

complex  $\text{Fe}(\eta^4\text{-C}_4\text{H}_6)(\text{CO})_3^{6b}$  which we found to be oxidized irreversibly at much more positive potential ( $E_{p,a} = +2.0$  V, Pt electrode,  $\text{CH}_3\text{CN}$ ). Controlled-potential macroscale electrolyses of **2**, in  $\text{CH}_3\text{CN}$ , have been carried out at 0 V (first step) and at +0.9 V (second step).<sup>25</sup> They showed that the first step is a 1-Faraday oxidation while the second step is a 4-Faraday oxidation. This is consistent with a decomposition of complex **2** at such a potential. These electrochemical studies confirmed that the green product arising from the oxidation of complex **2**, **3**, or **5** corresponds to a reversible one-electron process and can be formulated as the 17-electron paramagnetic stable salt of **2**<sup>+</sup>, **3**<sup>+</sup>, or **5**<sup>+</sup>.<sup>26</sup>

The ready access to complexes of type **2**, **3** or **5**, **6** allows the synthesis of new electron-rich complexes which may act as reducing reagents. The reversibility of their first step, a one-electron oxidation process, introduces new candidates among the class of reversible systems.

**Supplementary Material Available:** Figure S1 of the cyclic voltammetry of  $\text{Fe}(\eta^4\text{-C}_4\text{H}_6)(\text{PMe}_2\text{Ph})_3$ , tables of atomic coordinates, temperature factors, and bond lengths and angles (33 pages). Ordering information is given on any current masthead page.

(25) For the controlled-potential macroscale electrolyses were used (i) 150 mL of a solution of 0.27 g of **2** in acetonitrile and (ii) a cell, of a 4-cm diameter, equipped with a vitreous carbon anode and described in: Jacob, G.; Moinet, C. *Bull. Soc. Chim. Fr.* **1983**, 1, 291.

(26) However, no ESR signal was detected at low temperature, but magnetic measurements were consistent with paramagnetic species.

### Surprising Stereochemical Control of Wittig Olefination Involving Reaction of Fluorine-Containing Phosphoranium Salt and Aldehydes<sup>1</sup>

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The mechanistic pathway of the Wittig reaction is presently under active investigation.<sup>2-8</sup> Numerous mechanistic interpretations have been posited to account for the *Z* stereoselectivity observed with reactive ylides and the *E* stereoselectivity observed with stabilized ylides by the steric and electronic nature of substituents at phosphorus as well as at the carbon  $\alpha$  to phosphorus.<sup>2-5</sup>

We report herein the preliminary results of the synthesis of terminal HF-olefins from aldehydes and the surprising stereo-

(1) Presented in part at the 6th Winter Fluorine Conference, Daytona Beach, FL, Abstract 35.

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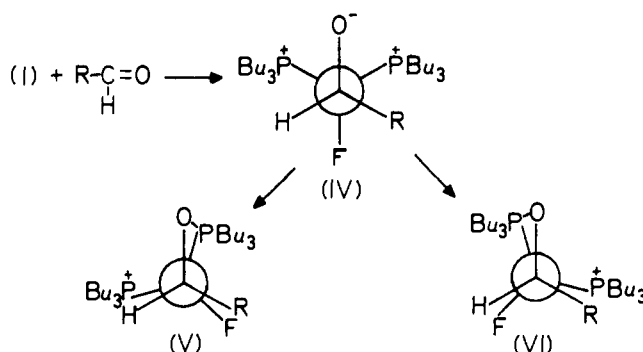
Table I.

$$\text{I} + \text{RCHO} \rightarrow [\text{Bu}_3\text{P}^+\text{CF}=\text{CHR}]\text{X}^- \xrightarrow{\text{NaOH(aq)}} \text{HCF}=\text{CHR} + \text{Bu}_3\text{PO}$$

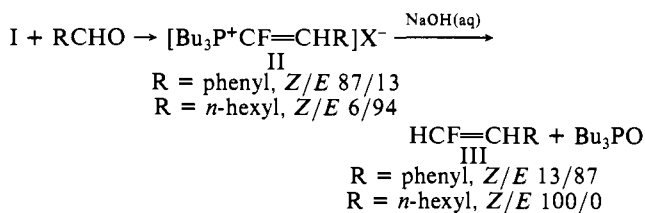
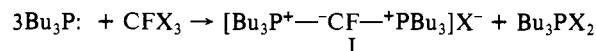
R	II <sup>a</sup>		III <sup>a</sup>	
	%	Z/E	%	Z/E
C <sub>6</sub> H <sub>5</sub>	(80)	56	87/13	(76) 61
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(83)		88/12	(74) 54
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	(96)		83/17	(78) 51
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	(94)		79/21	(81) 60
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	(75)		57/43	
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(85)		75/25	(73) 57
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(90)		100/0	50
<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	(92)		77/23	54
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	(89)		93/7	(64)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	(84)		3/97	(71) 51
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub>	(82)		6/94	(73) 57
C <sub>6</sub> H <sub>11</sub>	(85)		0/100	(77) 50

<sup>a</sup> Parentheses indicate <sup>19</sup>F NMR yield vs. benzotrifluoride. Z/E ratios were calculated by <sup>19</sup>F NMR.

Scheme I



chemical control exhibited by the fluorinated phosphoranium salt I,<sup>9</sup> a stabilized ylide. Wittig reaction of a variety of aldehydes



with the stabilized ylide I afforded the corresponding *Z* and *E* isomers<sup>10</sup> of the (1-fluoroalkenyl)-tri-*n*-butylphosphonium salt II. Subsequent cleavage of the P-C bond in II by alkaline hydrolysis led to the formation of the 1-fluoroalkene III stereospecifically with retention of configuration.<sup>9,11</sup> Since the vinylphosphonium salts II were produced in situ, the overall result is a one-pot conversion of aldehydes into vinyl fluorides. The results of these reactions are summarized in Table I.

The *E* stereoselectivity observed in the reaction of I with aliphatic aldehydes can be explained by current mechanistic proposals.<sup>2-5</sup> On the other hand, the *Z* stereoselectivity observed with aromatic aldehydes cannot be explained by such proposals. The aromatic moiety of the aldehydes appears to overcome the steric and electronic effects of the substituents, leading to the formation

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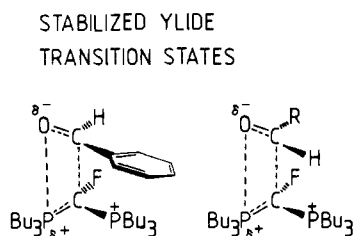
(10) The stereochemistry was assigned based on H,F coupling constants (trans *J*(F,H) = 43-54 Hz, cis *J*(F,H) = 22-30 Hz). (a) Burton, D. J.; Greenlimb, P. E. *J. Fluorine Chem.* **1973-1974**, 3, 447. (b) Burton, D. J.; Greenlimb, P. E. *J. Org. Chem.* **1975**, 40, 2796.

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of the sterically crowded *Z* isomer. To account for this dramatic shift in stereochemistry, we propose an intramolecular, through-space, charge-transfer complex<sup>12</sup> involving one of the tri-*n*-butylphosphonium groups in I and the  $\pi$ -electrons of the aromatic ring of the aldehyde.

If one envisions the classical Wittig mechanistic sequence<sup>4a</sup> (Scheme I) of the formation of betaine IV followed by cyclization to oxaphosphetane, then it can be seen that there is a choice as to which of the two diastereotopic phosphonium centers will be included in the ring. A concern in the classical Wittig reaction mechanism is the distribution of diastereomeric betaines. In this study diastereomeric betaines are not possible. Yet, on the basis of current mechanistic proposals, formation of the transoxaphosphetane V minimizes steric interaction between the R group of the aldehyde and the second phosphonium center of the ylide, thus resulting in the predominant formation of the *E* olefin. This line of reasoning is consistent with the *E* stereochemistry observed when aliphatic and alicyclic aldehydes react with I. However, aromatic aldehydes exhibit *Z* selectivity. Therefore, the more sterically hindered cis oxaphosphetane VI must predominate. The proposed through-space, charge-transfer complex between the aromatic ring and the positively charged phosphonium center accounts for this dramatic shift in stereochemistry. Therefore, *Z* stereoselectivity results when rotation of the betaine simultaneously allows for (a) the proposed through-space, charge-transfer complex and (b) the participation of the other phosphonium center in ring closure to oxaphosphetane.

The coplanar cycloaddition mechanism proposed by Giese and co-workers<sup>3</sup> for stabilized ylides can be similarly modified to account for the observed variations in stereochemistry. Accordingly, the effects of (a) steric crowding at phosphorus and (b) increased nucleophilicity of the ylide due to alkyl substituents result in formation of the carbon-carbon bond in advance of the phosphorus-oxygen bond; thus, steric interactions between substituents on the ylide carbon and carbonyl carbon favor the trans oxaphosphetane. This mechanistic interpretation predicts the



formation of the observed *E* isomer when utilizing aliphatic and alicyclic aldehydes. Invoking the proposed through-space, charge-transfer complex, the aromatic ring of the aldehyde interacts with one of the phosphonium centers as the ylide and carbonyl approach each other in a coplanar manner. Therefore, as the carbon-carbon bond forms, the aromatic ring and a phosphonium center are cis.

The proposed through-space, charge-transfer complex appears to be sensitive only to electron-withdrawing substituents on the aromatic ring. This causes the proposed interaction to weaken, allowing for the formation of significantly more of the *E* isomer; thus the steric and electronic nature of the ylide become dominant. Substituents in the ortho position on the ring enhance the *Z* selectivity. This *Z* selectivity appears to be unique, and we have no explanation for it at this time.

Operational details of the experimental procedure are outlined below for the preparation of 1-fluoro-2-phenylethene.

A 250-mL three-necked flask, equipped with magnetic stir bar, rubber septum, and nitrogen tee, was charged with 0.090 mol (18.2 g, 22.4 mL) of tri-*n*-butylphosphine and 30 mL of methylene chloride. The solution was cooled in an ice bath, and 0.030 mol (4.1 g, 2.8 mL) of trichlorofluoromethane was added in one portion via syringe. The resultant mixture was stirred at 0 °C for 1 h

and then at room temperature for 3 h.<sup>9</sup> To this phosphonium salt solution was added 0.024 mol (2.5 g, 2.4 mL) of freshly distilled benzaldehyde via syringe in one portion. The reaction was stirred for 8 h at room temperature. Further stirring did not effect the *Z/E* ratio or yield of II as calculated by <sup>19</sup>F NMR spectroscopy relative to the internal standard benzotrifluoride. The ambient temperature hydrolysis of II was accomplished by the slow addition of 36 mL of 10% NaOH to the reaction mixture followed by stirring at room temperature for 18 h. (<sup>19</sup>F NMR analysis of the reaction mixture revealed a *Z/E* ratio of 13/87, which is consistent with that of the isolated product.) The resultant organic layer was acidified and then steam distilled. The distillate was extracted with methylene chloride (2 × 25 mL), followed by washing with 40% sodium bisulfite (2 × 25 mL) and water (2 × 25 mL), and the organic portion dried with anhydrous magnesium sulfate. After solvent removal by distillation, the resulting oil was distilled, yielding 1.8 g (61% yield based on aldehyde, *Z/E* = 13/87) of 1-fluoro-2-phenylethene; bp<sup>13</sup> 71–74 °C (65 mmHg).

**Acknowledgment.** We thank the National Science Foundation and the Air Force Office of Scientific Research for financial support of this work.

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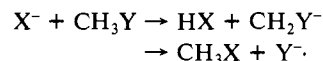
### Nucleophilic Displacement vs. Proton Transfer: The System OH<sup>-</sup>·(H<sub>2</sub>O)<sub>0,1,2</sub> + CH<sub>3</sub>Cl in the Relative Energy Range 0.03–5 eV

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When a Lewis base X<sup>-</sup> reacts with a methyl halide CH<sub>3</sub>Y, it may act as a Brønsted base or as a nucleophile



At thermal energies this competition is dominated by proton transfer when proton transfer is exothermic—and by nucleophilic displacement only when proton transfer is endothermic.<sup>3</sup> Here we show how proton transfer can still dominate when it is endothermic *provided there is sufficient energy available to drive it*, and we show further how this effect is suppressed by hydrating the base with one or two water molecules.

We have studied the system OH<sup>-</sup>·(H<sub>2</sub>O)<sub>0,1,2</sub> + CH<sub>3</sub>Cl in the relative energy range 0.2–5 eV, using the AFGL tandem mass spectrometer and techniques previously described.<sup>4,5</sup> For OH<sup>-</sup> + CH<sub>3</sub>Cl nucleophilic displacement alone is exothermic, and it alone is observed at 300 K.<sup>5–7</sup> However, with increasing trans-

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