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Iodofluorination of Phenyl-Substituted Olefins with Methyliodine(III) Difluoride[1]

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Methyliodine(III) difluoride reacts with phenyl-substituted olefins, e.g., 1,1-diphenylethylenes and styrenes, to form corresponding vicinal iodofluorides and not the rearranged 1,1-difluorides, obtained in a similar reaction with aryliodine(III) difluoride. Iodofluoride addition undergoes Markownikoff type regioselectivity, forming corresponding 1-phenyl-1-fluoro-2-iodoethanes.

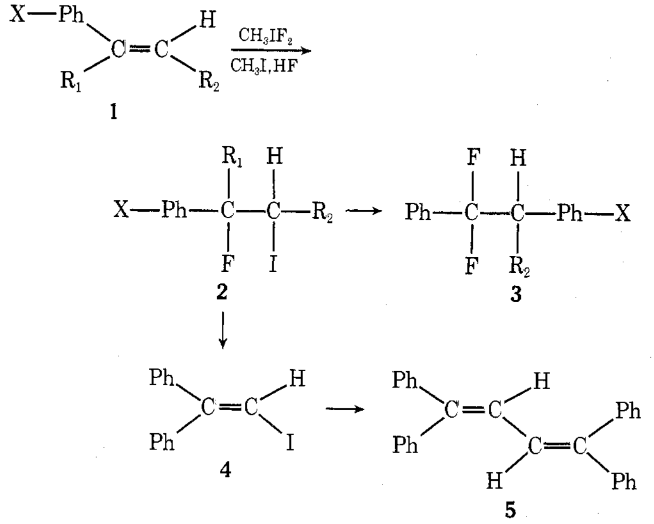
The addition of chlorine to olefinic double bonds using phenyliodine(III) dichlorides has received attention from several groups of workers.[2–4] The corresponding aryliodine(III) difluorides received much more limited attention as fluorinating agents, possibly because of the difficulties involved in their preparation and storage.[5–9] In our recent efforts to develop the polymeric fluorinating agent poly(*p*-iodostyrene difluoride),[10] we have also investigated the fluorination of 1-phenylethylenes with methyliodine(III) difluoride, the only stable representative of the alkyliodine(III) difluorides. The recent reported synthesis of methyliodine(III) difluoride by the reaction of xenon difluoride with an excess of methyl iodide[11] makes this potential fluorinating agent readily available.

Results and Discussion

The preparation of fluoroalkanes represents a different problem from that of the preparation of other haloalkanes and necessitates a specific method of fluorination.[12] Difficulties involve the handling of anhydrous hydrogen fluoride on the laboratory scale, the need for pressure equipment, low temperatures, and the ease of polymerization of alkenes.[12] Iodofluorination with a mixture of hydrogen fluoride–pyridine–*N*-iodosuccinimide avoids some experimental difficulties,[14] e.g., low temperature, high-pressure techniques, and polymerization of olefins.

Following the procedure reported by Gibson,[11] we prepared a solution of methyliodine(III) difluoride by the reaction of xenon difluoride with an excess of methyl iodide. A series of substituted 1-phenylethylenes (**1a–h**) were treated with methyliodine(III) difluoride (Scheme I). The pure product **2a** was isolated in a 55% yield from the crude reaction mixture by preparative TLC. The NMR spectra of the product **2a** showed a triplet signal at −157.5 ppm in ^{19}F NMR spectra and a doublet with coupling constant 23 Hz at 3.75 ppm in ^1H NMR spectra. The structure of 1,1-diphenyl-1-fluoro-2-iodoethanes was established also by chemical transformation. On heating **2a** at 80 °C, 1,1-diphenyl-2-iodoethene (**4**) and

Scheme I



1a, $X = H; R_1 = Ph; R_2 = H$
b, $X = p\text{-}Cl; R_1 = Ph; R_2 = H$
c, $X = p\text{-}OCH_3; R_1 = Ph; R_2 = H$
d, $X = H; R_1 = Ph; R_2 = CH_3$
e, $X = H; R_1 = Ph; R_2 = F$
f, $X = H; R_1 = R_2 = H$
g, $X = H; R_1 = CH_3; R_2 = H$
h, $X = H; R_1 = H; R_2 = Br$

smaller amounts of 1,1,4,4-tetraphenylbutadiene (**5**) were isolated. Products **4** and **5** were independently synthesized[15] and found to be identical with the products formed in the thermal elimination reaction. 2-Iodo-1,1-diphenylethylene (**4**) was also formed under basic elimination conditions, e.g., potassium *tert*-butoxide, from the corresponding **2a**.

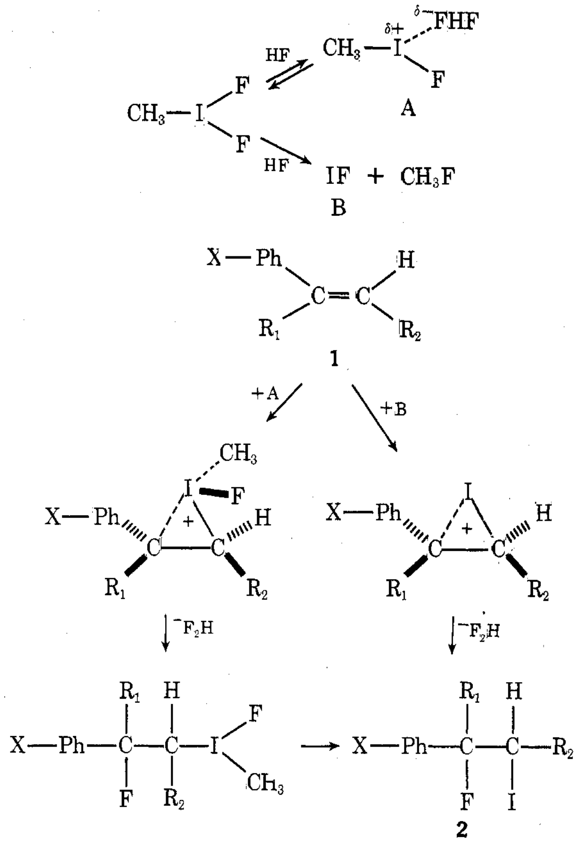
The reaction with *p*-chlorodiphenylethylene (**1b**) took place under similar conditions. On the other hand, reaction with *p*-methoxy derivative (**1c**) resulted in the rearranged product **3c**. The structure of the product was established on the basis of its NMR data (δ_F −105.5 ppm, t) which corresponds to that of the geminal difluorides. In the mass spectrum the fragments were methoxytropilium cation, *m/e* 121, and difluorobenzylium cation, *m/e* 127, which indicates *p*-methoxyphenyl-group migration. In order to detect the primary iodofluoride adduct, we reduced the reaction time from 1 h to 20 min. ^{19}F NMR spectra taken on the crude reaction mixture showed two triplets: one at −105.5 ppm and the other at −152 ppm with a coupling constant of 23 Hz, the former corresponding to the rearranged product and the latter to the unrearranged one. The unrearranged product was present in 20% abundance, as calculated from the integrals. We were not able to isolate the pure unrearranged product **2c**. The reaction with 1,1-diphenylpropene-1 (**1d**) under similar conditions resulted in the formation of a mixture of two products. One of them was rearranged 1,1-difluoro-1,2-diphenylpropene (**3d**) and another unrearranged primary iodofluoride (**2d**). The reduction of the reaction time to 30 min resulted in the formation of the rearranged product. The formation of difluorides could be explained by the S$_N$1 substitution reaction, and was observed in the reaction with olefins bearing at least one methyl or phenyl group (*cis*- or *trans*-phenylpropene, *cis*- and *trans*-stilbene),[16] which facilitates S$_N$1 substitution with its mesomeric or inductive effects. In the reaction with 1,1-diphenyl-2-fluoroethylene (**1e**), 2 h was needed for the completion of the reaction, while after 1 h only 50% conversion of the olefin to the corresponding iodofluoride (**2e**) was observed.

The reaction with substituted styrenes (**1f–h**) also resulted in the formation of unrearranged iodofluorides.

The addition of the elements of IF with methyliodine(III) difluoride to olefins is in sharp contrast to the reactivity of aryliodine(III) difluorides,[5,8] which were found to react with phenyl-substituted olefins forming 1,1-difluorides, accompanied by phenyl-group migration. We have also reinvestigated the latter reaction on a wider series of phenyl-substituted olefins with *m*-chlorophenyliodine(III) difluoride but were unable to detect any trace of iodofluorides.

There are two possible explanations for the unusual reactivity of methyliodine(III) difluoride (Scheme II). Either methyliodine(III) difluoride decomposes in the presence of hydrogen fluoride as a catalyst to methyl fluoride and a reactive species B, which subsequently adds the elements of IF to the olefinic double bond, or HF polarizes the I–F bond of methyliodine(III) difluoride, thus forming an electrophile A, which attacks the olefinic carbon, methyl fluoride being eliminated in the later stage of this iodofluorination reaction. Although the exact mechanism is not known at present, the addition of the elements of IF to 1-phenylethylenes with methyliodine(III) difluoride appears to be a regiospecific process in which the side reactions, e.g., competitive addition of hydrogen fluoride, exchange of iodine by the fluoride anion, or formation of phenyl-group migration products, can be avoided by adjusting the reaction conditions.

Scheme II

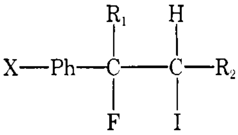


We feel that the methods outlined above may be preferable in some respects to the methods previously available for the in situ generation of the elements of IF.[13,14] One advantage which could be mentioned here is the low amount of HF required to catalyze the reaction, thus preventing the polymerization of olefins or other side reactions.

Experimental Section

Ir spectra were recorded by using a Perkin-Elmer 257 spectrometer, ^1H and ^{19}F NMR spectra by a JEOL JNM-PS-100 from CCl_4 solution with Me_4Si or CCl_3F as internal reference. Mass spectra and high-resolution measurements were taken on a CEC-21-110 spectrometer. Gas–liquid partition chromatography was carried out on a Varian

Table I. NMR Data for 1-Phenyl-1-fluoro-2-iodoalkanes (2)



$$X\text{—Ph—}\overset{R_1}{\underset{F}{C}}\text{——}\overset{H}{\underset{I}{C}}\text{—}R_2$$

Compd	δ_F, ppm	δ_H, ppm	δ_{X-Ph}, ppm	J_{FH}, Hz	δR_1, δR_2, ppm	Other coupling constants, Hz
2a	−157.5 (t)	3.75 (d)	7.1 (m)	23		
2b	−156.8 (t)	3.8 (d)	7.2 (m)	24		
2d	−162 (d)	4.85 (dq)	7.2 (m)	33	R_2 = 1.8 (d)	J_{HR_2} = 7.5
2e	−165 (dd)	7.3 (dd)	7.3 (m)	15	R_2 = −167.5 (dd)	J_{FF} = 30, J_{HR_2} = 49.5
2f	−163.1 (m)	3.3 (m)	7.3 (m)		R_1 = 5.35 (dt)	J_{FR_1} = 45, J_{R_1H} = 6
2g	−145.5 (qt)	3.54 (d)	7.3 (m)	21	R_1 = 1.87 (d)	J_{FR_1} = 21
2h	−165.3 (dd)	5.5 (m)	7.3 (m)	15	R_1 = 5.5 (m)	J_{FR_1} = 48

Aerograph Model 1800 and TLC on Merck PSC-fertigplatten silica gel F-254.

Materials. Pure samples of olefins were prepared by known methods: 1,1-diphenylethylene,[18] *p*-chloro-1,1-diphenylethylene,[18] *p*-methoxy-1,1-diphenylethylene,[18] 1,1-diphenylpropene,[19] 1,1-diphenyl-2-fluoroethene.[20,21] Other olefins were obtained from commercial sources and purified by VPC to conform with published physical and spectral data. Methyl iodide was purified and distilled before use.[17] Hydrogen fluoride of Fluka Purum quality was used. Xenon difluoride was prepared by the photosynthetic method[22] and its purity was better than 99.5%.

Addition and Isolation Procedures. Xenon difluoride (10 mmol) was dissolved in methyl iodide (10 ml) at room temperature and anhydrous hydrogen fluoride (1 mmol) was introduced to the reaction mixture. After 20 min, to the resulting brown-colored solution of methyliodine(III) difluoride 7 mmol of olefins **1a–h** was added and left to stand at room temperature for 1 h (2 h for **1e** and **1h**). Afterwards, methylene chloride (60 ml) was added, and the solution was washed with aqueous sodium bisulfite (50 ml, 10%), aqueous sodium hydrogen carbonate (50 ml, 10%), and water (50 ml, twice) and dried over anhydrous sodium sulfate. A catalytic amount of $N(n\text{-}C_4H_9)_3$ was added in order to prevent the decomposition of the product. Solvent was evaporated in vacuo at room temperature; the crude products (**2**) were separated by preparative TLC [SiO_2, activated 2 h at 120 °C, with a solution of cyclohexane (95%), methylene chloride (4%), $N(n\text{-}C_4H_9)_3$ (1%)]. The NMR data are given in Table I.

1-Fluoro-2-iodo-1,1-diphenylethane (2a): yellow oil (71.5%); mass spectra calcd for $C_{14}H_{12}FI$, *m/e* 325.9990; found, *m/e* 325.9983; *m/e* (rel intensity) 326 (M^+, 9), 306 (9), 199 (100), 185 (30), 142 (90), 77 (45).

1-Fluoro-2-iodo-1-phenyl-1-(4′-chlorophenyl)ethane (2b): yellow oil (59%); mass spectra calcd for $C_{14}H_{11}ClFI$, *m/e* 359.9599; found, 359.9587; *m/e* (rel intensity) 360 (M^+, 3), 340 (20), 242 (7), 235 (33), 233 (100), 142 (70), 77 (55).

1-Fluoro-2-iodo-1,1-diphenylpropane (2d): oily product (40%, reaction time 30 min); mass spectra calcd for $C_{15}H_{14}FI$, *m/e* 340.0146; found, *m/e* 340.0140; *m/e* (rel intensity) 340 (M^+, 4), 320 (10), 213 (100), 185 (25), 165 (40), 77 (45).

1,2-Difluoro-2-iodo-1,1-diphenylethane (2e): yellow oil (55%, reaction time 2 h); mass spectra calcd for $C_{14}H_{11}F_2I$, *m/e* 343.9896; found, 343.9896; *m/e* (rel intensity) 344 (M^+, 3), 217 (50), 185 (67), 142 (100).

1-Fluoro-2-iodo-1-phenylethane (2f): liquid product (70%); mass spectra calcd for C_8H_8FI, *m/e* 249.9677; found, *m/e* 249.9679; *m/e* (rel intensity) 250 (M^+, 11), 123 (100), 109 (40), 104 (34), 103 (50.4), 77 (30).

1-Iodo-2-fluoro-2-phenylpropane (2g): liquid product (60%); mass spectra calcd for $C_9H_{10}FI$, *m/e* 263.9833; found, *m/e* 263.9833; *m/e* (rel intensity) 264 (M^+, 7), 142 (16), 137 (100), 127 (20), 123 (65), 122 (16), 117 (67), 103 (29).

1-Fluoro-2-iodo-1-phenyl-2-bromethane (2h): liquid product (65%, reaction time 3 h); mass spectra calcd for C_8H_7BrFI, *m/e* 327.8783; found, *m/e* 327.8782; *m/e* (rel intensity) 330 (M + 2, 6), 328 (M^+, 6), 203 (72), 201 (72), 122 (100), 121 (15), 109 (68), 103 (21), 51 (34).

Reaction with *p*-Methoxy-1,1-diphenylethylene (1c). Under similar conditions we obtained 1,1-difluoro-1-phenyl-2-(4′-methoxyphenyl)ethane, which was separated by preparative TLC, and a yellow, oily product was isolated (63%): NMR δ_F −105.5 ppm (triplet), δ_H 3.3 ppm (triplet), δ_{OCH_3} 3.7 ppm (singlet), δ_{Ph} 7.2 ppm (multiplet), J_{FH} = 16.5 Hz; mass spectrum calcd for $C_{15}H_{14}F_2O$, *m/e* 248.1008; found, 248.1008; *m/e* (rel intensity) 248 (100), 209 (46), 197 (40), 165 (46), 139 (40), 127 (46), 121 (60), 77 (40).

Reaction with 1,1-Diphenylpropene-1 (1d). Under the conditions mentioned above, with the reaction time reduced to 30 min and workup procedure (separation by preparative TLC), gave 40% of oily product (**2d**) and 40% of unreacted olefin. In a 3-h experiment, the rearranged 1,1-difluoro-1,2-diphenylpropane resulted in 53% yield, its structure being determined by comparison with the product which resulted from the reaction of 1,1-diphenylpropene-1 with 3-chloroaryliodine(III) difluoride: NMR δ_F −109.8, −112.0 ppm (ABX), δ_H 3.7 ppm (m), δ_{CH_3} 1.5 ppm (d), δ_{Ph} 7.5 ppm (m), J_{FF} = 285, J_{FH} = 16.5, $J_{H\text{-}CH_3}$ = 7.5 Hz; mass spectrum calcd for $C_{15}H_{12}F_2$, *m/e* 232.1063; found, *m/e* 232.1055; *m/e* (rel intensity) 232 (M^+, 100), 179 (40), 165 (30), 127 (35), 115 (80), 91 (30).

Thermal Behavior of 1,1-Diphenyl-1-fluoro-2-iodoethane. 2a (0.32 g, 1 mmol) was heated for 10 h at 80 °C in the presence of a catalytic amount of hydrogen fluoride. To the resulting brown-colored product, methylene chloride (20 ml) was added, and the solution was washed with a saturated solution of sodium bisulfite (10 ml), a solution of sodium hydrogen carbonate (10 ml), and water (10 ml) and dried over anhydrous sodium sulfate. The products were separated by preparative TLC (SiO_2) and two products were isolated: 55 mg (17%) of yellow crystals, mp 200–202 °C, the product being identified by comparison with the independently prepared 1,1,4,4-tetraphenylbutadiene-1,3,[15] mp 202 °C; and 154 mg (55%) of yellow crystals, mp 41–43 °C, identical with the independently synthesized 1,1-diphenyl-2-iodoethylene (4).[15]

Elimination of Hydrogen Fluoride from 2a under Basic Conditions. 1-Fluoro-2-iodo-1,1-diphenylethane (0.32 g, 1 mmol) was dissolved in 4 ml of 0.3 M potassium *tert*-butoxide in *tert*-butyl alcohol. The reaction mixture was heated at 50 °C for 2 h, then cooled, 10 ml of water was added, and the mixture was extracted with 10 ml of methylene chloride. The methylene chloride solution was washed with water and dried with anhydrous sodium sulfate and the solvent was evaporated in vacuo. The product was purified by preparative TLC (SiO_2) and 171 mg (61%) of yellow crystals was isolated. The product was identical with 1,1-diphenyl-2-iodoethylene.

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Registry No.—**1a**, 530-48-3; **1b**, 18218-20-7; **1c**, 4333-75-9; **1d**, 778-66-5; **1e**, 390-75-0; **1f**, 100-42-5; **1g**, 98-83-9; **1h**, 103-64-0; **2a**, 58617-63-3; **2b**, 58617-64-4; **2d**, 58617-65-5; **2e**, 58617-66-6; **2f**, 17170-99-9; **2g**, 58617-67-7; **2h**, 58617-68-8; **3c**, 58617-69-9; **3d**, 1493-60-3; **4**, 19997-66-1; **5**, 1450-63-1; methyliodine(III) difluoride, 50994-96-2.

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Nucleophilic Displacements on Halogen Atoms. 8.[1] Reactions of α-Halo Sulfones with Triarylphosphines, Alkyldiphenylphosphines, and Phosphites

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A series of α-halo sulfones, m-(CN)$C_6H_4CHXSO_2Ph$, **1a** (where X = Cl, Br, and I), was treated with a set of substituted triarylphosphines (**2**) in aqueous DMF to give the reduced sulfone m-(CN)$C_6H_4CH_2SO_2Ph$ (**5a**) and the triarylphosphine oxides. Variation of the rates of reaction of **1a** with **2** correlated with normal Hammett σ constants for the substituents in **2** to yield (Cl)$\rho = -1.84$; (Br)$\rho = -3.03$; (I)$\rho = -3.30$. A similar study for the reactions of **1a** (X = Br) with alkyldiphenylphosphines showed a good correlation between Taft σ^* constants and log k_2 to give a $\rho = -4.21$. However, the rates of reaction of **1a** (X = Br) with trialkyl phosphites showed no correlation with Taft σ^* constants, and the triaryl phosphites contrary to expectation reacted more readily than trialkyl phosphites. The reactions of **1a** (X = Br and I) with optically active phosphine **6** gave the phosphine oxide **7** with inversion of configuration. Triphenylarsine and triphenylstibine were shown to be poor nucleophiles in these dehalogenation reactions.

Nucleophilic displacement reactions have occupied a central position in the studies of organic reaction mechanisms for over half a century.[2] Although the organic chemist has been concerned principally with nucleophilic substitutions at carbon atoms,[3] it is clear that many electrophilic sites such as oxygen,[4] nitrogen,[5] silicon,[6] sulfur,[7] phosphorus,[8] arsenic,[9] and many other inorganic elements[10] are open to nucleophilic attack if an appropriate leaving group is present. We have been examining nucleophilic displacement reactions on halogen atoms in α-halo sulfones with tertiary phosphines[11] and arenesulfinates as nucleophiles.[1]

The reactions of α-halobenzyl phenyl sulfones (**1**) with triphenylphosphine (TPP) in 90% aqueous dimethylformamide (DMF) (eq 1) are characterized by the following: (1)

$$\underset{\mathbf{1}}{ArCHXSO_2Ph} + \underset{\mathbf{2}}{Ar_3'P} \longrightarrow \underset{\mathbf{3}}{[ArCHSO_2Ph]^-}\ \underset{\mathbf{4}}{Ar_3'\overset{+}{P}X} \xrightarrow[DMF]{H_2O} \underset{\mathbf{5}}{ArCH_2SO_2Ph} + Ar_3'PO + HX \quad (1)$$

reduced sulfones **5** are produced quantitatively with no side reactions observed; (2) kinetics are second order, first order each in sulfone **1** and TPP; (3) large positive ρ values (ca. +6 for **1**, X = Br and I) were found; (4) the intermediate ions **3** and **4** are formed slowly and irreversibly, and their hydrolysis by protic solvent is very rapid; (5) for **1** (X = Cl, Br, and I), $k_{Br} > k_I \gg k_{Cl}$.[11a] These results and others obtained in a study of steric effects in the reactions of **1** with ortho-substituted triarylphosphines[11b] led us to maintain that a high degree of carbon–halogen bond breakage had occurred in the transition state. These results have encouraged us to examine more carefully the role of the phosphine nucleophile in these reactions. In particular, we now report the results of a study in which the variation in the phosphorus nucleophiles, tertiary phosphines and phosphites, has yielded detailed information on the mechanism of reaction 1 from the standpoint of the nucleophile.

Results and Discussion

A series of meta- and para-substituted triarylphosphines were prepared and allowed to react with the α-halo-m-cyanobenzyl phenyl sulfones [**1a**, Ar = m-(CN)C_6H_4] in 90% aqueous DMF (eq 2). The reactions were monitored by conductance readings (see Experimental Section) as a function of the formation of hydrohalic acid from the neutral starting materials. The rate data are reported in Tables I–IV. The data in Table IV can be compared with similar activation parameter data gathered from other SN2 reactions (Table V).

$$\underset{\mathbf{1a}\ (X = Cl, Br, I)}{m\text{-}(CN)C_6H_4CHXSO_2Ph} + \underset{\mathbf{2}}{Ar_3'P} \xrightarrow[DMF]{H_2O} \underset{\mathbf{5a}}{m\text{-}(CN)C_6H_4CH_2SO_2Ph} + Ar_3'PO + HX \quad (2)$$

Tertiary phosphines have been shown to be effective nonbasic nucleophiles of wide utility.[12] They are classed as soft nucleophiles[12,13] and owe their high nucleophilicity in large part to their polarizability. The collection of data in Table V is an attempt, albeit of limited success, to correlate the various enthalpies and entropies of activation associated with the nucleophilicity of TPP with the nature of the electrophilic centers. This problem is complicated by (1) inherent difficulties in interpreting relatively small differences in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values,[14] (2) relatively large errors in $\Delta S^{\ddagger}$ values,[15] and (3) use of different solvents for the reactions reported in Table V. In general, $\Delta S^{\ddagger}$ appears to be more negative for