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Fluorinated acetylenes Part 16 [☆]. The reactions of ethyl 4,4,4-trifluorobut-2-ynoate and hexafluorobut-2-yne with quadricyclane and the hydrogenation and thermal rearrangement of the resulting 1:1 cycloadducts

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Abstract

Thermal reaction of ethyl 4,4,4-trifluorobut-2-ynoate (**1**) and hexafluorobut-2-yne (**2**) with quadricyclane (**3**) gave the *exo*-1:1 adducts (**4a**) and (**4b**), respectively, by a $({}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s)$ cycloaddition pathway. Hydrogenation (1 mol equiv. of hydrogen) of adducts **4a** and **4b** using a Pd/C catalyst resulted in addition to the least substituted double bond to afford the alkenes **5a** and **5b**, respectively, and further hydrogenation of alkene **5a** gave the alkane **6**. Flow pyrolysis of adduct **4a** at 450 °C yielded *cis,cis,cis*-3-carboethoxy-4-trifluoromethylbicyclo[4.2.1]nona-2,4,7-triene (**7a**) (30%) and a ca. 1:1 mixture (55%) of *cis,cis,cis*-4-carboethoxy-3-trifluoromethylbicyclo[4.3.0]nona-2,4,7-triene (**8a**) and its 3-carboethoxy-4-trifluoromethyl isomer (**8b**). Compound **7a** arose by a non-concerted ring-opening of adduct **4a**, and compounds **8a** and **8b** were formed via an intramolecular Diels–Alder reaction of **7a** followed by rearrangement involving a 1,2-hydrogen shift. On flow pyrolysis under identical conditions, adduct **4b** afforded the rearranged triene **8c** exclusively, while flow pyrolysis of alkenes **5a** and **5b** gave the corresponding *cis,cis*-bicyclo[4.2.1]nona-2,4-dienes **9a** and **9b**, respectively. Attempted 1,3-dipolar cycloaddition between diene **9a** and diazomethane, and Diels–Alder reactions between diene **9b** and alkyne **1** or ethyl propynoate, were unsuccessful.

Keywords: Fluorinated acetylenes; NMR spectroscopy; IR spectroscopy; Mass spectrometry; Cycloaddition; Diels–Alder reaction

1. Introduction

We have reported recently the thermal reactions of ethyl 4,4,4-trifluorobut-2-ynoate (**1**) with (i) cyclopentadiene, buta-1,3-diene and 1,4-diphenylbuta-1,3-diene to give the corresponding Diels–Alder 1:1 cycloadducts in high yield [1], (ii) furan [2] and 3-carboethyoxyfuran [1] to afford Diels–Alder 1:1 and 2:1 cycloadducts with the 2:1 adducts formed by cycloaddition of the furan to the least substituted double bonds in the 1:1 adducts, and (iii) norbornadiene to yield the homo Diels–Alder cycloadduct [1]. The reaction of hexafluorobut-2-yne (**2**) with 3-carboethoxyfuran also afforded Diels–Alder 1:1 and 2:1 cycloadducts [3].

In the continuation of this study the thermal reactions of the alkynes **1** and **2** with quadricyclane (**3**) have been carried out and the resulting 1:1 adducts have been hydrogenated and subjected to flow pyrolysis.

$CF_3C{\equiv}CCO_2Et$ (1)

$CF_3C{\equiv}CCF_3$ (2)

(3)

2. Results and discussion

The reactions which have been investigated are summarised in Table 1.

It has been reported that thermal reactions of quadricyclane (**3**) with both electron-deficient alkenes [4] and alkynes [5] are stereospecific and take place by a $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ cycloaddition pathway to afford the *exo*-1:1 adducts exclusively, e.g. the reactions with dimethyl acetylenedicarboxylate and dicyanoacetylene gave the adducts **4c** and **4d**, respectively.

The reactions of **3** with the alkynes **1** and **2** were no exception and the *exo*-adducts **4a** and **4b**, respectively, were formed in high yield (Scheme 1). The *exo* stereochemistry was established by the ^{1}H NMR and H,H

[☆] For Part 15, see Ref. [1].

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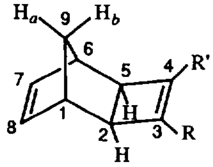
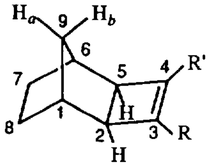
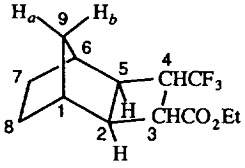


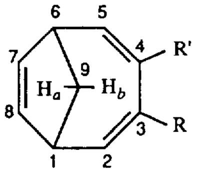
(**4**) **a**; R = CO_2Et, R' = CF_3
b; R = R' = CF_3
c; R = R' = CO_2Me
d; R = R' = CN



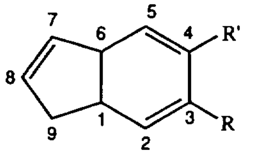
(**5**) **a**; R = CO_2Et, R' = CF_3
b; R = R' = CF_3



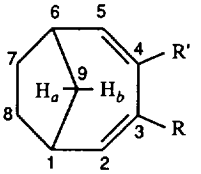
(**6**)



(**7**) **a**; R = CO_2Et, R' = CF_3
b; R = R' = CF_3
c; R = R' = H



(**8**) **a**; R = CF_3, R' = CO_2Et
b; R = CO_2Et, R' = CF_3
c; R = R' = CF_3
d; R = R' = H

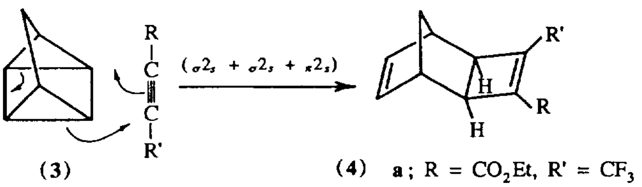


(**9**) **a**; R = CO_2Et, R' = CF_3
b; R = R' = CF_3

Table 1
Reactions of ethyl 4,4,4-trifluorobut-2-ynoate (**1**) and hexafluorobut-2-yne (**2**) with quadricyclane (**3**) and hydrogenation and flow pyrolysis of the products

Reactants	Molar ratio	Conditions		Products (%) [d]
		Temp. (°C)	Time	
1+**3** [a]	1:1	40 then 20	9 h 18 h	**4a** (96)
2+**3** [a]	1:1.74	70	9 d	**4b** (98) [e]
4a+H_2 [b]	1:1	20	9 h	**5a** (82)
4b+H_2 [b]	1:1	20	8 h	**5b** (92)
5a+H_2 [b]	1:1	20	6 h	**6** (94)
4a		450 [c]		**7a** (30); **8a**+**8b** (55) [f]
4b		450 [c]		**8c** (79)
5a		400 [c]		**9a** (80)
5b		500 [c]		**9b** (90)

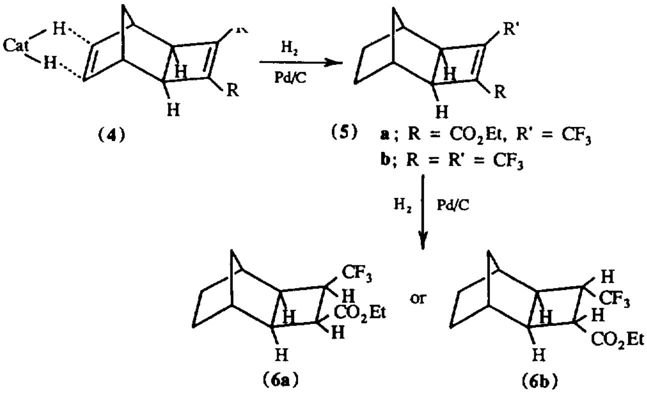
[a] In dichloromethane solvent.
[b] Using a Pd/C catalyst and anhydrous acetone as solvent.
[c] Flow pyrolysis.
[d] Based on fluorine-containing reactants.
[e] Reactant **2** (58%) was recovered.
[f] Compounds **8a** and **8b** were present in the ratio 52:48 (^1H NMR spectroscopy).



(**3**)

(**4**) **a**; R = CO_2Et, R' = CF_3
b; R = R' = CF_3

Scheme 1.



(**4**)

(**5**) **a**; R = CO_2Et, R' = CF_3
b; R = R' = CF_3

(**6a**) (**6b**)

Scheme 2.

COSY spectra which showed (i) an absence of coupling between H-1 and H-2 and between H-5 and H-6 and (ii) a four-bond coupling (W pathway) between H-2/5 and H-9a.

The NMR (^1H, ^{19}F and ^{13}C) spectra were entirely consistent with the proposed structures and showed the presence of two vinylic =CH groups (7/8), two vinylic =C carbons (3/4), four bridgehead $\geq$CH groups (1/2/5/6) and a bridging CH_2 group (9), together with a CF_3 group and a CO_2Et group or two CF_3 groups.

Hydrogenation of adducts **4a** and **4b** using a Pd/C catalyst and uptake of 1 mol equiv. of hydrogen in anhydrous acetone as the solvent resulted in addition across the least substituted double bond in each diene, to afford the alkenes **5a** and **5b**, respectively. Further hydrogenation of alkene **5a** gave alkane **6** but the ^1H NMR and H,H COSY spectra did not allow a differentiation to be made between structures **6a** and **6b** (see later) (Scheme 2).

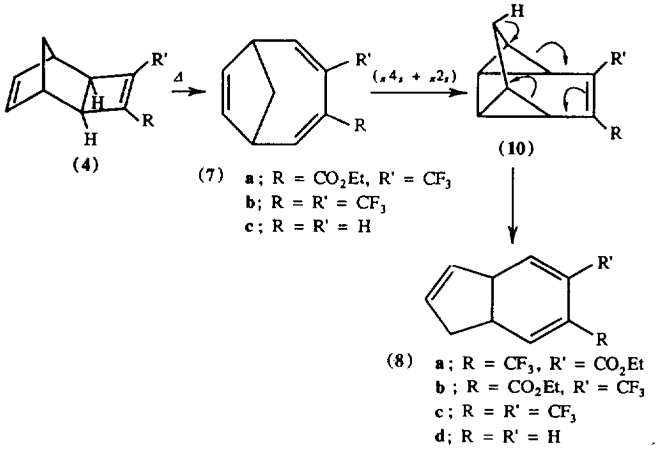
Exo-addition of hydrogen to the adducts **4a** and **4b** was expected, since it has been reported that hydrogenation of bridged polycyclic systems, e.g. 1,2-disubstituted norbornenes, under mild conditions takes place on the *exo* side to afford reduced products containing *endo* substituents [6]. A model indicated that reduction of alkene **5a** would be preferred sterically from the *endo* side relative to the bridging CH_2 group to give the alkane **6a**. The ^1H NMR spectrum showed a large *cis*-coupling ($J = 12.5$ Hz) between H-3 and H-4 and *cis*- or *trans*-couplings ($J = 8.5$ Hz) between H-3 and H-2 and between H-5 and H-4; reported H–H couplings in cyclobutane are $J(cis) = 4$–12 Hz and $J(trans) = 2$–10

Hz [7]. It was not possible therefore to determine whether the alkane had structure **6a** or **6b**.

The NMR spectra of compounds **5a**, **5b**, and **6** confirmed the structures proposed and showed the presence of two CH_2 groups (7/8), a bridging CH_2 group (9), four $\geqslant$CH groups (1/2/5/6) and either two vinylic carbons (3/4) and the substituent groups (**5a** and **5b**) or a $\geqslant CHCF_3$ group and a $\geqslant CHCO_2Et$ group (**6**). Fused cyclobutanes are relatively stable thermally, especially if the second ring is 5- or 6-membered. Thermally-allowed concerted ring-opening is a conrotatory process, which would result in the formation of 1,3-dienes containing one *trans* fused double bond. However, the fused cyclobutenes ring-open to give the thermally disallowed *cis,cis*-cyclic 1,3-dienes via a non-concerted process, e.g. thermolysis of bicyclo[4.2.0]oct-7-ene at 230–260 °C afforded *cis,cis*-cycloocta-1,3-diene [8]. It was therefore expected that pyrolysis of adducts **4a** and **4b** would afford the *cis,cis,cis*-bicyclo[4.2.1]nona-2,4,7-trienes **7a** and **7b**, respectively.

Flow pyrolysis of adduct **4a** at 450 °C gave the expected triene **7a** via a non-concerted ring-opening, but the major products comprised a mixture of the rearranged *cis,cis,cis*-bicyclo[4.3.0]nona-2,4,7-trienes **8a** and **8b** in the ratio 52:48 (^{1}H NMR spectroscopy); pyrolysis of adduct **4b** under identical conditions afforded only the rearranged bicyclo[4.3.0]nona-2,4,7-triene (**8c**).

It has been observed that the parent triene **7c** underwent intramolecular Diels–Alder cycloaddition at 290 °C, followed by rearrangement of the resulting adduct **10** involving a 1,2-H shift to give *cis,cis,cis*-bicyclo-[4.3.0]nona-2,4,7-triene (**8d**) [9,10]; it is considered that compounds **8a–c** are formed analogously from the intermediate trienes **7a** and **7b** (Scheme 3). Triene **7a** is apparently somewhat more stable thermally than triene **7b** and the two possible modes of rearrangement of the intermediate **10** formed from triene **7a** are equally facile, since a ca. 1:1 mixture of the products **8a** and **8b** was formed.



Scheme 3.

Flow pyrolysis of the dihydro derivatives **5a** and **5b** afforded the expected *cis,cis*-bicyclo[4.2.1]nona-2,4-dienes **9a** and **9b**, respectively; rearrangement of these compounds is precluded because of the absence of a double bond to interact with the diene system.

The NMR spectra of the bicyclo[4.2.1]nonatriene **7a** confirmed the structure and showed the presence of a CH=CH group, a $CH=C(CF_3)-C(CO_2Et)=CH$ grouping, two bridgehead $\geqslant$CH groups and a bridging CH_aH_b group [δ_H: 2.08 (9a) and 1.50 (9b) ppm; δ_c: 29.8 ppm]; the H,H COSY spectrum showed the expected coupling between H-6 and H-7 and between H-1 and H-8. Models indicate that the dihedral angle between H-9a and H-1/6 is ca. 30°, while that between H-9b and H1/6 is ca. 90°. The lower-field absorption which showed coupling to H-1/6 is therefore assigned to H-9a.

For the bicyclo[4.3.0]nonatriene **8c** the NMR spectra showed the presence of a CH=CH group, a $CH=C(CF_3)-C(CF_3)=CH$ grouping, two bridgehead $\geqslant$CH groups and an allylic CH_aH_b group for which the proton and carbon absorptions (δ_H: 2.74 and 2.27 ppm; δ_c: 40.7 ppm) appeared at lower field than those for the bridging CH_aH_b group in compound **7a**. The H,H COSY spectrum showed that (i) H-1 couples to H-2, H-6, H-9a and H-9b, but not to H-5, H-7 or H-8, (ii) H-6 couples strongly to H-1, H-5 and H-7 and only weakly to H-9a and H-9b, (iii) H-7 couples only to H-6 and H-8 and (iv) H-8 couples only to H-7, H-9a and H-9b. The above evidence confirms the structure of compound **8c**.

The isomers **8a** and **8b** could not be separated completely from each other, but sufficient separation was achieved to enable NMR assignments to be made and a CH=CH group, a $CH=C(CF_3)-C(CO_2Et)=CH$ grouping, two bridgehead $\geqslant$CH groups and an allylic CH_aH_b group were shown to be present in each isomer. From the ^{1}H NMR assignments of the diene protons in compound **8c** [δ: 6.52 (H-2) and 6.35 (H-4) ppm] a differentiation can be made between compounds **8a** and **8b** on the basis that replacement of CF_3 by CO_2Et results in the adjacent diene proton absorption being shifted downfield by ca. 0.2 ppm. Therefore, the isomer with chemical shifts for the diene protons of $\delta = 6.52$ (H-2) and 6.50 (H-4) ppm has structure **8a** and that with shifts of $\delta = 6.67$ (H-2) and 6.30 (H-4) ppm has structure **8b**.

The NMR spectra of the bicyclo[4.2.1]dienes **9a** and **9b** were comparable to those of triene **7a**, except for differences caused by replacement of CH=CH by CH_2-CH_2, and were entirely consistent with the structures proposed, i.e. a diene system $=CH-CR-CR^1=CH$ ($R = CO_2Et$, $R^1 = CF_3$ or $R = R^1 = CF_3$), two bridgehead $\geqslant$CH groups, two adjacent CH_2 groups and a bridging CH_aH_b group were shown to be present.

Neither of the double bonds in the diene system of compound **9a** underwent 1,3-dipolar cycloaddition with diazomethane and attempted Diels–Alder reactions between **9b** and alkyne **1** [up to 120 °C (3 d)] or ethyl propynoate [up to 100 °C (10 d)] were unsuccessful.

3. Experimental details

3.1. *Starting materials*

Ethyl 4,4,4-trifluorobut-2-ynoate (**1**) was prepared by reaction of the phosphonium bromide $Ph_3\overset{+}{P}CH_2CO_2Et\overset{-}{Br}$ with trifluoroacetic anhydride in the presence of triethylamine to afford the phosphorane $Ph_3P{=}C(CO_2Et)COCF_3$ [11] which was then pyrolysed at 190–200 °C and low pressure (ca. 10 mmHg) [12]. Hexafluorobut-2-yne (**2**) was a research sample available in the Department and quadricyclane (**3**) was a commercial sample, the purity of which was checked (^1H and ^{13}C NMR spectroscopy) before use.

3.2. *General techniques*

Reactions of quadricyclane (**3**) and the diene **9b** were carried out in vacuo in Pyrex ampoules (30–50 cm^3) fitted with Teflon Rotaflo taps. Hydrogenation and flow pyrolysis experiments were carried out as described in the text. Reaction products were purified by dry column flash chromatography (DCFC) using silica (Merck Kieselgel 60H, 15 μm) and eluants as given in the text (light petroleum is the petroleum ether fraction, b.p. 30–40 °C), liquid column chromatography (LC) using silica (Merck Kieselgel 60, 0.040–0.063 μm) and eluants described in the text, or distillation. Product mixtures were separated by DCFC or LC. Products were examined by IR spectroscopy (Perkin-Elmer DE783 spectrometer); ^1H NMR and H,H correlated spectroscopy (COSY) [Bruker AC300-FT (300 MHz) spectrometer; external reference Me_4Si]; ^{13}C NMR broad-band proton-decoupled spectroscopy (including DEPT 135°) [Bruker AC300-FT (75.0 MHz) instrument; lock signal D_2O and internal reference Me_4Si]; ^{19}F NMR spectroscopy [Bruker AC200 (188.3 MHz) instrument; external reference CF_3CO_2H]; and mass spectrometry [Kratos MS25 instrument operating at 70 eV under electron impact (EI) conditions]. The NMR spectra were recorded as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive.

Boiling points were determined by distillation or by Siwoloboff's method.

3.3. *Reactions of alkynes with quadricyclane (3)*

(a) Ethyl 4,4,4-trifluorobut-2-ynoate (1)

A solution of ester **1** (1.80 g, 10.84 mmol) and quadricyclane (**3**) (1.00 g, 10.86 mmol) in dichloromethane (3 cm^3) was heated at 40 °C (9 h) and then stored at room temperature (18 h). The tube contents were washed out with dichloromethane and the solvent was carefully removed on a rotary evaporator to afford an oil (2.80 g), which was shown by TLC (eluant: dichloromethane/light petroleum 3:1 v/v) to contain one major component ($R_F = 0.85$). Purification of the product by DCFC (same eluant) gave *exo*-3-carboethoxy-4-trifluoromethyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**4a**) (nc) (2.70 g, 10.46 mmol, 96%) (Analysis: Found: C, 60.2; H, 5.0; F, 22.3%; M$^+$, 258. $C_{13}H_{13}F_3O_2$ requires: C, 60.4; H, 5.0; F, 22.1%; M, 258), b.p. 115–116 °C.

(b) Hexafluorobut-2-yne (2)

A mixture of hexfluorobut-2-yne (**2**) (15.60 g, 66.30 mmol), quadricyclane (**3**) (3.50 g, 38.04 mmol) and dichloromethane (12 cm^3), heated at 70 °C (3 d), gave unchanged alkyne **2** (9.11 g, 56.26 mmol, 58% recovered). The residue was washed out of the tube with dichloromethane and the solvent was carefully removed on a rotary evaporator to afford an oil which was shown by TLC (eluant: light petroleum/dichloromethane 4:1 v/v) to consist of a single component ($R_F = 0.88$). The product was identified as *exo*-3,4-bis(trifluoromethyl)-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**4b**) (nc) (9.53 g, 37.50 mmol, 98%) (Analysis: Found: C, 51.9; H, 3.4; F, 45.2%; M$^+$, 254. $C_{11}H_8F_6$ requires: C, 52.0; H, 3.1; F, 44.9%; M, 254), b.p. 107–109 °C.

3.4. *Hydrogenation experiments*

(a) 3-Carboethoxy-4-trifluoromethyltricyclo[4.2.1.0^{2,5}]non-3-ene (4a)

A stirred mixture of diene **4a** (2.0 g, 7.75 mmol), palladium on charcoal (10% w/w, 0.03 g) and anhydrous acetone (12 cm^3) was connected to a standard hydrogenation apparatus and the take up of hydrogen monitored until 1 mol equiv. had reacted (9 h). The catalyst was filtered off and the solvent was removed by distillation to afford a colourless oil (1.98 g), which was shown by ^1H NMR spectroscopy and TLC (eluant: light petroleum/dichloromethane 2:1 v/v) to contain one major component ($R_F = 0.82$) and several minor components. Purification by DCFC (same eluant) gave 3-carboethoxy-4-trifluoromethyltricyclo[4.2.1.0^{2,5}]non-3-ene (**5a**) (nc) (1.65 g, 6.35 mmol, 82%) (Analysis: Found: C, 60.3; H, 6.0; F, 21.8%; M$^+$, 260. $C_{13}H_{15}F_3O_2$ requires: C, 60.0; H, 5.8; F, 21.9%; M, 260), b.p. 121–123 °C.

(b) 3,4-Bis(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (4b)

A stirred mixture of diene **4b** (3.50 g, 13.78 mmol), palladium on charcoal (10% w/w, 0.04 g) and anhydrous

Table 2
NMR data

Compound	δ: (ppm, assignment) [a]
4a	δ_H: 6.12 (mult., 2H, H-7/8); 4.18 (q, 2H, OCH_2, $J=7$ Hz); 2.68 (br., 1H, H-2); 2.60 (br., 1H, H-5); 2.56 (dd, 1H, H-1, $J_{8,1}=2.6$ Hz, $J_{6,1}=1.0$ Hz); 2.45 (dd, 1H, H-6, $J_{7,6}=2.8$ Hz; $J_{1,6}=1.0$ Hz); 1.40 (dmult., 1H, H-9a, $J_{9b,9a}=9.5$ Hz); 1.31 (br. d, 1H, H-9b, $J_{9a,9b}=9.5$ Hz); 1.25 (t, 3H, CH_3, $J=7$ Hz). δ_F: +14.5 (CF_3). δ_C: 160.3 (O–C=O); 143.3 (q, C-4, $^2J=35.6$ Hz); 141.9 (q, C-3, $^3J=5.3$ Hz); 135.8/135.3 (C-7/8); 119.0 (q, CF_3, $^1J=266.5$ Hz); 60.9 (OCH_2); 43.8/43.0 (C-2/5); 39.1 (C-9); 38.0/37.7 (C-1/6); 13.7 (CH_3)
4b	δ_H: 6.12 (mult., 2H, H-7/8); 2.63 (br., 2H, H-2/5); 2.53 (br., 2H, H-1/6); 1.44 (br.d, 1H, H-9a, $J_{9b,9a}=10$ Hz); 1.34 (br.d, 1H, H-9b, $J_{9a,9b}=10$ Hz). δ_F: +13.0 ($2CF_3$). δ_C: 140.1 (q, C-3/4, $^2J=35.0$ Hz); 135.7 (C-7/8); 118.6 (q, $2CF_3$, $^1J=271.6$ Hz); 43.3 (C-2/5); 38.9 (C-9); 38.0 (C-1/6)
5a	δ_H: 4.18 (q, 2H, OCH_2, $J=7$ Hz); 2.65/2.60 (2br., 2×1H, H-2/5); 2.23/2.17 (2 mult., 2×1H, H-1/6); 1.58 (mult., 2H, H-7a/8a or 7b/8b); 1.24 (dmult., 1H, H-9a or 9b, $J=11$ Hz); 1.22 (t, 3H, CH_3, $J=7$ Hz); 1.05 (complex, 3H, H-9b or 9a+7b/8b or 7a/8a). δ_F: +13.7 (CF_3). δ_C: 160.3 (O–C=O); 140.2 (q, C-4, $^2J=37.7$ Hz); 138.9 (q, C-3, $^3J=5.8$ Hz); 118.4 (q, CF_3, $^1J=274.4$ Hz); 60.9 (OCH_2); 46.8/46.2 (C-2/5); 33.7/33.5 (C-1/6); 30.2 (C-9); 27.7 (C-7/8); 14.0 (CH_3)
5b	δ_H: 2.62 (br., 2H, H-2/5); 2.19 (br., 2H, H-1/6); 1.58 (br., 2H, H-7a/8a or 7b/8b); 1.38 (br.d, 1H, H-9a, $J_{9b,9a}=11.5$ Hz); 1.10 (d, 1H, H-9b, $J_{9a,9b}=11.5$ Hz); 1.06 (mult., 2H, H-7b/8b or 7a/8a). δ_F: +13.0 ($2CF_3$). δ_C: 137.5 (q, C-3/4, $^2J=33.8$ Hz); 118.7 (q, $2CF_3$, $^1J=271.7$ Hz); 47.0 (C-2/5); 34.3 (C-1/6); 30.7 (C-9); 28.2 (C-7/8)
6	δ_H: 4.10 (q, 2H, OCH_2, $J=7$ Hz); 3.50 (dd, 1H, H-3, $J_{4,3}=12.0$ Hz, $J_{2,3}=9.5$ Hz); 3.28 (pentd, 1H, H-4, $J_{CF3,4}=J_{3,4}=12.0$ Hz, $J_{5,4}=9.5$ Hz); 2.52 (mult., 2H, H-2/5); 2.33 (mult., 2H, H-1/6); 1.83 (br.d, 1H, H-9a or 9b, $J_{9a,9b}=11.5$ Hz); 1.44 (mult., 2H, H-7a/8a or 7b/8b); 1.24 (br.d, 1H, H-9b or 9a, $J_{9b,9a}=11.5$ Hz); 1.22 (t, 3H, CH_3, $J=7$ Hz); 0.98 (mult., 2H, H-7b/8b or 7a/8a). δ_F +16.1 (d, $CHCF_3$, $J=12.0$ Hz). δ_C: 170.4 (O–C=O); 126.0 (q, CF_3, $^1J=278.8$ Hz); 60.6 (OCH_2); 42.5/41.5 (C-2/5); 40.2 (q, C-4, $^2J=30.0$ Hz); 39.4 (q, C-3, $^3J=6.4$ Hz); 37.1/36.9 (C-1/6); 33.6 (C-9); 29.2/27.6 (C-7/8); 14.2 (CH_3)
7a	δ_H: 6.97 (d, 1H, H-2, $J_{1,2}=8.0$ Hz); 6.72 (d, 1H, H-5, $J_{6,5}=8.0$ Hz); 5.41 (br., 2H, H-7/8); 4.21 (q, 2H, OCH_2, $J=7$ Hz); 3.32 (br.dd, 1H, H-1, $J_{2,1}=8.0$ Hz, $J_{9a,1}=6.5$ Hz); 3.28 (ddd, 1H, H-6, $J_{5,6}=8.0$ Hz, $J_{9a,6}=6.5$ Hz, $J_{7,6}=1.5$ Hz); 2.08 (dt, 1H, H-9a, $J_{9b,9a}=12.0$ Hz, $J_{1,9a}=J_{6,9a}=6.5$ Hz); 1.50 (d, 1H, H-9b, $J_{9a,9b}=12.0$ Hz); 1.32 (t, 3H, CH_3, $J=7$ Hz). δ_F +19.0 (CF_3). δ_C: 169.2 (O–C=O); 143.5 (C-2); 142.5 (q, C-5, $^3J=5.4$ Hz): 125.1 (C-7/8); 124.8 (q, C-3, $^3J=3.2$ Hz); 124.3 (q, C-4, $^2J=29.4$ Hz); 124.0 (q, CF_3, $^1J=275.8$ Hz); 61.7 (OCH_2); 42.7/42.4 (C-1/6); 29.8 (C-9); 14.0 (CH_3)
8a	δ_H: 6.52 (d, 1H, H-2, $J_{1,2}=4.5$ Hz); 6.50 (d, 1H, H-5, $J_{6,5}=5.0$ Hz); 5.92 (mult., 1H, H-7); 5.64 (mult., 1H, H-8); 4.16 (q, 2H, OCH_2, $J=7$ Hz); 3.60 (br., 1H, H-1); 3.17 (mult., 1H, H-6); 2.78/2.30 (2 mult., 2×1H, H-9a/9b); 1.24 (t, 3H, CH_3, $J=7$ Hz). δ_F +15.6 (CF_3). δ_C: 166.0 (O–C=O); 136.9/136.6 (C-2/5); 135.7 (q, C-4, $^3J=6.4$ Hz); 131.8 (C-8); 131.2 (q, C-3, $^2J=39.3$ Hz); 129.5 (C-7); 122.9 (q, CF_3, $^1J=272.4$ Hz); 61.1 (OCH_2); 43.4/34.9 (C-1/6); 40.9 (C-9); 13.9 (CH_3)
8b	δ_H: 6.67 (d, 1H, H-2, $J_{1,2}=5.2$ Hz); 6.30 (d, 1H, H-5, $J_{6,5}=4.0$ Hz); 5.96 (mult., 1H, H-7); 5.68 (mult., 1H, H-8); 4.21 (q, 2H, OCH_2, $J=7$ Hz); 3.65 (br., 1H, H-1); 3.22 (mult., 1H, H-6); 2.80/2.38 (2 mult., 2×1H, H-9a/9b); 1.22 (t, 3H, CH_3, $J=7$ Hz). δ_F: +15.2 (CF_3). δ_C: 166.8 (O–C=O); 141.4 (C-2); 137.3 (C-5); 136.8 (q, C-3, $^3J=6.4$ Hz); 132.5 (C-8); 132.4 (q, C-4, $^2J=39.3$ Hz); 130.2 (C-7); 123.5 (q, CF_3, $^1J=272.4$ Hz); 61.8 (OCH_2); 44.1/37.7 (C-1/6); 41.4 (C-9); 14.6 (CH_3)
8c	δ_H: 6.52 (d, 1H, H-2, $J_{1,2}=3.5$ Hz); 6.35 (d, 1H, H-5, $J_{6,5}=2.0$ Hz); 5.88 (br., 1H, H-7); 5.60 (br., 1H, H-8); 3.59 (br.d, 1H, H-6, $J\sim11$ Hz); 3.18 (br., 1H, H-1); 2.74 [br.dd, 1H, H-9a, $J_{9b,9a}=16$ Hz, $J_{1,9a}(cis)=10$ Hz]; 2.27 [br.dd, 1H, H-9b, $J_{9a,9b}=16$ Hz, $J_{1,9b}(trans)=4$ Hz]. δ_F: +16.0 (CF_3). δ_C: 137.1 (q, C-5, $^3J=2.7$ Hz); 133.0 (q, C-2, $^3J=3.2$ Hz); 131.9/129.1 (C-7/8); 122.3 (q, CF_3, $^1J=273.3$ Hz); 120.5 (q, C-3/4, $^2J=29.1$ Hz); 42.5 (C-6); 40.7 (C-9); 34.7 (C-1)
9a	δ_H: 6.78 (d, 1H, H-2, $J_{1,2}=8.0$ Hz); 6.75 (d, 1H, H-5, $J_{6,5}=8.0$ Hz); 4.14 (q, 2H, OCH_2, $J=7$ Hz); 2.80 (br., 2H, H-1/6); 1.96 (dt, 1H, H-9a, $J_{9b,9a}=12$ Hz, $J_{1,9a}=J_{6,9a}=6$ Hz); 1.83 (complex, 4H, H-7/8); 1.80 (d, 1H, H-9b, $J_{9a,9b}=12$ Hz); 1.23 (t, 3H, CH_3, $J=7$ Hz). δ_F: +18.7 (CF_3). δ_C: 168.7 (O–C=O); 148.1 (C-2/5); 145.2 (q, C-3, $^3J=5.1$ Hz); 125.7 (q, C-4, $^2J=38.5$ Hz); 123.8 (q, CF_3, $^1J=275.0$ Hz); 61.3 (OCH_2); 38.3 (C-1/6); 36.5/36.0/32.2 (C-7/8/9); 23.8 (CH_3)
9b	δ_H: 6.90 (d, 2H, H-2/5, $J_{1,2}=J_{6,5}=8.0$ Hz); 2.88 (br., 2H, H-1/6); 1.95 (dt, 1H, H-9a, $J_{9b,9a}=12.5$ Hz, $J_{1,9a}=J_{6,9a}=6.0$ Hz); 1.81 (complex, 4H, H-7/8); 1.79 (d, 1H, H-9b, $J_{9a,9b}=12.5$ Hz). δ_F: +16.9 ($2CF_3$). δ_C: 147.6 (q, C-2/5, $^3J=2.7$ Hz); 123.2 (q, CF_3, $^1J=275.6$ Hz); 121.9 (q, C-3/4, $^2J=42.4$ Hz); 38.3 (C-1/6); 35.4 (C-9); 33.6 (C-7/8)

[a] Singlet absorptions unless stated otherwise.

acetone (15 cm^3) was hydrogenated until 1 mol equiv. of hydrogen had been taken up (8 h). Work-up as in the previous experiment followed by distillation gave 3,4-bis(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-3-ene (**5b**) (nc) (3.25 g, 12.70 mmol, 92%) (Analysis: Found: C, 51.3; H, 3.8; F, 44.5%; M$^+$, 256. $C_{11}H_{10}F_6$ requires: C, 51.6; H, 3.9; F, 44.5%; M, 256), b.p. 114–116 °C.

(c) *3-Carboethoxy-4-trifluoromethyltricyclo[4.2.1.0^{2,5}]non-3-ene (5a)*

A stirred mixture of alkene **5a** (1.20 g, 4.46 mmol), palladium on charcoal (10% w/w, 0.05 g) and anhydrous acetone (8 cm^3) was hydrogenated until 1 mol equiv. of hydrogen had been taken up (6 h). Work-up as in experiment (b) gave 3-carboethoxy-4-trifluoromethyl-

Table 3
MS data

Compound	MS; *m/z* (%, assignment) [a]
4a	258 (50, M^+); 238 [41, $(M-HF)^+$]; 213 [22, $(M-OEt)^+$]; 189 [24, $(M-CF_3)^+$]; 185 [29, $(M-CO_2Et)^+$]; 165 (44, $C_{10}H_7F_2^+$); 164 (15, $C_{10}H_6F_2^+$); 116 (21, $C_6H_6F_2^+$); 115 (50, $C_6H_5F_2^+$); 69 (10, CF_3^+); 39 (20, $C_3H_3^+$); 29 (100, $CHO^+/C_2H_5^+$); 27 (32, $C_2H_3^+$)
4b	254 (74, M^+); 235 [11, $(M-F)^+$]; 227 [19, $(M-C_2H_3)^+$]; 185 [43, $(M-CF_3)^+$]; 165 (22); 164 (10); 116 (9); 115 (10); 69 (67); 66 (100, $C_5H_6^+$); 51 (22, $C_4H_3^+$); 47 (67, $C_2H_4F^+$); 39 (16)
5a	260 (3, M^+); 215 [11, $(M-OEt)^+$]; 212 [11, $(M-C_2H_4-HF)^+$]; 173 (26, $C_9H_8F_3^+$); 171 (24, $C_9H_6F_3^+$); 159 (15, $C_8H_6F_3^+$); 151 (37, $C_5H_2F_3O_2^+$); 147 (18, $C_6H_5F_2O_2^+$); 127 (54, $C_7H_5F_2^+$); 117 (18, $C_5H_6FO_2^+$); 86 (46, $C_4H_6O_2^+$); 84 (67, $C_4H_4O_2^+$); 51 (32); 49 (100, C_4H^+); 29 (25)
5b	256 (25, M^+); 237 [38, $(M-F)^+$]; 228 [68, $(M-C_2H_4)^+$]; 227 [46, $(M-C_2H_5)^+$]; 215 [35, $(M-C_3H_5)^+$]; 214 [29, $(M-C_3H_6)^+$]; 190 [90, $(M-C_3H_6-F)^+$]; 187 [24, $(M-CF_3)^+$]; 159 [49, $(M-C_2H_4-CF_3)^+$]; 127 (25); 69 (20); 42 (100, $C_3H_6^+$); 41 (20, $C_3H_5^+$); 39 (18)
6	262 (4, M^+); 214 [32, $(M-C_2H_4-HF)^+$]; 189 [25, $(M-CO_2Et)^+$]; 186 [25, $(M-C_3H_8O_2)^+$]; 127 (17); 95 (31, $C_5H_3O_2^+/C_3H_2F_3^+$); 67 (29, $C_5H_7^+$); 66 (100, $C_5H_6^+$); 43 (79, $C_3H_2O^+$); 41 (39); 39 (44); 29 (95); 27 (61)
7a	258 (68, M^+); 213 [37, $(M-OEt)^+$]; 185 [95, $(M-CO_2Et)^+$]; 184 [33, $(M-CO_2Et-H)^+$; 165 (99); 164 (42); 116 (45); 115 (100, $C_9H_7^+$); 85 (66); 84 (100); 66 (38); 51 (44); 49 (94); 29 (54)
8a + 8b	258 (63, M^+); 213 [33, $(M-OEt)^+$]; 21 [14, $(M-EtOH)^+$]; 189 [30, $(M-CF_3)^+$]; 185 [95, $(M-CO_2Et)^+$]; 184 [32, $(M-CO_2Et-H)^+$]; 183 [17, $(M-CO_2Et-2H)^+$]; 165 (96); 164 (43); 116 (45, $C_9H_8^+/C_6H_6F_2^+$); 115 (97, $C_9H_7^+$); 85 (65, $C_4H_5O_2^+/C_5H_6F^+$); 84 (98, $C_4H_4O_2^+/C_5H_5F^+$); 66 (44); 51 (48); 49 (100); 29 (69)
8c	254 (51, M^+); 235 [23, $M-F)^+$]; 185 [100, $(M-CF_3)^+$]; 165 (62); 164 (37); 145 (13, $C_7H_4F_3^+$); 133 (10, $C_6H_6F_2^+$); 115 (37); 86 (20, $C_5H_7F^+$); 84 (26, $C_5H_5F^+$); 69 (20); 66 (44); 51 (27); 49 (37); 39 (39)
9a	260 (13, M^+); 215 [12, $(M-OEt)^+$]; 190 [12, $(M-CF_3-H)^+$]; 173 (14, $C_9H_8F_3^+$); 171 (12, $C_9H_6F_3^+$): 151 (21, $C_9H_5F_2^+$): 147 (11, $C_6H_5F_2O_2^+$); 127 (29); 86 (39); 84 (60); 51 (32); 49 (100); 29 (24)
9b	256 (28, M^+); 228 [44, $(M-C_2H_4)^+$]; 215 [31, $(M-C_3H_5)^+$]; 195 [12, $[M-C_3H_5-HF)^+$]; 95 (47); 86 (31); 69 (39); 67 (59); 43 (40); 28 (100, $C_2H_4^+$)

[a] Expressed as percentage of base peak.

tricyclo[4.2.1.0^{2,5}]nonane (**6**) (nc) (1.14 g, 4.35 mmol, 94%) (Analysis: Found: C, 59.7; H, 6.6; F, 21.8%; M^+, 262. $C_{13}H_{17}F_3O_2$ requires: C, 59.5; H, 6.5; F, 21.8%; M, 262), b.p. 127–129 °C.

3.5. *Pyrolysis experiments*

*(a) 3-Carboethoxy-4-trifluoromethyltricyclo[4.2.1.0^{2,5}]-nona-3,7-diene (**4a**) (general procedure)*

Diene **4a** (3.50 g, 13.57 mmol), contained in a pressure-equalising dropping funnel connected to a Pyrex tube (2 × 20 cm) packed with glass beads, was added dropwise (0.5 h) in a slow flow of nitrogen to the tube which was heated to 450 °C. The product (3.37 g) was collected in a flask cooled to − 78 °C (Cardice/methylated spirits) and was shown by TLC (eluant: n-hexane) to contain two components (R_F = 0.72 and 0.58). Separation of the two components by LC (same eluant) gave (i) a mixture of *cis,cis,cis*-4-carboethoxy-3-trifluoromethylbicyclo-[4.3.0]nona-2,4,7-triene (**8a**) (nc) and *cis,cis,cis*-3-carboethoxy-4-trifluoromethylbicyclo[4.3.0]nona-2,4,7-triene (**8b**) (nc) (1.93, g, 7.48 mmol, 55%) (Analysis: Found: C, 60.4; H, 5.1; F, 21.9%; M^+, 258. $C_{13}H_{13}F_3O_2$ requires: C, 60.4; H, 5.0; F, 22.1%; M, 258), b.p. 158–160 °C, present in the ratio 52:48 (^1H NMR spectroscopy), and (ii) *cis,cis,cis*-3-carboethoxy-4-trifluoromethylbicyclo[4.2.1]nona-2,4,7-triene (**7a**) (nc) (1.04 g, 4.03 mmol, 30%) (Analysis: Found: C, 60.4; H, 4.7; F, 22.3%; M^+, 258. $C_{13}H_{13}F_3O_2$ requires: C, 60.4; H, 5.0; F, 22.1%; M, 258), b.p. 145–147 °C.

*(b) 3,4-Bis(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**4b**)*

Diene **4b** (1.50 g, 5.91 mmol), pyrolysed at 450 °C as in the previous experiment, gave an oil (1.38 g) which was shown by ^1H NMR spectroscopy and TLC (eluant: light petroleum) to contain one major component (R_F = 0.67). Purification by LC (same eluant) afforded *cis,cis,cis*-3,4-bis(trifluoromethyl)bicyclo-[4.3.0]nona-2,4,7-triene (**8c**) (nc) (1.04 g, 4.09 mmol, 79%) (Analysis: Found: C, 51.8; H, 3.2; F, 44.8%; M^+, 254. $C_{11}H_8F_6$ requires: C, 52.0; H, 3.1; F, 44.9%; M, 254), b.p. 137–138 °C.

*(c) 3-Carboethoxy-4-trifluoromethyltricyclo[4.2.1.0^{2,5}]-non-3-ene (**5a**)*

Alkene **5a** (2.00 g, 7.69 mmol), pyrolysed at 400 °C as in experiment (a), gave an oil (1.85 g) which was shown by TLC (eluant: light petroleum/dichloromethane 2:1 v/v) to contain a major product (R_F = 0.58) and some unchanged alkene **5a** (R_F = 0.82). Purification of the product by DCFC (same eluant) gave *cis,cis*-3-

carboethoxy-4-trifluoromethylbicyclo[4.2.1]nona-2,4-diene (**9a**) (nc) (1.60 g, 6.15 mmol, 80%) (Analysis: Found: C, 59.8; H, 6.1; F, 21.7%; M^+, 260. $C_{13}H_{15}F_3O_2$ requires: C, 60.0; H, 5.8; F, 21.9%; M, 260), b.p. 139–141 °C.

(*d*) *3,4-Bis(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-3-ene (5b)*

Alkene **5b** (2.00 g, 7.81 mmol), pyrolysed at 500 °C as in experiment (a), gave an oil (1.79 g) which was shown by ^1H NMR spectroscopy and TLC (eluant: light petroleum) to be a pure compound ($R_F = 0.72$) identified as *cis,cis*-3,4-bis(trifluoromethyl)bicyclo[4.2.1]nona-2,4-diene (**9b**) (nc) (1.79 g, 6.99 mmol, 90%) (Analysis: Found: C, 51.9; H, 4.0; F, 44.6%; M^+, 256. $C_{11}H_{10}F_6$ requires: C, 51.6; H, 3.9; F, 44.5%; M, 256), b.p. 127–129 °C.

3.6. Attempted reactions

(*a*) *3-Carboethoxy-4-trifluoromethylbicyclo[4.2.1]nona-2,4-diene (9a) with diazomethane*

A solution of diene **9a** (2.50 g, 9.62 mmol) in diethyl ether (10 cm^3) at 0 °C (ice bath) was treated with a cold (0 °C) solution of diazomethane (1.20 g, 28.6 mmol) in diethyl ether (200 cm^3). The mixture was stirred (24 h) with the excess of diazomethane allowed to evaporate slowly and the solvent was then removed (rotary evaporator) to afford unchanged diene **9a** (2.44 g, 9.38 mmol, 98% recovered).

(*b*) *3,4-Bis(trifluoromethyl)bicyclo[4.2.1]nona-2,4-diene (9b) with ethyl 4,4,4-trifluorobut-2-ynoate (1)*

A mixture of diene **9b** (1.50 g, 5.86 mmol), alkyne **1** (1.00 g, 6.02 mmol) and dichloromethane (1.5 cm^3) was heated at 100 °C (4 d) and then at 120 °C (3 d). The resulting material was washed from the tube with dichloromethane and the solvent was evaporated (rotary evaporator) to give a brown liquid (2.46 g), which was shown by ^1H and ^{19}F NMR spectroscopy and TLC (eluant: n-hexane/dichloromethane 2:1 v/v) to consist of unchanged reactants contaminated with a small amount of tar (TLC base line spot).

(*c*) *3,4-Bis(trifluoromethyl)bicyclo[4.2.1]nona-2,4-diene (9b) with ethyl propynoate*

A mixture of diene **9b** (1.50 g, 5.86 mmol), ethyl propynoate (0.74 g, 7.55 mmol) and dichloromethane (2 cm^3) was heated at 70 °C (7 d) and then at 100 °C (10 d). The ^1H and ^{19}F NMR spectra of the resulting material showed that only unchanged reactants were present.

The ^1H, ^{13}C and ^{19}F NMR spectra of the new compounds **4a**, **4b**, **5a**, **5b**, **6**, **7a**, **8a**, **8b**, **8c**, **9a** and **9b** are recorded in Table 2 and the mass spectra are summarised in Table 3. The IR spectra of all the new compounds showed bands (ν_{max}) (cm^{-1}) at 2950–2850 (m, aliph. C–H str.); ca. 1300 (s, C–F str.); and ca. 700 (m, CF_3 def.); in addition bands were present in the spectra of all the compounds (except **6**) at 3050–3000 (m, vinylic C–H str.) and 1700–1600 (m, C=C str.). Compounds **4a**, **5a**, **6**, **7a**, **8a/8b** and **9a** which contain a CO_2Et group showed additional bands in their spectra at 1750–1720 (s, ester C=O str.) and 1150–1120 (s, C–O str.).

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