Fluorinated acetylenes. Part 11. Reaction of [1,1-bis(3,3,3-trifluoropropynyl)]ethyl ethanoate with cyclohexa-1,3-diene and of [α,α-bis(3,3,3-trifluoropropynyl)]benzyl benzoate with norbornadiene and diazomethane*

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Abstract

The reaction of cyclohexa-1,3-diene with the dialkynyl ester $(CF_3C{\equiv}C)_2CMeO_2CMe$ (**1a**) at 70 °C gives a mixture of two diastereomers (ratio 9:2) of the Diels–Alder adduct [2-(2-acetoxy-5,5,5-trifluoropent-3-yn-2-yl)-3-trifluoromethyl]bicyclo[2.2.2]octa-2,5-diene (**3**), which on thermolysis at 100 °C affords mainly 2-(2-acetoxy-5,5,5-trifluoropent-3-yn-2-yl)benzotrifluoride (**4**) together with a small amount of its hydration product 2-(2-acetoxy-5,5,5-trifluoropent-3-one-2-yl)benzotrifluoride (**5**). Attempted cycloaddition between norbornadiene and the corresponding benzoate ester $(CF_3C{\equiv}C)_2CPhO_2CPh$ (**1b**) at 150 °C gave a complex mixture of unidentified products; reaction did not occur at 100 °C. Facile reaction occurred between diazomethane and the ester **1b** at 0 °C to give [α,α-bis(4-trifluoromethylpyrazol-3-yl)]benzyl benzoate (**16**) and [α-(1-methyl-4-trifluoromethylpyrazol-5-yl)-α-(4-trifluoromethylpyrazol-3-yl)]benzyl benzoate (**15**) and hence [α,α-bis(1-methyl-4-trifluoromethyl pyrazol-3-yl)benzyl benzoate (**17**), [α-(1-methyl-4-trifluoropyrazol-3-yl)-α-(1-methyl-4-trifluoromethylpyrazol-5-yl)]benzyl benzoate (**14**) (major product) and [α,α-bis(1-methyl-4-trifluoromethylpyrazol-5-yl)]benzyl benzoate (**13**).

Introduction

In the previous paper in this series [1] the preparation of the dialkynyl esters $(CF_3C{\equiv}C)_2CRO_2CR$, (**1a**) R = Me and (**1b**) R = Ph, in high yield from the reaction of the salt $CF_3C{\equiv}CLi$ with an excess of the appropriate acid chloride, and the thermal cycloaddition reactions of the esters **1** with furan and cyclopentadiene, were described. The novel 1:1 adducts which were isolated were formed via Diels–Alder reaction involving one acetylene triple bond followed by intramolecular $[{}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition to give an unstable intermediate adduct **2** containing a bridgehead double bond in fused 3- and 5-membered rings (Scheme 1). Various rearrangements of the intermediate adduct **2** then took place to give the observed products. A number of these results have been published as a preliminary communication [2].

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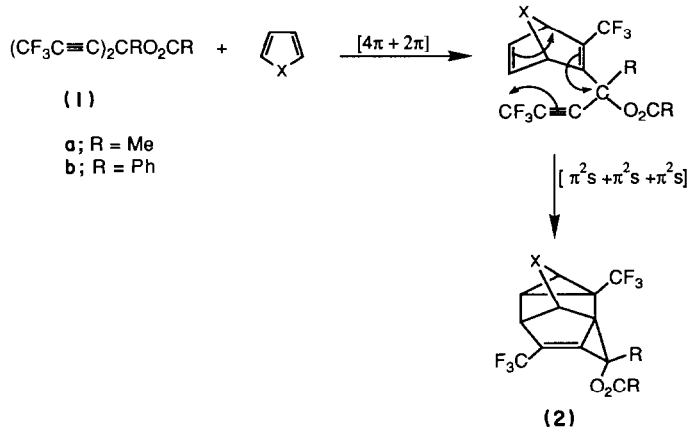


Scheme 1.

We now report an extension of this study covering the reactions of the ester **1a** with cyclohexa-1,3-diene and of the ester **1b** with norbornadiene and diazomethane.

Results and discussion

The reaction of ester **1a** with cyclohexa-1,3-diene [1:1 molar ratio at 70 °C in dichloromethane over 10 d after separation of the products by dry column flash chromatography (DCFC)] gave unchanged **1a** (20% recovered) and the two diastereomeric Diels–Alder 1:1 adducts **3** (45% and 20%). Models indicated a greater steric congestion between the O_2CMe group and the ring CH_2 groups in isomer **3b** than in isomer **3a**. Hence, it is concluded that the first eluted and major isomer has the structure **3a** and the minor isomer has the structure **3b**.

In a second experiment (1:1 molar ratio at 70 °C for 20 d) complete conversion of ester **1a** into the 1:1 adduct **3** occurred as shown by ^{19}F NMR spectroscopy. Adduct **3** was then heated at 100 °C for 13 d, and the two major products were separated by DCFC and identified as the 2-alkynylbenzotrifluoride **4** (61%) and the related ketone **5** (4%). When a mixture of compound **4** and dilute aqueous hydrochloric acid was heated at 100 °C for 10 d, the crude reaction mixture was shown (^{19}F NMR spectroscopy) to contain unchanged **4** and the ketone **5**, in a ratio of *c.* 1:2.

The molecular formulae of compounds **3–5** were determined as $C_{16}H_{14}F_6O_2$ (1:1 adduct), $C_{14}H_{10}F_6O_2$ (1:1 adduct $-C_2H_4$) and $C_{14}H_{12}F_6O_3$ (1:1 adduct $-C_2H_4+H_2O$) by elemental analysis and the presence in each mass spectrum of a parent ion peak, and their structures were established from the following spectral data.

The IR spectra of the 1:1 adduct isomers **3a** and **3b** and of compound **4** showed IR bands assigned to C≡C (2280 cm^{-1}) and ester carbonyl (1760 cm^{-1}) stretch, and the ^{19}F NMR spectra both consisted of two singlet absorptions (ratio 1:1) at *c.* +21 and +27 ppm in the regions expected for CF_3 groups bonded to vinylic and acetylenic carbons, respectively. The presence of the $CF_3C{\equiv}CCMeO_2CMe$ grouping in these compounds was confirmed by the ^1H and ^{13}C (including DEPT 135°) NMR spectra [δ_H *c.* 2.1 (CH_3CO_2); and 1.7–2.05 ($CH_3{-}C\leq$) ppm. δ_c *c.* 168 (s, ester C=O); *c.* 114 (q, CF_3, ^1J=258 Hz); *c.* 85 (q, $CF_3C{\equiv}C$, ^3J=6 Hz); *c.* 73 (q, $CF_3C{\equiv}C$, ^2J=53 Hz); *c.* 73 (s, $\geq C{-}O$); *c.* 40 (s, CH_3CO_2); and *c.* 20 (s, $CH_3{-}C\leq$) ppm]. Compounds **3a** and **3b** also contained two vinylic hydrogens (δ_H 6.3–6.5 ppm. δ_c *c.* 134 ppm), two bridgehead methine hydrogens [δ_H 3.9–4.1 ppm. δ_c *c.* 27; and *c.* 38 (q, $CF_3C{-}CH$, ^3J=4 Hz) ppm], two methylene groups (δ_H 1.3–1.8 ppm. δ_c 23.9–24.4 ppm) and a $CF_3C{=}C$ grouping [δ_c *c.* 123 (q, CF_3, ^1J=271 Hz); *c.* 129.5 (q, $CF_3C{=}C$), ^2J=33 Hz); and *c.* 149 (q, $CF_3C{=}C$, ^3J=4 Hz) ppm], thus confirming the structures of the 1:1 adducts.

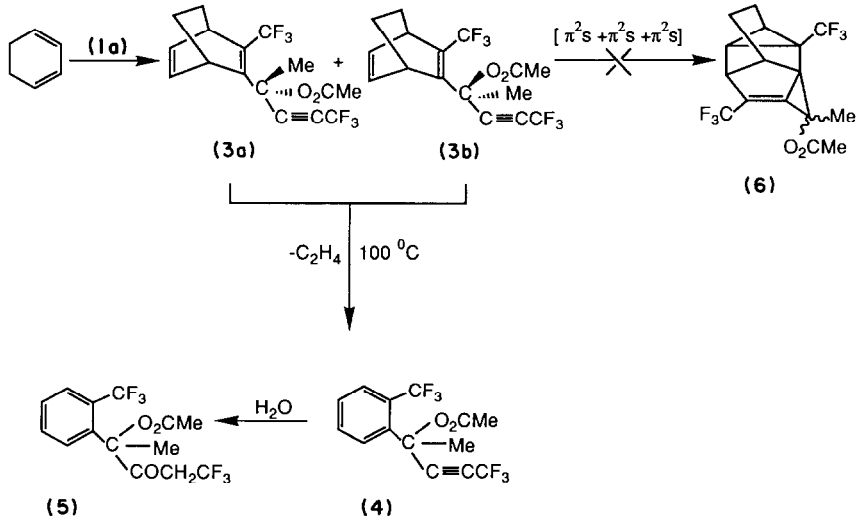
Compounds **4** and **5** were shown to be *ortho*-disubstituted benzenes containing a CF_3 substituent by their ^1H NMR (four adjacent aromatic hydrogens in the range δ_H 7.88–7.48 ppm with the appropriate couplings) and ^{13}C NMR spectra [δ_c *c.* 133–129 (3s, 3 aromatic=CH); *c.* 129 (q, aromatic =CH in $CF_3C{=}CH$ grouping, ^3J=6–7 Hz); *c.* 127 (q, ipso $=CCF_3$, ^2J=31 Hz); 140–136 (q, ipso $C{=}CCF_3$, ^3J=2 Hz); and *c.* 125 (q, CF_3, ^1J=273 Hz) ppm].

In compound **5** the acetylenic group $CF_3C{\equiv}C$ was replaced by the CF_3CH_2CO group [δ_H 3.53 (q, CF_3CH_2, J=10 Hz) ppm. δ_F+16.2 (t, CF_3CH_2, J=10 Hz) ppm. δ_c 197.7 (s, ketonic C=O); 124.4 (q, CF_3 ^1J=277 Hz); and 41.8 (q, CF_3CH_2, ^2J=29 Hz) ppm].

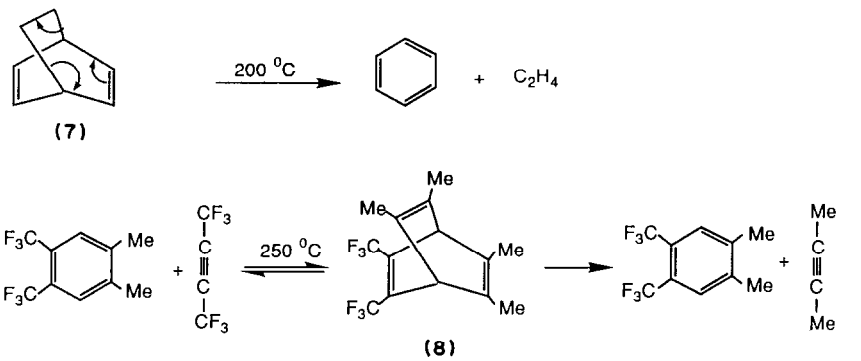
In the original experiment, ketone **5** is presumably formed from compound **4** and traces of water present in the reaction tube. Effective additions of water to alkynes normally take place only in the presence of catalysts such as mercury(II) salts. However, if a strong electron-withdrawing group is bonded to the alkynyl carbon, reaction can occur with water in the absence of a catalyst, e.g. conversion of the alkynes $PhC{\equiv}CSO_2CF_3$ [3] and $CF_3C{\equiv}CCHMeO_2CMe$ [4] into the ketones $PhCOCH_2SO_2CF_3$ and $CF_3CH_2COCHMeO_2CMe$, respectively. The products **3–5** are considered to be formed as shown in Scheme 2.

Under the reaction conditions, intramolecular [$_\pi2_s+{}_\pi2_s+{}_\pi2_s$] cycloaddition to give compound **6** did not compete with cleavage of ethene to form the arene **4**. Comparable retro-Diels–Alder reactions have been reported with bicyclo[2.2.2]octa-2,5-diene (**7**) [5] and its hexasubstituted derivative **8** [6] (Scheme 3).

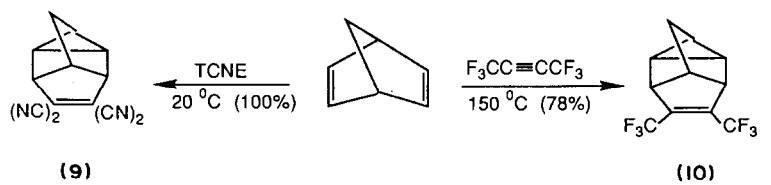
The two π-bonds of norbornadiene are reactive towards homo-Diels–Alder reactions with appropriate dienophiles, e.g. the formation of compounds **9** [7] and **10** [6] with tetracyanoethylene (TCNE) and hexafluorobut-2-yne, respectively.



Scheme 2.

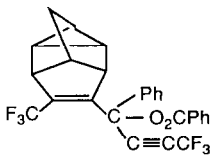


Scheme 3.



To determine whether norbornadiene would undergo a corresponding $[_{\pi}2_s + _{\pi}2_s + _{\pi}2_s]$ cycloaddition with ester **1b**, a mixture of the compounds (2:1 molar ratio) in dichloromethane was heated initially at 100 °C with the reaction monitored by TLC, but product formation was not detected over two weeks. The temperature was increased to 150 °C (14 d) after which the ^{1}H and ^{19}F NMR spectra of the resulting material indicated that a very complex mixture of products had been formed, none of which was major.

Thus, if cycloaddition had taken place, the resulting 1:1 and 2:1 adducts, **11** and **12**, respectively, were not stable at 150 °C.



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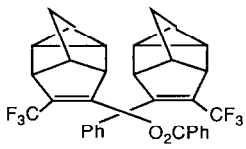


(12)

Two reactions of ester **1b** with diazomethane were carried out. In the first experiment, dropwise addition of an ethereal solution of diazomethane to a stirred ethereal solution of ester **1b** at 0 °C (*c.* 3.5:1 molar ratio), followed by removal of the ether, gave material which was shown by TLC to contain four major and several minor components. Separation of the major components by column chromatography gave (in order of elution) the bis(methylpyrazoles) **13** (6.5%) and **14** (45%), the monomethylbispyrazole **15** (10%) and the bispyrazole **16** (19%).

From a second experiment carried out under the same conditions but using an excess of diazomethane (*c.* 4.5:1 molar ratio), the three major products, which were separated by repeated DCFC, were the bis(methylpyrazoles) **13** (20%), **14** (39%) and **17** (18%).

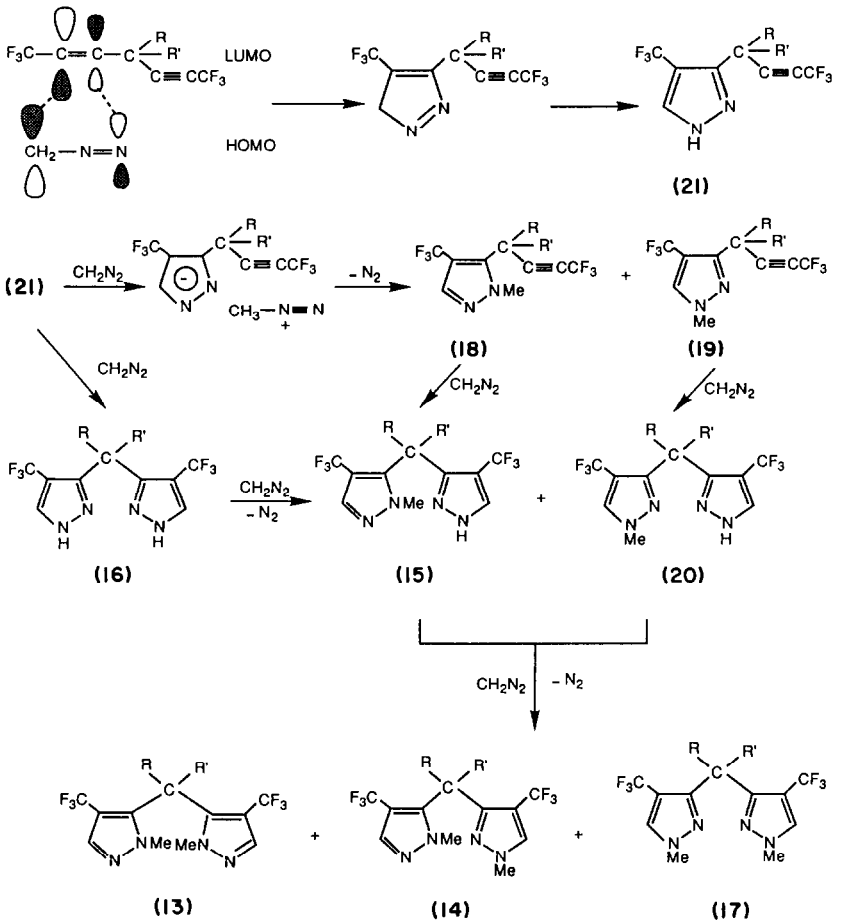
The products **13–17** are considered to be formed as shown in Scheme 4. The other expected products, the monomethylpyrazoles **18** and **19**, and the monomethylbispyrazole **20**, were not isolated, but may have been present in minor amounts.

The structures of compounds **13** and **14** were established by single-crystal X-ray studies [8], while those of compounds **15–17** were determined by a consideration of their NMR spectra (especially ^{13}C), including a comparison with the spectra of compounds **13** and **14**. The relevant ^{13}C NMR shifts are given in Table 1.

The IR spectra of compounds **15** and **16** showed a broad absorption at *c.* 3200 cm^{-1} (N–H str.). Compounds **16** and **17** each exhibited only one absorption in their ^{19}F NMR spectra at δ_F *c.* +24 ppm, indicating that both CF_3 groups were equivalent, and compound ***16*** showed an absence of an absorption at δ_H 3.5–3.9 ($N-CH_3$) ppm in its ^1H NMR spectrum.

A low-field absorption at δ_c *c.* 150 ppm observed in the ^{13}C spectrum of compound **14**, assigned to C=N (C-3), was also present in the spectra of compounds **15–17** but absent in that of compound **13**; the latter compound therefore is the only one which does not contain such a carbon atom doubly bonded to nitrogen. The HC= carbons (identified by DEPT 135° spectra) were γ to fluorine (^3J *c.* 3–4 Hz) and absorbed to lower field (δ_c 138.0–139.3 ppm) when doubly bonded to nitrogen [compounds **13–15**] than when doubly bonded to carbon (δ_c 132.6–135.2 ppm) [compounds **14–17**]. These spectral data prove unequivocally the structural identities of compounds **15–17**.

Diazomethane additions are generally dipole HOMO controlled, and the regiospecific addition to ester **1b** indicates that the larger frontier orbital in



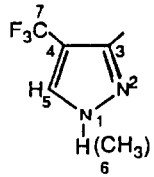
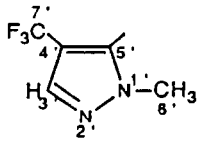
Scheme 4.

the LUMO of the alkyne is associated with the carbon bonded to CF_3. An analogous regiospecific addition has been observed in the reaction of diazomethane with the ester $CF_3C{\equiv}CCHMeO_2CMe$ [4].

The only compound isolated corresponding to reaction involving 2 equiv. of diazomethane was the bispyrazole **16**; the monomethylpyrazoles **18** and **19** were not detected. This indicates that addition to the triple bond in the 1:1 adduct **21** is faster than abstraction of the N–H proton. Of the two possible monomethylbispyrazoles **15** and **20**, only the former was isolated, although compound **20** must have been formed, as it is the precursor to the bis(methylpyrazole) (**17**) [and also probably **14**]. The reason why compound **20** is more reactive than **15** is not apparent. The major bis(methylpyrazole) was the unsymmetrical isomer **14**, presumably because it can be formed from two precursors, **15** and **20**; each of the other bis(methylpyrazoles), **13** and **17**, can only be formed from one precursor.

TABLE 1

^{13}C NMR chemical shifts (ppm)

Carbon					
	13	**14**	**15**	**16**	**17**
3[a]		148.9	151.2	147.6	151.4
4[b]		110.8	110.0	109.6	110.6
5[c]		132.6	133.1	135.1	135.2
6		41.2			41.1
7[d]		122.4	122.3	122.0	124.4
3'[c]	138.3	138.0	139.3		
4'[b]	112.8	112.4	111.5		
5'[e]	139.7	141.5	143.6		
6'[]	40.7	39.3	39.7		
7'[d]	121.8	122.0	121.6		

[a]Broad unresolved absorption.
[b]Quartet, ^2J c. 38 Hz.
[c]Quartet, ^3J c. 4 Hz.
[d]Quartet, ^1J c. 267 Hz.
[e]Quartet, ^3J c. 3 Hz.

Experimental

General techniques

Reaction product mixtures were examined by TLC methods and were separated by dry column 'flash' chromotography (DCFC) using silica gel (60 H Merck Kieselgel GF_{256}) with the eluants employed given in the text; light petroleum refers to the petroleum ether fraction of b.p. 40–60 °C.

^1H nuclear magnetic resonance (NMR) spectra were run on a Bruker AC (300 MHz) FT spectrometer, ^{13}C broad-band decoupled NMR (including DEPT 135°) spectra were recorded on the Bruker AC (75.0 MHz) machine and ^{19}F NMR spectra were recorded on a Perkin-Elmer R32 (84.6 MHz) spectrometer. External tetramethylsilane (TMS) and external trifluoroacetic acid (TFA) were used as the respective references, the samples being run as solutions in deuteriochloroform ($CDCl_3$) and chemical shifts to the low field of reference being 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) with ammonia gas] were run on Kratos MS 45 or MS 25 instruments operating at 70 eV.

Single-crystal X-ray structure determinations were carried out on a CAD4 diffractometer. Melting points are uncorrected.

Starting materials

The 1,4-dialkynyl esters **1a** and **1b** were prepared in high yield as reported previously [1] by reaction of an excess of the appropriate acid chloride with 3,3,3-trifluoropropynyl-lithium. Cyclohexa-1,3-diene and norbornadiene were commercial samples, the purities of which were checked before use.

*Reaction of [1,1,-bis(3,3,3-trifluoropropynyl)]ethyl ethanoate (**1a**) with cyclohexa-1,3-diene*

A mixture of the ester **1a** (3.40 g, 12.5 mmol), cyclohexa-1,3-diene (1.00 g, 12.5 mmol) and dichloromethane (5 cm^3) was heated *in vacuo* in a Rotaflo tube (*c.* 30 cm^3) at 70 °C (10 d) and the solvent then removed (rotary evaporator) to afford a thick liquid (4.02 g). The liquid was shown (^{19}F NMR spectroscopy) to consist of the unchanged ester **1b** and two products (ratio *c.* 2:1). Separation was achieved by repeated DCFC [light petroleum–dichloromethane (6:1 v/v)] which gave (in order of elution) unchanged ester **1a** (0.68 g, 2.5 mmol, 20% recovered) and the following two diastereomeric 1:1 adducts.

(i) [2-(2-Acetoxy-5,5,5-trifluoropent-3-yn-2-yl)-3-trifluoromethyl]bicyclo-[2.2.2]octa-2,5-diene (**3a**) (nc) (1.98 g, 5.6 mmol, 56%). (Analysis: Found C, 54.3; H, 4.0; F, 32.4%; mol. wt., 352. $C_{16}H_{14}F_6O_2$ requires: C, 54.5; H, 4.0; F, 32.4%; mol. wt., 352); b.p. 190 °C. ^1H NMR δ: 6.41–6.32 (mult., CH=CH); 4.14 (mult., CH); 3.91 (mult., CH); 2.13 (s, CH_3CO_2, 1.81 and 1.42–1.30 (AB mult. and mult., $2CH_2$); and 1.72 (s, CH_3) ppm. ^{19}F NMR δ: +27.5 (s, $CF_3C\equiv$); and +20.6 (s, $CF_3C=$) ppm. ^{13}C NMR δ: 168.5 (s, O−C=O); 148.4 (q, $CF_3C=C$, $^3J=4$ Hz); 134.4 and 133.9 (2s, CH=CH); 129.5 (q, $CF_3C=C$, $^2J=33$ Hz); 123.5 (q, $CF_3C=$, $^1J=271$ Hz); 114.1 (q, $CF_3C\equiv$, $^1J=258$ Hz); 85.8 (q, $CF_3C\equiv C$, $^3J=7$ Hz); 73.2 (q, $CF_3C\equiv C$, $^2J=53$ Hz); 73.0 (s >C−O); 41.4 (s, CH_3CO_2); 38.1 (q, CF_3C-CH, $^3J=4$ Hz); 27.5 (s, CH); 24.3 (s, CH_2); 24.2 (q, CH_2, $^4J=1.5$ Hz); and 21.1 (s, CH_3) ppm. IR (ν_{max}) (cm^{-1}): 2280 (s, C≡C str.); 1760 (s, ester C=O str.); 1650 and 1610 (m, C=C str.); 1360 and 1280 (s, C−F str.); and 1150 (s, C−O str.). Mass spectrum (EI) (*m/z*): 352 (5.4%, M^+); 310 [8.0, $M-CH_2CO)^+$]; 293 [3.9, $(M-CH_3CO_2)^+$]; 292 [5.0, $(M-CH_3CO_2H)^+$]; 277 (8.9, $C_{13}H_7F_6^+$); 245 (5.6, $C_{12}H_6F_5^+$); 85 (15.0, $C_4H_5O_2^+$); 69 (9.0, CF_3^+); and 43 (100.0, CH_3CO^+).

(ii) [2-(2-Acetoxy-5,5,5-trifluoropent-3-yn-2-yl)-3-trifluoromethyl]bicyclo[2.2.2]octa-2,5-diene (**3b**) (nc) (0.90 g, 2.6 mmol, 26%). (Analysis: Found: C, 54.5; H, 4.3; F, 32.0%; mol. wt, 352. $C_{16}H_{14}F_6O_2$ requires: C, 54.5; H, 4.0; F, 32.4%; mol. wt, 352); b.p. 184 °C. ^1H NMR δ: 6.45 (mult., =CH); 6.35 (ddd, =CH, $J_{6-5}=8$ Hz, $J_{4-5}=6$ Hz, $J_{7-5}=1.5$ Hz); 4.10 (mult., CH); 3.89 (mult., CH); 2.05 (s, CH_3CO_2); 1.78 (s, CH_3); and 1.52 and 1.35 (2 mult., $2CH_2$) ppm. ^{19}F NMR δ: +27.5 (s, $CF_3C\equiv$); and +20.9 (s, $CF_3C=$)

ppm. ^{13}C NMR δ: 167.8 (s, O–C=O); 149.0 (q, $CF_3C=C$, $^3J=4$ Hz); 133.7 and 133.3 (2s, CH=CH); 129.4 (q, $CF_3C=C$, $^2J=33$ Hz); 122.8 (q, $CF_3C=$, $^1J=271$ Hz); 114.0 (q, $CF_3C\equiv$, $^1J=258$ Hz); 85.5 (q, $CF_3C\equiv C$, $^3J=6$ Hz); 73.0 (q, $CF_3C\equiv C$, $^2J=53$ Hz); 72.3 (s, $\geq C-O$); 40.2 (s, CH_3CO_2); 37.6 (q, CF_3C-CH, $^3J=3$ Hz); 26.9 (s, CH); 24.4 (s, CH_2); 23.9 (s, CH_2); and 20.2 (s, CH_3) ppm. IR (ν_{max}) (cm^{-1}): 2280 (s, C≡C str.); 1760 (s, ester C=O str.); 1650 and 1610 (m, C=C str.); 1280 (s, C–F str.); and 1150 (s, C–O str.). Mass spectrum (EI) (*m/z*): 352 (29.5%, M^+); 310 [11.9, $(M-CH_2CO)^+$]; 293 [100.0, $(M-CH_3CO_2)^+$]; 292 [11.9, $(M-CH_3CO_2H)^+$]; 265 (8.2, $C_{12}H_7F_6^+$); 245 (8.4, $C_{12}H_6F_5^+$); and 43 (85.1, CH_3CO^+).

Thermolysis of the 1:1 adduct ***3***

A mixture of ester **1a** (3.40 g, 12.5 mmol), cyclohexa-1,3-diene (1.00 g, 12.5 mmol) and dichloromethane was heated *in vacuo* in a Rotaflo tube (*c.* 30 cm^3) at 70 °C for 20 d after which time it was shown (^{19}F NMR spectroscopy) that complete conversion of the reactants to the 1:1 adduct **3** had taken place. The tube was resealed, the contents reheated *in vacuo* at 100 °C (13 d) and the solvent removed to give a yellow solid (3.98 g) which was shown by TLC [petroleum ether–dichloromethane (2:1 v/v)] to contain two components (R_F 0.60 and 0.15). The components were separated by DCFC (same eluant) and were identified as follows.

(i) 2-(2-Acetoxy-5,5,5-trifluoropent-3-yn-2-yl)benzotrifluoride (**4**) (nc) (2.48 g, 7.6 mmol, 61%). (Analysis: Found: C, 51.9; H, 3.3; F, 35.0%; mol. wt., 324. $C_{14}H_{10}F_6O_2$ requires: C, 51.8; H, 3.1; F, 35.2%; mol. wt., 324); m.p. 220 °C. ^1H NMR δ: 7.88 (d, arom. 6-H, $J=8$ Hz); 7.81 (d, arom. 3-H, $J=8$ Hz); 7.59 (t, arom., 5-H, $J=8$ Hz); 7.45 (t, arom., 4-H, $J=8$ Hz); 2.12 (s, CH_3CO_2); and 2.04 (s, CH_3) ppm. ^{19}F NMR δ: +27.0, (s, $CF_3C\equiv$); and +21.9 (s, $CF_3C=$) ppm. ^{13}C NMR δ: 169.4 (s, O–C=O); 139.7 (s, ipso-C_6H_4); 133.1, 129.4 and 128.7 (3s, 3 arom. =CH); 129.2 (q, arom. =CH, $^3J=6$ Hz); 126.6 (q, ipso $=CCF_3$, $^2J=31$ Hz); 124.7 (q, $CF_3C=$, $^1J=273$ Hz); 114.9 (q, $CF_3C\equiv$, $^1J=258$ Hz); 87.5 (q, $CF_3C\equiv C$, $^3J=7$ Hz); 75.4 (s, $\geq C-O$); 74.8 (q, $CF_3C\equiv C$, $^2J=53$ Hz); 31.0 (s, CH_3CO_2); and 21.7 (s, CH_3) ppm. IR (ν_{max}) (cm^{-1}): 2280 (s, C≡C str.); 1760 (s, ester C=O str.); 1502 (m, arom. C=C str.); 1340 (s, C–F str.); and 1150 (s, C–O str.). Mass spectrum (EI) (*m/z*): 325 [35.9%, $(M+H)^+$]; 328 (21.6, M^+); 305 [7.1, $(M-F)^+$]; 282 [13.1, $(M-CH_2CO)^+$]; 281 (6.0, $M-CH_3CO)^+$]; 265 [99.6, $(M-CH_3CO_2)^+$]; 263 (13.4, $C_{12}H_8F_5O^+$); 262 (23.1, $C_{12}H_7F_5O^+$); 245 (17.2, $C_{12}H_6F_5^+$); 213 (35.5, $C_{11}H_8F_3O^+$); and 43 (100.0, CH_3CO^+).

(ii) 2-(2-Acetoxy-5,5,5-trifluoropent-3-one-2-yl)benzotrifluoride (**5**) (nc) (0.18 g, 0.50 mmol, 4%). (Analysis: Found: C, 49.3; H, 3.5; F, 33.0%; mol. wt., 342. $C_{14}H_{12}F_6O_3$ requires: C, 49.1; H, 3.5; F, 33.3%; mol. wt., 342); m.p. 63 °C. ^1H NMR δ: 7.48 (d, arom. H-6, $J=8$ Hz); 7.62 (d, arom. H-3, $J=8$ Hz); 7.53 (mult., arom. H-4 and H-5); 3.53 (q, CF_3CH_2, $J_{F-H}=10$ Hz); 2.17 (s, CH_3CO_2); and 2.03 (s, CH_3) ppm. ^{19}F NMR δ +21.7 (s, $CF_3C_6H_4$); and +16.2 (t, CF_3CH_2, $J=10$ Hz) ppm. ^{13}C NMR δ: 197.7 (br. C=O); 169.7 (s, O–C=O); 136.3 (q, $CF_3C=C$, $^3J=2$ Hz); 132.7, 129.6 and 129.4 (3s,

3 arom. =CH); 129.1 (q, arom. =CH, $^3J=7$ Hz); 127.3 (ipso $=CCF_3$, $^2J=31$ Hz); 124.8 (q, $CF_3C_6H_4$, $^1J=273$ Hz); 124.4 (q, CF_3CH_2, $^1J=277$ Hz); 84.7 (s, $\geq C-O$); 41.8 (q, CF_3CH_2, $^2J=29$ Hz); 23.6 (s, CH_3CO_2); and 22.1 (s, CH_3) ppm. IR (ν_{max}) (cm^{-1}): 1740 (br. C=O str.); 1310 and 1280 (s, C−F str.); and 1120 and 1105 (s, C−O str.). Mass spectrum (CI) (*m/z*): 360 [100.0%, $(M+NH_4)^+$]; 343 [5.5, $(M+H)^+$]; 342 (0.3, M^+); 327 [5.6, $(M-CH_3)^+$]; 299 [31.3, $(M-CH_3CO)^+$]; 206 (6.8, $C_9H_6F_4O^+$); 186 (9.7, $C_9H_5F_3O^+$); 173 (14.6, $C_8H_4F_3O^+$); 157 (30.0, $C_8H_4F_3^+$); 145 (3.3, $C_6H_4CF_3^+$); 77 (6.8, $C_6H_5^+$); and 60 (8.6, $C_2H_4O_2^+$).

Hydrolysis of 2-(2-acetoxy-5,5,5-trifluoropent-3-yn-2-yl)benzotrifluoride (4)

A solution of the arene **4** (0.05 g, 1.5 mmol) in dichloromethane (4 cm^3) and dilute hydrochloric acid (2 M, 4 cm^3) was heated *in vacuo* in a Rotaflo tube (*c.* 20 cm^3) at 100 °C (10 d). The tube was washed out with dichloromethane (3.3 cm^3), the organic layer separated, dried ($CaCl_2$) and the solvent removed (rotary evaporator) to give a residue (0.41 g) which was shown (^{19}F NMR spectroscopy) to consist of unchanged **4** and the ketone **5** in the ratio *c.* 1:2.

*Reactions of [α,α-bis(3,3,3-trifluoropropynyl)]benzyl benzoate (**1b**)*

(a) With norbornadiene

A mixture of ester **1b** (3.07 g, 7.75 mmol), norbornadiene (1.43 g, 15.5 mmol) and dichloromethane (10 cm^3) was heated *in vacuo* in a Rotaflo tube (*c.* 30 cm^3) at 150 °C (14 d) and the solvent then removed (rotary evaporator) to give a residue (4.30 g). The residue was shown (TLC and ^1H and ^{19}F NMR spectroscopy) to be a complex mixture of products, none of which was major; it was not examined further.

An attempted reaction (same molar ratio) carried out at 100 °C (14 d) gave only unchanged reactants.

(b) With diazomethane, experiment 1

A solution of diazomethane (0.80 g, 19.05 mmol) in diethyl ether (40 cm^3) was added dropwise to a stirred solution of ester **1b** (2.15 g, 5.43 mmol) in diethyl ether (30 cm^3) at 0 °C. The stirred reaction mixture was kept at 0 °C (1 h) and then slowly warmed to room temperature (1 h) and the diethyl ether removed (rotary evaporator). The solid residue (2.66 g) was shown by TLC [chloroform–methanol (98:2 v/v)] to contain four major ($R_F=0.75$, 0.67, 0.42 and 0.21) and several minor components, and the major components were separated by DCFC (same eluant). The separated products were found to be wet and so they were dissolved in diethyl ether, dried (P_2O_5) and the ether removed to give the anhydrous compounds which were identified as follows:

(i) [α,α-Bis(1-methyl-4-trifluoromethylpyrazol-5-yl)]benzyl benzoate (**13**) (nc) (0.18 g, 0.35 mmol, 6.5%). (Analysis: Found: C, 56.4; H, 3.4; F, 22.6; N, 10.8%; mol. wt., 508. $C_{24}H_{18}F_6N_4O_2$ requires: C, 56.7; H, 3.5; F, 22.4;

N, 11.0%; mol. wt., 508); m.p. 145 °C. ^{1}H NMR δ: 8.17 (d, *o*-$C_6H_5CO_2$, J=6.6 Hz); 7.80–7.17 (complex, C_6H_5 and *m*- and *p*-$C_6H_5CO_2$ and 2 =CH); and 3.65 (s, 2 N−CH_3) ppm. ^{19}F NMR δ: +24.0 (s, 2 CF_3) ppm. ^{13}C NMR δ: 164.6 (s, O−C=O); 139.7 (q, CF_3C=*C*, ^3J=2.8 Hz); 138.4 (q, CF_3−C−*C*H=N, ^3J=4.7 Hz); 135.3 (s, ipso-$C_6H_5CO_2$); 134.0, 129.9, 129.7, 128.8, 128.5 and 126.5 (6s, arom. =CH); 128.3 (s, ipso-C_6H_5); 121.8 (q, *C*F_3C=C, ^1J=267.3 Hz); 112.8 (q, CF_3C=C, ^2J=39.0 Hz); 80.9 (s, >C); and 40.8 (s, N−CH_3) ppm. IR (ν_{max}) (cm^{-1}): 1740 (s, ester C=O str.); 1600 (m, C=C str.); 1570 (s, C=N str.); 1265 (s, C−F str.); and 1105 (s, C−O str.). Mass spectrum (EI) (*m/z*): 508 (15.3%, M^+); 387 [67.6, $(M-PhCO_2)^+$]; 372 [85.2, $(M-PhCO_2-CH_3)^+$]; 353 (32.0, $C_{16}H_{10}F_5N_4^+$); 352 (14.4, $C_{16}H_9F_5N_4^+$); 332 (14.6, $C_{16}H_8F_4N_4^+$); 303 (22.5, $C_{15}H_{10}F_3N_4^+$); 283 (15.7, $C_9H_5F_6N_4^+$ and/or $C_{15}H_9F_2N_4^+$); 122 (15.9, $C_7H_6O_2^+$); 105 (100.0, $C_7H_5O^+$); and 77 (43.9, $C_6H_5^+$).

(ii) [α-(1-Methyl-4-trifluoromethylpyrazol-3-yl)-α-(1-methyl-4-trifluoromethylpyrazol-5-yl)]benzyl benzoate (**14**) (nc) (1.24 g, 2.44 mmol, 45%). (Analysis: Found: C, 56.4; H, 3.7; F, 22.4; N, 11.0%; mol. wt., 508. $C_{24}H_{18}F_6N_4O_2$ requires: C, 56.7, H, 3.5; F, 22.4; N, 11.0%; mol. wt., 508). ^{1}H NMR δ: 8.08 (d, *o*-$C_6H_5CO_2$, J=6.5 Hz); 7.77–7.20 (complex, C_6H_5, *m*- and *p*-$C_6H_5CO_2$ and 2 =CH); 3.88 and 3.51 (2s, 2 N−CH_3) ppm. ^{19}F NMR δ: +24.9 and +24.0 (2s, 2CF_3) ppm. ^{13}C NMR δ: 165.2 (s, O−C=O); 148.9 (br., CF_3−C−*C*=N); 141.5 (q, CF_3C=*C*, ^3J=3 Hz); 138.0 (q, CF_3−C−*C*H=N, ^3J=5 Hz); 137.4 (s, ipso-$C_6H_5CO_2$); 133.3 129.9, 128.4, 128.1, 127.9 and 127.8 (6s, arom =CH); 132.6 (q, CF_3C=*C*H, ^3J=4 Hz); 130.0 (s, ipso-C_6H_5); 122.0 (q, *C*F_3C=C, ^1J=267 Hz); 112.4 (q, CF_3C=C, ^2J=37 Hz); 110.8 (q, CF_3C=C*H*, ^2J=38 Hz); 81.4 (s, >C); 41.2 (s, N−CH_3); and 39.3 (s, N−CH_3) ppm. IR (ν_{max}) (cm^{-1}): 1740 (s, ester C=O str.); 1600 m (C=C str.); 1565 (s, C=N str.); 1265 (s, C−F str.); and 1105 (s, C−O str.). Mass spectrum (EI) (*m/z*): 508 (2.4%, M^+); 419 [23.2, $(M-CF_4)^+$]; 418 [33.3, $(M-CHF_4)^+$]; 403 [14.5, $(M-PhCO)^+$]; 387 [100.0, $(M-PhCO_2)^+$]; 372 [29.2, $(M-PhCO_2-CH_3)^+$]; 367 (29.2, $C_{17}H_{12}F_5N_4^+$); 349 (15.7, $C_{16}H_9F_4N_4O^+$); 283 (13.4, $C_9H_5F_6N_4^+$ and/or $C_{15}H_9F_2N_4^+$); 269 (15.8, $C_{11}H_5F_4N_4^+$); 122 (29.8, $C_7H_6O_2^+$); 105 (74.6, $C_7H_5O^+$); and 77 (56.5, $C_6H_5^+$).

(iii) [α-(1-Methyl-4-trifluoromethylpyrazol-5-yl)-α-(4-trifluoromethylpyrazol-3-yl)]benzyl benzoate (**15**) (nc) (0.27 g, 0.55 mmol, 10%). (Analysis: Found: C, 56.1; H, 3.3; F, 23.0; N, 11.2%. $C_{23}H_{16}F_6N_4O_2$ requires: C, 55.9; H, 3.2; F, 23.1; N, 11.3%); m.p. 108–109 °C. ^{1}H NMR δ: 8.05 (d, *o*-$C_6H_5CO_2$, J=7.1 Hz); 7.74–7.13 (complex, C_6H_5, *m*- and *p*-$C_6H_5CO_2$ and 2 =CH); and 3.94 (s, N−CH_3) ppm. ^{19}F NMR δ: +24.0 and +23.7 (2s, 2 CF_3C=C) ppm. ^{13}C NMR δ: 165.2 (s, O−C=O); 151.2 (br., CF_3−C−*C*=N ^3J=4 Hz); 133.4 (s, ipso-C_6H_5); 133.1 (q, CF_3C=*C*H, ^3J=5 Hz); 129.8, 128.45, 128.4, 128.1, 128.0 and 125.4 (6s, arom. =CH); 122.3 and 121.6 (2q, 2 *C*F_3C=C, ^1J=267 Hz); 111.5 (q, CF_3C=C, ^2J=38 Hz); 110.0 (q, CF_3C=CH, ^2J=39 Hz); 77.0 (s, >C); and 39.7 (s, N−CH_3) ppm. IR (ν_{max}) (cm^{-1}): 3240 (br., N−H str.); 1730 (s, ester C=O str.); 1600 (m, C=C str.); 1570 (m, C=N

str.); 1270 (s, C–F str.); and 1135 (s, C–O str.). Mass spectrum (EI) (*m/z*): 373 [14.5%, $(M-PhCO_2)^+$]; 354 [4.1, $(M-PhCO_2-F)^+$]; 353 [4.7, $(M-PhCO_2-HF)^+$]; 283 (28.0, $C_{15}H_9F_2N_4^+$); 122 (70.3, $C_7H_6O_2^+$); 105 (82.4, $C_7H_5O^+$); 77 (100.0, $C_6H_5^+$); 51 (18.8, $C_4H_3^+$ and/or C_3HN^+); and 29 (46.8, CHO^+).

(iv) [α,α-Bis(4-trifluoromethylpyrazol-3-yl)]benzyl benzoate (**16**) (nc) (0.49 g, 1.01 mmol, 19%). (Analysis: Found: C, 54.8; H, 3.1; F, 23.6; N, 11.7%. $C_{22}H_{14}F_6N_4O_2$ requires: C, 55.0; H, 2.9; F, 23.8; N, 11.6%); m.p. 102–104 °C. ^{1}H NMR δ: 8.13–7.92 (mult., *o*-$C_6H_5CO_2$); and 7.73–6.97 (mult., C_6H_5, *m*- and *p*-$C_6H_5CO_2$, 2 =CH and 2 NH) ppm. ^{19}F NMR δ: +23.7 (s, CF_3C=C) ppm. ^{13}C NMR δ: 165.5 (s, O–C=O); 147.6 (br., CF_3–C–*C*=N); 139.5 (s, ipso-$C_6H_5CO_2$); 135.1 (q, CF_3C=*C*H, ^3J=4 Hz); 133.6 (s, ipso-C_6H_5); 133.5, 130.0, 129.8, 128.5, 128.4 and 128.2 (6s, arom. =CH); 122.0 (q, *C*F_3C=C, ^1J=267 Hz); 109.6 (q, CF_3C=CH, ^2J=37.5 Hz); and 77.5 (s, >C) ppm. IR (ν_{max}) (cm^{-1}): 3200 (br., N–H str.); 1730 (s, ester C=O str.); 1605 (m, C=C str.); 1565 (s, C=N str.); 1260 (s, C–F str.); and 1130 (s, C–O str.). Mass spectrum (EI) (*m/z*): 359 [59.1%, $(M-PhCO_2)^+$]; 358 [92.5, $M-PhCO_2H)^+$]; 339 [42.5, $(M-PhCO_2-HF)^+$]; 338 (32.9, $C_{15}H_7F_5N_4^+$); 319 (17.9, $C_{15}H_7F_4N_4^+$); 318 (29.4, $C_{15}H_6F_4N_4^+$); 317 (21.5, $C_{15}H_5F_4N_4^+$); 299 (28.2, $C_{15}H_6F_3N_4^+$); 289 [25.4, $(M-PhCO_2H-CF_3)^+$]; 122 (19.2, $C_7H_6O_2^+$); 105 (67.9, $C_7H_5O^+$); 77 (100.0, $C_6H_5^+$); 69 (11.3, CF_3^+); 51 (39.6, $C_4H_3^+$ and/or C_3HN^+); and 29 (26.3, CHO^+).

(c) With diazomethane, experiment 2

A second experiment carried out under the same conditions as experiment 1, but using a larger excess of diazomethane (1.91 g, 45.5 mmol) and ester **1b** (4.50 g, 11.4 mmol), gave a solid residue (6.01 g) after removal of the ether. This residue was shown by TLC (dichloromethane–methanol (98:2 v/v) to contain three major (R_F=0.75, 0.68 and 0.63) and several minor components. The major components were separated by repeated DCFC (same eluant), then dissolved in ether, dried (P_2O_5) and the ether removed *in vacuo* to give (i) compound **13** (1.15 g, 2.31 mmol, 23%), (ii) compound **14** (2.25 g, 4.40 mmol, 39%) and (iii) [α,α-bis(1-methyl-4-trifluoromethylpyrazol-3-yl)]benzyl benzoate (**17**) (nc) (1.04 g, 2.05 mmol, 18%). (Analysis: Found: C, 56.5; H, 3.6; F, 22.3; N, 11.1%; mol. wt., 508. $C_{24}H_{18}F_6N_4O_2$ requires: C, 56.7; H, 3.5; F, 22.4; N, 11.0%; mol. wt., 508); m.p. 229 °C. ^{1}H NMR δ: 8.14 (dd, *o*-$C_6H_5CO_2$, J=7.5 and 1.5 Hz); 7.67–7.22 (complex, C_6H_5, *m*- and *p*-$C_6H_5CO_2$ and =CH); and 3.86 (s, N–CH_3) ppm. ^{19}F NMR δ: +24.4 (s, CF_3C=C) ppm. ^{13}C NMR δ: 166.6 (s, O–C=O); 151.4 (q, CF_3–C–*C*=N, ^3J=2 Hz); 140.3 (s, ipso-$C_6H_5CO_2$); 135.2 (q, CF_3C=*C*H, ^3J=3 Hz); 135.0, 131.5, 130.3, 129.9, 129.0 and 128.8 (6s, arom. =CH); 132.5 (s, ipso-C_6H_5); 124.4 (q, *C*F_3C=CH, ^1J=266 Hz); 110.6 (q, CF_3C=CH, ^2J=37 Hz); 84.5 (s, >C); and 41.1 (s, N–CH_3) ppm. IR (ν_{max}) (cm^{-1}): 1730 (s, ester C=O str.); 1600 (m, C=C str.); 1560 (s, C=N str.); 1320 and 1275 (s, C–F str.); and 1100 (s, C–O str.). Mass spectrum (CI) (*m/z*): 509 [0.3%,

$(M+H)^+$]; 387 [28.0, $(M-PhCO_2)^+$]; 373 (6.1, $C_{15}H_7F_6N_4O^+$); 185 (100.0, $C_{10}H_5N_2O_2^+$); 105 (55.3, $C_7H_5O^+$); and 78 (10.9, $C_6H_6^+$).

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