5-Fluorocyclopentadiene: Synthesis and Utility

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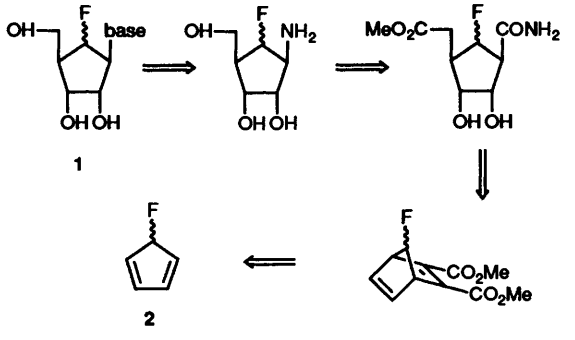
5-Fluorocyclopentadiene **2** has been prepared by the reaction of cyclopentadienylthallium and the F^+ source, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate). In their reactions with compound **2**, dieneophiles form adducts having exciusively *syn* orientation.

The success of specifically fluorinated analogues of biologically active molecules has led many workers to investigate the synthesis and biological activity of a wide range of fluorinated compounds.[1] Two general approaches to the synthesis of partially fluorinated compounds can be taken. The first involves fluorination in the latter part of a synthetic sequence and much success has been achieved using fluorinating reagents such as diethylaminosulfur trifluoride (DAST), tetrabutylammonium fluoride, xenon difluoride *etc.*[2] The alternative approach uses simple fluorinated compounds as building blocks for the synthetic procedure.[3]

The use of nucleosides and their carbocyclic analogues to treat viral infections has resulted in workers considering CHF and CF_2 moieties as isosteric replacements for the oxygen atom of the sugar ring.[4] Indeed some biologically active compounds have been prepared by fluorinating suitably substituted cyclopentanes.[5] However, retrosynthetic analysis of 6′-fluorocarbocyclic nucleosides **1** suggests that 5-fluorocyclopentadiene **2** may be a suitable fluorinated building block (Scheme 1).

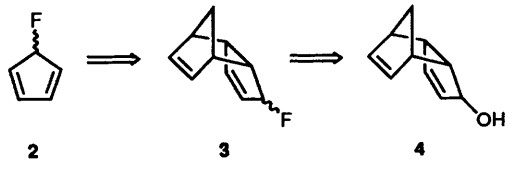


Scheme 1

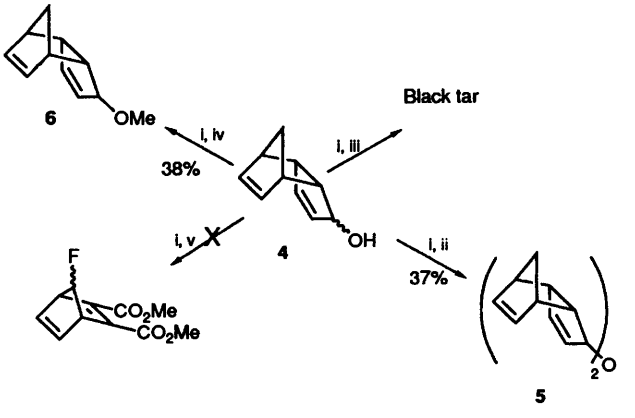
Surprisingly, although two reports do exist concerning 1- and 2-fluorocyclopentadiene,[6] there are no reports concerning 5-fluorocyclopentadiene. The aims of the work reported herein were to devise a method of preparing 5-fluorocyclopentadiene and examining its chemistry.

The first approach taken to synthesize this simple diene concentrated on the possibility of utilizing a retro Diels–Alder reaction, since this approach has proved successful in the preparation of a number of highly fluorinated cyclopentadienes.[7] 5-Fluorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene **3** was the first compound to be considered, since, although problems were envisaged with the simultaneous formation of cyclopentadiene, compound **3** should be readily available by the reaction of DAST with tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-ol **4**[8] (Scheme 2).

The first attempt to prepare compound **3** resulted, after aqueous work-up and column chromatography, in bis(tricyclo-[5.2.1.0^{2,6}]deca-3,8-dien-5-yl) ether **5** (Scheme 3). When the initial reaction product was purified by distillation instead (after any remaining DAST had been quenched with water and the



Scheme 2



Scheme 3 *Reagents and conditions:* i, DAST; ii, H_2O, then SiO_2; iii, air; iv, distil onto MeOH; v, distil onto DMAD

solvent removed) a colourless liquid was obtained. However, this liquid proved to be very sensitive to contact with air, since it rapidly decomposed after a short induction period to yield a black tar upon release of the vacuum.

If the liquid was distilled onto methanol and an inert atmosphere used, no decomposition was observed and the sweet smelling 5-methoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene **6** was obtained (Scheme 3). Further, no reaction was observed when the liquid was distilled onto dimethyl acetylenedicarboxylate (DMAD). These observations, coupled with a ^{1}H NMR spectrum of a rapidly decomposing sample of the colourless liquid, which contained a doublet of multiplets at δ 4.6 ($^2J_{HF}$ 60 Hz), suggest that compound **3** had been produced, but was very unstable in air. This was unexpected since there is no indication that the corresponding chloro analogue is unstable.[9]

Since this allylic fluoride proved to be so unstable an alternative approach to the synthesis of compound **2** was sought. A method which has previously been shown to be successful in the preparation of other 5-halogenocyclopentadienes, used the reaction between cyclopentadienylthallium with positive halogen sources such as *N*-bromosuccinimide and *N*-chlorosuccinimide.[10,11] The advent of available 'F^+' sources such as 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate) **7**[12] now makes it possible to attempt the preparation of 5-fluorocyclopentadiene using this methodology. The reaction of compound **7** with cyclopentadienylthallium did

Table 1 Reaction of cyclopentadienylthallium and compound **7** in the presence of dienophiles

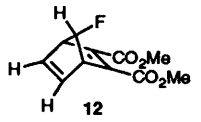
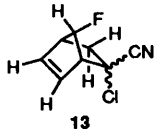
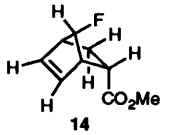
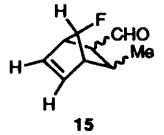
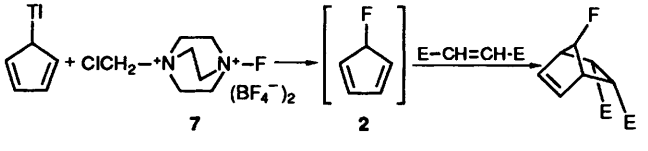
Dienophile	Adduct	Yield (%)
$(MeO_2CC)_2$	 **12**	35
CH_2=C(Cl)CN	 **13**	18
CH_2=$CHCO_2Me$	 **14**	17
MeCH=CHCHO	 **15**	0

Table 2 Reaction of cyclopentadienylthallium (CpTl), compound **7** and DMAD[a]

Solvent	T/°C	Yield (%)
MeCN	Room temp.	14
MeCN	0–Room temp.	14
MeCN	0–Room temp.	18[b,c]
MeCN	0–Room temp.	18[d]
MeCN	−78–Room temp.	16
CCl_4	0–Room temp.	0[e]
DMAD	0–Room temp.	20[b,f]
DMAD	0–Room temp.	35 (52[b])

[a] Unless otherwise stated the F^+ source was added to a solution of CpTl and DMAD; CpTl:F, 1:1.1. [b] GLC yield. [c] F^+ added over 10 min. [d] F^+:CpTl = 1:5; DMAD added after F^+. [e] DMAD added after 1 h. [f] CpTl added to F^+–DMAD.

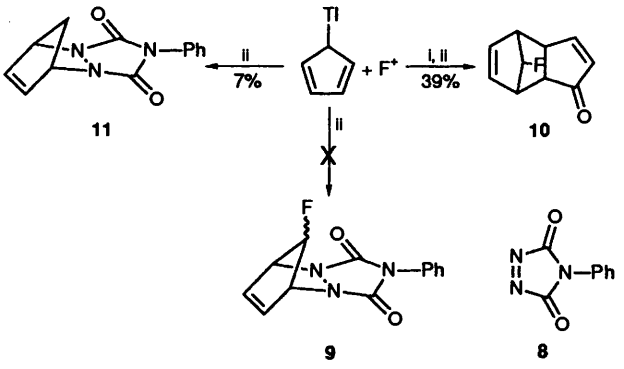
produce 5-fluorocyclopentadiene **2** *in situ*, which could be trapped by suitable dienophiles (Scheme 4).



Scheme 4

Initial studies on compound **2** concentrated on determining the rate of dimerisation. Since the monofluoro-analogue **3** had proved to be so unstable, it was envisaged that the dimer of 5-fluorocyclopentadiene would prove difficult to isolate. This was indeed the case, with no dimeric species being obtained even when methanol was added as a trap.

The rate of dimerisation of the other 5-halogenocyclopentadienes has been determined using the extremely reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione **8**, to trap out any remaining diene.[11] However, when the preparation of the Diels–Alder adduct **9** was attempted using the reported procedure, only 10-fluorotricyclo[5.2.1.$0^{2,6}$]deca-3,8-dien-5-one **10** was isolated (Scheme 5). The triazolinedione **8** is known to oxidise



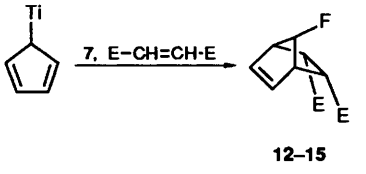
Scheme 5 *Reagents and conditions:* i, filter; ii, **8**

alcohols to carbonyl compounds,[13] and the formation of the alcohol possibly occurred while filtering the reaction mixture through Celite.

When the triazolinedione **8** was added to the reaction mixture of compound **7** and cyclopentadienylthallium without first filtering off any solids, the only product isolated was the non-fluorinated adduct **11** in low yield (see Scheme 5). In none of the experiments with the triazolinedione was the desired Diel–Alder adduct **9** produced.

If a less reactive dienophile is present when the fluorinating agent is added to the cyclopentadienylthallium, then the expected adducts are obtained, albeit in low yield (Table 1). In the case of DMAD, attempts to improve the yield by altering the temperature of the reaction, the order of addition, or reaction solvent, only succeeded in increasing the yield to 30–35% (Table 2). Although this yield is poor, it is comparable to those reported for other 5-halogenocyclopentadienes.[11]

A most interesting feature of this reaction is the position of the fluorine atom in the final adducts. In all cases, the addition of the dienophile yields 7-*syn*-fluorobicyclo[2.2.1]heptenes **12–15** (Scheme 6). The orientation of the fluorine was determined



Scheme 6

by NOE difference spectroscopy with enhancements shown in Fig. 1. Additional confirmation came from the *W* coupling between 7-H and 5-H in the norbornene skeleton.

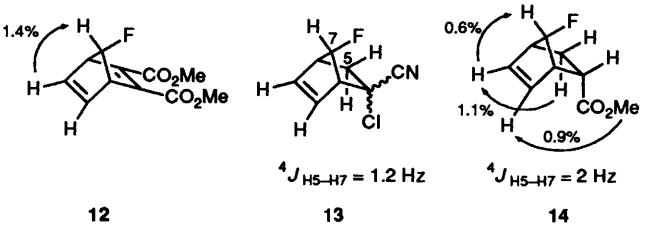


Fig. 1 NOE enhancements and *W* coupling

The preference of the dienophile to form *syn* adducts can be explained in terms of the Cieplak effect.[14] This effect results from the different abilities of the bond of the C-5 substituent to stabilize the transition state by donating electron density into the vacant σ* orbital associated with the forming σ bonds (Fig. 2). Since this stabilizing effect occurs only for the

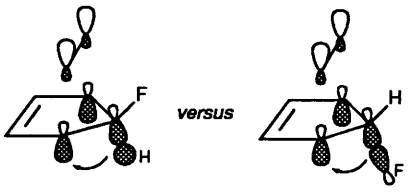


Fig. 2 σ bond formation transition states

substituent *anti* to the incoming dienophile, the best donor will be found on this side of the molecule. In the case of a C–F or C–H bond, the C–H bond must be the better donor. Interestingly, in the case of 5-bromocyclopentadiene addition occurs exclusively *anti* to the bromine, while addition occurs both *syn* and *anti* in the case of 5-chlorocyclopentadiene (the *anti* addition being more favoured).[11] These facts demonstrate a decrease in the ability of C–X bond to stabilise the transition state in the order C–Br > C–Cl ≥ C–H > C–F.

In conclusion, 5-fluorocyclopentadiene can be prepared *in situ* by the reaction of cyclopentadienylthallium with a F^+ source and it reacts with dienophiles to give Diels–Alder adducts. Investigations are currently underway to utilise these Diels–Alder adducts in the synthesis of carbocyclic nucleosides.

Experimental

General.—Unless noted otherwise, all starting materials were obtained from commercial suppliers and were used without further purification. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.0]octane bis(fluoroborate) was obtained from Air Products plc. Dichloromethane was distilled immediately prior to use from calcium hydride. Light petroleum refers to the fraction boiling in the range of 40–60 °C; this and ethyl acetate were distilled prior to use. Other solvents were distilled from suitable drying agents and stored over molecular sieves. Flash chromatography was carried out using silica gel 60 H (Merck 7385). TLC was performed on Merck 60-F-254 (0.25 mm thickness, Art. 571J) glass-backed silica gel plates. M.p.s were carried out in an 'Electrothermal' device and are uncorrected. IR spectra were recorded in a Perkin-Elmer 881 grating infrared spectrophotometer. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on either a Bruker WH400 at the Centre for Nuclear Magnetic Resonance at the University of Warwick, a Bruker AM250, A JOEL FX100 or a Hitachi Perkin-Elmer R24 spectrometer and *J* values are given in Hz. High resolution mass spectra were run at the SERC Mass Spectrometry Centre, Swansea, using a VG ZAB-E High Resolution Instrument or on a Kratos Profile Instrument.

5-Hydroxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene **4**,[8] cyclopentadienylthallium[15] and 4-phenyl-1,2,4-triazoline-3,5-dione **8**[16] were prepared according to the literature procedures.

Bis(tricyclo[5.2.1.0^{2,6}]*deca-3,8-dien-5-yl) Ether* **5**.—DAST (2 cm^3, 15 mmol) was slowly added to a solution of compound **4** (1.48 g, 10 mmol) in dichloromethane (50 cm^3) at 0 °C; the solution was allowed to warm to room temperature and was then stirred overnight. The reaction mixture was carefully poured onto a saturated solution of sodium hydrogen carbonate (50 cm^3) and the aqueous layer extracted with dichloromethane (1 × 50 cm^3), and the combined organic phase washed with water (2 × 50 cm^3), dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was then chromatographed over silica gel to give a colourless liquid (0.52 g, 1.9 mmol, 37%); ν(KBr)/cm^{-1} 3058, 2966, 1340 and 1056; δ_H(99.55 MHz, $CDCl_3$) 6.0–5.5 (8 H, m), 3.9 (2 H, s), 3.5–3.2 (2 H, m), 3.1–2.9 (2 H, m), 2.9–2.5 (4 H, m) and 1.5 (4 H, q, *J* 9); δ_C-(25 MHz, $CDCl_3$), 137.18, 135.19, 132.91, 132.09, 84.47, 54.52, 51.12, 50.59, 44.98 and 44.33 (Found: M^+, 278.1671. $C_{20}H_{22}O$ requires *M*, 278.1671).

5-*Fluorotricyclo*[5.2.1.0^{2,6}]*deca-3,8-diene* **3**.—DAST (4 cm^3, 30 mmol) was slowly added to a solution of compound **4** (2.96 g, 20 mmol) in dichloromethane (50 cm^3) at 0 °C. After 4 h the solution was carefully added to water (1 × 50 cm^3). The dichloromethane was distilled off under reduced pressure (10 mmHg) and the residue distilled (34 °C/0.6 mmHg) to give a colourless liquid (1.03 g) which after a short induction period rapidly and exothermically decomposed to give a black solid.

Repeating this experiment procedure but distilling the product onto deuteriochloroform (−78 °C) and filling the apparatus with nitrogen (upon release of the vacuum) gave a sample which decomposed while its ^1H spectrum was being recorded: δ_H(60 MHz, $CDCl_3$), 5.8–5.2 (4 H, m), 4.6 (1 H, d, *J* 60), 3.3–2.9 (1 H, m), 2.9–2.4 (2 H, m), 2.4–2.0 (1 H, m) and 1.5–1.0 (2 H, m).

5-*Methoxytricyclo*[5.2.1.0^{2,6}]*deca-3,8-diene* **6**.—The reaction was carried out as for the preparation of compound **3** [from **4** (0.5 g, 3.4 mmol)] except that the crude residue was distilled onto methanol (1 cm^3) at −78 °C, after which the apparatus was filled with argon. This mixture was allowed to warm to room temperature and was stirred under a positive pressure of nitrogen. No discolouration was noted even after 72 h and the reaction products were extracted into ether (20 cm^3). The ether layer was washed with water (1 × 20 cm^3) and the organic layer dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was chromatographed over silica to give a colourless sweet smelling liquid (0.21 g, 1.3 mmol, 38%); ν(KBr)/cm^{-1} 3058, 2967, 2816, 1340 and 1083; δ_H(99.55 MHz, $CDCl_3$) 5.9–5.5 (4 H, m), 3.7–3.6 (1 H, m), 3.3–3.2 (1 H, m), 3.2 (3 H, s), 3.0–2.8 (1 H, m), 2.8–2.6 (1 H, m), 2.6–2.4 (1 H, m) and 1.4 (2 H, q, *J* 8); δ_C(25 MHz, $CDCl_3$) 138.2, 135.3, 132.2, 131.8, 87.7, 55.4, 54.6, 51.2, 49.5, 45.2, 44.5; *m/z* 131 (100%), 66 (51), 91 (45), 117 (22), 82 (20), 53 (18), 146 (10) and 103 (5) (Found: M^+ − OMe, 131.0860. $C_{10}H_{11}$ requires 131.0861).

Treatment of Compound **3** *with DMAD.*—The attempted reaction was carried out as for the preparation of compound **3** except that the initial reaction residue was distilled onto DMAD (1 mol equiv.) at −78 °C. The mixture was placed under an argon atmosphere and allowed to warm to room temperature. TLC indicated that no desired reaction occurred and NMR of the crude reaction product showed only DMAD.

Dimerisation of 5-*Fluorocyclopentadiene* **2**.—Compound **7** (0.41 g/2.7 mmol g^{-1} F^+, 1.1 mmol) was added to a stirred solution of cyclopentadienylthallium (0.27 g, 1 mmol) in dichloromethane (2 cm^3) at 0 °C under a flow of nitrogen gas. After stirring for 1.5 h at room temperature, methanol (2 cm^3) was added, and TLC analysis showed that a reaction was occurring. The reaction mixture was filtered through a Celite plug (ether eluent). The ether was removed under reduced pressure and the residue chromatographed over silica; insufficient material was recovered for analysis.

Reaction of Compound **2** *with* 4-*Phenyl*-1,2-*triazoline*-3,5-*dione* **8**.—(a) Compound **7** (0.41 g/2.7 mmol g^{-1} F^+, 1.1 mmol) was added slowly over 10 min to a stirred solution of cyclo-

pentadienylthallium (0.27 g, 1 mmol) in acetonitrile. After a further 15 min the reaction mixture was filtered through a Celite pad (ether eluent) onto compound **8** (0.18 g, 1 mmol), and the reaction mixture was stirred for a further 4 h. The solvent was then removed under reduced pressure and the residue chromatographed over silica gel to yield 10-fluorotricyclo-[5.2.1.0^{2,6}]deca-3,8-dien-5-one **10** (0.032 g, 0.2 mmol, 39%) as a slightly yellow liquid; λ_{max}/nm (CCl_3H) 240; ν(KBr)/cm^{-1} 2929, 1698, 1344, 1251 and 1034; δ_H(250 MHz, $CDCl_3$) 7.41 (1 H, dd, *J* 5.8, 2.6), 6.03 (1 H, ddd, *J* 5.8, 1.6, 1.0), 5.90–5.84 (1 H, m), 5.77–5.71 (1 H, m), 4.63 (1 H, dt, *J* 59, 2), 3.70–3.63 (1 H, m), 3.26–3.19 (1 H, m) and 3.09–2.97 (2 H, m); δ_C(62.9 MHz, $CDCl_3$) 162.6 (CH), 137.7 (CH), 130.1 and 130.0 (2 × CH, overlapping d), 102.6 (CH, d, *J* 215), 47.3 (CH), 46.9 (CH, d, *J* 17), 46.3 (CH, d, *J* 17) and 45.2 (CH); δ_F(235.3 MHz, $CDCl_3$) −178.4 (d, *J* 59) (Found: M, 164.0631. $C_{10}H_9FO$ requires *M*, 164.0637).

(b) A slurry of cyclopentadienylthallium (0.27 g, 1 mmol) and compound **7** (0.41 g/2.7 mmol g^{-1} F$^+$, 1.1 mmol) in acetonitrile (10 cm^3) was added to a stirred solution of compound **8** (0.34 g, 1.9 mmol) in ether (20 cm^3). After 1 h the mixture was filtered through a Celite pad and the pad washed with ether. The solvents were removed under reduced pressure and the residue chromatographed (silica; light petroleum–ethyl acetate). A white solid (17.3 mg, 0.07 mmol, 7%) was produced which was identical with an authentic sample of 4-phenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione **11**.[17]

Dimethyl 7-syn-*Fluorobicyclo*[2.2.1]*hepta*-2,5-*diene*-2,3-*dicarboxylate* **12**.—Compound **7** (0.41 g/0.27 mmol g^{-1} F$^+$, 1.1 mmol) was added to a stirred solution of cyclopentadienylthallium (0.27 g, 1 mmol) in DMAD (2 cm^3) at 0 °C under a N_2 atmosphere. The reaction mixture was allowed to warm slowly to room temperature and was stirred for a further 3 h. The resultant mixture was filtered through Celite (ether eluent). The solvent was removed under reduced pressure and the residue chromatographed over silica gel using light petroleum–ethyl acetate. The title compound **12** (0.0800 g, 0.35 mmol, 35%) was obtained as a colourless oil which turned yellow upon standing; ν(KBr)/cm^{-1} 2959 and 1712; δ_H(250 MHz, $CDCl_3$) 6.74 (2 H, dd, *J* 2.2, 2.2), 4.50 (1 H, dt, *J* 62.5, 2.0) 3.98–3.94 (2 H, m) and 3.80 (6 H, s); δ_C(62.9 MHz, $CDCl_3$) 164.75 (C=O), 145.70 (C), 137.58 (CH, d, *J* 3.1), 109.47 (CH, d, *J* 231.5), 56.27 (CH, d, *J* 17.3) and 52.17 (CH_3); δ_F(235.3 MHz, $CDCl_3$) −163.9 (dt, *J* 62.5, 1.1) (Found: M$^+$ + H, 227.0720. $C_{11}H_{11}FO_4$ requires 227.0720).

2-*Chloro*-7-syn-*fluorobicyclo*[2.2.1]*hept*-5-*ene*-2-*carbonitrile* **13**.—Compound **7** (0.41 g/2.7 mmol g^{-1} F$^+$, 1.1 mmol) was added to a stirred solution of cyclopentadienylthallium (0.27 g, 1 mmol) in 2-chloroacrylonitrile (4 cm^3) at −41 °C under a N_2 atmosphere during 10 min. The reaction was allowed to warm to room temperature slowly and stirred for a total of 2.5 h. Excess of 2-chloroacrylonitrile was removed by distillation (10 mmHg) and the residue was dissolved in diethyl ether and filtered through a Celite plug. The Celite was washed with ether, the solvent removed under reduced pressure and the residue chromatographed (silica, light petroleum–ethyl acetate) to yield the title compound **13** as an off white solid (0.0315 g, 0.18 mmol, 18%) which was recrystallised (light petroleum–ether) at −26 °C; m.p. 78.5–80.0 °C; ν(KBr)/cm^{-1} 3007, 2245, 1336 and 725; δ_H(250 MHz, $CDCl_3$) 6.36–6.30 (1 H, m) 6.12–6.06 (1 H, m), 4.61 (1 H, dddd, *J* 57.1, 2, 2, 2), 3.54–3.48 (1 H, m), 3.14–3.08 (1 H, m), 2.98 (1 H, ddd, *J* 13.6, 3.8, 2.9) and 1.95 (1 H, ddd, *J* 13.6, 2.2); δ_C(100.62 MHz, $CDCl_3$) 135.96 (CH, d, *J* 7.4), 130.59 (CH, d, 6.9), 119.47 (C≡N), 97.97 (CH, d, *J* 216.7), 56.54 (CH, d, *J* 15.4), 55.08 (CCN, d, *J* 4.3), 45.29 (CH, d, *J* 17.7) and 41.67 (CH_2); δ_F(253.3 MHz, $CDCl_3$) −173.18 (d, *J* 57.1) (Found: M$^+$ + NH_4^+, 189.0595. $C_8H_{11}N_2ClF$ requires 189.0595).

Methyl 7-syn-*Fluorobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* **14**.—Compound **7** (0.41 g/2.7 mmol g^{-1} F$^+$, 1.1 mmol) was added to a stirred solution of cyclopentadientylthallium (0.27 g, 1 mmol) in methyl acrylate (2 cm^3) at 0 °C under a N_2 atmosphere over 15 min. Acetonitrile (2 cm^3) was then added to the viscous mixture. After 3 h of stirring at room temperature, the reaction mixture was filtered through a Celite pad (acetone eluent). The solvent was removed under reduced pressure and the residue chromatographed (silica; light petroleum–ethyl acetate). The title compound was obtained as a colourless liquid (0.0284 g, 0.17 mmol, 17%); ν(KBr)/cm^{-1} 2960, 1735 and 1199; δ_H(250 MHz, $CDCl_3$) 6.13–6.08 (1 H, m), 5.91–5.85 (1 H, m), 4.34 (1 H, d, *J* 59.2), 3.64 (s, 3 H), 3.19 (1 H, dddd, *J* 9.5, 4.4, 4.0, 1.8), 3.12–3.09 (1 H, m), 2.81 (1 H, m), 2.15 (1 H, dddd, *J* 11.4, 9.5, 4.0, 2.0) and 1.59 (1 H, ddd, *J* 11.4, 4.0, 1.2); δ_C(62.9 MHz, $CDCl_3$) 174.81 (C=O) 135.00 (CH, d, *J* 8.6), 130.58 (CH, d, *J* 8.0), 98.59 (CH, d, *J* 212.3), 51.63 (CH_3), 47.52 (CH, d, *J* 16.6), 44.55 (CH, d, *J* 17.5), 40.41 (CH) and 25.93 (CH_2); δ_F(253.3 MHz, $CDCl_3$) −178.48 (d, *J* 59.2) (Found: M$^+$, 170.0742. $C_9H_{11}FO_2$ requires *M*, 170.0744).

Attempted Formation of 7-syn-*Fluoro*-3-*methylbicyclo*[2.2.1]-*hept*-5-*ene*-2-*carbaldehyde* **15**.—Cyclopentadienylthallium was added to a stirred solution of compound **7** in but-2-enal (4 cm^3) at −41 °C. The solution was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered through a Celite pad and the pad was washed with ether. The solvents were removed under reduced pressure and the residue was chromatographed over silica using light petroleum–ethyl acetate. None of the fractions contained the desired product.

Acknowledgements

We wish to thank Air Products plc for their generous gift of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-(fluoroborate) and Professor S. M. Roberts for helpful discussions.

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Paper 2/02362H
Received 7*th May* 1992
Accepted 19*th May* 1992