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.

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(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]

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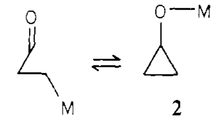
Received July 12, 1982

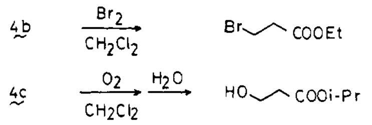
Metal homoenolate 1[2] is a highly intriguing class of reactive



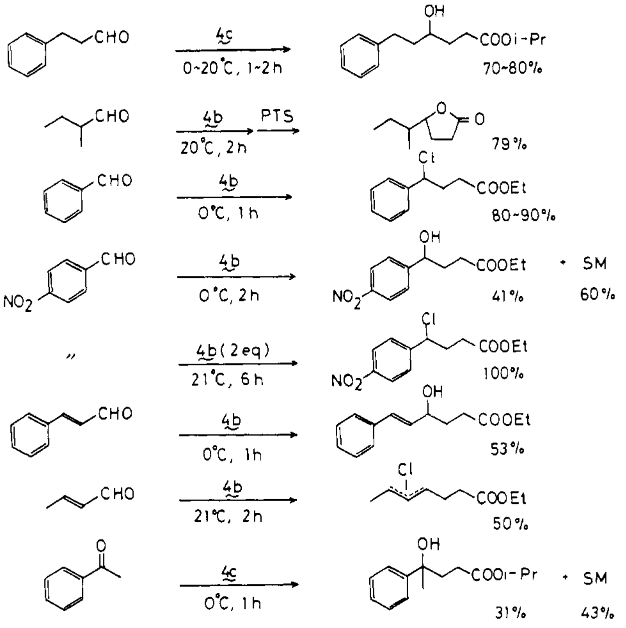
1 2

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]

Scheme I

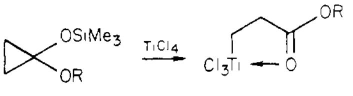


Scheme II[a]



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

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

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(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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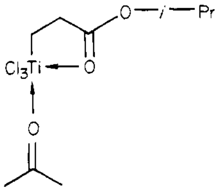
compound that is stable at room temperature for several months under vacuum and decomposes very slowly in solution ($t_{1/2}$ = 4 months; 26 °C, 0.1 M benzene). It melts at 90–95 °C with color change to reddish brown and sublimes with some decomposition at 90–110 °C (0.005 mmHg). Molecular weight by cryoscopy is 560–620, indicating a dimeric structure. Several lines of evidence suggest that **4** has the basic β-acylalkylmetal structure shown.[8] The ^{13}C NMR (proton noise decoupled) spectrum exhibits two nonequivalent methylene carbons, the broad signal at 100.6 ppm being assigned to the carbon bound to the metal. The ^{1}H NMR spectrum, showing a pair of A_2B_2-type triplets, resembles the spectrum of alkyl 3-(trichlorostannyl)propionate, which has a chelate structure similar to the one proposed here.[4b] The downfield shift of the carbonyl carbon (^{13}C NMR) and the weakening of the C=O bond (IR)[9] are also found for the stannylpropionate.[10] Undoubtedly, the internal coordination of the carbonyl group to the metal is responsible for the unusual thermal stability of **4**.[11] Bromine reacts with **4b** to give ethyl 3-bromopropionate, and oxidation of **4c** with molecular oxygen gives isopropyl 3-hydroxypropionate in good yield (Scheme I). Attempts to obtain diffractable crystals in order to get further information about the structure are in progress.

Having established the preparation of **4**, we then examined their reactivities with organic electrophiles. To our great satisfaction, the titanium alkyls smoothly transferred their propionate unit to aldehydes above 0 °C in methylene chloride (Scheme II).[12] Aliphatic aldehydes reacted cleanly with **4** to give the γ-hydroxy esters. The reaction provides a very efficient synthesis of this potentially useful class of compounds. Benzaldehyde initially gave the γ-hydroxybutyrate in moderate yield, but the product suffered in situ chlorination toward the end of the reaction. Chlorinated products were also obtained from *p*-nitrobenzaldehyde and crotonaldehyde. Ketones do not serve as reactive electrophiles for the titanium homoenolate. Addition of acetone to **4c** in benzene at once gave the monomeric addition complex **5**,[13] which remained quite stable. The reaction of acetophenone with **4c** gave the γ-hydroxy ester only in low yield. Chlorination of the initial adduct was a side reaction observed. Interestingly, **4** is inert to either benzoyl chloride or its more electrophilic derivative, the aluminum chloride complex. This inertness suggests that the trichlorotitanium alkyl **4** is substantially different in nature from the usual Grignard reagents.



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We have demonstrated that the purple powder of the trichlorotitanium homoenolate has considerable potentialities as a novel reagent for organic synthesis. Various points of interest including the modification of the reactivities by ligand exchange as well as the preparation of other metal complexes are under further study.

Acknowledgment. We thank Professor Takakazu Yamamoto for helpful discussions and for provision of an IR facility and Dr. Yoko Kaizu for the measurement of the resonance Raman spectra.

Registry No. 3a, 84098-43-1; **3b**, 27374-25-0; **3c**, 84098-44-2; **4a**, 84098-51-1; **4b**, 84098-52-2; **4c**, 84098-53-3; **5**, 84098-54-4; $TiCl_4$, 7550-45-0; Me_3SiCl, 75-77-4; $BrCH_2CH_2COOEt$, 539-74-2; $HOCH_2CH_2COO$-*i*-Pr, 84098-45-3; $PhCH_2CH_2CH(OH)CH_2CH_2COO$-*i*-Pr, 84098-46-4; $PhCH(Cl)CH_2CH_2COOEt$, 2125-35-1; O_2N-*p*-$C_6H_4CH(OH)CH_2CH_2COOEt$, 84098-47-5; O_2N-*p*-$C_6H_4CH(Cl)CH_2CH_2COOEt$, 84098-48-6; $PhCH{=}CHCH(OH)CH_2CH_2COOEt$, 84098-49-7; $PhC(OH)(CH_3)CH_2CH_2COO$-*i*-Pr, 84098-50-0; $PhCH_2CH_2CHO$, 104-53-0; $CH_3CH_2CH(CH_3)CHO$, 96-17-3; PhCHO, 100-52-7; O_2N-*p*-C_6H_4CHO, 555-16-8; $CH_3CH{=}CHCHO$, 4170-30-3; $PhCOCH_3$, 98-86-2; $PhCH{=}CHCHO$, 104-55-2; acetone, 67-64-1; isopropyl (trichlorostannyl)propionate, 70508-46-2; 1-methylpropyl-2-oxotetrahydrofuran, 77755-97-6; ethyl chloroheptenoate, 84129-71-5.

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(8) **4c**: ^{1}H NMR (0.3 M $CDCl_3$) δ 1.51 (d, 6 H, *J* = 6 Hz), 2.40 (CH_2Ti) and 3.38 (A_2B_2 t, 2 H, *J* = ca. 7 Hz), 5.65 (qq, 1 H, *J* = 6, 6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 44.1 (t), 77.7 (d), 100.6 (br, $w_{1/2}$ = ca. 45 Hz on PND), 189.8 (s); IR (0.1 M benzene) 2930 (s), 1603 (vs), 1425 (s), 1330 (m), 1260 (m), 1095 (s), 895 (m), 800 cm^{-1} (m); IR (0.02 M CL_4) 1608 cm^{-1}; IR (KBr) 1610 (br s), 1465 (m), 1390 (sh), 1375 (m), 1325 (s), 1095 (s), 880 (v br), 360 cm^{-1} (v br); resonance Raman (514.5 nm, solid) 360 (s), 285 (sh), 280 (br s), 265 (br s), 120 cm^{-1} (m). Anal. Calcd for $C_6H_{11}O_2Cl_3Ti$: C, 26.75; H, 4.12. Found: C, 26.59; H, 4.22. We owe the description of the homoenolate complex as **4** partly to a referee.

(9) (a) Driessen, W. L.; Groeneweld, W. L.; van der Wey, F. W. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 353. (b) Brun, L. *Acta Crystallogr.* **1966**, *20*, 739.

(10) Isopropyl (trichlorostannyl)propionate: ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 6 H, *J* = 6 Hz), 2.13 and 2.83 (A_2B_2 t, 2 H, J = ca. 7 Hz), 5.15 (qq, 1 H, *J* = 6, 6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.53 (q), 24.22 (t), 28.20 (t), 75.00 (d), 180.54 (s); IR (0.03 M CCl_4) 2960 (w), 1665 (vs), 1388 (s), 1330 (m), 1265 (m), 1230 (m), 1105 (s), 900 cm^{-1} (w). Anal. Calcd for $C_6H_{11}O_2Cl_3Sn$: C, 21.18; H, 3.26. Found: C, 21.32; H, 3.24.

(11) Cf.: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974; Chapter 2. Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 246.

(12) We thank H. Oshino for some experimental help.

(13) **5**: IR (0.1 M benzene) 2940 (m), 1675 (s), 1605 (s), 1420 (m), 1370 (m), 1325 (m), 1250 (sh), 1240 (m), 1090 (m), 860 cm^{-1} (s). Molecular weight by cryoscopy is 310.

Photosensitized [4 + 2] Cyclodimerization of 1,3-Cyclohexadiene

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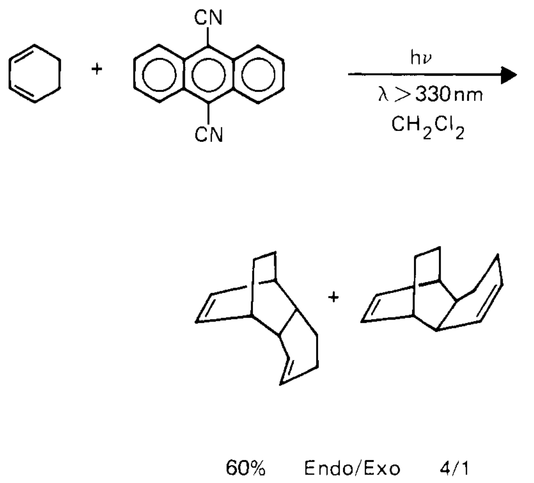
Excited state complexes (excimers and exciplexes) and/or photoinduced electron-transfer processes have been implicated in a variety of photochemical reactions.[1] One interesting consequence of these phenomena is that the course of the photoreaction may be drastically altered from that of excited singlet and/or triplet pathways. We have found that 1,3-cyclohexadiene (CHD), when irradiated through a uranyl oxalate filter (λ >330 nm) in CH_2Cl_2 at room temperature in an inert atmosphere in the presence of 9,10-dicyanoanthracene (DCNA), produces almost exclusively the [4 + 2] adducts *endo*- and *exo*-dicyclohexadiene (**1** and **2**; 4:1) in >60% isolated yield[2] (eq 1). This constrasts



(1)

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(1) Several reviews which include numerous references are as follows: (a) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (b) Caldwell, R. A.; Creed, D. *Ibid.* *1980*, *13*, 45–50. (c) Davidson, R. S. In "Molecular Association"; Foster, R., Ed.; Academic Press: London, 1975; p 215.

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