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A Novel One-pot Synthesis of Fluorinated α , β -unsaturated Esters

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Abstract: The reaction of pentafluorophenylmethylenetriphenylarsorane or p-chloro-tetrafluorophenylmethylenetriphenylarsorane, generated in situ from methylenetriphenylarsorane and hexafluorobenzene or chloropentafluorobenzene, with bromoacetates giving excellent yields of 3-pentafluorophenyl or 3-p-chloro-tetrafluorophenyl α , β -unsaturated esters with high steroselectivity is described.

 α , β -Unsaturated esters are important intermediates being essential synthetic organic chemistry, comin pounds in the synthesis of some natural products and capable of undergoing many useful organic transformations¹. Therefore reactions leading to the formation of them, especially fluorinated compounds, have attracted much attention.² Asato et al. have reported Wittig-Horner reactions to give trifluoromethylated α,β-unsaturated esters which have been applied to the synthesis products.³ some fluorinated natural However the of methods for the preparation of pentafluorophenylated or p-chloro-tetrafluorophenylated α,β-unsaturated esters have not been appeared in the literature.

Recently we found a novel double elimination of arsonium salts and its application to the preparation of 4-trifluoromethyl-2,4-dienyl carboxylates⁴. In our continuing investigation to exploit the synthetic utility of this reaction in organic synthesis, we now wish to report a novel one-pot synthesis of 3-pentafluorophenyl or 3-p-chloro-tetrafluorophenyl acrylates by the reaction of pentafluorophenylmethylenetriphenylarsorane or p-chloro-tetrafluorophenyltriphenylarsorane with bromoacetates.

The reaction sequence is shown as follows:



The fluorinated arsoranes 3 generated from the methylenetriphenylarsorane with hexafluorobenzene or chloro-pentafluorobenzene,⁵ without isolation, reacted with bromoacetates to give fluorinated products 7 in 94-99% yields(3 steps).

The reaction of 3 to 7 is initiated by nucleophilic attack of fluorinated arsonane 3 on the α -carbon atom of bromoacetate to give arsonium salt 4. 4 reacted with another molecule of 3 to give 5 which converted to 6 via hydrogen transfer, followed by elimination of triphenyl-

Compound	Х	R	b.p.(°C/2mmHg)	yield(%) ^a
7a	F	сн ₃	70	99
7b	F	^C 2 ^H 5	76	97
7c	F	C₄Hg−n	106	99
7đ	F	C ₄ H ₉ -i	96	95
7e	C1	СН _З	89	95
7 f	C1	с ₂ н ₅	96	94
7g	C1	C₄ ^H 9 ^{−n}	104	97
7 h	C1	^C 4 ^H 9 ⁻ⁱ	98	99

Table 1. Preparation of Fluorinated Products 7.

a Isolated yields.

arsine to afford product 7. It may be explained that 6 is more stable than 5 due to the negative charge can be stabilized by CO_2R group.

This one-pot synthesis of fluorinated α,β -unsaturated esters is quite convenient in excellent yields with high stereoselectivity under mild condition giving E-isomer exclusively as juaged on NMR spectrascopy and would be useful in the synthesis of fluorinated biologically active compounds.

Experimental

All boiling points were uncorrected. IR spectra of liquid products were obtained as film on a Shimadzu IR-440 spectrometer. ¹H NMR and ¹⁹F NMR spectra were recorded on a Varian EM-360 (60 MHz) or XL-200 (200 MHz) spectrameter with SiMe₄ and CF₃CO₂H (positive for upfield shifts) as external references, respectively. Mass spectra were measured on a GC-MS-4021 spectrameter.

General Procedure: Phenyllithium (4 mmol) in absolute diethyl ether (6 ml) was added dropwise to a stirred suspension of methyltriphenylarsonium iodide (4 mmol) in aksolute diethyl ether (25 ml) at 20°C under nitrogen. The mixture was stirred for lh and cooled to 0°C, the hexafluorobenzene or chloro-pentafluorobenzene (2 mmol) was slowly added over 5 min. After stirring for 15 min at 0°C, the mixture was warmed to 20°C and stirred for further 30 min. Then bromoacetate (1 mmol) was added and stirred for 1h at 20°C. The product 7 was isolated by column chromatography on silica gel with light petroleum (b.p. 60-90°C)-ethyl acetate (9:1) as eluent.

Methyl 3-pentafluorophenyl acrylate (7a) 993 yield; b.p. 70°C/2mmHg; IR(film): 1728s, 1650s, 1200s cm⁻¹; ¹H NMR(CCl₄/TMS): δ 3.73(3H,s), 6.58(1H, d,J= 16Hz), 7.42(1H,d,J=16Hz); ¹⁹F NMR(CCl₄/TFA): δ 62.0-64.0 (2I,m), 74.0-75.5(1F,m), 84.0-85.3(2F,m)ppm; MS m/z: 252 (M⁺,38%), 221(M⁺-OMe,100%), 193(M⁺-CO₂Me,56%) (Found: C, 47.52; H, 1.91; C₁₀H₅F₅O₂ requires C, 47.64; H, 1.98%)

Ethyl 3-pentafluorophenyl acrylate (7b) 97% yield; b.p. 78°C/2mmHg; IR(film): 1730s, 1650s, 1260s cm⁻¹; ¹H NMR(CCl₄/TMS): δ 1.32(3H, t,J=6Hz), 4.25 (2H,q, J=6Hz), 6.66(1H,d,J=16Hz), 7.60(1H,d,J=16Hz); ¹⁹F NMR(CCl₄/TFA): δ 61.3-63.0(2F, m), 73.3-74.7(1F,m), 83.7-85.)(2F,m)ppm; MS m/z: 266(M⁺,42%),221(M⁺-OEt,100%), 193 (M⁺-CO₂Et, 27%) (Found: C, 49.16; H, 2.53; C₁₁H₇F₅O₂ requires C, 49.65; H, 2.63%)

n-Butyl 3-pentafluorophenyl acrylate (7c) 99% yield; b.p. 106°C/2mmHg; IR(film): 1730s, 1650s, 1260s cm⁻¹; ¹H NMR(CCl₄/TMS): δ0.93(3H, t,J=6Hz), 1.10-1.80(4H,m), 4.08(2H,t,J=6Hz), 6.54(1H, d, J=16Hz), 7.46 (1H d,J=16Hz); ¹⁹F NMR(CCl₄/TFA):δ62.0-63.3(2F,m), 74.075.3(1F,m), 83.6-85.3(2F,m)ppm; MS m/z: 294(M⁺, 11%), 221(M⁺-OBu,100%), 193(M⁺-CO₂Bu, 53%)(Found: C, 52.69; H, 3.73; C₁₃H₁₁F₅O₂ requires C, 53.08; H, 3.74%)

i-Butyl 3-pentafluorophenyl acrylate (**7d**) 95% yield; b.p. 96°C/2mmHg; IR(film): 1720s, 1650s, 1260s cm⁻¹; ¹H NMR(CCl₄/TMS): δ0.87(3H,t,J=6Hz), 1.18(3H, d,J=6Hz),1.20-1.70(2H,m), 4.78(1H,m), 6.48(1H,d,J=16Hz), 7.40(1H,d,J=16Hz); ¹⁹F NMR(CCl₄/TFA): δ62.0-63.3(2F,m), 74.0-75.2(1F,m), 83.6-85.3(2F,m)ppm; Ms m/z: 294(M⁺,1%), 221(M⁺-OBu,100%), 193(M⁺-CO₂Bu,41%) (Found: C, 52.94; H, 3.75; C₁₃H₁₁F₅O₂ requires C, 53.08; H, 3.74%)

Methyl 3-p-chloro-tetrafluorophenyl acrylate (7e) 95% yield; b.p. 89°C/2mmHg; IR(film): 1720s, 1640s, 1240s cm⁻¹; ¹H NMR(CCl₄/TMS): δ 3.85(3H,s), 6.73(1H,d,J= 16Hz), 7.58(1H,d,J=16Hz) ¹⁹F NMR(CCl₄/TFA): δ 61.7-62.7 (2F,m), 62.7-63.7(2F,m)ppm; MS m/z: 268(M⁺,67%), 237(M⁺ -OMe, 100%), 209(M⁺-CO₂Me, 35%), 174(M⁺-CO₂Me-Cl, 53%) (Found: C, 44.66; H, 1.83; C₁₀H₅ClF₄O₂ requires C, 44.72; H, 1.86%)

Ethyl 3-p-chlorotetrafluorophenyl acrylate (7f) 94% yield; b.p. 96°C/2mmHg; IR(film): 1730s, 1640s, 1250s cm⁻¹; ¹H NMR(CCl₄/TMS):δ1.33(3H,t,J=6Hz), 4.24(2H, q,J=16Hz), 6.70(1H,d,J=16Hz), 7.64(1H,d,J=16hz); ¹⁹F NMR (CCl₄/TFA):δ62.0-63.0(2F,m), 63.0-64.0(2F,m)ppm; MS m/z: 282(M⁺,16%), 237(M⁺-OEt,52%), 209(M⁺-CO₂Et,58%), 174(M⁺-CO₂Et-Cl,100%) (Found: C, 46.36; H, 2.33; C₁₁H₇ClF₄O₂ requires C, 46.76; H, 2.48%)

n-Butyl 3-p-chloro-tetrafluorophenyl acrylate (**7g**) 97% yield; b.p. 98°C/2mmHg; IR(film): 1730s, 1642s, 1268s cm⁻¹; ¹H NMR(CCl₄/TMS): δ0.94(3H, t,J=6Hz), 1.14-1.90(4H,m), 4.10(2H,t, J=6Hz), 6.60(1H, d, J=16Hz), 7.52 (lH,d,J=16Hz); ¹⁹F NMR(CCl₄/TFA): 861.6-62.6(2F,m), 62.6-64.0(2F, m)ppm; MS m/z: 310(M⁺,15%), 237(M⁺-OBu,100%), 209(M⁺-CO₂Bu,38%), 174(M⁺-CO₂Bu-Cl,55%)(Found: C, 50.21; H. 3.51; C₁₃H₁₁ClF₄O₂ requires C, 50.27; H, 3.54%)

i-Butyl 3-p-chloro-tetraphenyl acrylate (7h) 99% yield; b.p. 98°C/2mmHg; IR(film): 1720s, 1640s, 1255s cm⁻¹; ¹H NMR(CCl₄/TMS): 80.87(3H,t,J=6Hz), 1.18(3H, d,J=6Hz),1.20-1.75(2H,m), 4.74(1H,m), 6.48(1H,d,J=16Hz), 7.48(1H,d,J=16Hz); ¹⁹F NMR(CCl₄/TFA): 861.4-62.4(2F,m), 62.4-64.0(2F,m)ppm; MS m/z: 310(M⁺,1%), 237(M⁺-OBu,29%), 209(M⁺-CO₂Bu, 7%), 174(M⁺-CO₂Bu-Cl,12%)(Found: C, 50.24; H, 3.49; C₁₃H₁₁ClF₄O₂ requires C, 50.27; H, 3.54%)

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