Fluorinated acetylenes. Part 9 [1]. Reaction of furan with the phenylethanoate esters derived from trifluoropropynyl secondary alcohols

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Abstract

The thermal reaction of furan with the ester $CF_3C{\equiv}CCHMeO_2CCH_2Ph$ (**2a**) (1.1:1 molar ratio) at 100 °C gives a mixture of Diels–Alder 1:1 (**3**) (51%), 2:1 (**4**) (20%) and 3:1 (**5**) (5%) adducts (each as two diastereomers). The 2:1 adducts are the *exo–endo* isomers arising from *exo*-addition to the least substituted double bond in the 1:1 adducts and the complete stereochemistry of both diastereomers has been established by X-ray crystallography; the 3:1 adducts are formed analogously by *exo*-addition to the 2:1 adducts. It is calculated that the 1:1 adduct diastereomers are initially formed in the ratio *c.* 55:45. Similarly, reaction of furan with the ester $CF_3C{\equiv}CCHPhO_2CCH_2Ph$ (**2b**) (*c.* 1.5:1 molar ratio) affords as major products the corresponding 1:1 (**10**) (44%) and 2:1 (**11**) (38%) adducts (each as two diastereomers).

Introduction

In a study of the chemistry of alkynes of type $CF_3C{\equiv}CR$ the reaction of furan with the ester ($R = CHMeO_2CMe$) was investigated, but the major product, a liquid, was not fully characterised although spectral data indicated it was probably a mixture of two hydrated 1:1 adduct isomers [1].

It was decided in the present work to re-investigate this reaction using a higher molecular weight ester, the phenylethanoate, in the hope that the products would be solids and their structures could be determined by X-ray crystallography.

Results and discussion

Treatment of the alcohol $CF_3C{\equiv}CCHMeOH$ (**1a**) [1] with the acid chloride $PhCH_2COCl$ gave the corresponding ester **2a** (80%).

Reaction of furan with ester **2a** (molar ratio *c.* 1.1:1.0) in dichloromethane at 100 °C over 9 d gave a mixture of three major components which were

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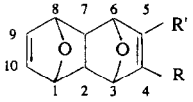
separated by DCFC to afford a hydrated, liquid 1:1 adduct (51%), a solid 2:1 adduct (20%) and a solid 3:1 adduct (5%) as shown by elemental analysis and their NMR and mass spectra. The NMR spectra indicated that the respective adducts each consisted of two isomers in the ratios 54:46; 56:44 and 59:41.

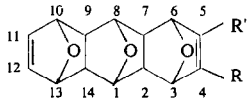
Careful separation by DCFC, taking early and late samples of each of the adducts, enabled pure samples to be obtained of both isomers of the 1:1 and 2:1 adducts and of the major isomer of the 3:1 adduct. The 1:1 adduct isomers were isolated as monohydrates and attempted dehydration ($MgSO_4$ and P_2O_5) using ethereal solutions of each isomer was unsuccessful.

The NMR (^1H, ^{13}C and ^{19}F) spectra of each 1:1 adduct isomer showed the presence of a 2,5-dihydrofuran ring, the ester $-CHMeO_2CCH_2Ph$ group and a $CF_3C{=}C$ grouping. This is consistent with the two diastereomeric adducts **3a** and **3b** each formed as a racemate.

Similarly, each 2:1 adduct isomer was shown (NMR) to contain a $-CH{=}CH-$ group, four ring CH−O and two tertiary hydrogens, the ester $-CHMeO_2CCH_2Ph$ group and a $CF_3C{=}C$ grouping, which is consistent with the two racemic diastereomers **4a** and **4b**. Furthermore, the isomers were identified as the expected *exo–endo* adducts from their ^1H spectra (including decoupling experiments) and a comparison of the coupling constants obtained with those of the *exo–endo* 2:1 adduct **6** formed from the reaction of furan with dimethyl acetylenedicarboxylate (DMAD) at 100 °C [2] (see Table 1).

In the *exo–endo* configuration, the dihedral angle between H-1 and H-2 (and H-7 and H-8) should be *c.* 45° leading to a coupling constant of *c.* 5 Hz as observed, while the dihedral angle between H-2 and H-3 (and H-6 and H-7) should be close to 90°; the lack of observed coupling is consistent with this.



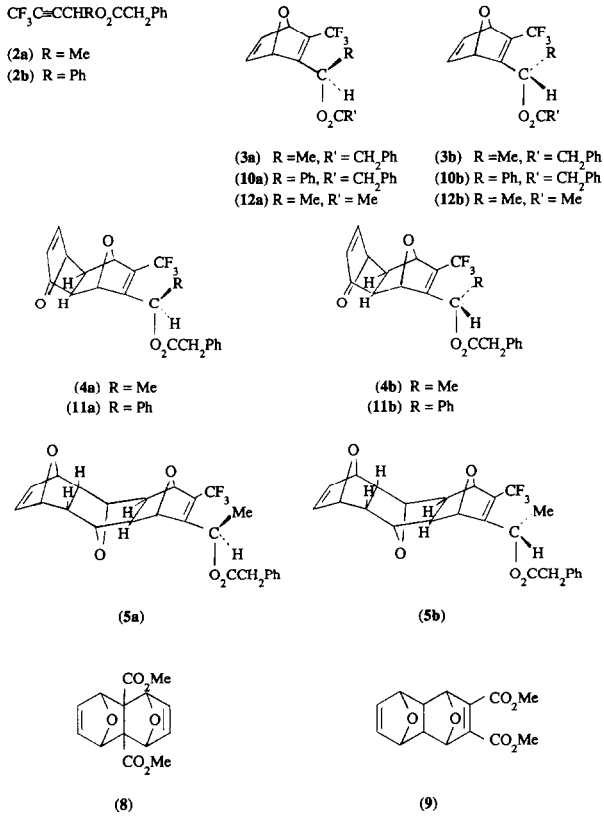


(**4**) R = CF_3, R′ = $CHMeO_2CCH_2Ph$ (**5a**) R = CF_3, R′ = $CHMeO_2CCH_2Ph$
(**6**) R = R′ = CO_2Me (**7**) R = R′ = CO_2Me

TABLE 1

2:1 Adduct coupling constant (Hz)				3:1 Adduct coupling constants (Hz)		
J	**4a**	**4b**	**6**	*J*	**5a**	**7**
9–10	6.0	5.0	6.0	2–3	4.5	4.9
1–10	1.5	1.0	1.8	6–7	4.5	4.9
8–9	1.5	1.0	1.8	8–9	5.5	5.6
2–7	7.5	7.0	7.5	1–14	5.5	5.6
1–2	5.0	[a]	4.9	9–14	8.5	8.7
7–8	5.0	[a]	4.9	2–7	7.5	7.3

[a]Broad, unresolved absorption.



Scheme 1.

These conclusions were confirmed by single-crystal X-ray studies [3], which showed that the major diastereomer had structure **4a** and the minor isomer structure **4b**.

The ^{1}H NMR data obtained for the major 3:1 adduct isomer **5a** is compared in Table 1 with that reported [2] for the *exo–endo–exo* 3:1 adduct **7** formed from the reaction of furan with DMAD, thus establishing the stereochemistry.

A sample of the separated major 1:1 adduct isomer on reaction with furan (1:1 molar ratio) at 100 °C gave the unchanged 1:1 adduct (20% recovered), the 2:1 adduct **4a** (*c.* 77%), the major 3:1 adduct isomer (*c.* 18%) and several minor components. This reaction established that the major 1:1 and 3:1 adduct diastereomers had structures **3a** and **5a**, respectively.

It can therefore be calculated that in the reaction of furan with ester **2a** the 1:1 adduct diastereomers **3a** and **3b** are formed in the ratio *c.* 55:45. Models did not indicate why the diastereomer **3a** should be favoured.

It is well established that in a number of Diels–Alder reactions involving unsymmetrical oxanorbornadienes, the cycloadducts formed at room temperature are different from those obtained at elevated temperature [4–6].

At room temperature, addition is kinetically controlled and involves the most substituted double bond of the dienophile, whilst at elevated temperature the thermodynamically stable products are formed via addition to the least substituted double bond, e.g. the 2:1 adducts **8** and **9** are formed from the reaction of furan with DMAD at 20 °C and 100 °C, respectively [6]. In the present study, evidence was not obtained for reactions involving the most substituted double bond of the 1:1 adduct **3**.

The hydrated 1:1 adducts **3a** and **3b** were sticky oils and so it was decided to prepare the phenylethanoate ester **2b** of the phenyl-substituted alcohol $CF_3C{\equiv}CCHPhOH$ (**1b**) [7] and investigate the reaction with furan, in the hope that hydrated, solid, diastereomeric 1:1 adducts would be formed that could be separated and their structure determined (especially the position of hydration).

The ester **2b** (82%) was prepared by reaction of phenylethanoyl chloride with the corresponding alcohol, and a mixture of furan and ester **2b** (1.5:1.0 molar ratio) in dichloromethane heated at 100 °C over 10 d afforded a mixture of two major and several minor components. The major components were separated by DCFC and identified as a monohydrated 1:1 adduct **10** (44%) and a 2:1 adduct **11** (38%); the adducts were each present as a mixture of diastereomers in the ratio 52:48 and 51:49, respectively (^1H and ^{19}F NMR spectroscopy).

Sufficient purification of the diastereomers was achieved to enable NMR assignments to be made to the individual isomers and to establish that they had analogous structures to the 1:1 and 2:1 adduct isomers obtained from ester **2a**. It was assumed that the major isomers had structures **10a** and **11a**. Unfortunately, the 1:1 adduct isomers were also sticky oils and X-ray crystallographic studies could not be carried out.

The results obtained in this study indicate that the products formed from the reaction of furan with the ethanoate $CF_3C{\equiv}CCHMeO_2CMe$, and which were not fully characterised [1], were the diastereomeric 1:1 adducts **12a** and **12b**.

Experimental

Starting materials

The alcohols $CF_3C{\equiv}CHROH$ (**1a**) R = Me [1] and (**1b**) R = Ph [7] were prepared by treatment of the salt $CF_3C{\equiv}CLi$ with the appropriate aldehyde followed by acidification.

General techniques

Reaction products were purified and reaction product mixtures were separated by dry column 'flash' chromatography (DCFC) using silica gel (60H Merck GF_{256}) purchased from BDH Chemicals, Ltd.

^1H nuclear magnetic resonance spectra (NMR) were run on a Bruker AC (300 MHz) FT spectrometer, ^{13}C broad-band decoupled NMR spectra

(including DEPT 135°) were recorded on the Bruker AC machine (at 75.0 MHz) and ^{19}F NMR spectra were recorded on a Perkin-Elmer R32 (84.6 MHz) spectrometer. The spectra were run on solutions ($CDCl_3$) with internal tetramethylsilane (TMS) and external trifluoroacetic acid (TFA) used as the respective references; chemical shifts to low field to the reference are designated positive.

Infrared (IR) spectra were recorded on a Perkin-Elmer 783 spectrometer using KBr discs for solid samples and CsI plates for liquid films.

Low-resolution [electron impact (EI) or chemical ionisation (CI) as noted in the text] mass spectra were run on Kratos MS 45 or MS 25 instruments operating at 70 eV, and high-resolution spectra (accurate mass measurement) were recorded on a Kratos Concept 1S mass spectrometer.

X-Ray crystallography used Rigaka AFC 65 and CAD-4 diffractometers.

Melting points are uncorrected.

Reactions of acetylenic alcohols with phenylethanoyl chloride

*(a) 5,5,5-Trifluoropent-3-yn-2-ol (**1a**)*

Phenylethanoyl chloride (3.36 g, 21.75 mmol) was added dropwise to the stirred alcohol **1a** (2.00 g, 14.5 mmol) under an atmosphere of nitrogen at room temperature and the mixture was then heated at 60–70 °C (6 h) until evolution of hydrogen chloride had ceased. The excess of phenylethanoyl chloride was removed on a rotary evaporator and the residue was purified by DCFC [eluant: light petroleum–CH_2Cl_2 (1:1 v/v)] to afford 5,5,5-trifluoropent-3-yn-2-yl phenylethanoate (**2a**) (nc) (2.97 g, 11.6 mmol, 80%) (Analysis: Found: C, 60.7; H, 4.5; F, 22.1%; mol. wt., 256. $C_{13}H_{11}F_3O_2$ requires: C, 60.9; H, 4.3; F, 22.3%; mol. wt. 256). ^1H NMR δ: 7.30 (mult., 5H, C_6H_5); 5.48 (broad, 1H, O–C*H*Me); 3.55 (s, 2H, CH_2); and 1.40 (d, 3H, CH_3, $J = 6.5$ Hz) ppm. ^{19}F NMR δ: +27.20 (d, $CF_3C{\equiv}C$, $J_{CH-CF} = 3.0$ Hz) ppm. ^{13}C NMR δ: 170.0 (s, O–C=O); 133.1 (s, *ipso*-C_6H_5); 129.1, 128.6 and 127.3 (3s, *o*-, *m*- and *p*-C_6H_5); 113.8 (q, CF_3, $^1J = 257$ Hz); 85.0 (q, $CF_3C{\equiv}C$, $^3J = 6$ Hz); 72.6 (q, $CF_3C{\equiv}C$, $^2J = 56$ Hz); 59.1 (s, CH–O); 40.8 (s, CH_2); and 19.9 (s, CH_3) ppm. IR ($\nu_{max.}$): 3040 (w, arom. C–H str.); 2940 (w, aliph. C–H str.); 2285 (m, C≡C str.); 1750 (s, C=O str.); 1600 and 1500 (m, arom, C=C str.); 1285 (s, C–F str.); 1145 and 1040 (s, C–O str.); and 750 and 700 (m, arom. C–H out-of-plane def.) cm^{-1}. Mass spectrum *m/z*: 256 (16.3%, M^+); 121 [3.6, $(M - PhCH_2CO)^+$]; 119 (3.5, $C_7H_7CO^+$); 101 (5.2, $C_5H_3F_2^+$); 91 (100.0, $C_7H_7^+$); 51 (5.2, $C_4H_3^+$); and 39 (5.5, $C_3H_3^+$).

*(b) 1-Phenyl-4,4,4-trifluorobut-2-yn-1-ol (**1b**)*

Treatment of the alcohol **1b** (3.80 g, 19.0 mmol) with phenylethanoyl chloride (4.41 g, 28.5 mmol) as described in the previous experiment gave material (7.40 g) which was purified by DCFC [eluant: light petroleum–CH_2Cl_2 (2:1 v/v)] to give 1-phenyl-4,4,4-trifluorobut-2-yn-1-yl phenylethanoate (**2b**) (nc) (4.95 g, 15.6 mmol, 82%) (Analysis: Found: C, 68.2; H, 4.0; F, 17.9%; mol. wt., 318. $C_{18}H_{13}F_3O_2$ requires: C, 67.9; H, 4.1; F, 17.9%; mol. wt., 318). ^1H NMR δ: 7.42–7.10 (mult., 10H, 2 C_6H_5); 6.48 (q, 1H, CH–O,

J_{CF-CH} = 4.5 Hz); and 3.50 (s, 2H, CH_2) ppm. ^{19}F NMR δ: +27.6 (d, $CF_3C{\equiv}C$, J_{CH-CF} = 4.5 Hz) ppm. ^{13}C NMR δ: 169.7 (s, O−C=O); 134.3 and 132.9 (2s, 2 *ipso*-C_6H_5); 129.5, 129.1, 128.8, 128.5, 127.5 and 127.2 (6s, *o*-, *m*- and *p*-C_6H_5); 113.9 (q, CF_3, ^1J = 258 Hz); 83.5 (q, $CF_3C{\equiv}C$, ^3J = 6 Hz); 73.5 (q, $CF_3C{\equiv}C$, ^2J = 53 Hz); 64.4 (s, CH−O); and 40.6 (s, CH_2) ppm. IR ($\nu_{max.}$): 3080 and 3040 (w, arom. C−H str.); 2940 (w, aliph. C−H str.); 2280 (m, C≡C str.); 1750 (s, C=O str.); 1610 and 1500 (m, arom. C=C str.); 1290 and 1240 (s, C−F str.); 1150 (s, C−O str.); and 760 and 700 (m, arom. C−H out-of-plane def.) cm^{-1}. Mass spectrum *m/z*: 318 (10.9%, M^+); 183 [30.0, $(M-PhCH_2CO_2)^+$]; 182 [7.6, $(M-PhCH_2CO_2H)^+$]; 133 (10.8, $C_9H_6F^+$); 91 (100.0, $C_7H_7^+$); 77 (7.3, $C_6H_5^+$); 51 (4.5, $C_4H_3^+$); and 29 (37.2, CHO^+).

*Reaction of 5,5,5-trifluoropent-3-yn-2-yl phenylethanoate (**2a**) with furan*

A mixture of ester **2a** (4.03 g, 15.7 mmol) and furan (1.16 g, 17.1 mmol) in dichloromethane (10 cm^3), contained in a Rotaflo tube (*c.* 30 cm^3), was heated *in vacuo* at 100 °C for 9 d. Removal of the solvent (rotary evaporator) gave a residue (5.2 g) which was shown by TLC [eluant: light petroleum–CH_2Cl_2 (1:2 v/v)] to contain three major components (R_F, 0.70; 0.16; and 0.01). The products were separated by repeated DCFC with the first component eluted with light petroleum–CH_2Cl_2 (1:2 v/v), the second with CH_2Cl_2 (R_F, 0.38) and the third with $CH_3CO_2Et-CH_2Cl_2$ (1:24 v/v; R_F, 0.40); unchanged ester **2a** (0.52 g, 2.03 mmol, 13% recovered) was eluted before the first product component.

(i) The first product was identified as a mixture of monohydrates of the two diastereomers (ratio 54:46; ^1H NMR) of the 1:1 adducts **3** (2.75 g, 8.0 mmol, 51%). Pure samples of the two isomers were obtained by repeated DCFC (same eluant) from the early and late fractions, respectively. The first eluted isomer was identified as a monohydrate of 2-[phenylacetoxy)ethyl]-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene (**3a**) (nc) (0.92 g, 2.7 mmol, 17%) (Analysis: Found: C, 60.0; H, 4.6; F, 16.4%; mol. wt., 342. $C_{17}H_{15}F_3O_3 \cdot H_2O$ requires: C, 59.6; H, 5.0; F, 16.7%; mol. wt., 342). ^1H NMR δ: 7.25 (mult., 5H, C_6H_5); 6.95 (dd, 1H, =CH, J = 5.5 and 2.0 Hz); 6.35 (dd, 1H, =CH, J = 5.5 and 2.0 Hz); 5.85 (qd, 1H, Me*CH*−O, J = 6.5 and 1.0 Hz); 5.35 (broad, 1H, >CH−O); 5.30 (broad, 1H, >CH−O); 3.53 (s, 2H, CH_2); and 1.43 (d, 3H, CH_3, J = 6.5 Hz) ppm. ^{19}F NMR δ: +15.90 (s, $CF_3C{=}C$) ppm. ^{13}C NMR δ: 169.6 (s, O−C=O); 160.9 (q, $CF_3C{=}C$, ^3J = 5 Hz); 143.1 and 142.3 (2s, CH=CH); 138.4 (q, $CF_3C{=}C$, ^2J = 36 Hz); 133.6 (s, *ipso*-C_6H_5); 129.1, 128.5 and 127.2 (3s, *o*-, *m*- and *p*-C_6H_5); 123.0 (q, CF_3, ^1J = 268 Hz); 83.4 and 82.1 (2s, 2 ring CH−O); 65.5 (s, CH−O); 41.1 (s, CH_2); and 19.2 (s, CH_3) ppm. IR ($\nu_{max.}$): 3040 (w, arom. C−H str.); 2940 (w, aliph. C−H str.); 1745 (s, C=O str.); 1500 (m, arom. C=C str.); 1245 (s, C−F str.); 1160 and 1120 (s, C−O str.); and 710 (s, arom. C−H out-of-plane def.) cm^{-1}. Mass spectrum *m/z*: 342 [0.6% $(M+H_2O)^+$]; 324 (0.5, M^+); 205 (9.5, $C_9H_8F_3O_2^+$); 193 (35.1, $C_{10}H_6FO_3^+$); 189 (16.7, $C_9H_8F_3O^+$); 163 (22.4, $C_{10}H_{11}O_2^+$); 161 (27.8, $C_7H_4F_3O^+$); 141 (23.8, $C_7H_3F_2O^+$); 136

(39.4, $C_8H_8O_2^+$); 119 (33.1, $C_8H_7O^+$); 91 (100.0, $C_7H_7^+$); 51 (27.2, $C_4H_3^+$); and 29 (41.0, CHO^+).

The second eluted isomer was also identified as a monohydrate of 2-[(phenylacetoxy)ethyl]-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene (**3b**) (nc) (0.53 g, 1.55 mmol, 10%) (Analysis: Found: C, 59.4; H, 4.9; F, 16.4%; mol. wt., 342. $C_{17}H_{15}F_3O_3 \cdot H_2O$ requires: C, 59.6; H, 5.0; F, 16.7%; mol. wt., 342). ^{1}H NMR δ: 7.25 (mult., 5H, C_6H_5); 7.10 (dd, 1H, =CH, J=5.0 and 2.0 Hz); 7.05 (dd, 1H, =CH, J=5.0 and 2.0 Hz); 5.95 (qd, 1H, MeC*H*—O, J=6.5 and 1.0 Hz); 5.60 (broad, 1H, >CH—O); 5.30 (broad, 1H, >CHO); 3.60 (s, 2H, CH_2); and 1.15 (d, 3H, CH_3, J=6.5 Hz) ppm. ^{19}F NMR δ: +15.90 (s, CF_3C=C) ppm. ^{13}C NMR δ: 170.0 (s, O—C=O); 160.5 (q, CF_3C=*C*, ^3J=5 Hz); 143.4 and 142.8 (2s, CH=CH); 138.4 (q, CF_3*C*=C, ^2J=36 Hz); 133.5 (s, *ipso*-C_6H_5); 129.2, 128.7 and 127.2 (3s, *o*-, *m*- and *p*-C_6H_5); 123.0 (q, CF_3, ^1J=268 Hz); 82.5 and 82.1 (2s, 2 ring CH—O); 65.2 (s, CH—O); 41.0 (s, CH_2); and 16.5 (s, CH_3) ppm. IR ($\nu_{max.}$): 3040 (w, arom. C—H str.); 2940 (w, aliph. C—H str.); 1740 (s, C=O str.); 1500 (m, arom. C=C str.); 1255 (s, C—F str.); 1160 and 1135 (s, C—O str.); and 710 (s, arom. C—H out-of-plane def.) cm^{-1}. Mass spectrum *m/z*: 342 [0.2%, $(M+H_2O)^+$]; 324 (0.1, M^+); 221 (2.0, $C_{12}H_7F_2O_2^+$); 205 (3.1, $C_9H_8F_3O_2^+$); 189 (4.3, $C_9H_8F_3O^+$); 163 (9.6, $C_{10}H_{11}O_2^+$); 136 (6.5, $C_8H_8O_2^+$); 119 (7.1, $C_8H_7O^+$); 118 (10.2, $C_8H_6O^+$); 91 (100.0, $C_7H_7^+$); 90 (4.2, $C_7H_6^+$); 77 (3.3, $C_6H_5^+$); 69 (3.1, CF_3^+); and 65 (7.7, $C_5H_5^+$).

Attempts to remove water from the 1:1 adducts by treatment of solutions in ether with $MgSO_4$ and P_2O_5 were unsuccessful.

(ii) The second product, a white crystalline solid, was identified as a mixture of two diastereomers of the 2:1 adduct **4** (1.20 g, 3.1 mmol, 20%) in the ratio 56:44 (^{1}H NMR). The isomers were separated by DCFC (eluant: CH_2Cl_2) and the first isomer eluted was identified as *exo–endo*-4-[(phenylacetoxy)ethyl]-5-trifluoromethyl-11,12-dioxatetracyclo[6.2.1.1.^{3,6}0^{2,7}]dodeca-4,9-diene (**4a**) (nc) (0.60 g, 1.5 mmol, 10%) (Analysis: Found: C, 64.3; H, 5.0; F, 14.2%; mol. wt., 392. $C_{21}H_{19}F_3O_4$ requires: C, 64.3; H, 4.8; F, 14.5%; mol. wt., 392), m.p. 118 °C, by an X-ray crystallographic study [3]. The minor second isomer eluted was recrystallised [light petroleum–CH_2Cl_2 (3:1 v/v)] and was also identified as *exo–endo*-4-[(phenylacetoxy)ethyl]-5-trifluoromethyl-11,12-dioxatetracyclo[6.2.1.1.^{3,6}O^{2,7}]dodeca-4,9-diene (**4b**) (nc) (0.51 g, 1.3 mmol, 8%) (Analysis: Found: C, 64.1; H, 4.9; F, 14.3%; mol. wt., 392. $C_{21}H_{19}F_3O_4$ requires: C, 64.3; H, 4.8; F, 14.5%; mol. wt., 392), m.p. 93 °C, by an X-ray crystallography study [3].

Spectral details: major isomer (minor isomer). ^{1}H NMR ($CDCl_3$) δ: 7.30 (7.35) (mult., 5H, C_6H_5), 6.25 (6.30) [dd, 1H, =CH (10), J_{9-10}=6.0 (5.0), J_{1-10}=1.5 (0.8) Hz]; 6.20 (6.10) [dd, 1H, =CH (9), J_{10-9}=6.0 (5.0), J_{8-9}=1.5 (0.8) Hz]; 5.90 (5.75) [qd, (q), 1H, MeC*H*—O, J_{Me-H}=6.5 (6.5), J_{3-H}=1.5 Hz]; 4.75 (4.55) [dd, (broad), 1H, H-1, J_{2-1}=5.0, J_{10-1}=1.5 Hz]; 4.55 (4.75) [broad (broad), 1H, H-3]; 4.45 (4.75) [broad (broad), 1H, H-6]; 4.40 (4.30) [dd, (broad), 1H, H-8, J_{7-8}=5.0, J_{9-8}=1.5 Hz]; 3.63 (3.56) [s, (s), 2H, CH_2]; 2.68 (2.65) [dd, (broad), 1H, H-2, J_{7-2}=7.5, J_{1-2}=5.0 Hz]; 2.28 (2.65) [dd

(broad), 1H, H-7, $J_{2-7}=7.5$, $J_{8-7}=5.0$ Hz]; and 1.40 (1.35) [d, (d), 3H, CH_3, $J_{H-Me}=6.5$ Hz] ppm. ^{19}F NMR δ: +18.4 (+19.0) [s (s), $CF_3C=C$] ppm. ^{13}C NMR δ: 170.5 (169.8) (s, O−C=O); 156.0 (155.6) [q, $CF_3C=C$, $^3J=5(4)$ Hz]; 134.4 (133.2) [q, $CF_3C=C$, $^2J=35$ (34) Hz]; 134.1 (133.4) (s, *ipso*-C_6H_5); 129.8, 129.3, and 128.0 (129.0, 128.3 and 126.9) (3s, *o*-, *m*- and *p*-C_6H_5); 123.0 (122.2) [q, CF_3, $^1J=268$ (270) Hz]; 79.1, 79.0, 78.5 and 77.7 (78.2, 78.0, 77.2 and 77.1) (4s, 4 ring CH−O); 65.9 (65.5) (s, side-chain CH−O); 49.0 and 47.9 (48.6 and 47.7) (2s, 2 ring CH); 42.2 (40.9) (s, CH_2); and 20.5 (19.2) (s, CH_3) ppm. IR ($\nu_{max.}$): 3040 (m, arom. C−H str.); 2990 and 2970 (w, aliph. C−H str.); 1745 (1735) (s, C=O str.); 1675 (1680) (m, CH=CH str.); 1500 (m. arom. C=C str.); 1260 (1255) (s, C−F str.); 1160, 1115 and 1070 (1170 and 1110) (s, C−O str.); and 700 (m, arom. C−H out-of-plane def.) cm^{-1}. Mass spectrum *m/z*: 392 [0.0% (5.4), M^+]; 375 [0.8 (3.7), $(M-OH)^+$]; 257 [0.4 (83.8), $(M-PhCH_2CO_2)^+$]; 256 [1.9 (37.9), $(M-PhCH_2CO_2H)^+$]; 239 [7.4 (100.0), $C_{12}H_9F_2O_3^+$]; 189 [2.8 (13.7), $C_8H_4F_3O_2^+$]; 163 [12.0 (45.0), $C_{10}H_{11}O_2^+$]; 136 [1.9 (25.3), $C_8H_8O_2^+$]; 91 [100.0 (77.3), $C_7H_7^+$]; 68 [26.0 (16.6), $C_4H_4O^+$]; and 51 [4.9 (22.1), $C_4H_3^+$].

(iii) The final product was identified as a mixture of the two diastereomers of the 3:1 adduct **5** (0.38 g, 0.80 mmol, 5%) in the ratio 59.41 (^{19}F NMR: δ +19.1 and +15.8 ppm). On attempted separation of the isomers by DCFC [eluant: CH_3CO_2Et–CH_2Cl_2 (1:24 v/v)], only the major isomer could be obtained pure and this was identified as *exo–endo–exo*-4-[phenylacetoxy)ethyl]-5-trifluoromethyl-15,16,17-trioxahexacyclo[6.6.1.1.^{3,6}1.^{10,13}0.^{2,7}0^{9,14}]heptadeca-4,11-diene (**5a**) (nc) (0.12 g, 0.25 mmol, 2%) (Analysis: Found: C, 65.6; H, 4.9; F, 12.5%; mol. wt., 460.1509. $C_{25}H_{23}F_3O_5$ requires: C, 65.2; H, 5.0; F, 12.5%; mol. wt., 460.1497). ^1H NMR δ: 7.45–7.25 (mult., 5H, C_6H_5); 6.25 (broad, 2H, CH=CH); 5.85 (qd, 1H, MeC*H*=O, $J_{Me-H}=6.5$, $J_{3-H}=1.5$ Hz); 4.80 (broad d, 2H, H-3 and H-6, J_{2-3} and $J_{7-6}=4.5$ Hz); 4.75 and 4.70 (2s, 2H, H-10 and H-13); 4.05 (d, 1H, H-1, $J_{14-1}=5.5$ Hz); 3.65 (d, 1H, H-8, $J_{9-8}=5.5$ Hz); 3.60 (s, 2H, CH_2); 2.60 (dd, 1H, H-2, $J_{7-2}=7.5$, $J_{3-2}=4.5$ Hz); 2.50 (dd, 1H, H-7, $J_{2-7}=7.5$, $J_{6-7}=4.5$ Hz); 2,45 (dd, 1H, H-14, $J_{9-14}=8.5$, $J_{1-14}=5.5$ Hz); 2.10 (dd, 1H, H-9, $J_{14-9}=8.5$, $J_{8-9}=5.5$ Hz); and 1.42 (d, 3H, CH_3, $J_{H-Me}=6.5$ Hz) ppm. ^{19}F NMR δ: +19.1 (s, $CF_3C=C$) ppm. ^{13}C NMR δ: 170.6 (s, O−C=O); 156.3 (q, $CF_3C=C$, $^3J=4$ Hz); 135.1 and 134.9 (2s, CH=CH); 134.6 (q, $CF_3C=C$, $^2J=35$ Hz); 134.2 (s, *ipso*-C_6H_5); 130.0, 129.4 and 128.0 (3s, *o*-, *m*- and *p*-C_6H_5); 122.9 (q, CF_3, $^1J=269$ Hz); 78.7 (s, ring CH−O, C-3); 77.9 (q, ring CH−O, C-6, $^3J=2$ Hz); 80.2, 80.1, 75.5 and 75.4 (4s, 4 ring CH−O); 66.1 (s, side-chain CH−O); 52.9 and 52.0 (2s, 2CH, C-2 and C-7); 46.3 and 46.2 (2s, 2CH, C-9 and C-14); 42.3 (s, CH_2); and 20.7 (s, CH_3) ppm. IR ($\nu_{max.}$): 3090 and 3040 (w, arom. C−H str.); 2960 and 2930 (w, aliph. C−H str.); 1740 (s, C=O str.); 1680 (m, CH=CH str.); 1500 (m, arom. C=C str.); 1250 (s, C−F str.); 1160, 1120 and 1110 (s, C−O str.); and 700 (m, arom. C−H out-of-plane def.) cm^{-1}. Mass spectrum (CI, NH_3) *m/z*: 478 [27.2%, $(M+NH_4)^+$]; 461 (12.5, $(M+H)^+$]; 341 [17.5, $(M-PhCH_2CO)^+$]; 325 [100.0,

$(M-PhCH_2CO_2)^+$]; 315 (20.3, $C_{15}H_{14}F_3O_4^+$); 154 (48.8, $C_8H_7FO_2^+$); 145 (65.8, $C_{10}H_9O^+$); 108 (27.5, $C_7H_8O^+$); 91 (38.9, $C_7H_7^+$); and 68 (31.8, $C_4H_4O^+$).

Reaction of 2-[(phenylacetoxy)ethyl]-3-trifluoromethyl-7-oxabicyclo-[2.2.1]hepta-2,5-diene isomer ***3a*** *with furan*

A mixture of the 1:1 adduct **3a** (0.50 g, 150 mmol) and furan (0.10 g, 1.47 mmol) in dichloromethane (2 cm^3) was heated *in vacuo* in a Rotaflo tube (*c.* 25 cm^3) at 100 °C for 10 d. After removal of the solvent *in vacuo*, the residue (0.60 g) was shown by ^1H, ^{19}F and ^{13}C NMR spectroscopy to contain the unchanged 1:1 adduct **3a** (20% recovered), the 2:1 adduct **4a** (*c.* 77%), the 3:1 adduct **5a** (*c.* 18%) and minor components (*c.* 5%).

*Reaction of 1-phenyl-4,4,4-trifluorobut-2-yn-1-yl phenylacetate (****2b****) with furan*

A mixture of the ester **2b** (5.33 g, 16.76 mmol) and furan (1.66 g, 24.41 mmol) in dichloromethane (10 cm^3) was heated *in vacuo* in a Rotaflo tube (*c.* 30 cm^3) at 100 °C for 10 d. After removal of the solvent *in vacuo*, the residue (6.98 g) was shown by TLC methods [eluant: light petroleum–CH_2Cl_2 (1:2 v/v)] to contain two major (R_F, 0.72 and 0.45) and a number of minor components. The two major components were separated by DCFC (same eluant) and were identified as follows.

(i) A mixture of monohydrates of the two diastereomers of 2-[(phenylacetoxy)benzyl]-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene (**10**) (nc) (2.82 g, 7.31 mmol, 44%) (Analysis: Found: C, 65.1; H, 4.4; F, 14.4%; mol. wt., 404.1473. $C_{22}H_{17}F_3O_3 \cdot H_2O$ requires: C, 65.3; H, 4.7; F, 14.1%; mol. wt., 404.1458) present in the ratio 52:48 (^1H NMR). IR ($\nu_{max.}$: 1730 (s, C=O str.); 1250 (s, C–F str.); and 1170 and 1125 (s, C–O str.) cm^{-1}. Mass spectrum *m/z*: 404 [53.1%, $(M+H_2O)^+$]; 386 (19.0, M^+); 268 [22.7, $(M-PhCO_2H)^+$]; 267 (8.0, $C_{14}H_{10}F_3O_2^+$); 251 (53.1, $C_{14}H_{10}F_3O^+$); 242 (13.6, $C_{12}H_9F_3O_2^+$); 225 (42.8, $C_{15}H_{13}O_2^+$); 108 (39.0, $C_7H_8O^+$); and 91 (100.0, $C_7H_7^+$).

(ii) A mixture of two diastereomers of 4-[(phenylacetoxy)benzyl]-5-trifluoromethyl-11,12-dioxatetracyclo[6.2.1.1.^{3,6}0^{2,7}]dodeca-4,9-diene (**11**) (nc) (2.92 g, 6.29 mmol, 38%) (Analysis: Found: C, 68,4; H, 4.6; F, 12.8%; mol. wt., 454. $C_{26}H_{21}F_3O_4$ requires: C, 68.7; H, 4.6; F, 12.6%; mol. wt., 454) present in the ratio 51:49 (^1H and ^{19}F NMR). IR ($\nu_{max.}$): 1730 (s, C=O str.); 1260 (s, C–F str.); and 1175 (s, C–O str.) cm^{-1}. Mass spectrum (CI, NH_3) *m/z*: 472 [100.0%. $(M+NH_4)^+$]; 455 [26.2, $(M+H)^+$]; 454 (4.6, M^+); 377 [9.3, $(M-C_6H_5)^+$]; 335 [66.8, $(M-PhCH_2CO)^+$]; 318 [21.8, $(M-PhCH_2CO_2H)^+$]; 251 (40.7, $C_{14}H_{10}F_3O^+$); 241 (45.0, $C_{12}H_8F_3O_2^+$); 225 (92.8, $C_{15}H_{13}O_2^+$); and 108 (15.9, $C_7H_8O^+$).

Although pure isomers could not be separated by repeated DCFC (same eluant), sufficient purification was achieved to allow the following NMR assignments to be made.

^{1}H NMR ($CDCl_3$) δ (**10a**): 7.35–7.25 (mult., 10H, 2 C_6H_5); 6.95 (s, 1H, CH—O); 6.85 [dd, 1H, =CH (H-6), $J_{5-6}=5$, $J_{1-6}=2$ Hz]; 6.40 [dd, 1H, =CH (H-5), $J_{6-5}=5$, $J_{4-5}=2$ Hz]; and 5.50 and 5.25 (broad, 2H, 2 ring CH—O) ppm; δ (**10b**); 7.50–7.25 (mult., 10H, 2 C_6H_5); 6.90 (s, 1H, CH—O); 7.00 [d, 1H, =CH (H-6), $J_{5-6}=5$ Hz]; 6.35 [d, 1H, =CH (H-5), $J_{6-5}=5$ Hz]; and 5.45 and 5.25 (broad; 2H, 2 ring CH—O) ppm; δ (**11a**): 7.45–7.20 (mult., 10H, 2 C_6H_5); 6.90 (s, 1H, CH—O); 6.30–6.05 (mult., 2H, CH=CH); 4.75 [d, ring CH—O (H-3), $J_{2-3}=5$ Hz]; 4.55 [broad, 1H, ring CH—O (H-1)]; 4.45 [d, 1H, ring CH—O (H-6), $J_{7-6}=5$ Hz]; 4.40 [broad, 1H, ring CH—O (H-8)]; 3.70 (s, 2H, CH_2); 2.70 (dd, 1H, H-2, $J_{7-2}=7.5$, $J_{3-2}=5$ Hz); and 2.20 (dd, 1H, H-7, $J_{2-7}=7.5$, $J_{6-7}=5$ Hz) ppm; δ (**11b**); 7.45–7.20 (mult., 10H, 2 C_6H_5); 6.81 (s, 1H, CH—O); 6.30–6.05 (mult., 2H, CH=CH); 4.73 [d, 1H, ring CH—O (H-3), $J_{2-3}=5$ Hz]; 4.60 [broad, 1H, ring CH—O (H-1)]; 4.50 [d, 1H, ring CH—O (H-6), $J_{7-6}=5$ Hz]; 4.40 [broad, 1H, ring CH—O (H-8)]; 3.74 (s, 2H, CH_2); 2.65 (dd, 1H, H-2, $J_{7-2}=7.5$, $J_{3-2}=5$Hz); and 1.90 (dd, 1H, H-7, $J_{2-7}=7.5$; $J_{6-7}=5$ Hz) ppm.

^{19}F NMR δ (**10a**): +16.0 ppm; δ (**10b**): +16.1 ppm; δ (**11a**): +18.6 ppm; δ (**11b**): +19.3 ppm.

^{13}C NMR δ (**10a**): 170.4 (s, O—C=O); 158.6 (q, $CF_3C=C$, $^3J=5$ Hz); 143.2 and 141.8 (2s, CH=CH); 139.0 (q, $CF_3C=C$, $^2J=36$ Hz); 134.2 and 134.1 (2s, 2 *ipso*-C_6H_5); 130.0, 129.5, 129.3, 129.2, 128.0 and 126.5 (6s, *o*-, *m*- and *p*-C_6H_5); 123.8 (q, CF_3, $^1J=268$ Hz); 84.0 [s, ring CH—O (C-4)]; 83.3 [q, ring CH—O (C-1), $^3J=2$ Hz]; 70.3 (s, CH—O); and 42.1 (s, CH_2) ppm; δ (**10b**): 170.2 (s, O—C=O); 158.7 (q, $CF_3C=C$, $^3J=5$ Hz); 144.0 and 143.0 (2s, CH=CH); 139.0 (q, $CF_3C=C$, $^2J=36$ Hz); 136.6 (s, 2 *ipso*-C_6H_5). 129.9, 129.6, 129.4, 129.2, 128.2 and 127.1 (6s, *o*-, *m*- and *p*-C_6H_5); 123.8 (q, CF_3, $^1J=268$ Hz); 84.9 [s, ring CH—O (C-4)]; 83.3 [q, ring CH—O (C-1), $^3J=2$ Hz]; 70.8 (s, CH—O); and 42.0 (s, CH_2) ppm; δ (**11a**): 169.3 (s, O—C=O); 153.1 (q, $CF_3C=C$, $^3J=4$ Hz); 136.5 and 128.8 (2s, 2 *ipso*-C_6H_5); 135.1 (q, $CF_3C=C$, $^2J=35$ Hz); 133.9 and 133.8 (2s, CH=CH); 129.2, 128.7, 128.65; 128.6, 127.4 and 126.1 (6s, *o*-, *m*- and *p*-C_6H_5); 122.3 (q, CF_3, $^1J=269$ Hz); 78.35, 78.3, 78.25 and 77.4 (4s, 4 ring CH—O); 69.5 (s, CH—O); 48.4 and 47.4 (2s, 2 ring $\rangle$CH); and 41.4 (s, CH_2) ppm; δ (**11b**); 169.6 (s, O—C=O); 153.3 (q, $CF_3C=C$, $^3J=4$ Hz); 135.5 and 128.9 (2 *ipso*-C_6H_5); 135.2 (q, $CF_3C=C$, $^2J=35$ Hz); 133.3 and 133.2 (2s, CH=CH); 128.9, 128.75, 128.7, 128.5, 127.1 and 125.6 (6s, *o*-, *m*- and *p*-C_6H_5); 122.3 (q, CF_3, $^1J=270$ Hz); 78.35, 78.3, 77.2 and 77.0 (4s, ring CH—O); 69.5 (s, CH—O); 48.9 and 47.6 (2s, 2 ring $\rangle$CH); and 41.4 (s, CH_2) ppm.

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