imized when adjacent π-type lone pairs are orthogonal (A) rather than parallel (B) and/or that stability is maximized when the π lone pair at neutral sulfur can donate electrons to the σ^* orbital of the adjacent Me–S$^+$ bond, as in A (or **1a**).[10]

Evidence of n–σ^* donation is also seen in the ^{1}H NMR spectra of **1–4** (Table I); the axial C3 proton is almost as deshielded as the axial C6 proton, consistent with extensive charge delocalization, —CHŜS$^+$CH— ↔ —CHS$^+$=SCH—.

Unlike 1,2-dithianes, methylation of 1,2-dithiolanes **15–18** was nonselective. Methyl lipoate **18** gave the four possible regio- and stereoisomers **8a,b** and **9a,b** in the ratio 26:11:33:30. A remarkable dynamic NMR effect was observed whereby ^{1}H and ^{13}C resonances for pairs of diastereomers **6a,b**, **7a,b**, **8a,b**, and **9a,b** became indistinguishable on addition of traces of sulfide (e.g., Me$_2$S). The ^{1}H spectrum of the chiral ion **5** (six nonequivalent ring protons) collapsed to one with planar symmetry (three pairs of nonequivalent ring protons) on adding Me$_2$S, indicating rapid interconversion of enantiomers. No net change occurred as the salts could be recovered unchanged. We attribute these results to a rapid and *reversible* ring opening by the sulfide nucleophile whereby chirality at pyramidal sulfur is destroyed.[11] Reclosure to either of two configurations results in the interconversion of enantiomers for **5** and diastereomers for **6–9** (eq 2).

$$n = 1, 2 \qquad\qquad\qquad \mathbf{19} \qquad\qquad\qquad (2)$$
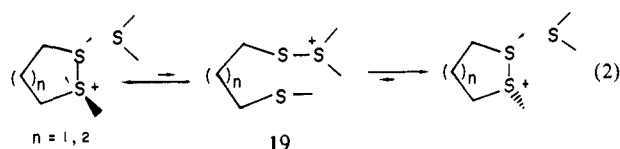
The ^{1}H spectrum of the chiral dithianium ion **1a** also collapsed to that of a symmetrical ring on addition of Me$_2$S—consistent with rapid equilibration of enantiomers through an achiral acyclic intermediate (**19**). Reclosure to an equatorial MeS$^+$ orientation does *not* occur. Similar sulfide-induced ring opening may be expected of ions **2–4** but there was no change in the ^{1}H or ^{13}C spectra on addition of Me$_2$S, and no interconversion of diastereomers of **2–4** could be detected. We regard this as evidence that reclosure of **19** to a configuration in which MeS$^+$ is equatorial is energetically disfavored over reclosure to the axial form.

In comparison, 1,2-dithiolanium diastereomers are comparable in energy, which suggests that the five-membered ring is torsionally flexible and can adopt twist conformations that avoid destabilizing interactions[12] while retaining the stereoelectronic advantage of a pseudoaxial MeS$^+$. Most importantly, ring-opening equilibria (eq 2) strongly favor ring closure, which means that ring strain is *not* the source of reactivity in 1,2-dithiolanium ions, as has been suggested for 1,2-dithiolanes.[13] Rather, reactivity is best attributed to the rapid cleavage of S–S$^+$ bonds by nucleophiles. The ready polymerization of 1,2-dithiolanes[14] can likewise be attributed to initial thiolanium ion formation followed by monomer-induced ring cleavage. The process can be reversed, as we have shown by the successful preparation of **5** (eq 1) by methylation of 1,2-dithiolane polymer.

(9) For examples of the use of Fourier series for the analysis of conformational behavior, see: (a) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. (b) Defrees, D. J.; Hehre, W. J.; Sunko, D. E. *Ibid.* **1979**, *101*, 2323.

(10) n–σ^* donation in B (or **1b**) is not a factor since it could occur only from a less accessible σ-type lone pair at neutral sulfur. See also: Andretti, G. D.; Bernadi, F.; Bottoni, A.; Fava, A. *J. Am. Chem. Soc.* **1982**, *104*, 2176.

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Electron-Rich, Hydrocarbon–Metal Complexes: Synthesis and Reversible One-Electron Oxidation. X-ray Structure of a 17-Electron Iron Cation

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Electron-rich metal complexes containing hydrocarbon fragments have recently attracted interest, because they offer evidence for new organometallic processes such as C–H–M intramolecular interaction,[2] C–H activation,[3] or radical-promoted reactions.[4] Among unstable conjugated hydrocarbon fragments, the trapping by an electron-rich metal center of the formally cross-conjugated trimethylenemethane (TMM) dianion[5] is of special interest. Although electron-poor metal–TMM complexes have been characterized,[6] electron-rich metal–TMM complexes have never been isolated even though they have been found to be key intermediates as sources of the trimethylenemethane group in carbon–carbon bond formation reactions.[7] We now wish to describe a simple route to electron-rich metal–TMM complexes, starting directly from FeCl$_2$, and to show their facile oxidation by a reversible one-electron process to produce 17-electron species; the X-ray structure of one of these, the paramagnetic piano-stool complex Fe(η^4-C$_4$H$_6$)(PMe$_3$)$_3$$^+$(CF$_3SO_3$)$^-$, is reported.

To a THF solution containing 1 equiv of FeCl$_2$(PMe$_2$Ph)$_2$[8] and of PMe$_2$Ph were added successively, under inert atmosphere, an excess of magnesium and of CH$_2$=C(CH$_2$Cl)CH$_2$Cl (**1**) to give an orange complex **2**, isolated to a 40% yield[9] (Scheme I). A similar reaction using FeCl$_2$(PMe$_3$)$_2$[8] and 1 equiv of PMe$_3$ in THF yielded an orange oil **3** in 47% yield.[10] By direct addition of the

(1) (a) Laboratoire de Chimie de coordination Organique (UA-CNRS 415). (b) Laboratoire d'Electrochimie (UA-CNRS 439). (c) Laboratoire de Physique Cristalline (UA-CNRS 804).

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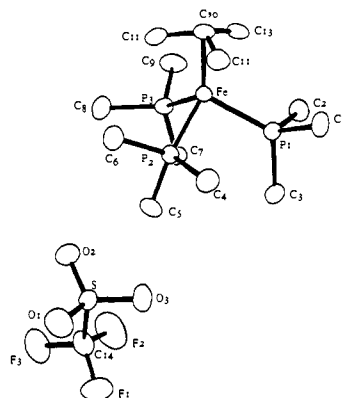
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(8) The mixture FeCl$_2$L$_2$/L (L = PMe$_2$Ph, PMe$_3$) is obtained by simple addition of 3 equiv of L to FeCl$_2$ in THF. follwed by a 1-h reflux. Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272.
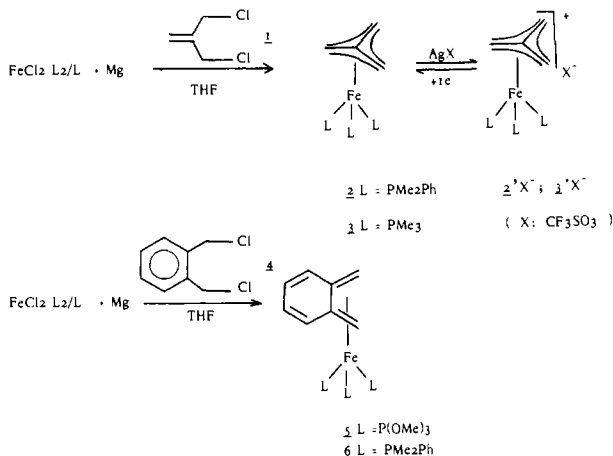
(9) Complex 2. Anal. Calcd for C$_{28}$H$_{39}$P$_3$Fe: C, 64.12; H, 7.44; P, 17.74; Fe, 10.68. Found: C, 63.73; H, 7.44; P, 17.42; Fe, 11.27. Mass spectrum, *m/e* 524.162 (calcd for (M)$^+$ 524.161), 386 [(M – PMe$_2$Ph)$^+$], 248 [M – 2PMe$_2$Ph)$^+$], 332 [(M – C$_4$H$_6$)$^+$].

(10) Complex 3. Anal. Calcd for C$_{13}$H$_{33}$P$_3$Fe: C, 46.15; H, 9.76. Found: C, 46.87; H, 9.74. Mass spectrum, *m/e* 338.113 (calcd for M$^+$ (C$_{13}$H$_{33}$P$_3$Fe) 338.114), 262 [(M – PMe$_3$)$^+$], 208 [(M – PMe$_3$ – C$_4$H$_6$)$^+$], 186 [(M – 2PMe$_3$)$^+$], 132 [(M – 2PMe$_3$ – C$_4$H6)$^+$].

Figure 1. ORTEP drawing of $Fe(\eta^4\text{-}C_4H_6)(PMe_3)_3{}^+(CF_3SO_3)^-$; hydrogens are omitted.

Scheme I

corresponding Grignard of **1** to a THF solution of $FeCl_2$-$(PR_3)_2/PR_3$, complexes **2** and **3** were obtained in very low yield. For both complexes **2** and **3**, NMR spectra[11] showed equivalent (C_4H_6) ^{1}H nuclei as well as ^{31}P nuclei.

A similar approach was used for the fixation of the o-xylylene ligand to the electron-rich $Fe(PR_3)_3$ moiety. Typically, to a THF solution of $FeCl_2[P(OMe)_3]_3$[12] were added successively an excess of magnesium and of o-(chloromethyl)benzyl chloride **4**. Yellow crystals of **5** (45% yield) were obtained.[13]   From $FeCl_2$-$(PMe_2Ph)_2/PMe_2Ph$ in THF the same reaction led to the yellow complex **6** (33% yield)[14] (Scheme I). The ^{31}P NMR of complexes **5** and **6** showed two types of ^{31}P nuclei in the ratio 1:2,[15] and their ^{1}H NMR spectra were consistent with an η^2,η^2-o-xylylene ligand coordinated to iron(0).[16]

Complexes **2** and **3** in THF or CH_3CN solution were air sensitive and their color turned slowly (**2**) or immediately (**3**) from yellow to deep green upon exposure to air. In acetonitrile, both complexes **2** and **3** reacted readily with Ag^+, Cu^+, or ferricinium salts to give a stable green solution; however, both were decomposed by addition of iodine. Both complexes **2** and **3**, in acetonitrile, were oxidized with 1 equiv of $Ag(CF_3SO_3)$ to afford a green product which was precipitated by addition of ether.

After purification by silica gel column chromatography, the green solution obtained from **3** and $Ag(CF_3SO_3)$ afforded crystals, in CH_2Cl_2-ether, suitable for X-ray analysis at 128 K.[17]   The molecular structure, as shown by the ORTEP view in Figure 1 corresponds to the 17-electron complex $3^+(CF_3SO_3)^-$. It shows a staggered conformation having a C_{3v} symmetry cation and an umbrella-shaped η^4-C_4H_6 ligand where the central C(10) atom is away from the iron atom with regard to the C(11), C(12), C(13) plane. The hydrogens of the four ligands are displayed approximately on a sphere around the iron atom and may contribute to the stability of the 17-electron cation 3^+.[18,19]

The green oxidation complexes of **2** and **3** reacted slowly with $NaCH(CO_2Et)_2$ in THF and immediately with a suspension of $NaBH_4$ in THF to give back the starting yellow complexes **2** and **3**. These reactions are consistent with an electron transfer from $(CH(CO_2Et)_2^-$ or H^- to the oxidized species.

These oxidation and reduction processes of complexes **2** and **3** have been investigated by an electrochemical study. Cyclic voltammetry of **2** in acetone, using a platinum electrode, showed a two-step oxidation:[20] the first step is a *reversible* oxidation ($E_{1/2}$ = -0.29 V);[21] the second step is an *irreversible* process ($E_{p,a}$ = +0.76 V).[22]   Complex **3** behaved similarly as **2** in cyclic voltammetry but was more readily oxidized ($E_{1/2}$ = -0.43 V). Also the green form resulting from the first oxidation step is much more stable for **3** than the corresponding **2** species.[23] Complex **5** also gave a reversible oxidation process but at a less negative potential ($E_{1/2}$ = -0.05 V)[24] than either **2** or **3**. The higher stability of 3^+X^- may be due to both the high donating capability of the PMe_3 groups and the bulkiness of the ligands around the iron atom. This electrochemical study showed the striking effect of the phosphorus groups in complexes **2**, **3**, and **5** as compared to the carbonyl

(11) ^{1}H NMR (80 MHz, 305 K, C_6D_6) δ, **2**, [1.40 (d, PMe_2Ph, $^2J_{PH}$ = 5 Hz), 0.75 (d, CH_2C, J_{PH} = 10.5 Hz), **3**, [1.11 (d, PMe_3, $^2J_{PH}$ = 6.1 Hz), 0.80 (d, CH_2C, J_{PH} = 11 Hz); ^{31}P NMR (32.38 MHz, 309 K, C_6D_6) δ, **2**, 34.71 (s), **3**, 26.84 (s).

(12) Muetterties, E. L.; Harris, T. V.; Rathke, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

(13) **5**. Anal. Calcd for $C_{17}H_{35}O_9FeP_3$: C, 38.34; H, 6.57; P, 17.47; Fe, 10.52. Found: C, 38.36; H, 6.49; P, 17.98; Fe, 11.92. Mass spectrum, m/e 532.085 (calcd for (M)$^+$ 532.084), 501 [(M – OMe)$^+$], 408 [(M – P-(OMe)$_3$)$^+$], 428 [(M – C_8H_8)$^+$].

(14) **6**, yellow oil; decomposes in the mass spectrometer; unstable for powder analysis.

(15) 1H NMR (80 MHz, 309 K, C_6D_6) δ, **6**, 7.23 (s), 7.06 (m) (C_6H_5), 7.66–7.40 (m), 6.71 (m)(C_6H_4), 1.72 (d, 1 PMe_2Ph, J_{PH} = 6.2 Hz), 1.14 (d, 2 PMe_2Ph, $(J_{PH} + J_{P'H})$ = 12.8 Hz), 1.42 (m, H_{syn}), -1.35 (br d, H_{anti}, $^3J_{PH}$ = 12 Hz). ^{31}P NMR (32.38 MHz, 309 K, C_6D_6) δ, **5**, 192.0 and 176.2 (br s in the ratio 1:2), **6**, 42.4, 26.2 (sh s in the ratio 1:2). The ^{31}P NMR spectra are consistent with[2c] (i) a mirror plane bisecting the CH_2-C_6H_4-CH_2 ligand and containing Fe and one phosphorus atoms and (ii) a J_{PP} = 0.

(16) Analogous complexes with an η^2,η^2-o-xylylene (C_8H_8) ligand have been reported (a) $(C_8H_8)Fe(CO)_3$: Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053. Johnson, B. F. G.; Lewis, J.; Thompson, D. J. *Tetrahedron Lett.* **1974**, 3789 (b) $C_8H_8Co(C_5H_5)$: Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 6992. (c) $(C_8H_8)Ru(PR_3)_3$.[2c]

(17) Crystals slowly decomposed at room temperature and data were collected at 128 K with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.71069 Å, ± = 1.001 nm⁻¹): monoclinic space group $P2_1/c$, a = 12.313(2) Å, b = 11.016(2) Å, c = 17.064 (3) Å, β = 103.1 (2)°, Z = 4, M_r = 487.3; 4323 reflections were collected of which 3177 have $I > 3 \sigma(I)$. The structure was solved by a comparison of Multan and Patterson and several Fourier differences. All the hydrogen atoms were found with one Fourier difference (between 0.67 and 0.43 e⁻ Å⁻³); the better refinement with a unit scheme gives R = 0.024.

(18) Main distances (Å): Fe-C(10), 1.930 (2); Fe-C(11), 2.134 (2); Fe-C(12), 2.118 (3); Fe-C(13), 2.115(3); C(10)-C(11), 1.418 (4); C(10)-C(12), 1.417 (4); C(10)-C(13), 1.425 (4); Fe-P(1), 2.268 (1); Fe-P(2), 2.266 (1); Fe-P(3), 2.280 (1). Main angles (deg): C(11)-C(10)-C(12), 115.1 (3); C(11)-C(10)-C(13), 115.2 (3); C(12)-C(10)-C(13), 114.9 (3); P(1)-Fe-P-(2), 96.90 (3); P(1)-Fe-P(3), 100.53 (3); P(2)-Fe-P(3), 97.91 (2).

(19) An X-ray structure of a related 18-electron iron complex $Fe(CO)_3$-$(\eta^4$-$C_4H_5Ph)$ has been reported. Churchill, M. R.; Gold, K. *J. Chem. Soc., Chem. Commun.* **1968**, 693.

(20) The cyclic voltammograms at a platinum (or vitrous carbon) electrode were recorded with a three electrode polarograph UAP 4-Tacussel. All the measurements were carried out at 25 °C under a nitrogen atmosphere with a solution of the complex (1.4–1.5. 10⁻³ M). All the potentials are referred to a saturated calomel electrode. $E_{p,a}$ and $E_{p,c}$ stand for anodic potential peak and cathodic potential peak, respectively.

(21) The first oxidation step of **2** was also found to be reversible in various conditions: (a) in DMF with a Pt electrode ($E_{p,a}$ = -0.29 V; $E_{p,c}$ = -0.38 V), (b) in CH_3CN with a Pt electrode ($E_{p,a}$ = -0.33 V; $E_{p,c}$ = -0.42 V), (c) in acetone with a vitrous carbon electrode ($E_{p,a}$ = -0.34 V; $E_{p,c}$ = -0.42 V).

(22) The second irreversible wave ($E_{p,a}$ = +0.76 V) occurred with a poisoning of the anode. This is attributed to PMe_2Ph freed by decomposition of the complex at this potential, for the same phenomenum was observed during oxidation of PMe_2Ph at the same potential. Decomposition of **2** by addition of I_2 corresponds to its oxidation at the second wave. (I_2 is reduced in acetonitrile, Pt electrode at $E_{p,c}$ = +0.57 V and $E_{p,c}$ = +0.4 V.)

(23) **3**, cyclic voltammetry, in acetone, Pt electrode: reversible first step ($E_{p,a}$ = -0.40 V; $E_{p,c}$ = -0.46 V), irreversible second step oxidation ($E_{p,a}$ = +0.63 V). The one-electron oxidized, green form of **3** decomposes only slowly at room temperature in the presence of water or oxygen.

(24) **5**, cyclic voltammetry in acetone, Pt electrode: first wave ($E_{p,a}$ = -0.02 V; $E_{p,c}$ = -0.11 V), second wave ($E_{p,a}$ = +0.65 V).

complex $Fe(\eta^4\text{-}C_4H_6)(CO)_3$[6b] which we found to be oxidized *irreversibly* at much more positive potential ($E_{p,a}$ = +2.0 V, Pt electrode, CH_3CN). Controlled-potential macroscale electrolyses of **2**, in CH_3CN, have been carried out at 0 V (first step) and at +0.9 V (second step).[25] 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^+, 3^+, or 5^+.[26]

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 $Fe(\eta^4\text{-}C_4H_6)(PMe_2Ph)_3$, 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 vitrous 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[1]

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The mechanistic pathway of the Wittig reaction is presently under active investigation.[2-8] 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 α to phosphorus.[2-5]

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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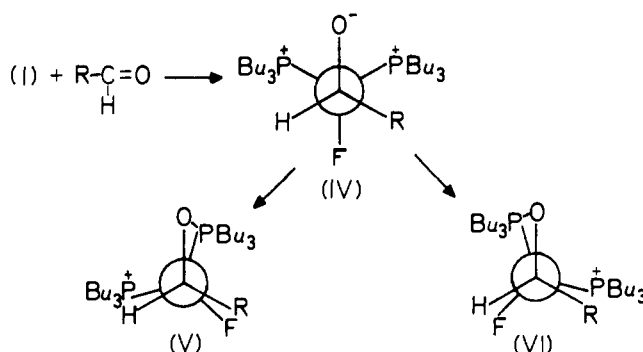
Table I.

$$I + RCHO \rightarrow [Bu_3P^+CF{=}CHR]X^- \xrightarrow{NaOH(aq)}$$
$$II$$

$$HCF{=}CHR + Bu_3PO$$
$$III$$

R	II[a]		III[a]	
	%	Z/E	%	Z/E
C_6H_5	(80) 56	87/13	(76) 61	13/87
$p\text{-}CH_3C_6H_4$	(83)	88/12	(74) 54	12/88
$p\text{-}CH_3OC_6H_4$	(96)	83/17	(78) 51	17/83
$p\text{-}ClC_6H_4$	(94)	79/21	(81) 60	25/75
$p\text{-}NO_2C_6H_4$	(75)	57/43		
$m\text{-}CF_3C_6H_4$	(85)	75/25	(73) 57	25/75
$o\text{-}CH_3C_6H_4$	(90)	100/0	50	0/100
$o\text{-}CH_3OC_6H_4$	(92)	77/23	54	20/80
$o\text{-}ClC_6H_4$	(89)	93/7	(64)	5/95
$CH_3(CH_2)_5$	(84)	3/97	(71) 51	100/0
$CH_3(CH_2)_6$	(82)	6/94	(73) 57	100/0
C_6H_{11}	(85)	0/100	(77) 50	100/0

[a] Parentheses indicate ^{19}F NMR yield vs. benzotrifluoride. Z/E ratios were calculated by ^{19}F NMR.

Scheme I

chemical control exhibited by the fluorinated phosphoranium salt I,[9] a stabilized ylide. Wittig reaction of a variety of aldehydes

$$3Bu_3P: + CFX_3 \rightarrow [Bu_3P^+{-}^-CF{-}^+PBu_3]X^- + Bu_3PX_2$$
$$I$$

$$I + RCHO \rightarrow [Bu_3P^+CF{=}CHR]X^- \xrightarrow{NaOH(aq)}$$
$$II$$
$$R = phenyl, Z/E\ 87/13$$
$$R = n\text{-hexyl}, Z/E\ 6/94$$

$$HCF{=}CHR + Bu_3PO$$
$$III$$
$$R = phenyl, Z/E\ 13/87$$
$$R = n\text{-hexyl}, Z/E\ 100/0$$
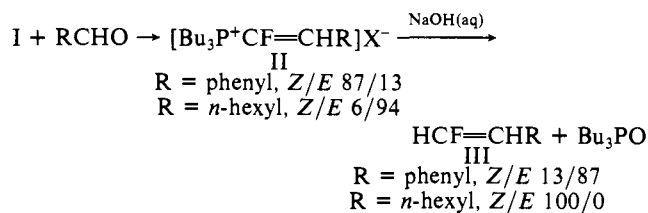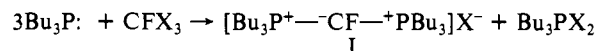
with the stabilized ylide I afforded the corresponding *Z* and *E* isomers[10] of the (1-fluoroalkenyl)-tri-*n*-butylphosphonium salt II. Subsequent cleavage of the P–C bond in II by alkaline hydrolysis led to the formation of the 1-fluoroalkene III stereospecifically with retention of configuration.[9,11] 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.[2-5] 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

(9) Burton, D. J.; Cox, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 650.

(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.

(11) Burton, D. J.; Shin-ya, S.; Howells, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 3689.