Registry No. 1, 15687-27-1; 2, 51407-46-6; 3, 38861-78-8; 4, 40150-92-3; 5, 105899-75-0; Co(II) stearate, 1002-88-6; Mn(II) stearate, 3353-05-7.

Supplementary Material Available: Table documenting the effect of different metals and their complexes on the autoxidation of 2 (1 page). Ordering information is given on any current masthead page.

Facile Synthesis of Ethyl 3,3-Difluoroacrylate from Dibromodifluoromethane and Diels-Alder Cycloaddition with Furan[1]

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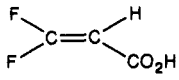
Received December 11, 1985

Esters of acrylic acid have received continuous interest as reagents in organic synthesis. On the contrary, their β-fluorinated analogues were somewhat deserted,[2] albeit they potentially allow the direct introduction of one or several fluorine atoms into a molecule. Thus, for an attempted route to 6,6-difluoroshikimic acid, we needed esters of 3,3-difluoroacrylic acid (1). Previously, such



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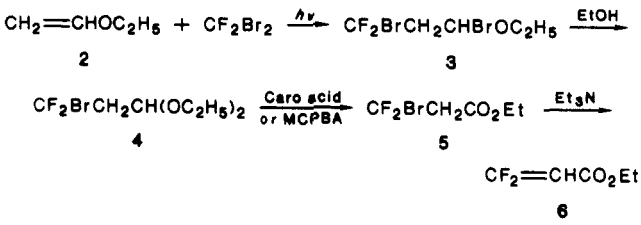
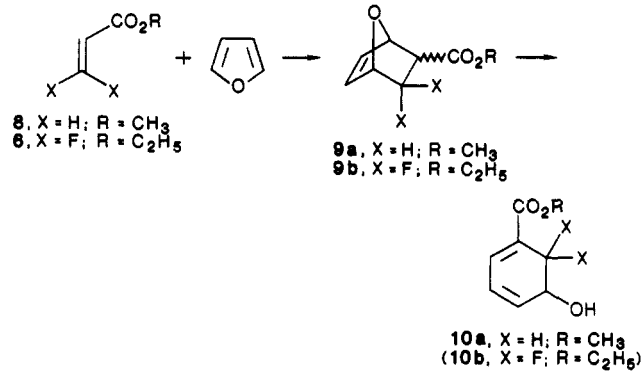
esters were prepared by multistep synthesis from not easily available materials by tedious or not clear procedures.[3-6] Recently, an elegant but delicate one-pot synthesis of the acid 1 was described starting from 1,1-difluoroethylene via (2,2-difluorovinyl)lithium.[7] Nevertheless, the authors did not describe the esters. We developped an easy synthesis of ethyl 3,3-difluoroacrylate (6) in 36% overall yield, starting from ethyl vinyl ether 2 and dibromodifluoromethane.

In the first step, the two reagents were condensed under ultraviolet irradiation; then the resulting α-bromo ether 3 was treated with ethanol to give the bromodifluoroacetal 4,[8] following Tarrant's procedure[9] (see Scheme I). The next step was the direct oxidation of the acetal 4 to the ethyl ester 5 either with Caro acid[10] or *m*-chloroperoxybenzoic acid[11,12] in comparable yields. Attempted oxidations by ozone[13] gave only complex mixtures of fluorinated compounds.

Scheme I



Scheme II



Rapid dehydrobromination of the ester 5 was carried out with triethylamine in dichloromethane at 0 °C to give ethyl 3,3-difluoroacrylate (6) in 74% yield. For this step, the temperature must be carefully controlled and the reaction quenched as soon as the addition of the amine is finished, in order to avoid the formation of ethyl 3,3,3-trifluoropropanoate. We had previously shown that dehydrochlorination of cyclohexyl 3-chloro-3,3-difluoropropanoate, prepared by Bayer-Villiger oxidation of the corresponding ketone, led to an unresolvable mixture of the expected acrylate and cyclohexyl 3,3,3-trifluoropropanoate[2] due to fluoride ion random. Obviously, replacing chlorine by the better leaving group bromine enhances the selectivity of the reaction.

In a recent work, it was shown that the [4 + 2] cycloaddition reaction between furan and acrylic monomers, to give the 7-oxabicyclo[2.2.1]heptyl system, was greatly accelerated by the addition of zinc iodide[14] or boron trifluoride etherate.[15] As a route to (±)-shikimic acid and to its epimers[16] the Diels-Alder adduct **9a** obtained from furan and methyl acrylate (8) led, upon the base induced cleavage of the oxygen bridge, to the cyclohexadienol **10a**[14,16] (see Scheme II).

With the aim of preparing the difluorocyclohexadienol **10b**, we reacted first furan with ethyl 3,3-difluoroacrylate (6) in the presence of zinc iodide (boron trifluoride etherate or aluminum chloride[17] were ineffective). Although ex-

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(7) Gillet, J. P.; Sauvêtre, R.; Normant, J. F. *Synthesis* **1982**, 297.
(8) We failed to hydrolize 4 to the corresponding aldehyde, a precursor of 3,3-difluoroacrolein. The diethyl acetal 7 was obtained in 85% yield by treating 4 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature. We failed also to hydrolize 7.

CF_2=CHCH$(OEt)_2$
7

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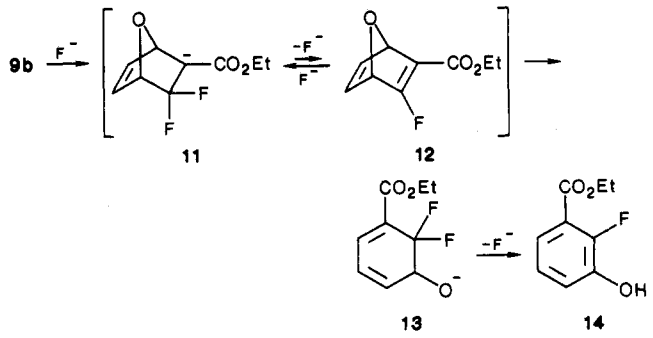
Scheme III



tensive decomposition took place (in contrast with the very clean reaction of furan with methyl acrylate), we isolated a 40% yield from **6** of the adduct **9b** (85h heating at 80 °C, instead of 48 h at 40 °C, starting from 8[14]), as a mixture of epimers (**9b(endo)**/**9b(exo)** ≃ 4/1). Their configuration was determined by the value of the coupling constant in **9b(endo)**, $J_{H1,H2}$ = 4.4 Hz and in **9b(exo)**, $J_{H1,H2}$ = 0 Hz.[18,19] We found that the condensation could also be conducted without a catalyst; but then, the yield was the half of that with zinc iodide: 72 h heating at 100 °C gave a mixture of **9b** (**9b(endo)**/**9b(exo)** ≃ 13/1) in 20% isolated yield. Further heating did not improve the yield but increased the formation of polymeric material. By comparison, a month or more is required to obtain 20% of **9a** from furan and **8**.[14] Thus, without a catalyst, ethyl 3,3-difluoroacrylate (**6**) appears to be much more reactive than methyl acrylate (**8**). In the presence of zinc iodide, the comparison is less obvious since the reaction was accompanied by decomposition. Attempts of base-promoted ring opening of **9b** by lithium hexamethyldisilazide at −78 °C[14] led to a complex mixture from which the expected cyclohexadienol **10b** was absent.

In order to prevent a possible elimination of a fluoride ion from the anion **11**, we used "anhydrous" tetrabutylammonium fluoride[20] which might act as a strong base on **9b** and add a fluoride ion to the hypothetic vinylic fluoride **12**, giving back **11**. This objective was partially thwarted as the reaction did not stop to the anion **13** of the cyclohexadienol **10b**, giving rise to the fluorophenol **14**, after hydrolysis (see Scheme III). Some other bases (potassium hydride or even tri-*n*-butylmethylfluorophosphorane[21] [$(n\text{-}C_4H_9)_3P(CH_3)F$]) were found to be ineffective at opening the adduct **9b** under mild conditions, to prevent easy aromatization. Nevertheless, the isolation of **14** was proof that the anion of **10b** (**13**) was obtained as an intermediate.

Experimental Section

General Methods. ^1H NMR and ^{19}F NMR spectra, unless otherwise specified, were recorded respectively at 60 MHz and 56.45 MHz with a Varian EM 360 L NMR spectrometer equipped with a proton/fluorine probe. Higher field NMR spectra were recorded at 90 MHz (^1H) and 84.715 MHz (^{19}F) on a Brüker WH-90 apparatus and at 250 MHz and at 500 MHz, respectively, on Brüker WM-250 and WM-500 spectrometers by Mr. Davoust and Mrs. Platzer, Université P. & M. Curie, Paris. COSY experiments were done at 500 MHz. ^1H chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane. ^{19}F NMR chemical shifts are given in ppm downfield relative to $CFCl_3$. IR spectra were recorded on a Perkin-Elmer 167 spectrometer and are expressed in cm^{-1}. Elemental analyses were performed either by the Service Central d'Analyse du CNRS, Vernaison or by the Service de Microanalyse, Université P. & M. Curie, Paris. Melting points were taken on a Mettler FP61 instrument.

3-Bromo-3,3-difluoropropanal diethyl acetal (4) was prepared by Tarrant's procedure[9] in 65% yield from ethyl vinyl ether: ^1H NMR ($CDCl_3$) 1.2 (t, 6 H, CH_3), 2.75 (td, 2 H, $J_{2,F}$ = 14 Hz, $J_{2,1}$ = 5 Hz, $(C_2)H_2$), 3.6 (≃qd, 4 H, CH_2), 4.9 (t, 1 H, $J_{1,2}$ = 5 Hz, $(C_1)H$); ^{19}F NMR ($CDCl_3$) −42 (t, $J_{F,2}$ = 14 Hz).

Ethyl 3-Bromo-3,3-difluoropropanoate (5). Caro Acid Procedure. To a vigorously stirred solution of **4** (24.7 g, 0.1 mol) in absolute ethanol (200 mL) at 5–10 °C is added the Caro acid prepared from 85% sulfuric acid (144 g) and ammonium persulfate (114 g, 0.5 mol).[10] After being stirred for 16 h at room temperature, the mixture was diluted with cold water (600 mL) and extracted with ether (3 × 250 mL). The organic phase was washed with brine (2 × 200 mL) and then dried over Na_2SO_4. Concentration under vacuum (20 mmHg) and distillation afforded **5** (16.3 g, 0.075 mol, 75%): bp 60–61 °C (20 mmHg); IR ($CHCl_3$) 1750, 1570, 1380, 1180, 1100, 1030; ^1H NMR ($CDCl_3$) 1.3 (t, 3 H, CH_3), 3.5 (t, 2 H, $J_{2,F}$ = 13 Hz, $(C_2)H_2$), 4.3 (q, 2 H, CH_2); ^{19}F NMR ($CDCl_3$) −43 (t, $J_{F,2}$ = 13 Hz). Anal. Calcd for $C_5H_7BrF_2O_2$: C, 27.67; H, 3.25. Found: C, 27.55; H, 3.42.

3-Chloroperoxybenzoic Acid (MCPBA) Procedure. A stirred mixture of **4** (12.3 g, 0.05 mol), CH_2Cl_2 (25 mL), MCPBA (tech. 80%, 15 g, 0.07 mol), and concentrated sulfuric acid (4 drops) was refluxed overnight. After cooling, the mixture was filtered and the solid washed with cold CH_2Cl_2 (3 × 50 mL). The filtrate was washed with 20% sodium bisulfite solution (10 mL), cold saturated $NaHCO_3$ (2 × 15 mL), and then with brine (2 × 30 mL). After drying (Na_2SO_4) and concentration (20 mmHg), the residue was bulb-to-bulb distilled (0.1 mmHg) to give **5** (7.7 g, 71%).

Ethyl 3,3-Difluoroacrylate (6). To a well-stirred solution of **5** (13.0 g, 0.06 mol) in CH_2Cl_2 (30 mL) was added dropwise triethylamine (8.35 mL, 0.06 mol) at 0 °C. At the end of the addition the mixture was filtered and the solid rinsed with cold CH_2Cl_2 (2 × 40 mL). The filtrate was washed with 15% hydrochloric acid (15 mL) and brine (2 × 30 mL) and dried over Na_2SO_4. The solvent was distilled off in an efficient column. Distillation of the residue in a smaller equipment (Vigreux column) gave 6.04 g of **6** (0.044 mol, 74%): bp 97–98 °C; IR ($CHCl_3$) 1745, 1732 (shoulder), 1710, 1400, 1380, 1355, 1280, 1145; ^1H NMR ($CDCl_3$) 1.3 (t, 3 H, CH_3), 4.3 (q, 2 H, CH_2), 5.05 (dd, 1 H, J_{2,F_t} = 22.0 Hz, J_{2,F_c} = 2.8 Hz, $(C_2)H$); ^{19}F NMR ($CDCl_3$) −66 (dd, $J_{F_t,2}$ = 22.0 Hz, $J_{F,F}$ = 16.0 Hz, F trans to $(C_2)H$), −70 (dd, $J_{F_c,2}$ = 2.8 Hz, $J_{F,F}$ = 16.0 Hz, F cis to $(C_2)H$). Anal. Calcd for $C_5H_6F_2O_2$: C, 44.13; H, 4.44; F, 27.92. Found: C, 44.34; H, 4.57; F, 27.46.

2-Carbethoxy-3,3-difluoro-7-oxabicyclo[2.2.1]hept-5-ene (9b). Ethyl 3,3-difluoroacrylate (**6**) (1 g, 7.3 mmol), furan (3 mL, 2.8 g, 0.041 mol), and hydroquinone (ca. 0.03 g) were placed in a Teflon-stoppered, heavy-walled glass (Pyrex) bulb. The mixture was heated in an oil bath for 72 h at 100 °C with magnetic stirring. After evaporation of the furan, the residue was bulb-to-bulb distilled at 90–100 °C (bath temperature) under 0.05 mmHg to give 0.3 g of **9b** (mixture of endo/exo ≃ 13/1) as a partially crystallized colorless oil (1.5 mmol, 20%).

Zinc Iodide Procedure. A mixture of ethyl 3,3-difluoroacrylate (**6**) (2 g, 14.6 mmol), furan (6 mL), anhydrous zinc iodide (2 g, 6.3 mmol), and hydroquinone (ca. 0.03 g) was placed in a 50-mL, Teflon-stoppered, round-bottomed flask. The mixture was heated in an oil bath for 80 to 85 h at 80 °C, with magnetic stirring and occasional manual shaking. The black mixture was carefully triturated with diethyl ether and filtered through a pad of Celite. The ether phase was washed with water and dried ($MgSO_4$). The solvent and excess of reagents were removed under vacuum to give a clear brown oil which was bulb-to-bulb distilled as above to give 1.2 g of **9b** (6.0 mmol, 40%, mixture of endo/exo ≃ 4/1). Anal. Calcd for $C_9H_{10}F_2O_3$: C, 52.94; H, 4.94. Found:

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(19) The approximate dihedral angle between vicinal H_2 and F being 0° for F_e and 120° for F_a in **9b(endo)** (respectively 120° and 0° in **9b(exo)**) it can be assumed that $J_{2,F_a} < J_{2,F_e}$ in **9b(endo)** and $J_{2,F_a} > J_{2,F_e}$ in **9b(exo)**.[18]
(20) Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3219.
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C, 52.78; H, 4.89. The two epimers were separated by column chromatography (CH_2Cl_2, silica gel) **9b(endo)** was first eluted ($R_f \simeq 0.6$, by TLC) as a colorless solid: mp 47.4 °C; IR (CCl_4) 1740 (COOR), 1340, 1310, 1190. ^1H NMR ($CDCl_3$, 250 MHz) 1.26 (t, 3 H, CH_3), 3.42 (dt, 1 H, $J_{2,F_e} = 20.7$ Hz, $J_{2,F_a} = 4.4$ Hz, $J_{2,1} = 4.4$ Hz, $(C_2)H$), 4.16 (m, 2 H, CH_2), 4.83 ($\simeq$dtd, $J_{4,F_e} = 6.0$ Hz, $J_{4,F_a} \simeq 2.2$ Hz, $J_{4,5} \simeq 2.2$ Hz, $J = 1.1$ Hz, $(C_4)H$), 5.13 (mbr, 1 H, $(C_1)H$), 6.42 ($\simeq$ddt, 1 H, $J_{5,6} = 5.8$ Hz, $J = 1.8$ and 1.5 Hz, $(C_5)H$), 6.91 (dt, 1 H, $J_{6,5} = 5.8$ Hz, $J_{6,1} = 1.6$ Hz, $J_{6,F_a} = 1.6$ Hz, $(C_6)H$) [H_1 and H_4, H_4 and H_5 are coupled as determined by COSY experiments at 500 MHz]; ^{19}F NMR ($CDCl_3$, 84.7 MHz) -98.4 (dddd, $J_{F_a,F_e} = 222$ Hz, $J_{F_e,2} = 20.7$ Hz, $J_{F_e,4} = 6.0$ Hz, $J = 0.7$ Hz, F_e), -107.0 (dm, $J_{F_e,F_e} = 222$ Hz, $w_{1/2} = 9.6$ Hz, F_a). Then **9b(exo)** ($R_f \simeq 0.4$, by TLC) as a colorless oil: ^1H NMR ($CDCl_3$, 250 MHz) 1.31 (t, 3 H, CH_3), 2.80 (dd, 1 H, $J_{2,F_a} = 11.4$ Hz, $J_{2,F_e} = 6.2$ Hz, $(C_2)H$), 4.27 (m, 2 H, CH_2), 4.78 (d(mbr), 1 H, $J_{4,F_e} \simeq 6.0$ Hz, $(C_4)H$), 5.35 (sext br, 1 H, $(C_1)H$), 6.54 (d($\simeq$qbr), 1 H, $J_{5,6} = 5.8$ Hz, $(C_5)H$), 6.69 (dm, 1 H, $J_{6,5} = 5.8$ Hz, $(C_6)H$); ^{19}F NMR ($CDCl_3$, 84.7 MHz) -101.4 (dd quint, $J_{F_a,F_e} = 225$ Hz, $J_{F_a,2} = 11.4$ Hz, $J = 1.1$ Hz, F_a), -110.0 (dt, $J_{F_e,F_a} = 225$ Hz, $J_{F_e,2} = 6.2$ Hz, $J_{F_e,4} = 6.2$ Hz, F_e).

Ethyl 2-Fluoro-3-hydroxybenzoate (14). Tetrabutylammonium fluoride trihydrate (2 g, 6.3 mmol) was heated for 48 h in a round-bottomed flask with magnetic stirring at 45 °C under vacuum (0.05 mmHg). The melted adduct **9b** (0.4 g, 1.9 mmol) was added at this temperature under an inert atmosphere. The paste liquefied and the mixture was heated for 2 h with stirring. After cooling, the reaction was quenched with water and extracted with ether. Drying ($MgSO_4$) and concentration gave a viscous brown oil which was purified by preparative TLC (20% AcOEt/C_6H_6, silica gel) giving pure **14** (0.1 g, 0.54 mmol) as a solid: ^1H NMR ($CDCl_3$) 1.39 (t, 3 H, CH_3), 4.39 (q, 4 H, CH_2), 6.44 (s br, 1 H, OH), $\simeq$ 6.90-7.50 (m, 3 H, H Ar); ^{19}F NMR ($CDCl_3$) -137 (t, $J = 6.3$ Hz); mass spectrum, m/e (relative intensity) 184 (M^+), 156, 139 (100), 111, 83.

Registry No. **2**, 109-92-2; **3**, 1993-81-3; **4**, 1645-58-5; **5**, 105836-29-1; **6**, 35245-99-9; *endo*-**9b**, 105836-30-4; *exo*-**9b**, 105836-31-5; **14**, 105836-28-0; CF_2Br_2, 75-61-6; furan, 110-00-9.

A Stereospecific Synthesis of All Four Isomers of 9,11-Tetradecadienyl Acetate Using a General Method Applicable to 1,3-Dienes

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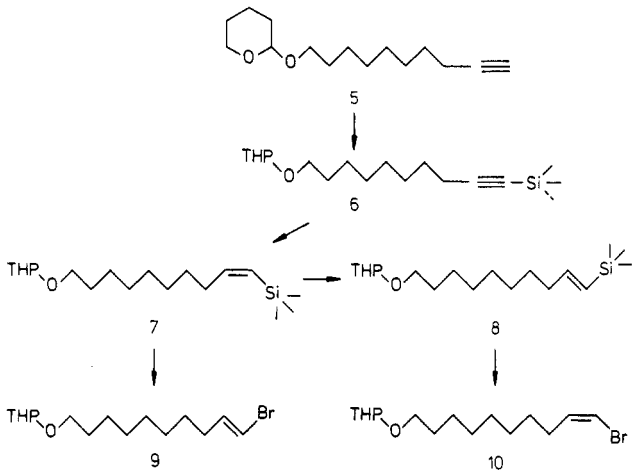
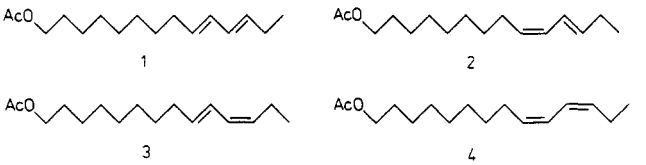
Received March 11, 1986

An important structural feature of many insect pheromones and other biologically active compounds is a conjugated diene system. The need for regio- and stereochemically pure compounds for biological tests is well-recognized,[1] and a large number of methods for the stereoselective synthesis of conjugated dienes have been developed.[2-4] Among the more recent and promising methods is the direct coupling of two alkenyl moieties in the presence of a catalyst.[5-8] This strategy is also used in the present study where we now report a convergent and general synthesis of all four isomers of 9,11-tetradecadienyl acetate (**1**-**4**). The 9*Z*,11*E*-isomer **2** is the main pheromone component of the Egyptian cotton leafworm *Spodoptera littoralis*[9] and the cone pyralid *Dioryctria abietella*.[10] In order to perform biological tests, all four isomers are needed.

Scheme I

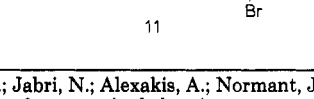




Preparation of the isomerically pure *E* and *Z* vinyl bromides **9** and **10** from the acetylene **5** via the corresponding vinylsilanes[11] **7** and **8** and the cross-coupling of these bromides with alkenylboranes using a palladium catalyst[5,6,12] is shown to be an attractive method for the synthesis of these diene systems.

Silylation of 1-(2-tetrahydropyranyloxy)-9-decyne[13] (**5**) with trimethylsilyl chloride gave the alkynylsilane **6** in a 90-95% yield (Scheme I). Hydroalumination of the triple bond with diisobutylaluminum hydride followed by protonation gave the *Z* vinylsilane **7** in a 79% yield of >97% isomeric purity. Isomerization of **7** (NBS, pyridine, $h\nu$)[14] yielded the corresponding *E* vinylsilane **8** in a 70% yield of >98% isomeric purity. The two *Z* and *E* vinylsilanes **7** and **8** were obtained isomerically pure (>99.9%) by chromatography on $AgNO_3$-impregnated silica gel.[15]

Bromination of the *Z* vinylsilane **7** followed by desilicohalogenation with sodium methoxide according to a method previously described[11] gave the vinyl bromide **9** together with 10-15% of the product **11** formed by undesired hydrogen bromide elimination. However, bro-



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