes. The *para*-substituted arylcopper analogs also successfully undergo the addition reaction.

Introduction

The stereospecific preparation of polysubstituted alkenes and dienes presents a major challenge in organic synthesis. A variety of natural products contain one or more double bonds and these molecules must be synthesized with an extremely high factor of stereochemical integrity, as minute percentages of the undesired isomer can inhibit the biological activity of the target natural product.[2] Of the many methods currently in use for alkene syntheses, recent attention has been focused on the carbometalation of alkynes, which efficiently generates vinyl organometallic intermediates, which can be further transformed *via* subsequent coupling reactions.[2-13] Although several metals have exhibited varying degrees of success (magnesium, lithium, zinc, aluminum), the most useful reagents for carbometalation of alkynes are those derived from copper. The addition occurs exclusively in a *syn* mode, and the vinylic copper intermediate thus produced is reactive toward many electrophiles with complete retention of configuration.

While copper-mediated carbometalation of alkynes enjoys increasing popularity in hydrocarbon syntheses, very little work has been done to broaden the scope of this reaction to the synthesis of the corresponding substituted fluorinated alkenes. The first preparation of this type was accomplished in our laboratories by Hansen,[14] who reported that perfluorinated vinyl copper reagents underwent a stereospecific *syn* addition to hexafluoro-2-

butyne in DMF at room temperature to afford the desired conjugated dienylcopper species. In this paper, we extend this reaction to fluorinated arylcopper reagents.

Discussion

(Pentafluorophenyl)copper, C_6F_5Cu, is an excellent reagent for a variety of synthetic uses. It is completely soluble in a number of organic solvents and exhibits a remarkable thermal stability compared to its hydrocarbon analog, C_6H_5Cu.[15]

The earliest syntheses of (pentafluorophenyl)copper involved metathesis reactions between cuprous halide and a pentafluorophenyl organometallic reagent.[15-22] Tamborski and co-workers prepared C_6F_5Cu by reaction of CuI with the thermally labile (pentafluorophenyl)lithium.[16] C_6F_5Cu was also obtained from the corresponding Grignard reagent.[17] Cairncross and Sheppard reported that C_6F_5Cu exists as a tetramer when isolated from its dioxane complex.[18] More recently, Rieke prepared C_6F_5-Cu from C_6F_5I and a highly reactive, specially activated copper powder in an ethereal solvent.[23-25]

In subsequent reactions of C_6F_5Cu, it was generally found that the rate of reaction and the product distribution were strongly dependent on the mode of arylcopper synthesis.[19] Of particular significance was the effect of solvent on certain reactions, when the desired pathway would only be followed after a solvent exchange to a highly complexing medium, such as DMAC.[17]

As a result of the positive effects of more complexing solvents and the success of the carbometalation with fluorinated vinylcopper reagents in DMF, we have designed a novel, efficient synthesis of C_6F_5Cu, which can

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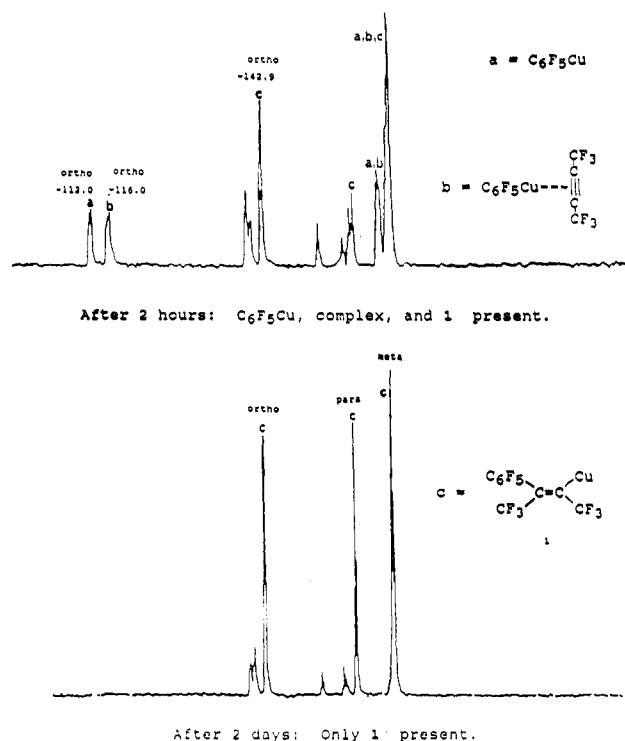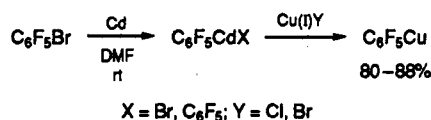(25) Ebert, G. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 4482.

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Figure 1. Ortho, para, and meta regions of ^{19}F NMR spectrum of reaction mixture for $C_6F_5Cu + CF_3C{\equiv}CCF_3$.

be carried out in DMF without the need for solvent exchange. Thus, the arylcopper species is synthesized from the corresponding cadmium reagent, which is readily prepared from bromopentafluorobenzene and cadmium metal as described by Heinze.[26] Once formed, the soluble cadmium reagent is simply decanted away from the excess cadmium metal and salts, and 1 equiv of cuprous halide is added at room temperature. After stirring for 15 min, the nearly quantitative reaction is complete, and the expected copper reagent is present in an ^{19}F NMR yield of 80–88%, based on bromopentafluorobenzene.

$$C_6F_5Br \xrightarrow[\substack{DMF \\ rt}]{Cd} C_6F_5CdX \xrightarrow{Cu(I)Y} C_6F_5Cu$$

$$80\text{–}88\%$$

$$X = Br, C_6F_5; \ Y = Cl, Br$$

Hexafluoro-2-butyne may be condensed directly into the C_6F_5Cu reaction mixture. After the mixture is stirred vigorously for 2 h, the ^{19}F NMR spectrum reveals that three species are present in solution (see Figure 1), as exhibited by three discrete signals in the o-fluorine region. The first of these (–112.0 ppm from $CFCl_3$) indicates the presence of the starting material, C_6F_5Cu, and another (–142.9 ppm) corresponds to the expected adduct. The third o-fluorine signal occurs at –116.0 ppm and is tentatively assigned to a transient complex between the copper atom and the triple bond of the butyne (see Scheme I).

The extent of the reaction between C_6F_5Cu and the fluorinated alkyne can thus be easily monitored by the gradual disappearance of the signal at –116.0 ppm and concomitant enhancement of the –142.9 ppm peak, signifying the conversion of the intermediate complex to the desired vinyl copper reagent 1.

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Scheme I
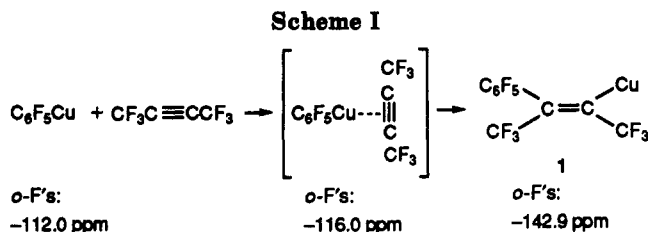
A typical 100-mmol reaction requires 2–3 days for completion, and 1 is formed in ^{19}F NMR yields of 60–80%, based on bromopentafluorobenzene. The only significant impurity is C_6F_5H, which is formed during the synthesis of the cadmium reagent. However, this problem can be readily resolved by a low pressure room temperature distillation designed to remove the volatile contaminants before the vinylcopper species is quenched with an electrophile. A variable temperature NMR study revealed that 1 exhibits an extremely high thermal stability, with no noticeable decomposition occurring at temperatures up to 150 °C. The C_6F_5Cu can be generated in large quantities in DMF and stored (in the absence of oxygen) for days or weeks without noticeable decomposition. No attempt was made to isolate the C_6F_5Cu in a solid form.

The stereochemistry of the addition of C_6F_5Cu to hexafluoro-2-butyne was *syn*, as determined from the characteristic *cis*-CF_3–CF_3 coupling constant of 12 Hz in the ^{19}F NMR spectrum, a magnitude which would be close to 0 if the CF_3 moieties were *trans* to one another.

Further confirmation of the structure of 1 was afforded by hydrolysis and iodination. When a solution of 1 was treated with dilute acid or molecular iodine, spectroscopic data of the resulting products were consistent with 2 and 3, respectively. Both reactions occurred with complete retention of stereochemistry to afford reasonable yields of products.
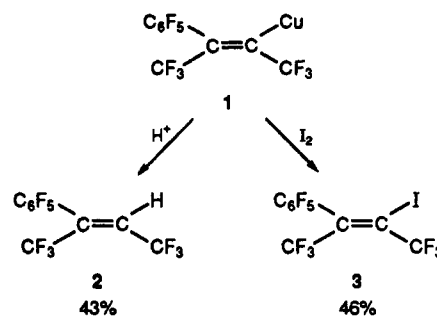
Although the stereochemistry of the carbometalation reaction can be easily assigned, the utilization of the symmetrical F-2-butyne does not allow us to determine whether or not the addition reaction exhibits any regiospecificity. We therefore attempted the reaction of C_6F_5Cu with an unsymmetrical alkyne, $C_6F_{13}C{\equiv}CCF_2H$. ^{19}F NMR data revealed that the product was 4, indicating complete regiospecificity. This result was not unexpected as organocopper reagents typically add to alkynes with the copper atom associated with the least-hindered carbon of the triplet bond.[2]