Fluorinated acetylenes. Part 12*. Reaction of 3,3,3-trifluoropropynyl-lithium with benzil and α-haloacetophenones

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Abstract

Treatment of 3,3,3-trifluoropropynyl-lithium (**4**) with benzil (2:1 molar ratio) in diethyl ether at −50 °C, followed by addition of an excess of benzoyl chloride, affords 1-benzoyl-5-benzoyloxy-5-phenyl-2,3-bis(trifluoromethyl)cyclopenta-1,3-diene (**11**) (61%) and the 1,4-dialkynyl ester $(CF_3C{\equiv}C)_2CPhO_2CPh$ (**1b**) (8%). Similar reaction of the salt **4** with α-chloroacetophenone (2:1 molar ratio) in diethyl ether at −50 °C, followed by addition of a slight excess of benzoyl chloride, gives the ester $CF_3C{\equiv}CCPh(CH_2Cl)O_2CPh$ (**14a**) (55%) and a compound considered to be 2,5-diphenyl-2,5-bis(3,3,3-trifluoropropynyl)-1,4-dioxan (**15**) (30%). Under the same conditions, α-bromoacetophenone yields the corresponding bromo ester $CF_3C{\equiv}CCPh(CH_2Br)O_2CPh$ (**14b**) (39%), 2-phenyl-2-(3,3,3-trifluoropropynyl)oxirane (**16**) (25%) and the dialkynyl ester (**1b**) (7%). The oxirane **16**, conveniently prepared (51%) by treatment of salt **4** with the bromoketone (1:1 molar ratio) in THF at −60 °C, on reaction with lithium phenylacetylide followed by addition of benzoyl chloride (*c.* 1:1:1 molar ratio) in THF at −60 °C gives a compound identified as 2-phenyl-2-(1-phenyl-5,5,5-trifluoropent-3-en-1-yn-3-yl)oxirane (**17**) or possibly 2-phenyl-2-(3-phenylprop-2-yn-1-yl)-3-(2,2,2-trifluoroethylidene)oxirane (**18**) in 28% yield.

Introduction

In previous papers in this series [1, 2] we have reported the preparation of the 1,4-diynyl esters $(CF_3C{\equiv}C)_2CRO_2CR$, (**1a**; R = Me) and (**1b**; R = Ph), and the interesting and novel results of an investigation of their cycloaddition reactions with various 1,3-dienes and diazomethane. As an extension to this work, it was decided to investigate routes to fluorinated 1,5-diynes so that their cycloaddition reactions could also be studied.

The chemistry of 1,5-diynes has not been studied in detail and the few reports in the literature indicate that there are two general routes to such compounds, i.e. (i) coupling of propargyl halides via intermediate Grignard or lithium reagents [3–5] or coupling of propargyl sodium salts [6] and (ii) coupling of propargyl radicals generated by homolytic fission of a propargyl

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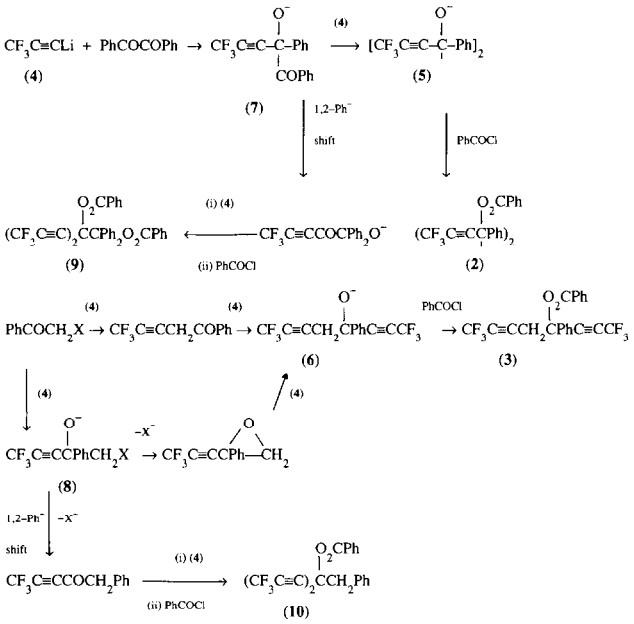
C—H bond under photochemical conditions [7, 8]. The parent compound, hexa-1,5-diyne, has been prepared in good yield by coupling of allyl bromide using magnesium to afford hexa-1,5-diene, followed by addition of bromine to the double bonds and then dehydrobromination [9].

However, it was considered possible that the 1,5-diynyl esters **2** and **3** could be synthesised by reaction of 3,3,3-trifluoropropynyl-lithium (**4**) with benzil and an α-haloacetophenone, respectively, with the intermediate alkoxides **5** and **6** trapped by addition of benzoyl chloride. It was realised that in these reactions the expected first-formed anions **7** and **8** could rearrange by a 1,2-phenide shift before being trapped by the acid chloride, cf. the benzil–benzylic acid rearrangement, and if this occurred the 1,4-diynes **9** and **10** could be produced (Scheme 1; however, this did not take place).

The results obtained from the reaction of salt **4** with benzil, phenacyl chloride and phenacyl bromide are now discussed.

Results and discussion

An ethereal solution of salt **4** was treated with an ethereal solution of benzil at −50 °C (2:1 molar ratio) followed by addition of an excess of benzoyl chloride in ether at −60 °C. After hydrolysis of the excess of benzoyl chloride with aqueous sodium hydroxide, the organic material was shown to consist of two major and a number of minor components. The major



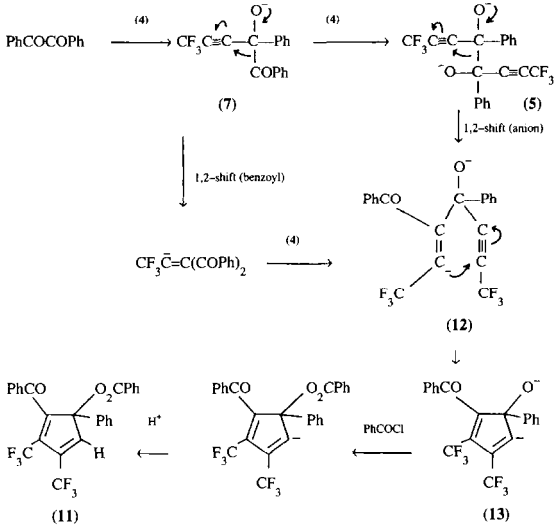
Scheme 1.

components were separated (DCFC) and identified as the diynyl ester **1b** (8%) [2] and the pentasubstituted cyclopentadiene (**11**) (61%). The former compound, **1b**, is formed by reaction of unreacted **4** with benzoyl chloride, while the diene **11** (an unexpected product) is considered to arise via rearrangement either of the 1:1 adduct **7** or the 2:1 adduct **8**, as shown in Scheme 2. The structure of compound **11** rests largely upon NMR spectral data. The ^{19}F spectrum indicated the presence of two coupled, and thus adjacent, CF_3 groups. The ^{13}C spectrum indicated the presence of the groups, $CF_3C{=}C$, $CF_3C{=}CH$, C–O, Ph, PhCO and $PhCO_2$, and the ^1H spectrum, and the IR and mass spectra were entirely consistent with the suggested structure.

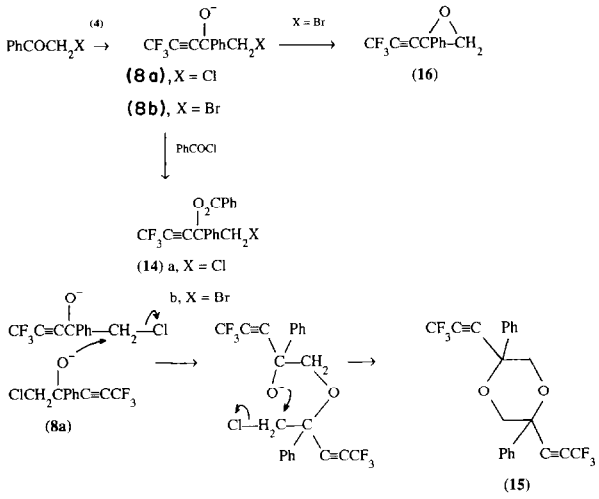
It is apparent that in this system a 1,2-phenyl shift is less favourable than either a 1,2-shift of the anion $CF_3C{\equiv}CCPhO^-$ in **5** or, perhaps more likely, a 1,2-benzoyl shift in **7**. The intermediate dianion **12** then cyclised via a favourable 5-centre transition state to afford **13**. Since the reaction was carried out with anhydrous solvents under a nitrogen atmosphere, it is considered that **13** then reacted with benzoyl chloride at the oxygen atom and protonation took place on work-up.

Treatment of salt **4** with α-chloroacetophenone (2:1 molar ratio) in ether at −50 °C followed by addition of benzoyl chloride gave two major products, the trifluoropropynyl ester (**14a**) (55%) and a compound thought to be the substituted dioxan (**15**) (*c.* 30%). An analogous reaction with α-bromoacetophenone afforded ester **1b** (7%), the trifluoropropynyl ester (**14b**) (39%) and the oxirane **16** (25%). These products (**14–16**) are considered to be formed as shown in Scheme 3.

The major products, esters **14a** and **14b**, resulted from the initial nucleophilic attack at carbonyl carbon to give the alkoxides **8a** and **8b**, respectively, which were sufficiently stable and hence long-lived to be trapped



Scheme 2.



Scheme 3.

by benzoyl chloride; products resulting from the initial displacement of the halide ion were not isolated. Only with alkoxide **8b** did intramolecular displacement of halide ion take place to afford the oxirane **16**, in keeping with the bromide ion being a better leaving group than the chloride ion.

The remaining product, the suspected dioxan **15**, could not be obtained pure, being contaminated with the ester $PhCO_2Bu^n$ (*c.* 8:1). The mass spectrum (CI) of the mixture showed a highest mass peak for $(M+NH_4)^+$, together with peaks for $(M+H)^+$ and M^+; peaks for ions containing chlorine were absent. In the IR spectrum a strong absorption at 2270 cm^{-1} was assigned to C≡C str., while the ^{19}F NMR spectrum showed only a singlet absorption at δ +28.0 ($CF_3C{\equiv}C$) ppm. ^1H NMR absorptions were observed in the aromatic region (δ 7.7–7.2 ppm) and at 3.85 and 3.75 (AB, CH_AH_B, $J_{AB}=11$ Hz) ppm in the region expected for CH_2-O. The ^{13}C NMR spectrum was very informative and showed singlet absorptions for phenyl carbons, $\rangle C-O$ and CH_2O, and quartet absorptions in the expected regions and with the expected coupling constants for the three carbons in the $CF_3C{\equiv}C$ grouping. This provides strong evidence for the proposed structure.

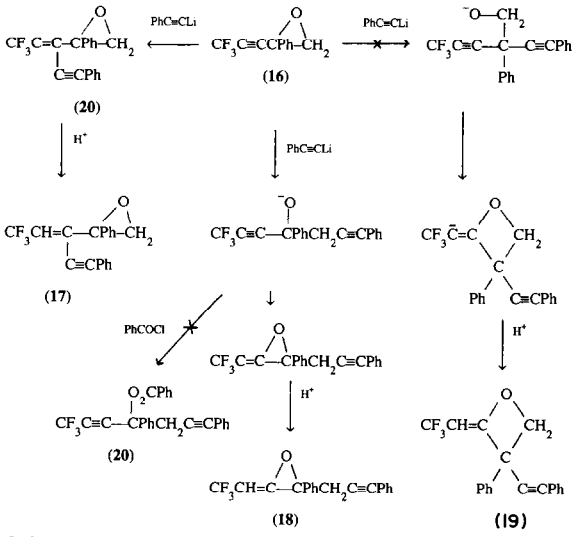
The dioxan was formed presumably via intermolecular nucleophilic attack involving displacement of the chloride ion in **8a** by the alkoxide oxygen in a second molecule of **8a**. It could also have arisen by nucleophilic attack of **8a** on the oxirane **16**, but this is considered less likely since oxirane **16** was not detected in the products and dioxan **15** was not detected in the products from the bromoketone reaction in which oxirane **16** was formed in the presence of alkoxide **8b**. It is not clear why intermolecular displacement of the chloride ion to give **15** should be favoured while intramolecular displacement to give oxirane **16** is not, or why dioxan **15** was not formed in the bromoketone reaction.

The presence of the ester $PhCO_2Bu^n$ was confirmed by the spectral data obtained, and it is probable that the ester was formed by reaction of n-butoxy lithium (from the oxidation of Bu^nLi prior to use) with the benzoyl chloride.

One interesting observation is that rearrangement of alkoxides **8a** and **8b** by 1,2-shifts is not favourable in contrast to the alkoxide intermediates **5** and **7** in the benzil reaction. The results obtained show that the oxirane **16** can be made from α-bromoacetophenone and that at low temperatures its further reaction with the excess of salt **4** present did not occur to any great extent. It was decided to prepare oxirane **16** from the bromoketone and then to investigate its reaction with a different lithium acetylide to determine if a 1,5-diyne could be made this way (see Scheme 4).

Reaction of salt **4** with the bromoketone (1:1 molar ratio) in THF at −60 °C gave oxirane **16** (51%) after purification by DCFC. Treatment of lithium phenylacetylide with oxirane **16** in THF at −30 °C then at 0 °C, followed by addition of benzoyl chloride at −50 °C, gave one major product which was separated by DCFC but could not be obtained completely pure. It was identified as the oxirane **17**, or possibly **18**, (28%), on the basis of the following evidence.

The ^1H NMR spectrum showed the presence of two phenyl groups, a $CF_3CH=$ grouping and two non-equivalent methylene protons (δ 3.35 and 3.25 ppm, $J_{AB}=7.5$ Hz); the doublet absorption in the ^{19}F NMR spectrum confirmed the $CF_3CH=$ grouping. Apart from absorptions for eight different aromatic carbons ($2C_6H_5$) in the ^{13}C NMR spectrum, C≡C and $CF_3CH=C$ groupings were confirmed, together with a quaternary carbon (δ 61.4 ppm) and a methylene carbon (δ 55.3 ppm). An accurate mass determination confirmed the molecular formula as $C_{19}H_{13}F_3O$ and a strong absorption at



Scheme 4.

1130 cm^{-1} in the IR spectrum was assigned to C–O str. The relevant NMR data for oxirane **16** [CH_2–O; δ_H 3.36 and 2.95 ppm (J_{AB} = 6 Hz) and δ_C 59.1 ppm, *C*Ph–O; δ_C 50.6 ppm] are in reasonable agreement with those of structure **17**. In the parent oxirane, $^2J_{HH}$ = +5.5 Hz, whereas outside a three-membered ring it usually lies in the range −11 to −17 Hz [10]. Neighbouring π-electrons cause a negative contribution to $^2J_{HH}$. The observed magnitude of 7.5 Hz appears reasonable for an oxirane derivative (**17**), but too small for compound **18** where the CH_2 group is not part of a ring.

It is therefore more likely that the product has structure **17**, but structure **18** cannot be completely ruled out. The observation that the CH_2–O carbons in the oxetane absorb at δ 72.6 ppm [11] strongly ruled against the alternative oxetane structure **19** for the present product.

The formation of compounds **17** and **18** can be explained as shown in Scheme 4.

Nucleophilic attack on oxirane **16** could take place on the acetylenic carbon rendered electrophilic by the β-trifluoromethyl group, and would give compound **17** on protonation. Alternatively, attack could occur on the oxirane ring at either the least or more substituted carbon. With phenyloxirane, nucleophilic attack can take place at either carbon depending upon the nucleophile used and its bulk [12, 13], but attack on oxiranes at the more open site is normally preferred. The desired 1,5-diyne **20** was not isolated.

The reactions studied gave interesting results, but the desired 1,5-diynes were not detected in the products. Other routes to fluorinated 1,5-diynes are under investigation and will be reported in due course.

Experimental

Starting materials

3,3,3-Trifluoropropyne was prepared from 1,1,2-trichloro-3,3,3-trifluoropropene [14] and its lithium salt was generated by passage of the alkyne into a stirred solution of n-butyl-lithium (1.6 M solution in hexane) in anhydrous diethyl ether or THF at −78 °C under a nitrogen atmosphere. Phenylacetylene, benzil, α-chloroacetophenone and α-bromoacetophenone were commercial samples and the purity of each was checked before use.

General techniques

Reaction product mixtures were separated by dry column 'flash' chromatography (DCFC) using silica gel (Merck Kieselgel 60 H) and eluants as given in the text; light petroleum refers to the petroleum ether fraction of b.p. 40–60 °C.

IR, NMR [^1H (220 MHz), ^{19}F (84.6 MHz) and ^{13}C (75.0 MHz and including DEPT 135°) with samples as solutions in $CDCl_3$ and external tetramethylsilane (TMS), external trifluoroacetic acid (TFA) and internal TMS as the respective references; chemical shifts to low field of the reference designated positive] and routine mass [under electron impact (EI) or chemical ionisation (CI,

with NH_3 gas) conditions] spectra were recorded on instruments described previously [2]. Accurate mass measurements were carried out on a Kratos Concept high-resolution mass spectrometer.

Reactions of 3,3,3-trifluoropropynyl-lithium (4)

(a) With benzil

A solution of benzil (2.21 g, 10.5 mmol) in diethyl ether (50 cm^3) was added dropwise to a stirred solution of the salt **4** [prepared from n-butyl-lithium (1.34 g, 20.9 mmol) and trifluoropropyne (2.25 g, 23.9 mmol) in diethyl ether (100 cm^3)] at −50 °C and stirring was continued (1 h) while the reaction mixture warmed up to room temperature. The mixture was cooled to −60 °C, and a precooled (−50 °C) solution of benzoyl chloride (5.90 g, 42.0 mmol) in diethyl ether (20 cm^3) was added in one batch, and stirring was continued at −60 °C (0.5 h). After warming the mixture to room temperature, the solvent was removed (rotary evaporator) and the residue treated with aqueous sodium hydroxide (2 M, 100 cm^3). The organic layer was separated, the aqueous layer washed with diethyl ether (3×20 cm^3), the combined organic material dried ($CaCl_2$) and the solvent removed (rotary evaporator) to afford a yellow semi-solid (4.9 g). This material was shown by TLC methods [light petroleum–dichloromethane (1:1 v/v)] to contain two major (R_F = 0.90 and 0.65) and a number of minor components, and the two major components were separated by DCFC (same eluant) to give (i) [α,α-bis(3,3,3-trifluoropropynyl)]benzyl benzoate (**1b**) (0.32 g, 0.80 mmol, 8%), which was identified by a comparison of its ^1H and ^{19}F NMR spectra with those reported [2], and (ii) 1-benzoyl-5-benzoyloxy-5-phenyl-2,3-bis(trifluoromethyl)cyclopenta-1,3-diene (**11**) (61%) (nc). (Analysis: Found: C, 64.2; H, 3.0; F, 22.6%; mol. wt., 502. $C_{27}H_{16}F_6O_3$ requires: C, 64.5; H, 3.2; F, 22.7%; mol. wt., 502); m.p. 112 °C. ^1H NMR δ: 7.95 (d, 2H, *o*-C_6H_5CO, J = 7.5 Hz); and 7.65–7.20 (complex, 13 arom. =CH and 1 vinylic =CH) ppm. ^{19}F NMR δ: +18.4 and +15.4 (2q, $2CF_3C=$, J = 4.3 Hz) ppm. ^{13}C NMR δ: 189.9 (s, C=O); 164.4 (s, O−C=O); 152.1 (q, $CF_3C=C$, ^3J = 4 Hz); 143.7 (q, $CF_3C=CH$, ^3J = 5 Hz); 135.9 (s, ipso-C_6H_5CO); 134.8, 133.8, 129.9, 129.6, 129.3, 129.0, 128.6, 128.5 and 124.6 (9s, arom. =CH); 132.3 (q, $CF_3C=C$, ^2J = 37 Hz); 130.8 (s, ipso-$C_6H_5CO_2$); 128.7 (s, ipso-C_6H_5); 127.2 (q, $CF_3C=CH$, ^2J = 38 Hz); 120.5 (q, $CF_3C=$, ^1J = 270 Hz); 120.1 (q, $CF_3C=$, ^1J = 272 Hz); and 90.8 (s, C−O) ppm. IR (ν_{max}) (cm^{-1}): 1740 and 1660 (s, C=O str.); 1590 and 1580 (s, C=C str.); 1260 (C−F str.); and 1160 and 1135 (s, C−O str.). Mass spectrum (CI) (*m/z*): 520 [100.0%, $(M+NH_4)^+$]; 503 [10.0, $(M+H)^+$]; 502 (1.4 M^+); 397 (11.1, $C_{20}H_{11}F_6O_2^+$); 381 (14.9, $C_{20}H_{11}F_6O^+$); 343 (13.6, $C_{20}H_{11}F_4O^+$); and 105 (24.5, $C_7H_5O^+$).

(b) With α-chloroacetophenone

A solution of α-chloroacetophenone (1.70 g, 11.0 mmol) in diethyl ether (250 cm^3) was added slowly (0.5 h) to a stirred solution of the salt **4** [prepared from n-butyl-lithium (1.40 g, 21.9 mmol) and trifluoropropyne (2.30 g, 24.5 mmol) in diethyl ether (100 cm^3)] at −50 °C and stirring was continued while the reaction mixture slowly warmed up to room temperature

(1.5 h). The temperature was again decreased to −50 °C and a solution of benzoyl chloride (1.96 g, 14.0 mmol) in diethyl ether (10 cm^3) was added in one batch and stirring was continued at −50 °C (0.5 h). Work-up as in the previous experiment gave a crude product (4.13 g), which was shown by TLC [light petroleum–dichloromethane (2:1 v/v)] to contain two major components (R_F = 0.62 and 0.56) and unchanged chloroketone (R_F = 0.44). On separation by DCFC (same eluant), unchanged α-chloroacetophenone (0.10 g, 0.71 mmol, 6% recovered) (eluted last) and the following two products were obtained:

(i) [α-(Chloromethyl)-α-(3,3,3-trifluoropropynyl)]benzyl benzoate (**14a**) (nc) (2.14 g, 6.1 mmol, 55%). (Analysis: Found: C, 61.5; H, 3.6; F, 15.9%; mol. wt., 352. $C_{18}H_{12}ClF_3O_2$ requires: C, 61.3; H, 3.4; F, 16.2%; mol. wt., 352); m.p. 40 °C. ^{1}H NMR δ: 8.07 (d, 2H, *o*-$C_6H_5CO_2$, J = 7.5 Hz); 7.68–7.27 (complex, 8H, C_6H_5 and *m*- and *p*-$C_6H_5CO_2$); and 4.08 and 3.95 (AB, CH_AH_BCl, J_{AB} = 11 Hz) ppm. ^{19}F NMR δ: +27.9 (s, $CF_3C{\equiv}C$) ppm. ^{13}C NMR δ: 163.4 (s, O−C=O); 136.3 (s, ipso-$C_6H_5CO_2$); 133.8, 129.9, 129.4, 128.6, 128 and 125.2 (6s, arom. =CH); 129.1 (s, ipso-C_6H_5); 113.9 (q, $CF_3C{\equiv}C$, ^1J = 258 Hz); 82.9 (q, $CF_3C{\equiv}C$, ^3J = 6 Hz); 76.9 (s, C−O); 75.8 (q, $CF_3C{\equiv}C$, ^2J = 53 Hz); and 51.1 (s, CH_2Cl) ppm. IR (ν_{max}) (cm^{-1}): 2280 (m, C≡C str.); 1725 (s, ester C=O str.); 1300 and 1265 (s, C−F str.); and 1145 (s, C−O str.). Mass spectrum (EI) (*m/z*): 352 (0.9%, M^+); 317 [11.6, $(M-Cl)^+$]; 231/233 [100.0, $(M-PhCO_2)^+$]; 230/232 [20.7, $(M-PhCO_2H)^+$]; 212/214 (13.6, $C_{11}H_7F_2Cl^+$); 211/213 (15.8, $C_{11}H_6F_2Cl^+$); 196 (61.6, $C_{11}H_7F_3^+$); 195 (41.6, $C_{11}H_6F_3^+$); 105 (37.7, $C_7H_5O^+$); 77 (35.7, $C_6H_5^+$); and 51 (21.0, $C_4H_3^+$).

(ii) A semi-solid (0.74 g), which was identified as a mixture of 2,5-diphenyl-2,5-bis(3,3,3-trifluoropropynyl)-1,4-dioxan (**15**) (0.70 g, 1.60 mmol, 30%) and n-butyl benzoate (0.036 g, 0.20 mmol) in the ratio *c.* 8:1 (^{1}H NMR spectroscopy); attempts to separate the mixture by preparative-scale TLC methods were unsuccessful. ^{1}H NMR δ: (compound **15**): 7.7–7.2 (C_6H_5); and 3.85 and 3.75 (AB, $-CH_AH_B-O$, J_{AB} = 11 Hz) ppm; ($PhCO_2Bu^n$): 8.0–7.4 ($C_6H_5CO_2$); 4.35 (t, CH_2CH_2-O, J = 7.5 Hz); 1.71 (quin., $CH_2CH_2CH_2$); 1.52 (sextet, $CH_3CH_2CH_2$); and 1.00 (t, CH_3CH_2) ppm. ^{19}F NMR δ: +28.0 ($CF_3C{\equiv}C$) ppm. ^{13}C NMR δ: (Compound **15**): 138.1 (ipso-C_6H_5); 129.4, 128.8 and 128.4 (3s, arom. =CH); 113.9 (q, $CF_3C{\equiv}C$, ^1J = 258 Hz); 86.5 (q, $CF_3C{\equiv}C$, ^3J = 6 Hz); 73.4 (q, $CF_3C{\equiv}C$, ^2J = 53 Hz); 72.5 (s, C−O); and 53.6 (s, CH_2-O) ppm; ($PhCO_2Bu^n$): 167.2 (O−C=O); 132.9 (ipso-$C_6H_5CO_2$); 130.2, 129.5 and 128.3 (arom. =CH); 65.0 (CH_2-O); 30.6 (CH_2); 19.2 (CH_2); and 13.6 (CH_3) ppm. IR (ν_{max}) (cm^{-1}): (compound **15**): 2270 (s, C≡C str.); 1275 (s, C−F str.); and 1145 (s, C−O str.); ($PhCO_2Bu^n$): 1750 (s, ester C=O str.). Mass spectrum (CI) (*m/z*): (compound **15**): 460 [3.9%, $(M+NH_4)^+$]; 443 [1.2, $(M+H)^+$]; 442 (0.4, M^+); ($PhCO_2Bu^n$): 178 (4.3%, M^+); 122 (14.5, $PhCO_2H^+$); and 105 (100.0, $C_7H_5O^+$).

(c) With α-bromoacetophenone (2:1 molar ratio)

The reaction of salt **4** [generated from n-butyl-lithium (1.90 g, 29.7 mmol) and 3,3,3-trifluoropropyne (3.29 g, 35.0 mmol)] with α-bromoaceto-

phenone (2.99 g, 15.0 mmol), carried out under identical conditions to the previous experiment, gave a crude product (5.90 g) which was shown by TLC methods [light petroleum–dichloromethane (2:1 v/v)] to contain three components (R_F = 0.94, 0.78 and 0.40). The components were separated by DCFC (same eluant). They were identified as follows:

(i) Ester **1b** (0.40 g, 1.0 mmol, 7%), identified by a comparison of its ^{1}H and ^{19}F NMR spectra with those reported [2].

(ii) 2-Phenyl-2-(3,3,3-trifluoropropynyl)oxirane (**16**) (nc) (0.78 g, 3.70 mmol, 25%). (Analysis: Found: C, 62.0; H, 3.4; F, 27.2%; mol. wt., 212. $C_{11}H_7F_3O$ requires: C, 62.3; H, 3.3; F, 26.4%; mol. wt., 212). ^{1}H NMR δ: 7.38–7.25 (complex, 5H, C_6H_5); and 3.36 and 2.95 (AB, $-CH_AH_B-O$, J_{AB} = 6 Hz) ppm. ^{19}F NMR δ: +29.0 ($CF_3C{\equiv}C$) ppm. ^{13}C NMR δ: 135.1 (s, ipso-C_6H_5); 129.5, 129.4 and 125.9 (3s, arom. =CH); 114.6 (q, $CF_3C{\equiv}C$, ^1J = 258 Hz); 88.7 (q, $CF_3C{\equiv}C$, ^3J = 6 Hz); 71.3 (q, $CF_3C{\equiv}C$, ^2J = 53 Hz); 59.1 (s, CH_2-O); and 50.6 (s, C–O) ppm. IR (ν_{max}) (cm^{-1}): 2280 (s, C≡C str.); 1240 (s, C–F str.); and 1150 (s, C–O str.). Mass spectrum (CI) (*m/z*): 230 [100.0%, $(M+NH_4)^+$]; 213 [98.4, $(M+H)^+$]; 212 (63.8, M^+); 193 [21.0, $(M-F)^+$]; 182 [48.6, $(M-CH_2O)^+$]; 164 (15.9, $C_{10}H_6F_2^+$); and 105 (20.9, $C_7H_5O^+$).

(iii) [α-(Bromomethyl)-α-(3,3,3-trifluoropropynyl)]benzyl benzoate (**14b**) (nc) (2.30 g, 5.81 mmol, 39%). (Analysis: Found: C, 54.4; H, 3.0; F, 14.2%; mol. wt., 397. $C_{18}H_{12}BrF_3O_2$ requires: C, 54.4; H, 3.0; F, 14.4%; mol. wt., 397); m.p. 54 °C. ^{1}H NMR δ: 8.08 (d, 2H, *o*-$C_6H_5CO_2$, J = 7 Hz); 7.69–7.25 (complex, 8H, C_6H_5 and *m*- and *p*-$C_6H_5CO_2$); and 3.95 and 3.85 (AB, CH_AH_BBr, J_{AB} = 11 Hz) ppm. ^{19}F NMR δ: +28.4 (s, $CF_3C{\equiv}C$) ppm. ^{13}C NMR δ: 163.4 (s, O–C=O); 136.7 (s, ipso-$C_6H_5CO_2$); 133.8, 130.0, 129.5, 129.0, 128.6 and 125.1 (6s, arom. =CH); 129.1 (s, ipso-C_6H_5); 113.9 (q, $CF_3C{\equiv}C$, ^1J = 259 Hz); 83.2 (q, $CF_3C{\equiv}C$, ^3J = 7 Hz); 76.3 (s, C–O); 75.8 (q, $CF_3C{\equiv}C$, ^2J = 54 Hz); and 39.0 (s, CH_2Br) ppm. IR (ν_{max}) (cm^{-1}): 2270 (m, C≡C str.); 1750 (s, ester C=O str.); 1310 and 1240 (s, C–F str.); and 1150 (s, C–O str.). Mass spectrum (CI) (*m/z*): 414/416 [39.2%, $(M+NH_4)^+$]; 396/398 (3.0, M^+); 317 [3.9, $(M-Br)^+$]; 291/293 [46.8, $(M-PhCO)^+$]; 275/277 [16.1, $(M-PhCO_2)^+$]; 196 (20.6, $C_{11}H_7F_3^+$); 105 (100.0, $C_7H_5O^+$); and 30 (29.6, CH_2O^+).

(d) With α-bromoacetophenone (1:1 molar ratio)

A solution of the bromoketone (2.99 g, 15.0 mmol) in THF (6 cm^3) was added dropwise to a stirred solution of salt **4** [prepared from n-butyllithium (0.96 g, 15.0 mmol) and 3,3,3-trifluoropropyne (1.53 g, 16.3 mmol) in THF (30 cm^3)] at −60 °C, stirring was continued until the reaction mixture had warmed up to room temperature (1.5 h) and the mixture was then heated at 50 °C (1 h). Removal of the solvent (rotary evaporator) gave a residue (3.06 g) which was shown (^{1}H and ^{19}F NMR spectroscopy) to consist mainly of the oxirane **16** together with some unchanged bromoketone and a number of minor products. Purification by DCFC [light petroleum–dichloromethane (2:1 v/v)] gave oxirane **16** (1.63 g, 7.7 mmol, 51%).

*Reaction of 2-phenyl-2-(3,3,3-trifluoropropynyl)oxirane (**16**) with lithium phenylacetylide*

Oxirane **16** (1.13 g, 5.3 mmol) was added dropwise to a stirred solution of lithium phenylacetylide [prepared from n-butyl-lithium (0.44 g, 6.9 mmol) and phenylacetylene (0.71 g, 7.0 mmol) in THF (20 cm^3) at −30 °C] at −30 °C and stirring was continued at −30 °C (0.5 h) and then at 0 °C (2 h). The temperature was then lowered to −50 °C and a solution of benzoyl chloride (0.98 g, 6.7 mmol) in THF (3 cm^3) was added slowly. Finally, the mixture was allowed to warm slowly to room temperature and stirring was continued (2 h). Work-up as in the first experiment gave a residue (2.50 g) which was shown by TLC methods [light petroleum–dichloromethane (1:1 v/v)] to contain one major component; reactants were absent (^1H and ^{19}F NMR spectroscopy). Attempted purification of the major component gave slightly impure 2-phenyl-2-(1-phenyl-5,5,5-trifluoropent-3-en-1-yn-3-yl)-oxirane (**17**) or 2-phenyl-2-(3-phenylprop-2-yn-1-yl)-3-(2,2,2-trifluoroethylidene)oxirane (**18**) (0.47 g, 1.5 mmol, 25%). (Analysis: Found: C, 73.6; H, 4.1; F, 17.1%; mol. wt., 314.3919. $C_{19}H_{13}F_3O$ requires: C, 72.6; H, 4.1; F, 18.1%; mol. wt., 314.4264). ^1H NMR δ: 7.49–7.27 (complex, 10H, $2C_6H_5$); 6.20 (q, 1H, $CF_3CH=$, $J_{F-H}=8.5$ Hz); and 3.34 and 3.26 (AB, CH_AH_B, $J_{AB}=7.5$ Hz) ppm. ^{19}F NMR δ: +19.0 (d, $CF_3CH=$, $J=8.5$ Hz) ppm. ^{13}C NMR δ: 135.9 (s, ipso-C_6H_5); 133.4 (q, $CF_3CH=C$, $^3J=6$ Hz); 131.8, 129.5, 128.8, 128.45, 128.4 and 127.7 (6s, arom. =CH); 123.8 (q, $CF_3CH=C$, $^2J=35$ Hz); 122.6 (q, $CF_3CH=C$, $^1J=271$ Hz); 121.7 (s, ipso-C_6H_5); 101.7 (s, $PhC\equiv C$); 82.0 (s, $PhC\equiv C$); 61.4 (s, C−O); and 55.3 (s, CH_2) ppm. IR (ν_{max}) (cm^{-1}): 2205 (s, C≡C str.); 1275 (s, C−F str.); and 1130 (s, C−O str.). Mass spectrum (CI) (*m/z*): 332 [82.1%, $(M+NH_4)^+$]; 315 [100.0, $(M+H)^+$]; 314 (40.0, M^+); 297 [34.8, $(M-OH)^+$]; and 105 (28.1, $C_7H_5O^+$).

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