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A simple synthesis of fluoroalkyl substituted dihydrofurans by rhodium(II)-catalyzed 1,3-dipolar reactions

Yanli Wang and Shizheng Zhu*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

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Abstract—The rhodium(II)-catalyzed reactions of ethyl 2-diazo-fluoroalkylacetoacetate **1** with vinyl ethers have been studied. The reactions of **1a–e** with isobutyl vinyl ethers afforded dihydrofuroates **3a–e** in good to excellent yields. Further transformation of the dihydrofuroates by acid-catalyzed alcohol elimination could give α-fluoroalkyl-β-furoates readily. Similarly, stable diazo compounds **1a** and **b** reacted with cyclic vinyl ethers to give 1,3-dipolar cycloaddition products. Interestingly, only vinyl C–H insertion compound was obtained concerning the reaction of **1a** with 2,5-dimethylfuran. The reaction mechanism was also discussed.

1. Introduction

Introduction of fluoroalkyl, especially trifluoromethyl group, into organic molecules often results in dramatic modification of their physical and chemical properties as well as their biological activity profile.[1] In recent years, an increasing need for fluorine-containing molecules both for bio-active and for functional materials has prompted the development of methods for the preparation of versatile fluoro-containing synthons. Although fluoroalkylation of aromatics could be achieved rather readily with a variety of methods, most notably by using trifluoromethyl copper and related oganometallics, there also exists a lack of appropriate means for constructing various fluoroalkyl-containing aliphatic compounds.[2] During our development of new versatile fluoroalkyl-containing building blocks, we were attracted by the fact that an enormous number of transformations (e.g. cyclopropanation, Wolff rearrangement, dipolar addition, dimerization, oxidation and ylide formation followed by sigmatropic rearrangement) occurred with the diazo carbonyl compounds, thus making them extremely versatile reactants.[3] Furthermore, the fast development of new chiral catalysts for diazo compounds makes the diazocarbonyls more useful in organic synthesis.[3] Due to the former reasons, in line with our search for new fluoroalkyl-containing synthons, our strategy has been to prepare appropriate fluoroalkyl-substituted 2-diazo-1,3-dicarbonyls and utilize them as precursors for carbenoid intermediates, which would enable us to synthesize a variety of fluoroalkyl-containing molecules with high regio- and chemoselectivity.

We have recently reported the 1,3-dipolar reactions of ethyl 2-diazo-fluoroalkylacetoacetate **1** with alkyl and aromatic nitriles to synthesize a series of 5-fluoroalkyl substituted oxazoles.[4] In an extension of this study, we now describe herein further synthetic utility of **1** in its rhodium(II)-catalyzed decomposition to produce, in situ, a fluoroalkyl-containing carbenoids which reacts with alkyl vinyl ethers to give fluoroalkyl-substituted dihydrofuroates. Since many molecules which contain one or more of a furan or dihydrofuran ring could be extensively used as agricultural and industrial organic chemicals,[5] synthesis of a series of fluoroalkyl-substituted dihydrofurans would be meaningful.

2. Results and discussions

Diazo compounds **1a–e** were easily prepared through simple diazo transfer reaction from 1,3-dicarbonyls.[4] **1a–c** were stable enough for storage at room temperature while **1d** and **e** would decompose partly during purification and storage,[4] so they must be freshly prepared before use. The different stability should be attributed to the different electron-withdrawing ability of the fluoroalkyl. Previously, Hoffmann et al. have reported that decomposition of **1a** in the presence of a catalytic amount of $Rh_2(OAc)_4$ in ethyl vinyl ether at 100°C in a sealed tube gave rise to ethyl 5-ethoxy-2-trifluoromethyl-4,5-dihydro-3-furancarboxylate in 92% yield.[6] However, the reactions of fluorinated 1,3-dicarbonyls with vinyl ethers have not been studied comprehensively. To demonstrate the general applicability of this approach, we have extended this rhodium-catalyzed reaction to the fluoroalkyl-substituted 2-diazo-1,3-dicarbonyls

Keywords: fluorinated diazo compounds; vinyl ethers; carbenoids; rhodium acetate; 1,3-dipolar cycloaddition.

* Corresponding author. Tel.: +86-21-6416-3300/3525; fax: +86-21-6416-6128; e-mail: zhusz@pub.sioc.ac.cn

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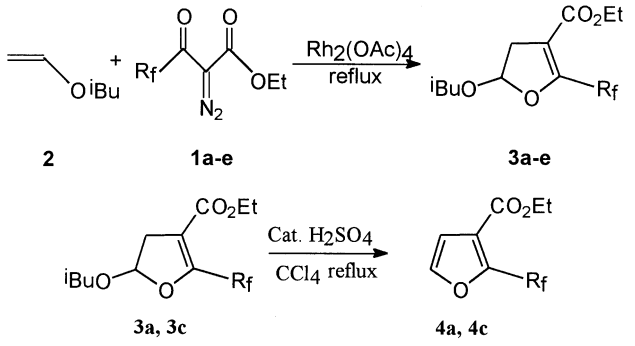
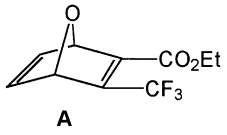


R_f = CF_3 (1a); CF_2Cl,(1b); CF_2Br (1c); C_3F_6Cl (1d); C_5F_{11} (1e).

Scheme 1.



A

Figure 1.

Table 1. Reaction results of fluorinated diazo compounds **1** with vinyl ethers

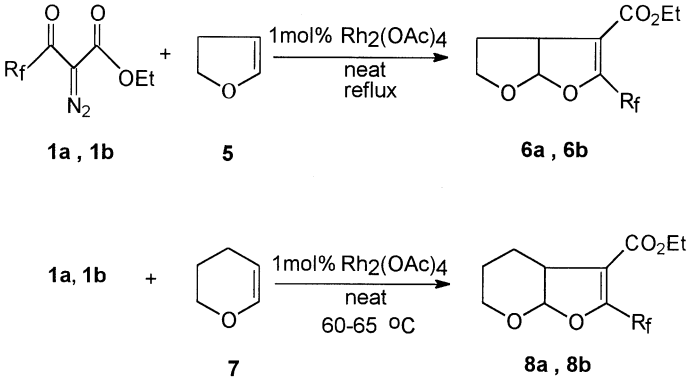
Entry	Diazo compounds	Vinyl ethers	Products	Yield (%)[a]
1	**1a**	**2**	**2a**	95
2	**1b**	**2**	**2b**	95
3	**1c**	**2**	**2c**	88
4	**1d**	**2**	**2d**	72
5	**1e**	**2**	**2e**	83
6	**1a**	**5**	**6a**	62
7	**1b**	**5**	**6b**	64
8	**1a**	**7**	**8a**	70
9	**1b**	**7**	**8b**	68

[a] Isolated yields of pure compounds.

1a–e. Similarly, the reactions of **1a–e** with isobutyl vinyl ethers catalyzed by 0.5 mol% of $Rh_2(OAc)_4$ gave dihydrofuroates **3a–e** in good to excellent yields (72–95%). The results indicated that different fluoroalkyl substituents on the diazo compounds, either trifluoromethyl or perfluoropentyl, exhibited little effect on the reaction yields. Meanwhile, **1d** and **e** gave slightly lower yields than those of **1a–c** because of their instability.

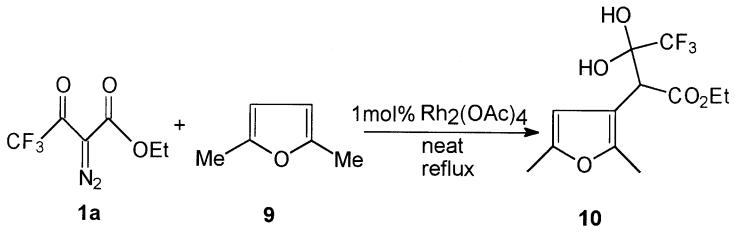
The dihydrofuroic esters **3a** and **c** could be further converted to α-fluoroalkyl-β-furoates **4a** and **c** by refluxing in carbon tetrachloride catalyzed by sulfuric acid in 45 and 38% yields, respectively (Scheme 1). Previously, the 3-ethoxycarbonyl-4-trifluoromethylfuran had been prepared through two different methods from 2-ethoxycarbonyl-3-fluoroalkyl-7-oxabicyclo[2.2.1]hepta-2,5-diene **A** (Fig. 1): one method reported by Cambon et al. was by thermolysis at 150°C in xylene of the Diels–Alder cycloaddition of compound **A** and tetracyclone in low yield (38%);[8a] the other method reported by Tipping et al. was controlled hydrogenation of compound **A** followed by the pyrolysis of the product at 400°C to give 3-ethoxycarbonyl-4-trifluoromethylfuran and ethylene,[8b] but these two methods required extremely severe conditions and the synthesis of 2-fluoroalkyl-3-ethoxycarbonylfurans had not been reported till now, so we had to provide a practical and direct method for the preparation of α-fluoroalkyl-β-furoates.

After success with the former reactions, we tried the rhodium(II)-catalyzed reactions of **1a–c** with cyclic enol ethers, such as dihydrofuran and 3,4-dihydro-2*H*-pyran. With **1a** and **b**, only 1,3-dipolar cycloaddition products **6** and **8** were isolated after the diazo compound was heated in neat cyclic enol ether in the presence of 1 mol% of $Rh_2(OAc)_4$ for about 20 h at 60°C. The reaction results are summarized in Table 1. The structures of **6** and **8** assigned to these substituted dihydrofurans were based on the ^1H NMR spectra, which were identical with those of their analogues (Scheme 2).[7] However, in the case of **1c**, bromodifluoromethyl acetyl diazoacetate, only a sticky polymeric substrate was obtained, but no expected cycloaddition compound was detected. We assumed that with heating **1c** might undergo a radical polymerization reaction with cyclic enol ethers initiated by the bromodifluoromethyl group. Nevertheless, when some radical inhibitors, such as hydroquinone and nitrosobenzene, were added to the reaction system to improve the reaction results, no encouraging results were observed. Further attempts by conducting the reaction in different solvents such as chloroform, hexane, and benzene also failed.



R_f = CF_3 (1a); CF_2Cl,(1b).

Scheme 2.

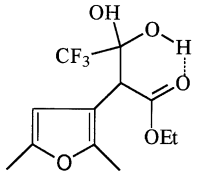


1a 9 10

Scheme 3.

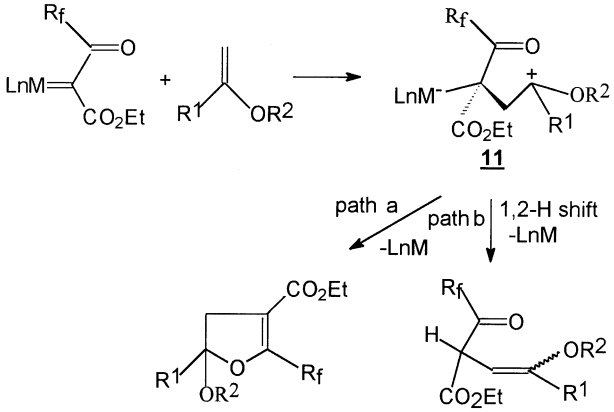
Earlier studies indicated that the copper- or rhodium(II)-catalyzed reaction of furan or mono-substituted furan with acyclic α-diazo carbonyl compounds underwent a cyclopropanation followed by a ring-opening process, to afford the *Z*–*E* diene adducts.[9] Meanwhile, the cyclic metal carbenoids, such as 2-diazo-1,3-cyclohexanedione, showed a distinct departure from the reactivity of acyclic diazo compounds by producing 1,3-dipolar cycloadducts rather than dienals. In addition, allylic or vinyl C–H insertion products were also detected by the reactions of a cyclic carbenoid with 2-methylfuran.[10] However, we observed a different result in our experiments. After **1a** was refluxed with 5 equiv. of 2,5-dimethylfuran in benzene or hexane in the presence of 1 mol% of $Rh_2(OAc)_4$ for 14 h, the only product isolated was 3-position vinyl C–H insertion product **10** (Scheme 3).

The structure assigned as **10** was based on its analytical and spectroscopic data: ^{19}F NMR spectrum, ^1H NMR spectrum, IR absorptions and the electron impact mass spectrum. Firstly, the ^{19}F NMR spectrum exhibited a single peak at +5.9 ppm (with TFA as external standard, and with upfield positive), which suggested the signal of a hydrated trifluoroacetyl.[11] Secondly, the peaks of chemical shift 4.79 and 4.65 in the ^1H NMR were easily exchanged by D_2O, which further suggested the presence of an active hydroxyl group. In addition, IR spectra also showed strong hydroxyl absorption at 3376 cm^{-1}, but no carbonyl group absorption was detected. Another proof was that the electron impact mass spectrum showed a molecular ion peak at 296, which matched with the molecular mass of **10** exactly. Moreover, there were no vinyl proton signals in the ^1H NMR spectrum, but only a distinctive peak of furan proton at chemical shift 6.03, which further confirmed the structure of **10** as vinyl hydrogen insertion product of carbenoid from **1a** to 2,5-dimethylfuran followed by hydration of the trifluoroacetyl. Previously, some aryltrifluoromethyl ketone was reported to form stable *gem*-diols, both for the inductive effects of the trifluoromethyl, and also for the intramolecular H-bond formation.[11] The stable **10** showed two nonequivalent OH



10

Figure 2.



Scheme 4.

groups in the ^1H NMR spectrum, suggesting an intramolecular interaction of one of its OH groups with the ethoxycarbonyl group, as shown in Fig. 2.

The mechanism of 1,3-dipolar ketocarbene addition with vinyl ethers had been represented as initial cyclopropanation followed by catalytic rearrangement.[12] However, we were prone to another interpretation of the accumulated results outlined in Scheme 4 to accommodate our experimental results.[13] Charge development in the metal carbenoid derived from **1**, followed by addition to the electron-rich alkenes, afforded a reaction intermediate **11** capable of reacting with the nucleophilic carbonyl oxygen to form dihydrofurans (path a) or by forming vinyl C–H insertion products by a 1,2-hydrogen transfer reaction (path b). According to this mechanism, when the carbenoid reacted with 2,5-dimethylfuran, the hydrogen transfer surpassed the dihydrofurans formation due to the steric factors, so only vinyl C–H insertion product **10** was yielded.

3. Conclusions

In this paper, we have studied the 1,3-dipolar reaction of 2-fluoroalkyl-substituted 1,3-dicarbonyls with vinyl ethers to synthesize a series of fluoroalkyl-containing dihydrofuroates. Moreover, ethyl 2-fluoroalkyl-3-furoates could be obtained easily by the acid-catalyzed alcohol elimination. Since a very important derivatization in the synthesis of biological active compounds consists of the introduction of perfluoroalkyl, especially trifluoroalkyl group, these easily available fluoroalkyl-containing diazo compounds will play an important role in the synthesis of fluoroalkyl-containing heterocycles.

4. Experimental

4.1. General

Melting points were measured in Temp-Melt apparatus. ^1H and ^{19}F NMR spectra were recorded on Varian-360L or Bruker AM-300 instruments with Me_4Si and TFA (with upfield positive) as internal and external standards, respectively. NMR spectra were recorded in chloroform-d unless otherwise stated. IR spectra were obtained with a Perkin Elmer 983G spectrophotometer using KBr disks of the compounds. Low mass spectrum was obtained with HP 5989a instrument. Elemental analyses were performed by this Institute. All reactions as well as column chromatography were monitored routinely with the aid of TLC or ^{19}F NMR spectroscopy. Benzene and hexane were dried over sodium wire; reagents were purified before use according to the standard methods. **1a–c** were prepared by diazo transfer reaction of ethyl fluoroalkylacetoacetate with tosyl azide. **1d,e** were prepared according to the procedures reported.[4]

4.2. General procedure for the reaction of perfluoroalkanesulfonyl azide with ethyl perfluoroalkylacetoacetate to prepare 2-diazo fluoroalkylacetoacetates 1d,e

A solution of ethyl fluoroalkylacetoacetate (ca. 1 mmol, 2 ml) and an equimolar amount of polyfluoroalkanesulfonyl azide in anhydrous diethyl ether at 0°C was treated dropwise with an equimolar amount of TEA. TLC analysis showed that the reaction was complete within 0.5 h. The solvent was evaporated and the residue was chromatographed on a silica column using petroleum ether–ether (6:1) as eluant; two products, ethyl 2-diazo-3-oxo-fluoroalkylacetoacetate and ethyl diazoacetate, were obtained, evaporated under vacuum and gave the pure compounds **1d,e** as light yellow oil.

4.3. General procedure for the reactions of diazo compounds with isobutyl vinyl ether

A solution of **1a** (0.420 g, 2.0 mmol) in isobutylvinyl ether (2 ml) was added over a 10 min period to a stirring, refluxing solution of $Rh_2(OAc)_4$ (4 mg, 1 mmol) in isobutylvinyl ether (2 ml), and the mixture then heated for another 20 min until ^{19}F NMR indicated completion of the reaction. The reaction mixture was concentrated under vacuum and chromatographed. Elution with petroleum ether–diethyl ether (15:1 v:v) yielded the ester **3a** (0.536 g, 1.9 mmol, 95%) as a colorless liquid.

4.3.1. Ethyl 2-trifluoromethyl-5-*iso*-butoxy-4,5-dihydro-3-furancarboxylate 3a. Colorless liquid: δ_H ($CDCl_3$): 5.65 (1H, dd, J=7.3, 3.0 Hz), 4.23 (2H, q, J=7.0 Hz), 3.24–3.61 (2H, m), 2.90–3.15 (2H, m), 1.90 (1H, m), 1.28 (3H, t, J=7.0 Hz), 0.93–0.97 (6H, m). δ_F ($CDCl_3$): −12.0 (s). ν_{max} (neat)/cm^{-1}: 1715s, 1661m, 1377–1153vs. m/z 282 (M^+, 0.66) 236 (M^+-HOEt, 7.50), 197 ($M^+-C_4H_9OC^+$, 27.95), 181 ($M^+-C_4H_9CO_2^+$, 15.58), 151 (M^++1−CO_2Et–$C_4H_9^+$, 12.91), 69 (CF_3^+, 3.94), 57 ($C_4H_9^+$, 100). (Found: C, 50.88; H, 6.20%. Calcd for $C_{12}H_{17}O_4F_3$: C, 51.06; H, 6.03%.)

4.3.2. Ethyl 2-chlorodifluoromethyl-5-*iso*-butoxy-4,5-dihydro-3-furancarboxylate 3b. Colorless liquid: δ_H ($CDCl_3$): 5.65 (1H, dd, J=7.2, 2.7 Hz), 4.22 (2H, q, J=7.0 Hz), 3.33–3.64 (2H, m), 2.89–3.25 (2H, m), 1.89 (1H, m), 1.30 (3H, t, J=7.0 Hz), 0.90–0.96 (6H, m). δ_F ($CDCl_3$): −24.3 (s). ν_{max} (neat)/cm^{-1}: 1714s, 1651m, 1331–1152vs. m/z 299 (M^+, 68.88), 254 (M^+-OEt, 17.06), 225 (M^+−1−CO_2Et, 67.55), 213 (M^+-CF_2Cl, 80.31), 57 ($C_4H_9^+$, 100). (Found: C, 48.27; H, 5.91%. Calcd for $C_{12}H_{17}ClO_4F_2$: C, 48.24; H, 5.70%.)

4.3.3. Ethyl 2-bromodifluoromethyl-5-*iso*-butoxy-4,5-dihydro-3-furancarboxylate 3c. Colorless liquid: δ_H ($CDCl_3$): 5.65 (1H, dd, J=7.2, 2.7 Hz), 4.21 (2H, q, J=7.0 Hz), 3.26–3.69 (2H, m), 2.90–3.25 (2H, m), 1.91 (1H, m), 1.29 (3H, t, J=7.0 Hz), 0.87–0.92 (6H, m). δ_F ($CDCl_3$): −28.3 (s). ν_{max} (neat)/cm^{-1}: 1715s, 1649m, 1373–1154vs. m/z 345/343 (M^++2/M^+, 4.03/4.75), 298 (M^+-OEt, 3.51), 269 (M^+−1−CO_2Et, 3.43), 57 ($C_4H_9^+$, 100). (Found: C, 42.33; H, 4.90%. Calcd for $C_{12}H_{17}O_4F_2Br$: C, 41.98; H 4.96%.)

4.3.4. Ethyl 2-(3-chloro-1,1,2,2,3,3-hexafluoropropyl)-5-*iso*-butoxy-4,5-dihydro-3-furancarboxylate 3d. Colorless liquid: δ_H ($CDCl_3$): 5.63 (1H, dd, J=7.2, 2.4 Hz), 4.24 (2H, q, J=7.0 Hz), 3.24–3.62 (2H, m), 2.9–3.2 (2H, m), 1.95 (1H, m), 1.25 (3H, t, J=7.0 Hz), 0.82–0.94 (6H, m). δ_F ($CDCl_3$): −10.1 (t), 34.2 (m), 43.1 (m). ν_{max} (neat)/cm^{-1}: 1708s, 1654m, 1358–1122vs. m/z 399 (M^+, 7.02), 325 (M^+−1−CO_2Et, 23.81), 267 (M^+−1−CO_2Et–$C_4H_{10}^+$, 20.05), 57 ($C_4H_9^+$, 100), 41 ($C_3H_5^+$, 45.13). (Found: C, 42.46; H, 4.67%. Calcd for $C_{14}H_{17}ClO_4F_6$: C, 42.16; H, 4.27%.)

4.3.5. Ethyl 2-perfluoropentyl-5-*iso*-butoxy-2,5-dihydro-3-furancarboxylate 3e. Colorless liquid: δ_H ($CDCl_3$): 5.62 (1H, dd, J=7.2, 2.0 Hz), 4.20 (2H, q, J=7.0 Hz), 3.26–3.56 (2H, m), 2.9–3.2 (2H, m), 1.86(1H, m), 1.24 (3H, t, J=7.0 Hz), 0.89–0.93 (6H, m). δ_F ($CDCl_3$): 3.40 (s), 35.2 (m), 55.2 (m), 59.0 (m). ν_{max} (neat)/cm^{-1}: 1705s, 1650m, 1350–1153vs. m/z 482 (M^+, 1.06), 436 (M^++1−OEt, 7.92), 409 (M^+−CO_2Et, 5.23), 351 (M^+−CO_2Et–$C_4H_9^+$, 44.34), 57 ($C_4H_9^+$, 100), 41 ($C_3H_5^+$, 28.93). (Found: C, 39.81; H, 3.55%. Calcd for $C_{16}H_{17}O_4F_{11}$: C, 39.83; H 3.53%.)

4.3.6. Ethyl 3-trifluoromethyl-2-furancarboxylate 4a. A solution of **3a** (0.8 g, 2.8 mmol) in carbon tetrachloride (5 ml) was added dropwise to a stirring mixture of concentrated sulfuric acid (0.2 g, 4 mmol) in carbon tetrachloride (65 ml) at reflux over a 3 h period, and the heating was continued for 2 h. Then the mixture was washed with water, 5% sodium bicarbonate solution and water, again dried with Na_2SO_4, and evaporated (temperature of water bath <30°C). Chromatography of the residue on silica gel and elution with 30:1 petroleum ether (30–60°C)–ether produced a light yellow liquid **4a** (0.239 g, 1.1 mmol) in 41% yield. δ_H ($CDCl_3$): 7.40 (1H, m), 6.70 (2H, m), 4.25 (2H, q, J=7.0 Hz), 1.23 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): −16.2 (s). ν_{max} (neat)/cm^{-1}: 1730s, 1601m, 1324–1149vs. m/z 208 (M^+, 1.06), 180 (M^++1−Et, 43.18), 163 (M^++1−OEt, 100), 135 (M^++1−CO_2Et, 10.33). (Found: 208.03147. HRMS calcd for $C_8H_7O_3F_3$: 208.03310.)

4.3.7. Ethyl 3-bromodifluoromethyl-2-furancarboxylate 4c. The same reaction and workup on **3c** (0.6 g,

1.7 mmol) yielded a light yellow liquid **4c** (0.175 g, 0.65 mmol) in 38% yield. δ_H ($CDCl_3$): 7.35 (1H, m), 6.73 (2H, m), 4.25 (2H, q, J=7.0 Hz), 1.25 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): −16.2 (s). ν_{max} (neat)/cm^{-1}: 1724s, 1592m, 1498m, 1313–1167vs. *m/z* 270/268 (M^++2/M^+, 10.95), 223 (M^+−1−OEt, 15.44), 195 (M^+−1−CO_2Et, 8.64), 189 (M^+−Br, 60.22), 161 (M^++1−C_2H_5−Br, 71.02), 141 (M^++2−$BrCF_2$, 100). (Found: C, 35.57; H, 2.79%. Calcd for $C_8H_7BrO_3F_2$: C, 35.70; H, 2.60%.)

4.4. General procedure for the reactions of diazo compounds with cyclic vinyl ethers

A solution of **1a** (0.210 g, 1 mmol) in 2,3-dihydrofuran (1.5 ml) was added over a 6 h period to a stirring, refluxing solution of $Rh_2(OAc)_4$ (4 mg, 1 mmol) and 2,3-dihydrofuran (1.5 ml), and the stirring continued for another 13 h. Then the mixture was concentrated. Chromatography and elution with petroleum ether–ethyl acetate (8:1 v:v) gave the ester **6a** (157 mg, 0.62 mmol, 62%) as a light yellow liquid.

4.4.1. Ethyl 3-trifluoromethyl-2,8-dioxabicyclo[3.3.0]oct-3-ene-4-carboxylate 6a. δ_H ($CDCl_3$): 6.25 (1H, d, J=6.0 Hz), 4.23 (2H, q, J=7.0 Hz), 3.90–4.20 (2H, m, OCH_2), 3.75 (1H, m), 2.21 (2H, m), 1.30 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): −13.3 (s). ν_{max} (neat)/cm^{-1}: 1715s, 1652m, 1381–1161vs. *m/z* 252 (M^+, 6.26), 206 (M^+−1−OEt, 100), 179 (M^+−CO_2Et, 28.81), 109 (M^+−1−CO_2Et−CF_3, 33.24), 81 ($C_2F_3^+$, 23.94), 69 (CF_3^+, 23.67). (Found: C, 47.64; H, 4.53%. Calcd for $C_{10}H_{11}O_4F_3$: C, 47.62; H, 4.37%.)

4.4.2. Ethyl 3-chlorodifluoromethyl-2,8-dioxabicyclo-[3.3.0]oct-3-ene-4-carboxylate 6b. δ_H ($CDCl_3$): 6.24 (1H, dd, J=6.0, 3.0 Hz), 4.25 (2H, q, J=7.0 Hz), 3.91–4.16 (2H, m, OCH_2), 3.78 (1H, m), 2.17 (2H, m), 1.30 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): −24.0 (s). ν_{max} (neat)/cm^{-1}: 17145s, 1635m, 1319–1144vs. *m/z* 269 (M^+, 40.73), 224 (M^+−OEt, 40.19), 183 (M^+−CF_2Cl, 28.81), 155 (M^+−CF_2Cl−OEt, 18.82), 109 (M^+−1−CF_2Cl−CO_2Et, 28.26). (Found: C, 44.89; H, 4.36%. Calcd for $C_{10}H_{11}O_4F_2Cl$: C, 44.69; H, 4.10%.)

4.4.3. Ethyl 3-trifluoromethyl-2,9-dioxabicyclo[4.3.0]-non-3-ene-4-carboxylate 8a. δ_H ($CDCl_3$): 5.94 (1H, d, J=7.5 Hz), 4.12 (2H, q, J=7.0 Hz), 3.85 (2H, m), 3.05–3.18 (1H, m), 1.6–2.1 (4H, m), 1.25 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): −12.6 (s). ν_{max} (neat)/cm^{-1}:1715s, 1647m, 1377–1111vs. *m/z* 266 (M^+, 9.65), 220 (M^+−1−OEt, 100), 192 (M^+−1−CO_2Et, 65.86), 169 (M^+−1−CO2Et−CF_3, 66.75), 69 (CF_3^+, 39). (Found: C, 49.34; H, 4.78%. Calcd for $C_{11}H_{13}O_4F_3$: C, 49.62; H, 4.89%.

4.4.4. Ethyl 3-chlorodifluoromethyl-2,9-dioxabicyclo-[4.3.0]non-3-ene-4-carboxylate 8b. δ_H ($CDCl_3$): 5.94 (1H, d, J=7.5 Hz), 4.25 (2H, q, J=7.0 Hz), 3.88 (2H, m), 3.17–3.30 (1H, m), 1.62–2.13 (4H, m), 1.29 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): −26.9 (s). ν_{max} (neat)/cm^{-1}: 1715s, 1647m, 1377–1111vs. *m/z* 285/283 (M^++2/M^+, 18.52/6.07), 238 (M^+−OEt, 38.00), 211 (M^++1−CO_2Et, 11.98), 123 (M^+−1−CO_2Et−CF_2Cl, 14.39. (Found: C, 46.85; H, 4.66%. Calcd for $C_{11}H_{13}O_4F_2Cl$: C, 46.72; H, 4.60%.)

4.4.5. Ethyl 2-(2,2,2-trifluoro-1,1-dihydroxyethyl)-3-furanacetate 10. A solution of **1a** (0.210 g, 1 mmol) in benzene (1.5 ml) was added over a 6 h period to a stirring, refluxing solution of $Rh_2(OAc)_4$ (4 mg, 1 mmol) and 2,5-dimethylfuran (1.5 ml), and the stirring continued for another 13 h. The mixture was concentrated. Chromatography and elution with 4:1 petroleum ether–ethyl acetate gave the ester **10** (0.157 g, 0.62 mmol, 62%) as a light yellow liquid. δ_H ($CDCl_3$): 6.03 (1H, s), 4.79 (1H, s), 4.65 (1H, s), 4.32 (1H, q, J=7.0 Hz), 3.90 (1H, s), 2.25 (6H, s), 1.25 (3H, t, J=7.0 Hz). δ_F ($CDCl_3$): +5.9 (s). ν_{max} (KBr)/cm^{-1}: 3376vs, 1699s, 1466m, 1438m, 1375–1020vs. *m/z* 296 (M^+, 8.18), 279 (M^++1−H_2O, 29.51), 205 (M^+−H_2O−CO_2Et, 23.82), 182 (M^+−CF_3CO_2H, 25.03). (Found: C, 48.81; H, 5.11%. Calcd for $C_{12}H_{15}O_5F_3$: C, 48.65; H, 5.07%.)

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References

1. Welch, J. T. *Selective Fluorination in Organic and Bioorganic Chemistry*; *ACS Symposium Series*; American Chemical Society: Washington, DC, 1991; p. 456.
2. Shi, G. Q.; Xu, Y. Y.; Xu, M. *Tetrahedron* **1991**, *47*, 1629–1648.
3. (a) Doyle, M. P.; Mckervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds, From Cyclopropanes to Ylides*; Wiley: New York, 1998. (b) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.
4. Wang, Y. L.; Zhu, S. Z. *J. Fluorine Chem.* **2000**, *103*, 139–144.
5. Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. In *Comprehensive Heterocyclic Chemistry, Vol. II*; Pergamon: Oxford, 1996; pp. 395–413.
6. Hoffmann, M. G.; Wenkert, E. *Tetrahedron* **1993**, *49*, 1057–1062.
7. Wenkert, E.; Ananthanaravan, T. P.; Ferreira, V. F.; Hoffmann, M. G.; Kim, H. *J. Org. Chem.* **1990**, *55*, 4975–4975.
8. (a) Nezis, A.; Fagn, J.; Cambon, A. *J. Fluorine Chem.* **1991**, *53*, 297–299. (b) Barlow, M.; Suliman, G.; Nadia, N. E.; Tipping, A. E. *J. Fluorine Chem.* **1995**, *70* (1), 59–69.
9. Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1124–1125.
10. Pirrung, M. C.; Zhang, J. C.; Lackey, K.; Sternbach, D. D.; Brown, F. *J. Org. Chem.* **1995**, *60*, 2112–2124.
11. (a) Salvador, R. L.; Saucier, M. T. *Tetrahedron* **1971**, *27*, 1221. (b) Guthrie, J. P. *Can. J. Chem.* **1975**, *53*, 898.
12. (a) Alonso, M. E.; Jano, P.; Hernandez, M. I.; Greenberg, R. S.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 3047–3050. (b) Alonso, M. E.; Morales, A.; Chitty, A. W. *J. Org. Chem.* **1982**, *47*, 3747–3754.
13. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds, From Cyclopropanes to Ylides*; Wiley: New York, 1998; pp. 206 (and references therein).