Journal of Fluorine Chemistry, 47 (1990) 45–57

Received: April 13, 1989; accepted: August 24, 1989

FLUORINATED ACETYLENES, PART 7 [1]. PREPARATION AND SOME REACTIONS OF 4,4,4-TRIFLUOROBUT-2-YNOIC ACID AND 1-PHENYL-4,4,4-TRIFLUOROBUT-2-YN-1-OL

SABIHA TAJAMMAL AND ANTHONY E. TIPPING*

Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD (U.K.)

SUMMARY

Treatment of the salt $CF_3C{\equiv}CLi$ with alkyl chloroformates affords the compounds $CF_3C{\equiv}CCO_2R$ (R = Et and CH_2Ph) in relatively low yield and with gaseous carbon dioxide yields the acid $CF_3C{\equiv}CCO_2H$. Reaction of the acid with diazomethane gives the methyl ester which, with an excess of the reagent, undergoes regiospecific 1,3-dipolar cycloaddition to produce 3-carbomethoxy-4-trifluoromethylpyrazole and hence the 3- and 5-carbomethoxy-1-methyl-4-trifluoromethylpyrazoles. Oxidation of the alcohol $CF_3C{\equiv}CCH(OH)Ph$ (active MnO_2) affords a 70:23 mixture of 3-benzoyl-2,4-bis(trifluoromethyl)-2-hydroxy-6-phenyl-α-pyran and E-1,3-dibenzoyl-2-trifluoromethylpropene (via the ketone $CF_3C{\equiv}CCOPh$).

INTRODUCTION

Acetylenic esters and ketones of type $R_FC{\equiv}CX$ (R_F = perfluoroalkyl, X = CO_2R and COR) have been prepared [2-4] via intramolecular Wittig reactions and the esters have been reported to (i) rearrange to vinyl ethers on treatment with aqueous base [2,3] and (ii) undergo 1,3-dipolar cycloaddition with C,N-diphenylnitrone and aryl nitrile oxides to afford indoles [5] and isoxazoles [6], respectively.

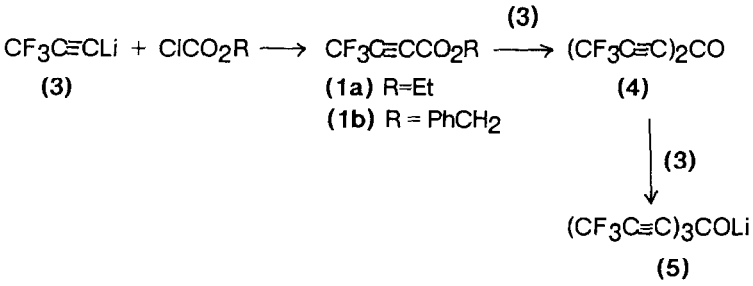
In our hands the preparation of ethyl 4,4,4-trifluorobut-2-ynoate **(1a)** by the Wittig procedure gave variable yields and alternative methods of synthesis of such esters and of phenyl 3,3,3-trifluoropropynyl ketone **(2)** were investigated so that a general study of the utility of such alkynes as dienophiles and dipolarophiles in cycloaddition reactions could be undertaken.

* To whom enquiries should be addressed.

0022-1139/90/$3.50

DISCUSSION

Initial studies were directed to the reaction of 3,3,3-trifluoropropynyl-lithium **(3)** with chloroformate esters, although further reaction of the product esters with salt **(3)** could occur to form the ketone **(4)** and the salt of the tertiary alcohol **(5)** as has been reported [7] for the reaction of hex-1-ynyl-lithium with ethyl chloroformate.



Treatment of the salt **(3)** (generated by bubbling $CF_3C{\equiv}CH$ into a stirred solution of n-BuLi-C_6H_{14} in n-Bu_2O under nitrogen at -78 °C followed by evaporation of the hexane at -23 °C in vacuo) with ethyl chloroformate (1:1 molar ratio, dropwise addition at -60 °C)gave (after hydrolysis of unreacted ethyl chloroformate) volatile material, which on fractional condensation in vacuo afforded a mixture of ester **(1a)** (34%) and hexane in the ratio 8:1 (^{1}H n.m.r.) from which pure ester could not be isolated. In a second reaction an excess of ethyl chloroformate was added in one portion at -78 °C to the salt **(3)** in di-n-butyl ether. Difficulty was encountered in hydrolysing completely the excess of chloroformate and a mixture of ester **(1a)** (39%) (b.p. 96-98 °C), hexane and ethyl chloroformate (b.p. 93 °C) was obtained.

In an attempt to obviate the separation problems the lithium salt **(3)** in diethyl ether was treated with an excess of the higher-boiling benzyl chloroformate at -78°C. After filtration and removal of the ether a mixture of unreacted benzyl chloroformate, ester **(1b)** (43%) and bis(3,3,3-trifluoropropynyl) ketone **(4)** (43%) was obtained. Attempts to separate the components by chromatography using a variety of solvents was unsuccessful because of the similar R_F values of the compounds.

Because the reactions gave relatively low yields of the ester **(1)**, the synthesis of 4,4,4-trifluorobut-2-ynoic acid **(6)** followed by its reaction with an excess of diazomethane, was undertaken so that the direction of 1,3-dipolar cycloaddition of diazomethane to the initially formed methyl ester **(1c)** could be determined. Dry carbon dioxide gas was bubbled into a stirred solution of salt **(3)** in diethyl ether at -30 °C followed by acidification (HCl aq.) at room temperature. Repeated fractional

condensation of the dried ether layer in vacuo gave a mixture of acid **(6)** (49%) and diethyl ether in the ratio 3.53:1.0 (^{1}H n.m.r. and elemental analysis), which on treatment with an excess of an ethereal solution of diazomethane at 0 °C afforded 5-carbomethoxy-1-methyl-4-trifluoromethylpyrazole **(7)** (32%), 3-carbomethoxy-1-methyl-4-trifluoromethylpyrazole **(8)** (6.5%) and 3-carbomethoxy-4-trifluoromethylpyrazole **(9)** (45%). These products are formed via the methyl ester **(1c)** and the cycloadduct **(10)** as shown in Scheme 1; pyrazole **(11)** was not detected.

The structures of compounds **(8)** and **(9)** were established by single crystal X-ray studies while that of the semi-solid product **(7)** was confirmed mainly by a comparison of its ^{13}C n.m.r. spectrum with those of the other pyrazoles (Table).

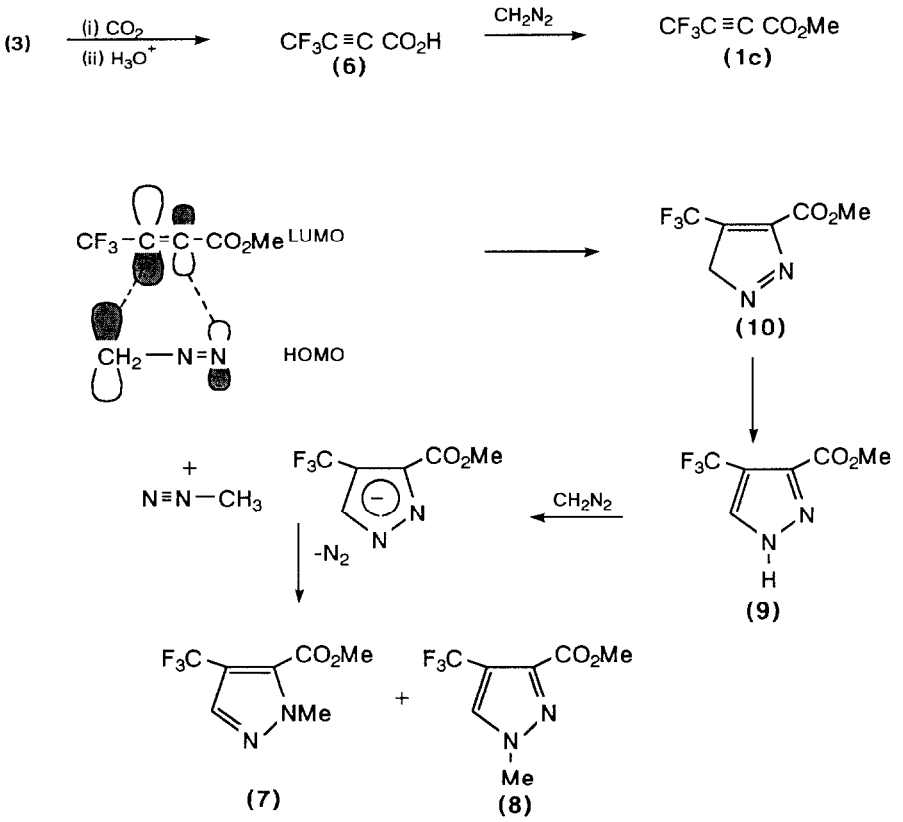
The higher field chemical shift of the -C(O)-C carbon in compound **(7)** relative to those in compounds **(8)** and **(9)** is consistent with the carbon being singly bonded

TABLE

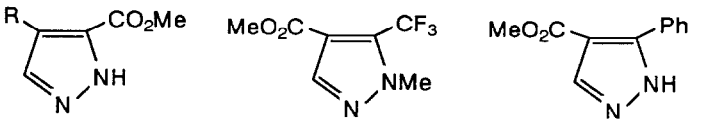
^{13}C NMR shifts* (p.p.m. to low field of TMS)

Assignment	(7)	(8)	(9)
NMe	39.19 s	38.80 s	-
OMe	51.27 s	51.11 s	52.65 s
CF_3-C	114.8 (q, J 38.7)	113.8 (q, J, 39.3)	114.2 (q, J 43.5)
CF_3	120.5 (q, J 266.9)	120.5 (q, J 266.9)	121.8 (q, J 266.4)
-C(=O)-C	129.4 (q, J 2.4)	138.6 (broad)	139.6 (broad)
CF_3-C-CH	135.65 (q, J 4.0)	131.5 (q, J 4.6)	132.4 (broad)
C=O	157.6s	159.5 s	161.2 s

*Broad band proton decoupled; coupling constants $J_{F_3\text{-}C}$ (Hz) in brackets.



Scheme 1



(11) R = CF_3

(13) R = H

(14) R = Ph

(12)

(15)

to nitrogen in the former compound rather than doubly bonded as in the latter two compounds. Similarly, only in compound **(7)** is the CH carbon doubly bonded to nitrogen and the absorption is at lower field than that in either compound **(8)** or **(9)**. The possibility that the compound assigned structure **(7)** was the other regioisomer **(12)** was discounted because of the coupling observed between the fluorines and the CH carbon (of the magnitude expected for a γ coupling); in compound **(12)** the CH carbon is δ to the fluorines and coupling would not be expected.

Diazomethane additions are generally dipole HOMO controlled and the regiospecific addition to ester **(1c)** can be explained by the larger frontier orbital coefficient in the alkyne being associated with the carbon bonded to CF_3, i.e. the electron-withdrawing -I/-M effect of the CO_2Me group outweighs the -I effect of the CF_3 group.

Adduct **(13)** has been reported to be formed regiospecifically with ethyl propiolate [8], but the ester $PhC{\equiv}CCO_2Me$ afforded both cycloadducts **(14)** and **(15)** (ratio 52.5:47.5) [9] and this non-regiospecific addition has been attributed to the steric bulk of the phenyl group [10].

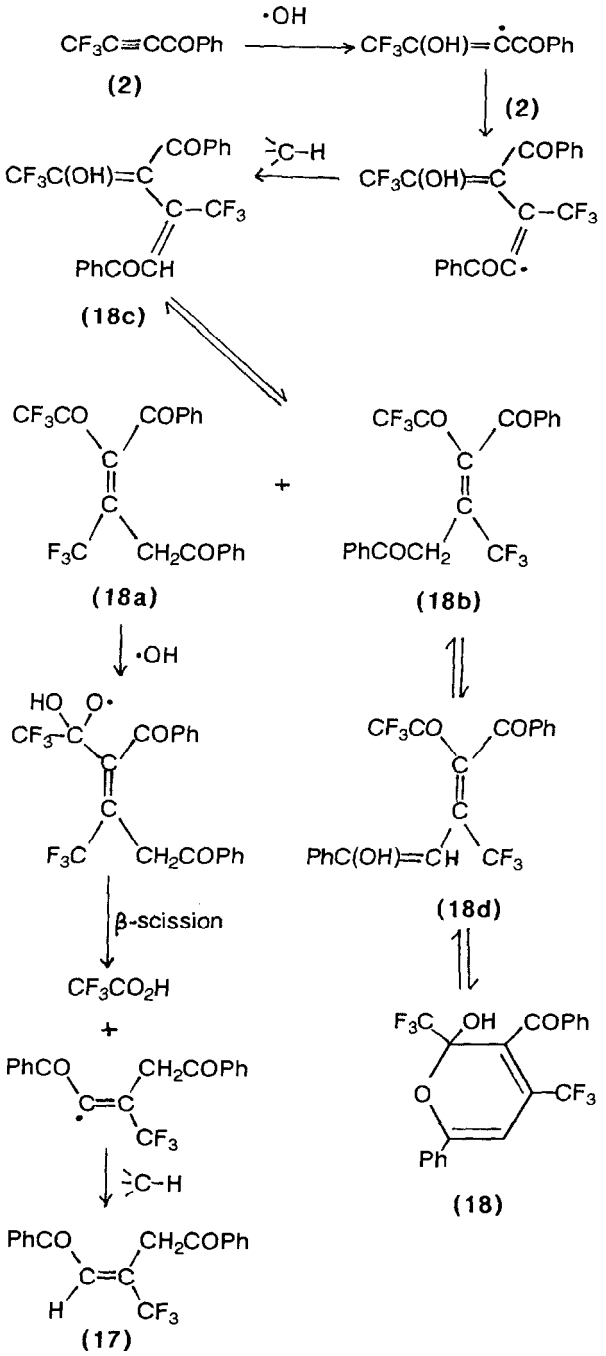
The synthesis of ketone **(2)** was investigated by the following route.

$$\textbf{(3)} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) PhCHO}} CF_3C{\equiv}CCH(OH)Ph \textbf{ (16)} \xrightarrow{[O]} CF_3C{\equiv}CCOPh \textbf{ (2)}$$

It has been reported [11] that the salt **(3)** undergoes facile reaction with various aldehydes and ketones to afford the corresponding secondary and tertiary alcohols, respectively, in good yield after acidification.

In the present work treatment of salt **(3)** with benzaldehyde followed by acid work up gave alcohol **(16)** (83%), but surprisingly, attempted oxidation to the ketone **(2)** with a variety of reagents (including pyridinium chlorochromate/CH_2Cl_2/20 °C, CrO_3/H_2SO_4(aq.)/20 °C and HgO/$CHCl_3$/reflux) gave almost quantitative recoveries of the alcohol. Since the successful oxidation of 1-phenylbut-2-yn-1-ol to phenyl propynyl ketone in high yield (80%) has been reported using active manganese (IV) oxide at room temperature (1:10 molar ratio) [12], the oxidation of alcohol **(16)** with this reagent was investigated.

Treatment of alcohol **(16)** in dichloromethane with an excess of oxidant (1:10 molar ratio) at 20 °C for one day afforded a minor product (TLC) identified as ketone **(2)** (17% conversion) by a comparison of the i.r. and ^{19}F n.m.r. spectra of the mixture with those reported [4]. In an attempt to improve the yield the mixture was treated with further oxidant (1:20 molar ratio) and heated under reflux in



Scheme 2

dichloromethane (14 days) to afford E-1,3-dibenzoyl-2-trifluoromethylpropene **(17)** (23%) and 3-benzoyl-2,4-bis(trifluoromethyl)-2-hydroxy-6-phenyl-α-pyran **(18)** (70%) the structures of which were established by X-ray diffraction.

A free-radical mechanism has been proposed [13] for the oxidation of benzyl alcohols to the corresponding aldehydes using active MnO_2 and the participation of hydroxyl radicals (presumed to be generated from hydrated MnO_2, present in the oxidant) has been postulated to account for the formation of 1,6- and 1,8-pyrene diones in the oxidation of pyrene [14].

It is proposed that alcohol **(16)** is first oxidised to ketone **(2)** (detected in the initial oxidation) and the products **(17)** and **(18)** are then formed via hydroxyl radical attack on compound **(2)** as shown in Scheme 2.

Keto-enol tautomerism involving compound **(18c)** would give the isomers **(18a)** and **(18b)** and only with the latter E-isomer is cyclisation to the α-pyran **(18)** favourable. Further hydroxyl radical attack on the Z-isomer **(18a)** followed by β-scission and hydrogen abstraction would afford the E-alkene **(17)**.

The crystal structures of compounds **(8)**, **(9)**, **(17)** and **(18)** will be published in due course [15].

EXPERIMENTAL

Starting Materials

Ethyl chloroformate, benzyl chloroformate and benzaldehyde were commercial samples whose purity was checked before use. 3,3,3-Trifluoropropyne was prepared (73%) by the reaction of 1,1,2-trichloro-3,3,3-trifluoropropene with zinc dust and zinc (II) chloride in DMF at 100 °C followed by addition of water at 60 °C [16] and its lithium salt (3) was made by bubbling the alkyne into a stirred mixture of n-butyl-lithium (1.55M solution in hexane) in the appropriate anhydrous solvent maintained at -60 to -78 °C under a nitrogen atmosphere in a flask fitted with a dropping funnel and a cold finger (-78 °C). Active manganese (IV) oxide was prepared by the method of Attenburrow et al [17].

General Techniques

Individual components of liquid and solid reaction product mixtures were separated by column chromatography using silica (Kieselgel 60, 0.40 to 0.063 mm)

or dry column 'flash' chromatography (DCFC) using silica (Kieselgel 60H, 15 μm) after examination by TLC.

Products were examined by i.r. spectroscopy (Perkin-Elmer 783 instrument), ^{1}H n.m.r. (Perkin-Elmer R34 spectrometer operating at 220 MHz; reference Me_4Si), ^{19}F n.m.r. (Perkin-Elmer R32 spectrometer operating at 84.6 MHz; reference CF_3CO_2H) and ^{13}C n.m.r. spectroscopy (Bruker WP80 spectrometer operating at 20.1 MHz with broad band proton decoupling using D_2O as the deuterium lock signal and Me_4Si as internal reference) and mass spectrometry (Kratos MS45 instrument with an electron beam energy of 70 eV).

X-ray crystallography was carried out on a CAD-4 diffractometer.

Compounds (7), (8), (9), (16), (17) and (18) are new.

Reactions of 3,3,3-Trifluoropropynyl-lithium(3)

(a) With ethyl chloroformate

Ethyl chloroformate (1.80 g, 16.9 mmol) in di-n-butyl ether (10 cm^3) was added slowly to a stirred solution of the salt **(3)** [prepared from n-butyl-lithium (1.08 g, 16.9 mmol) and trifluoropropyne (1.90 g, 20.2 mmol) in di-n-butyl ether (50 cm^3) with the hexane removed as far as possible by evaporation in vacuo at -23 °C before addition of the alkyne] at -60 °C and stirring was continued (1 h). Water (20 cm^3) was added at ambient temperature and the mixture was stirred (4 h). The material volatile in vacuo at -23 °C from the dried ($CaCl_2$) organic layer was repeatedly fractionated (2 mmHg) to give a mixture (1.01 g) (-64 °C trap) of hexane and ethyl 4,4,4-trifluorobut-2-ynoate **(1a)** (0.95 g, 5.75 mmol, 34%) in the ratio 1:8 (^{1}H n.m.r.); the ester was identified by a comparison of its i.r. [1740 s (C=O str.) cm^{-1}] and ^{1}H [δ_H + 1.05 (t, 3 H, CH_3) and + 4.05 (q, 2 H, OCH_2)p.p.m.] and ^{19}F n.m.r. [δ_F + 25.0 (s, $CF_3C{\equiv}C$) p.p.m.] spectra with those reported [3].

A second experiment employing n-butyl-lithium (1.28 g, 20.0 mmol) in di-n-butyl ether (50 cm^3) and the alkyne (2.04 g, 21.7 mmol) and carried out under the same conditions, except that an excess of ethyl chloroformate (3.28 g, 30.2 mmol) in di-n-butyl ether (10 cm^3) was added at -78 °C in one portion, gave a -64 °C fraction (2.89 g) shown by ^{1}H and ^{19}F n.m.r. spectroscopy to consist of unchanged ethyl chloroformate (1.48 g, 13.6 mmol, 45% recovered), ester **(1a)** (1.30 g, 7.9 mmol, 39%) and hexane (0.11 g).

(b) With benzyl chloroforomate

Benzyl chloroformate (3.38 g, 19.82 mmol) in diethyl ether (10 cm^3) cooled to -40 °C was added in one portion to a stirred solution of the salt **(3)** [prepared from n-butyl-lithium (0.63 g, 9.92 mmol) in diethyl ether (25 cm^3) and trifluoropropyne (1.17 g, 12.45 mmol)] at -78 °C and stirring was continued during 45 minutes. The resulting material was filtered and the ether removed from the filtrate by evaporation to give a mixture (4.12 g) of unreacted benzyl chloroformate (2.70 g, 15.86 mmol, 80% recovered), benzyl 4,4,4-trifluorobut-2-ynoate **(1b)** (0.97 g, 4,25 mmol, 43%), $\nu_{max.}$ 1740s (C=O str.) cm^{-1}, δ_H 7.35 (broad, Ph) and 5.10 (s, OCH_2) p.p.m., δ_F + 26.8 (s, $CF_3C{\equiv}C$) p.p.m. and bis(3,3,3-trifluoropropynyl) ketone (4) (0.45 g, 2.12 mmol, 43%), $\nu_{max.}$ 1720s (C=O str.) cm^{-1}, δ_F + 26.3 (s, $CF_3C{\equiv}C$), p.p.m. Attempts were made to separate the three compounds by DCFC using a wide range of solvents, but even the best mixture (CH_2Cl_2 and C_5H_{12}, 3:1 v/v R_F values 0.91, 0.88 and 0.82) was not satisfactory to effect a separation.

(c) With carbon dioxide

Gaseous carbon dioxide was slowly passed (2.5 h) into a stirred solution of salt **(3)** [prepared from n-butyl-lithium (5.9 g, 93.0 mmol) in diethyl ether (200 cm^3) and trifluoropropyne (11.52 g, 122.5 mmol)] at -34 °C and the resulting material was warmed to room temperature. Aqueous hydrochloric acid (100 cm^3, 2M) was added and stirring was continued during 30 minutes. The organic layer was separated, dried ($MgSO_4$) and the ether removed by distillation to leave a liquid residue, which was fractioned at 2 mmHg to afford a -23 °C fraction (7.14 g) identified as a mixture of 4,4,4-trifluorobut-2-ynoic acid **(6)** (6.20 g, 44.92 mmol, 49%) and diethyl ether (0.94 g) in the ratio 3.53:1.0 (Found: C, 39.0; H, 2.7; F, 35.4%. Calc. for a mixture of $C_4HF_3O_2$ and $C_4H_{10}O$ in the ratio 3.53:1.0:C, 38.75; H, 2.4; F, 35.8%), b.p. 126 °C at 755 mmHg, $\nu_{max.}$ 3380 broad (O-H str.), 2260s (C≡C str.), 1720 vs (C=O str.) 1260s (C-F str.) and 1150s (C-O str.) cm^{-1}, δ_H ($CDCl_3$) 11.15 (s, CO_2H) p.p.m., δ_F ($CDCl_3$) + 24.0 (s, $CF_3C{\equiv}C$) p.p.m., m/z 138 (1.5%, M^+), 121 [17.6%, $(M\text{-}OH)^+$], 93 (69%, $C_3F_3^+$) 75 (100%, $C_3HF_2^+$) and 69 (32%, CF_3^+). All attempts to isolate the pure acid (6) were unsuccessful.

(d) With benzaldehyde

Benzaldehyde (6.26 g, 59.1 mmol) in diethyl ether (30 cm^3) was added dropwise to a stirred solution of salt **(3)** [prepared from n-butyl-lithium (5.54 g, 55.8

mmol) in diethyl ether (200 cm^3) and trifluoropropyne (6.10 g, 64.9 mmol)] at -34 °C and stirring was continued (2 h) while the solution warmed to room temperature. Hydrochloric acid (50 cm^3, 2M) was added, the ether layer was separated and dried ($CaCl_2$) and the ether removed by evaporation to give impure product (11.16 g). Purification by DCFC [eluant petrol (b.p. 40-60 °C) and dichloromethane (1:2 v/v)] gave 1-phenyl-4,4,4-trifluorobut-2-yn-l-ol **(16)** (9.27 g, 46.35 mmol, 83%) (Found: C, 60.1; H, 3.8; F, 28.0%; M^+ 200. $C_{10}H_7F_3O$ requires C, 60.0; H, 3.5; F, 28.5%; M, 200), b.p. 96 °C at 9 mmHg, $\nu_{max.}$ 3450s (O-H str.), 3040w (C-H str.) 2275 w (C≡C str.), 1600s, 1490s, and 1450s (aromat. C=C str.), 1275s (C-F str.) and 1140s (C-O str.) cm^{-1}, δ_H ($CDCl_3$) 4.85 (s, 1H, CH), 5.20 (s, 1H, OH) and 7.30 (s, 5 H, C_6H_5) p.p.m., δ_F ($CDCl_3$) + 27.3 ($CF_3C{\equiv}C$) p.p.m., δ_C 63.56 (s, CH) 73.17 (q, CF_3C, J 53.0 Hz), 86.45 (q, CF_3C C, J 6.4 Hz), 114.2 (q, CF_3, J 257.5 Hz) and 126.65, 128.88, 129.12 and 137.66 (phenyl) p.p.m., m/z 200 (100%, M^+), 199 [67.1%, $(M\text{-}H)^+$], 183 [70.2%, $(M\text{-}OH)^+$], 182 [21.6%, $(M\text{-}H_2O)^+$], 131 [29.1%, $(M\text{-}CF_3)^+$] 121 (22.5%, $C_4F_3O^+$), 105 (14.4%, $C_7H_5O^+$) and 77 (27.9%, $C_6H_5^+$).

Reaction of Acid **(6)** with Diazomethane

A solution containing an excess of diazomethane (2.73 g, 65.0 mmol) in diethyl ether was added dropwise to a stirred solution of hexane and 4,4,4-trifluorobut-2-ynoic acid (4.1 g, 29.8 cm^3) in diethyl ether (100 cm^3) at 0 °C. The resulting solution was slowly allowed to warm to room temperature (2 h) and the ether was removed by distillation to afford a semi-solid residue (5.16 g), shown by TLC (C_6H_{14}/CH_2Cl_2 1:2 v/v) to contain three components (R_F 0.82, 0.45 and 0.10). These were separated by DCFC (eluants C_6H_{14}/CH_2Cl_2 1:2 v/v for components 1 and 2 and CH_2Cl_2 for component 3) and were identified as (i) 5-carbomethoxy-1-methyl-4-trifluoromethylpyrazole **(7)** (1.98 g, 9.5 mmol, 32%) (Found: C, 40.7; H, 3.8; N 13.3; F, 27.3%; M^+, 208. $C_7H_7F_3N_2O_2$ requires C, 40.4; H, 3.4; N, 13.5; F, 27.4%; M, 208), $\nu_{max.}$ 2945, 2910 and 2840 m (C-H str.), 1730 s (C=O str.), 1460 and 1510 s (C=N str.), 1260 s (C-F str.), 1145 s (C-O str.) and 1090 and 800 s (N-CH_3 str.) cm^{-1}, δ_H ($CDCl_3$) 3.80 (s, 3H N-CH_3), 4.05 (s, 3 H, O-CH_3) and 7.60 (1 H, CH), p.p.m. , δ_F ($CDCl_3$) + 20.7 (CF_3) p.p.m. m/z 208 (17.5%, M^+), 189 [55.3%, $(M\text{-}OH)^+$], 188 [51.7%, $(M\text{-}OH_2)^+$], 177 [100% $(M\text{-}OCH_3)^+$], 149 [16.8%, $(M\text{-}CO_2CH_3)^+$] and 129 (34.1%, $C_5H_3F_2N^+$), (ii) 3-carbomethoxy-1-methyl-4-trifluoromethyl-pyrazole **(8)** (0.39 g, 1.88 mmol, 6.5%) (Found C, 40.4; H, 3.4; N, 13.5%; M^+ 208), m.p. 89 °C, $\nu_{max.}$ 2945, 2910 and 2840s (C-H str.), 1725 s(C=O str.), 1440 and 1570 s (C=N str.), 1260 s(C-F str.), 1100s (C-O str.) and 1095 and 800 s (N-CH_3 str.) cm^{-1}, δ_H ($CDCl_3$) 3.90 (s, 3 H, N-CH_3), 4.02 (s, 3H, O-CH_3) and 7.81 (s, 1 H,

CH) p.p.m., δ_F ($CDCl_3$) + 21.4 (CF_3) p.p.m., m/z 208 13.5%, M^+), 189 [13.3%, (M-OH)$^+$], 177 (100%, (M-OH_2)$^+$] and 42 (16.0%, $C_2H_2O^+$), and (iii) 3-carbomethoxy-4-trifluoromethylpyrazole **(9)** (2.6 g, 13.4 mmol 45%) (Found: C, 37.1; H, 2.3; N, 14.1; F, 29.4%; M^+, 194. $C_6H_5F_3O_2$ requires C, 37.1; H, 2.6; N, 14.4; F, 29.4%; M, 194),m.p. 151 °C, $\nu_{max.}$ 3145 m (N-H str.), 2890 s(C-H str.), 1730s (C=O str.), 1460 and 1510s (C=N str.) 1300 s (C-F str.) and 1140s (C-O str.) cm^{-1}, δ_H ($CDCl_3$) 4.20 (s, 3 H, O-CH_3), 8.35 (s, 1H, CH) and 12.35 (s, 1 H, NH) p.p.m., δ_H ($CDCl_3$) + 20.4 (CF_3) p.p.m., m/z 194 (45.5%, M^+), 175 [50.6%, (M-F)$^+$], 163 [100%, (M-OCH_3)$^+$], 144 (29.8% $C_5H_2F_2N_2O^+$) and 143 (60.1%, $C_5HF_2N_2O^+$).

Reaction of Alcohol (16) with Active Manganese (IV) Oxide

A mixture of 1-phenyl-4,4,4-trifluorobut-2-yn-1-ol **(16)** (0.80 g, 4.0 mmol) and active manganese(IV) oxide (4.0 g, 45.8 mmol) in dichloromethane (25 cm^3) was stirred under an atmosphere of nitrogen at room temperature (24 h) with the reaction monitored by TLC and a minor product (R_F 0.77, CH_2Cl_2 and C_5H_{12} 2:1 v/v) was detected. The mixture was filtered and the solvent removed by evaporation to give a mixture (0.80 g) of unchanged alcohol **(16)** (0.66 g, 3.32 mmol, 83% recovered) and phenyl 3,3,3-trifluoropropynyl ketone **(2)** (0.13 g, 0.68 mmol, 17% conversion) which was identified by a comparison of its i.r. and ^{19}F n.m.r. spectra with those reported [4], $\nu_{max.}$ 2190w (C≡C str.) and 1655s (C=O str.) cm^{-1}, δ_F +26.3 (s, CF_3) p.p.m.

The mixture was treated with a further quantity of the oxidant (6.90 g, 79.0 mmol) in dichloromethane (30 cm^3) and heated under reflux (14 days). Filtration and removal of the solvent by evaporation afforded a residue (0.78 g) which was shown by TLC to contain two components (R_F 0.80 and 0.37, CH_2Cl_2 and C_5H_{12} 2:1 v/v). These were separated by DCFC using the same solvent mixture to give (i) E-1,3-dibenzoyl-2-trifluoro-methylpropene **(17)** (0.15 g, 0.46 mmol, 23%) (Found: C, 67.7; H, 4.0; F, 18.1%; M^+, 318. $C_{18}H_{13}F_3O_2$ requires C, 67.9; H, 4.1; F, 17.9%; M, 318), m.p. 76 °C, $\nu_{max.}$ 3095 and 3070 m (arom.C-H str.), 2935 m (aliph. C-H str.), 1690 and 1675 s (C=O str.), 1600 and 1580 m (C=C str.), 1450m (C-H def.), 1325, 1305 and 1220s (C-F str.) and 890s (arom. C-H def.) cm^{-1}, δ_H ($CDCl_3$) 4.45 (s, 2H, CH_2), 7.35 to 7.70 (mult., 7 H, = CH and meta and para phenyl hydrogens) and 7.85 to 8.05 (mult, 4 H, ortho phenyl hydrogens) p.p.m., δF ($CDCl_3$) + 8.0 (d, CF_3, J, 1.9 Hz), δ_C ($CDCl_3$), 36.79 (s, CH_2), 123.14 (q, CF_3, J 274.9 Hz), 127.92 (q, = CH, J 5.45 Hz), 128.18, 128.52, 128.69, 128.81, 133.48, 133.83, 136.21 and 137.09 (all s, C_6H_5), 137.14 (q, CF_3-C=, J 31.05 Hz) 190.02 (s, CH_2C=O) and 192.84 (s, =CH-C=O) p.p.m., m/z 318 (2.5%, M^+), 301 [27,8% (M-

OH)$^+$], 106 (26.0%, PhCHO$^+$), 105 (100%, PhCO$^+$) and 77 (51.0%, $C_6H_5^+$), and (ii) a product (0.60 g) which on recrystallisation ($CHCl_3/C_5H_{12}$ 1:10 v/v) afforded colourless crystals of 3-benzoyl-2,4-bis(trifluoromethyl)-2-hydroxy-6-phenyl-α-pyran **(18)** (0.57 g, 1.40 mmol, 70%) (Found: C, 58.3; H, 3.1; F, 27.7%; M$^+$, 414. $C_{20}H_{12}F_6O_3$ requires C, 58.0; H, 2.9; F, 27.5%; M, 414), m.p. 124 °C, $\nu_{max.}$ 3190 m (O-H str.), 1650s C=O str.) 1600 and 1580 m (C=C str.), 1450 m (C-H def.), 1270, and 1140s (C-F str.), 1200s (C-O str.) and 900s (arom. C-H def.) cm^{-1}, δ_H ($CDCl_3$) 5.45 (s, 1H, OH), 6.20 (s, 1H, CH=), 7.30 to 7.85 (mult.,8 H, Ph and meta and para-hydrogens of PhCO) and 8.01 (d, 2 H, ortho hydrogens of PhCO) p.p.m., δ_F($CDCl_3$) -2.0 (s, 3 F, CF_3) and + 16.0 (s, 3F, CF_3C=) p.p.m., δ_C ($CDCl_3$) 91.24 (q, CF_3C-CH, J 2.7 Hz), 96.42 (q, CF_3C-O, J 35.0 Hz), 119.84 (q, C-C=O, J 2.58 Hz), 121.51 (q, CF_3C-O, J 276 Hz), 121.61 (q, CF_3C=C, J 288 Hz), 125.75, 128.71, 128.81, 129.92, 131.09, 131.14, 134.88 and 135.66 (all s, 2 x C_6H_5), 130.00 (q, CF_3C=C, J 33.3 Hz), 153.98 (s, PhC=CH) and 193.95 (s, C=O), p.p.m., m/z 414 (8.0%, M$^+$), 397 [100%, (M-OH)$^+$], 293 (15.7%, $C_{13}H_7F_6O^+$), 105 (88.8%, PhCO$^+$) and 77 (10.4%, $C_6H_5^+$).

In a second experiment a mixture of alcohol **(16)** (0.80 g, 4.0 mmol) and active manganese (IV) oxide (4.10 g, 45.8 mmol) in dichloromethane (45 cm^3) stirred under nitrogen at room temperature (24 h), gave alkene **(17)** (0.15 g, 0.48 mmol, 24%) and the α-pyran **(18)** (0.54 g, 1.3 mmol, 65%).

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