visual pigment would have a broad ($W_{1/2}$ ca. 4000 $cm^{-1}$) blue-shifted absorption band. Attempts to form cyanine analogues of bovine rhodopsin are currently underway.

**Acknowledgment.** We are grateful to Hillary Rodman for her assistance in carrying out the calculations and to Dr. Valeria Balogh-Nair for discussions. This work has been supported by NSF Grants PCM82-07145 and GM-30519 (to B.H.) and NSF Grant CHE-8110505 (to K.N.).

**Registry No.** Retinal, 116-31-4.

## Wittig Olefination via Reaction of Fluorine-Containing Phosphoranium Salts and *F*-Acyl Fluorides. A New Approach to Fluoroolefin Synthesis[1]

Donald J. Burton* and Daryl G. Cox

*Department of Chemistry, University of Iowa*
*Iowa City, Iowa 52242*

*Received September 29, 1982*

The normal course of reaction between phosphonium ylides and acyl halides is acylation of the ylide. If the new acylated salt contains a hydrogen on the carbon atom $\alpha$ to the phosphonium salt center, further acid–base reaction (transylidation) occurs to afford a new ylide:

$$\underset{\text{I}}{R_3P^+-{}^-CHR^1} + R^2C(O)Cl \rightarrow [R_3P^+-CHR^1C(O)R^2]Cl^- \xrightarrow{\text{I}} [R_3P^+-{}^-CR^1C(O)R^2]$$

We report the first preparation of a fluorine-containing phosphoranium salt[2] via reaction of fluorotrihalomethanes and tertiary phosphines:[3]

$$\underset{\text{II}}{3\ R_3P:} + \underset{\text{III}}{CFX_3} \rightarrow \underset{\text{IV, 90–95\%}}{[R_3P^+-{}^-CF-{}^+PR_3]X^-} + R_3PX_2$$

R = Bu, Ph; X = Cl, Br

When R = Bu, salt IV[4] readily undergoes a Wittig reaction with *F*-acyl fluorides (V) to give *F*-vinylphosphonium salts (VII) (only the *Z* isomer is observed). Subsequent hydrolysis of the vinylphosphonium salt provides a stereospecific route to the chain-extended (*E*)-1-hydro-*F*-olefin[5] VIII (Scheme I). The use of V introduces a stronger carbon–halogen bond into VI and retards elimination of halide ion (which leads to the acylation product).[6] In addition, the use of IV assures that the charged oxygen atom in VI must occupy a gauche position with respect to one of the two phosphorus atoms. Thus, this system permits one to compare the resultant rate of ring closure of VI to loss of halide ion and to determine whether Wittig olefination can compete with the acylation route.

When R = Bu(alkyl) in IV, reaction with V is rapid and VII is formed in 70–82% yields (as determined by $^{19}F$ NMR analysis). Little or none of the acylated product is observed.[7] In addition,

Scheme I

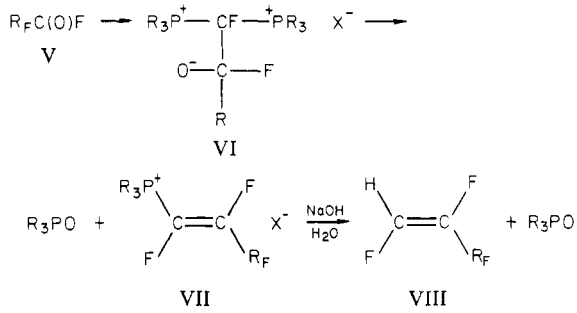


Table I

$$IV^a + V \rightarrow VII \xrightarrow[H_2O]{NaOH} VIII$$

| $R_F$ | VII,[b] % | VIII,[c,d] % |
|---|---|---|
| $CF_3$ | 73 | 45 |
| $CF_3CF_2$ | 80 | 62 |
| $CF_3CF_2CF_2$ | 82 | 52 |
| $CF_2Cl$ | 73 | 50 |
| $CH_3O_2CCF_2$ | 70 | 20 |
| $CF_3(CF_2)_2OCF(CF_3)$ | 75 | 49 |

[a] The phosphoranium salt was generated in all but the last case from 0.150 mol of $Bu_3P$ and 0.050 mol of $CFCl_3$. In the $CF_3(CF_2)_2OCF(CF_3)COF$ case, $CFBr_3$ was utilized. [b] $^{19}F$ NMR yield vs. $C_6F_6$. [c] Isolated yield of pure olefin. [d] The NMR, MS, and IR data were fully consistent with the assigned structures.

*only one isomer* of VII is detected by $^{19}F$ NMR—the *Z* isomer as noted in Scheme I. None of the *E* isomer was detected within the limits of $^{19}F$ NMR analysis. Table I summarizes the data for representative examples of V. Halogen, ether, and ester functionality is tolerated without any difficulty.

Stereospecific hydrolysis of VII occurs readily with addition of 50% NaOH, and the resultant chain-extended fluoroolefin is obtained in modest isolated yields. Table I illustrates typical examples. Since the preparation of IV, reaction with V, and the hydrolysis of VII can be carried out in a one-pot sequence, this novel approach to the synthesis of fluoroolefins from acyl fluorides provides a convenient synthetic entry to these versatile materials.

In contrast to the facile reaction of IV and V to give VII,[8] when the corresponding *F*-acyl chloride $R_FC(O)Cl$ is utilized in this reaction sequence (Scheme I), VII is *not* detected in any appreciable amount. Only acylation and cleavage products of IV were observed. Thus, the effect of the introduction of the stronger carbon–fluorine bond in VI is dramatically illustrated.

Operational details of the experimental procedure are outlined below for the preparation of (*E*)-1,2,3,3,4,4,5,5,5-nonafluoro-1-pentene.

A 250-mL three-necked flask, equipped with magnetic stir bar, rubber septum, and nitrogen tee, was charged with 0.150 mol (30.3 g, 37.4 mL) of tri-*n*-butylphosphine and 60 mL of dry benzonitrile.[9] The solution was cooled in an ice bath, and 0.050 mol (6.9 g, 4.7 mL) of trichlorofluoromethane was added in one portion via syringe. The resultant reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 3 h. $^{19}F$ NMR analysis indicated a 95% yield of $[Bu_3{}^+PC^-FP^+Bu_3]Cl^-$. To this phosphoranium salt solution was added ~0.050 mol of *F*-butanoyl fluoride [prepared from 0.055 mol (11.8 g, 7.2 mL) of *F*-butanoic acid]. Rapid reaction occurred to give 85% (*Z*)-$[Bu_3{}^+PCF{=}CFC_3F_7]X^-$. Addition of 6 mL of 50% NaOH, followed by flash distillation, drying over anhydrous $MgSO_4$, and fractional distillation gave 6.0 g (bp 32–34 °C) of >95% pure (*E*)-

(1) Presented in part at the 10th International Symposium of Fluorine Chemistry, Vancouver, Canada, Aug 1982, Abstract O-5.

(2) Cf. Ramirez et al. (Ramirez, F.; Pilot, J. F.; Desai, N. B.; Smith, C. P.; Hansen, B.; McKelvie, N. *J. Am. Chem. Soc.* **1967**, *89*, 6273) for the use of the term phosphoranium salt.

(3) To our knowledge these fluorine-containing phosphoranium salts are the first examples of fluoromethylene ylides that have been detectable.

(4) When R = Ph, the phosphoranium salts are inert to V.

(5) Cf. Burton et al. (Burton, D. J.; Inouye, Y.; Headley, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3980) for a previous report of chain-extention reactions as routes to fluoroolefins and fluorodienes.

(6) The use of acyl fluorides in place of acyl chlorides with simple ylides such as $Ph_3{}^+PC^-(Me)_2$ is not sufficient by itself to divert the overall process from acylation to olefination. It's the combination of effects in the process outlined in Scheme I that results in overall Wittig olefination.

(7) When a nonfluorinated acyl fluoride is utilized, olefination is not observed—only acylation results.

(8) In contrast to the facile reactions observed with IV, $[Bu_3{}^+PC^-ClP^+Bu_3]Cl^-$ did not react with $CF_3CF_2CF_2COF$.

(9) Solvents such as methylene chloride, chlorobenzene, dioxane, and *o*-chlorotoluene can also be utilized to prepare IV. Best results in subsequent reactions of IV were obtained with benzonitrile and *o*-chlorotoluene.

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1,2,3,3,4,4,5,5,5-nonafluoro-1-pentene (52% isolated yield).[10]

In conclusion, the use of IV illustrates the first example of Wittig olefination of an acid halide. Since the precursor methanes $CFCl_3$ and $CFBr_3$, the tertiary phosphines, and a variety of *F*-acids are commercially available, this approach to fluoroolefin synthesis provides a synthetically useful route to 1-hydro-*F*-olefin precursors that are easily metalated and can be elaborated further to other functional derivatives.[11] Also, since acyl fluorides are employed as precursors and chain-extension results, this route nicely complements the preparation of *F*-vinylphosphonium salts available via the tertiary phosphine–fluoroolefin reaction.[12]

**Acknowledgment.** We thank the National Science Foundation and the Air Force Office of Scientific Research for support of this work. We also thank Drs. N. Gurusamy and A. R. Bailey for technical assistance.

**Registry No.** II (R = Bu), 998-40-3; III (X = Cl), 75-69-4; IV (R = Bu; X = Cl), 84215-05-4; V ($R_F = CF_3$), 354-34-7; V ($R_F = CF_3CF_2$), 422-61-7; V ($R_F = CF_2Cl$), 354-27-8; V ($R_F = CH_3O_2CCF_2$), 69116-71-8; V ($R_F = CF_3(CF_2)_2OCF(CF_3)$), 2062-98-8; (*Z*)-VII ($R_F = CF_3$; R = Bu; X = Cl), 84195-33-5; (*Z*)-VII ($R_F = CF_3CF_2$; R = Bu; X = Cl), 84195-34-6; (*Z*)-VII ($R_F = CF_3CF_2CF_2$; R = Bu; X = Cl), 84195-35-7; (*Z*)-VII ($R_F = CF_2Cl$; R = Bu; X = Cl), 84195-36-8; (*Z*)-VII ($R_F = CH_3O_2CCF_2$; R = Bu; X = Cl), 84195-37-9; (*Z*)-VII ($R_F = CF_3(CF_2)_2OCF(CF_3)$; R = Bu; X = Br), 84195-38-0; (*E*)-VIII ($R_F = CF_3$), 5595-10-8; (*E*)-VIII ($R_F = CF_3CF_2$), 84195-39-1; (*E*)-VIII ($R_F = CF_3CF_2CF_2$), 75180-13-1; (*E*)-VIII ($R_F = CF_2Cl$), 84195-40-4; (*E*)-VIII ($R_F = CH_3O_2CCF_2$), 84195-41-5; (*E*)-VIII ($R_F = CF_3(CF_2)_2OCF(CF_3)$), 84195-42-6.

**Supplementary Material Available:** NMR data of the phosphoranium salts IV (R = Bu, Ph), NMR data of VII ($R_F = CF_2CF_2CF_3$), and NMR, IR, and MS data of olefin VIII ($R_F = CF_2CF_2CF_3$) (3 pages). Ordering information is given on any current masthead page.

(10) Purity was determined via GLPC analysis on OV-101 and Carbowax 20 M columns.

(11) Burton, D. J.; Hahnfeld, J. L. *Tetrahedron Lett.* **1975**, 773.

(12) Burton, D. J.; Shin-ya, S.; Howells, R. D. *J. Fluorine Chem.* **1980**, *15*, 543.

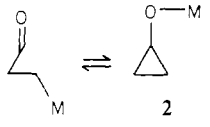
## Isolation and Reactions of Titanium Homoenolates of Esters[1]

Eiichi Nakamura and Isao Kuwajima*

*Department of Chemistry, Tokyo Institute of Technology Meguro, Tokyo 152, Japan*

*Received July 12, 1982*

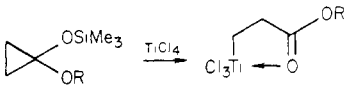
Metal homoenolate **1**[2] is a highly intriguing class of reactive



**1** **2**

species, yet its importance in organic chemistry has so far been underrated. Only the least reactive of the metal homoenolates (**1**, M = Hg[3] and Sn[4]) have been isolated, whereas the nature of the reactive ones, e.g., M = Na, remained elusive owing in part to their ready cyclization to the cyclopropanolate **2**[5,6] and in part to the absence of the suitable preparative approaches.[7]

We have found that the titanium homoenolate **4** can be prepared

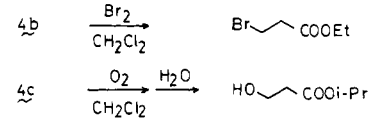


**3a**, R = Me
**b**, R = Et
**c**, R = *i*-Pr

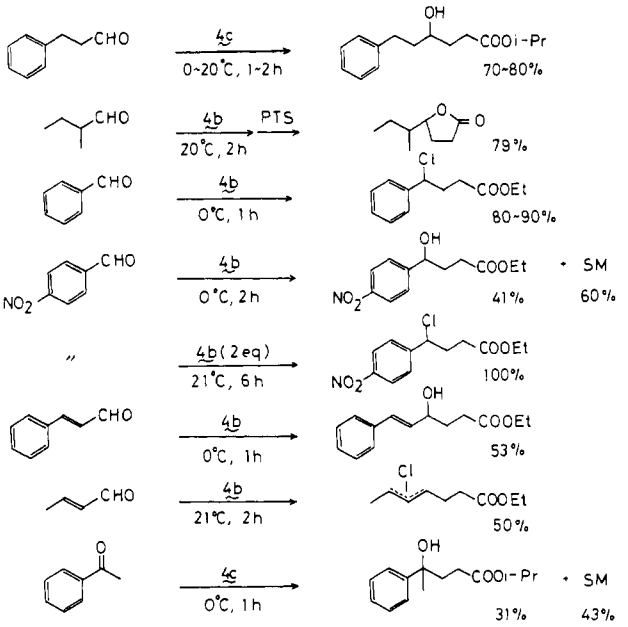
**4a–c**

in high yield by the reaction of the cyclopropane **3** with $TiCl_4$ and that this species does work as the nucleophilic homoenolate anion of alkyl propionates. When the cyclopropane **3c** was treated with $TiCl_4$ in $CDCl_3$ (or in $CH_2Cl_2$) at 25 °C, the initially formed yellowish suspension soon turned to a homogeneous wine-red solution with evolution of heat. The $^1H$ NMR spectrum indicated the formation of **4c** (89% yield) along with chlorotrimethylsilane (100%). The reaction of the methyl (**3a**) and the ethyl ether (**3b**) also proceeded smoothly (70% and 83% yield, respectively). No reaction took place when $TiCl_4$ was replaced by $TiCl_3$. The product was precipitated as microcrystalline powder after dilution with hexane. The deep purple **4c** is a moderately air-sensitive

Scheme I



Scheme II[a]



[a] About 1.2 equiv of **4** was used unless otherwise noted. SM stands for the starting carbonyl compound recovered.

(1) Metal homoenolate chemistry. For the previous report, see: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360.

(2) Because of the general lack of serious concern about the chemistry of metal homoenolates (except their synthetic equivalents), the word "homoenolate" has been related only loosely to the carbon anion **1**. Etymologically, however, "homoenolate" anion should mean the oxygen anion **2**, similar to the case of "enolate". In spite of such formalism, we prefer using "metal homoenolate" as the term for **1**; for **2** is more commonly called cyclopropanol and usually behaves as such.[5] In this way, we can avoid using rather awkward names such as β-oxido esters and β-acylalkylmetals. In view of the tautomeric relationship between **1** and **2**, however, it may also be justified to call **4** the homoenol *O*-silyl ether of alkyl propionates. It is to be noted that the definition of **1** as the homoenolate anion has been proposed by the initiator of this chemistry (Nickon, A.; Lambert, J. L. *J. Am. Chem. Soc.* **1962**, *84*, 4604).

(3) DeBoey, A.; De Puy, C. H. *J. Am. Chem. Soc.* **1970**, *92*, 4008.

(4) (a) Review: Omae, I. *Rev Silicon, Germanium, Tin Lead Compd.* **1973**, *1*, 59. (b) X-ray: Harrison, P. G.; King, T. J.; Healy, M. A. *J. Organomet. Chem.* **1979**, *132*, 17.

(5) Hamon, O. P. G.; Sinclair, R. W. *J. Chem. Soc., Chem. Commun.* **1968**, 890. Freeman, J. P.; Plonka, J. H. *J. Am. Chem. Soc.* **1966**, *88*, 3662.

(6) The cyclopropanes **3** were prepared from 3-chloropropionic esters (ca. 60% yield) on a 20-g scale by the reported method: Ruhlman, K. *Synthesis* **1971**, 236.

(7) For previous approaches to this problem, see: (a) Caine, D.; Frobest, A. S. *Tetrahedron Lett.* **1978**, 883. Goswami, R.; Corcorn, D. E. *Ibid.* **1982**, *23*, 1463. (b) Goswami, R. *J. Am. Chem. Soc.* **1980**, *102*, 5973. (c) Giese, B.; Horler, H.; Zwick, W. *Tetrahedron Lett.* **1982**, *23*, 931. (d) Ryu, I., Matsumoto, K., Ando, M.; Murai, S.; Sonoda, N. *Ibid.* **1980**, *21*, 4283.

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