

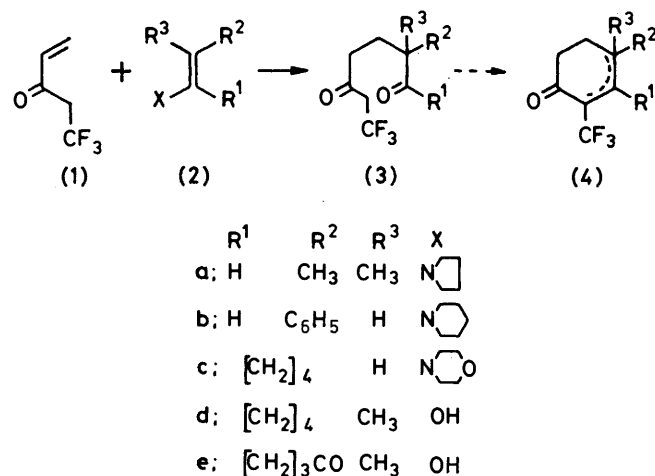
## Synthesis of 2-Trifluoromethylcyclohexenones from 2,2,2-Trifluoroethyl Vinyl Ketone

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2,2,2-Trifluoroethyl vinyl ketone is prepared in two steps from  $\beta$ -chloropropionyl fluoride and 1,1-difluoroethylene. Condensation of this reagent with enamines or ketols leads to the formation of 2-trifluoromethylcyclohexenones.

As opposed to monofluorinated cycloalkanones, which have been extensively studied for their biological properties,<sup>1,2</sup> cyclohexanones and cyclohexenones  $\alpha$ -substituted by a trifluoromethyl group have hardly been investigated.

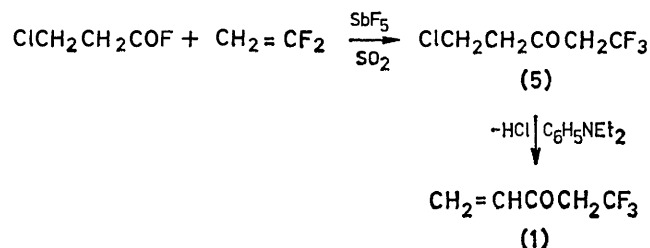
Until recently, only the radical addition of trifluoromethyl iodide to dienones<sup>3</sup> or enamines<sup>4</sup> enabled the preparation of some of these compounds. Another synthesis of trifluoromethylcyclohexenones is now possible, based on the annelation of ketones, or their derivatives, with a methyl vinyl ketone substituted by a trifluoromethyl group (we have previously used a similar methodology for the synthesis of monofluorocyclohexenones<sup>5</sup>). In order to apply this method the annelation reagent must be stable enough and easily available. As far as we know 2,2,2-trifluoroethyl vinyl ketone (1) has not been previously obtained. Here we describe its preparation and the Michael condensations with the enamines or enols (2), leading to  $\delta$ -diketones (3) which are then cyclised into 2-trifluoromethylcyclohexenones (4) (Scheme 1).



SCHEME 1

*Preparation of 2,2,2-Trifluoroethyl Vinyl Ketone (1).*—The ketone was prepared from 1,1-difluoroethylene. Acylation of this olefin with  $\beta$ -chloropropionyl fluoride,<sup>6</sup> in the presence of antimony pentafluoride, leads to 5-chloro-1,1,1-trifluoropentan-3-one (5) (Scheme 2). Our observations give no evidence of  $\beta$ -diketone and enol acetate formation, for the acylation with acetyl fluoride as described.<sup>7</sup> Dehydrochlorination of (5) by diethyl-aniline<sup>5,8</sup> produces 2,2,2-trifluoroethyl vinyl ketone (1)

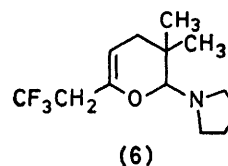
in an overall yield of 45%. Compound (1) is stable for several weeks at  $-30^\circ\text{C}$  in the presence of small amounts of hydroquinone.



SCHEME 2

*Condensation of 2,2,2-Trifluoroethyl Vinyl Ketone with Enamines.*—The reactions were performed in pentane at  $20^\circ\text{C}$  with the enamines derived from 2-methylpropanal and phenylacetaldehyde, in refluxing benzene with *N*-cyclohex-1-enylmorpholine.

An intermediate (6) with a dihydropyran structure,<sup>9</sup> is isolated in the case of the condensation of (1) with *N*-(2-methylprop-1-enyl)pyrrolidine (2a), a  $\beta$ -disubstituted enamine. Hydrolysis of (6) with hot 5*N*-hydrochloric acid gives 4,4-dimethyl-2-trifluoromethylcyclohex-2-en-1-one (4a) with 76% yield.

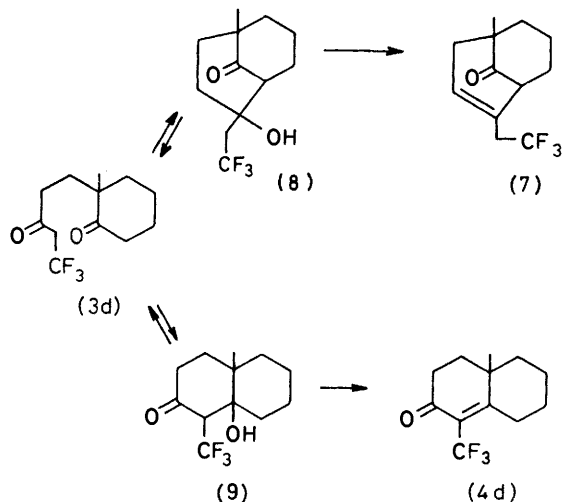


From  $\beta$ -monosubstituted enamines (derived from phenylacetaldehyde and cyclohexanone), condensation, followed by hydrolysis, leads to diketones (3b and c). Cyclisation into cyclohexenones (4b and c) occurs slowly at reflux in the presence of 5*N*-hydrochloric acid. In the case of compound (3b), ketolisation is not complete; if reflux is maintained, the yield of cyclised product is lowered. The reaction produces a mixture of two isomers of 4-phenyl-2-trifluoromethyl cyclohexenone (4b) which can be separated by chromatography on a silica gel column.

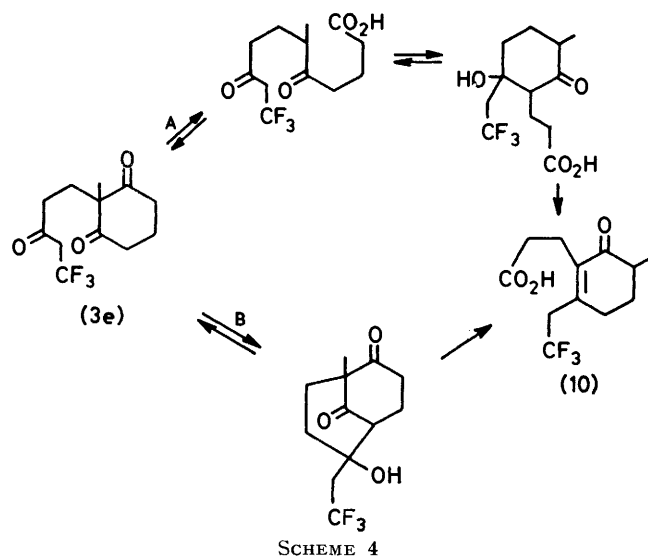
In the case of diketone (3c), the main product is the 1-trifluoromethyl- $\Delta^{9,10}$ -octalin-2-one (4c). Traces of 1-trifluoromethyl- $\Delta^{1,9}$ -octalin-2-one have been detected on the <sup>19</sup>F n.m.r. spectrum of the crude cyclisation product.

**Condensation of 2,2,2-Trifluoroethyl Vinyl Ketone with Ketones.**—An attempt to condense an enolate, formed from ethanolic potassium hydroxide solution, shows that reagent (1) loses its fluorine atoms and is transformed into a  $\beta$ -keto-ester under such conditions. Consequently the annelations are catalysed by acid; they occur, in fact, on the enolic form of the ketones.

**Condensation of (1) with 2-methylcyclohexanone.** The condensation was carried out in refluxing benzene in the presence of concentrated sulphuric acid.<sup>10</sup> After 7 h,



the alkylation product, diketone (3d), was obtained. If reflux was continued for 36 h, (3d) was converted into the bicyclo[3.3.1]nonenone (7) in 71% yield. From isolated (3d) kept in refluxing benzene for 26 h, toluene-*p*-sulphonic acid-catalysed cyclisation produced a mixture of (7) and (4d) in a 2 : 1 ratio. Formation of the two ketols occurred during this cyclisation.<sup>11</sup> In the presence of sulphuric acid, rapid dehydration of the kinetic product (8) produced (7). In the presence of toluene-*p*-sulphonic acid, which is weaker than sulphuric acid, de-



hydration was slower and occurred simultaneously with the kinetic product (8) and the thermodynamic product (9); thus 10-methyl-1-trifluoromethyl- $\Delta^{1,9}$ -octalin-2-one (4d) can be obtained (Scheme 3).

**Condensation of (1) with 2-methylcyclohexanone-1,3-dione.** The condensation, performed in ethanol at 20 °C in the presence of triethylamine, produced triketone (3e) in 89% yield. Thermal cyclisation in the presence of 5*N*-hydrochloric acid led to acid (10). The formation of (10) can be explained in two ways:<sup>12</sup> the opening of the  $\beta$ -diketone ring can happen before (route A) or after (route B) the ketolisation dehydration step (Scheme 4).

Hydrolysis of the trifluoromethyl group of (3e) occurred in basic medium and the formation of (4e) was not observed. Therefore the annelation method is limited to monoketone derivatives; it allows the preparation of 2-trifluoromethylcyclohexenones from the readily available 2,2,2-trifluoroethyl vinyl ketone.

#### EXPERIMENTAL

<sup>1</sup>H and <sup>19</sup>F N.m.r. spectra were recorded with a JEOL C.60 HL instrument; chemical shift values ( $\delta_H$  and  $\delta_F$ ) are expressed in p.p.m. relative to Me<sub>4</sub>Si (for <sup>1</sup>H n.m.r. spectra) or CCl<sub>3</sub> (for <sup>19</sup>F n.m.r. spectra) as internal standard. Spectra at 90 MHz were obtained with a Bruker WH90 DS instrument. I.r. spectra were recorded with a Perkin-Elmer 167 spectrometer, and u.v. spectra with a Varian Techtron 635 instrument. Preparative g.l.c. were performed with a Varian Aerograph model 920 chromatograph. Mass spectra were obtained on an A.E.I. MS30 instrument. M.p.s were determined on a Mettler FP61 apparatus.

**Preparation of 2,2,2-Trifluoroethyl Vinyl Ketone (1).**—5-Chloro-1,1,1-trifluoropentan-3-one (5). 1,1-Difluoroethylene was bubbled through a solution of 3-chloropropionyl fluoride (5.5 g, 0.05 mol) and SbF<sub>5</sub> (10.9 g, 0.05 mol) in liquid SO<sub>2</sub> (15 ml) at -20 °C, until there was no more absorption. The mixture was then poured into ice and extracted with diethyl ether. The organic extracts were washed with aqueous sodium hydrogencarbonate, dried (MgSO<sub>4</sub>), and evaporated. Distillation yielded 5-chloro-1,1,1-trifluoropentan-3-one (5.5 g, 63%); b.p. 69 °C at 14 Torr;  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 730 cm<sup>-1</sup>;  $\delta_H$  (CDCl<sub>3</sub>) 3.0 (2 H, t,  $J_{HH}$  6 Hz, CH<sub>2</sub>), 3.45 (2 H, q,  $J_{FH}$  10 Hz, CH<sub>2</sub>CF<sub>3</sub>), and 3.75 (2 H, t,  $J_{HH}$  6 Hz, CH<sub>2</sub>Cl);  $\delta_F$  (CDCl<sub>3</sub>) 64 p.p.m. (t,  $J_{FH}$  10 Hz);  $m/e$  176/174 ( $M^+$ ) and 139 ( $M - Cl$ ) (Found: C, 34.05; H, 3.5; Cl, 19.85; F, 32.25. C<sub>5</sub>H<sub>6</sub>ClF<sub>3</sub>O requires C, 34.4; H, 3.45; Cl, 20.32; F, 32.6%).

**2,2,2-Trifluoroethyl vinyl ketone (1).** The  $\beta$ -chloro-ketone (5) (7 g, 0.04 mol) with diethylaniline (9 g, 0.06 mol) and small amounts of hydroquinone was heated to 80 °C. Reaction progress was controlled by <sup>19</sup>F n.m.r. and heating was stopped when the  $\beta$ -chloro-ketone signal disappeared. The 2,2,2-trifluoroethyl vinyl ketone was separated from the mixture by bulb-to-bulb distillation at 1 Torr and then, distilled. 2,2,2-Trifluoroethyl vinyl ketone (1) (4 g, 72%) was stabilised by small amounts of hydroquinone and kept at -30 °C; b.p. 110–112 °C at ca. 760 Torr;  $\nu_{\max}$  (CHCl<sub>3</sub>) 1 708, 1 688, and 1 615 cm<sup>-1</sup>;  $\lambda_{\max}$  (hexane) 217 nm;  $\delta_H$  (CDCl<sub>3</sub>; 90 MHz) 3.4 (2 H, q,  $J_{HF}$  10.5 Hz, CH<sub>2</sub>CF<sub>3</sub>), 6 (1 H, dd,  $J_{HH}$  0.95, 10.5 Hz, H *trans* to COCH<sub>2</sub>CF<sub>3</sub>), 6.3 (q,  $J_{HH}$  0.95, and 17 Hz, H *cis* to COCH<sub>2</sub>CF<sub>3</sub>), and 6.45 (q,  $J_{HH}$  10.5, and 17 Hz, *gem*-H);  $\delta_F$  (CDCl<sub>3</sub>) 64 p.p.m. (t,  $J_{FH}$  10.5

Hz);  $m/e$  138 ( $M^+$ ), 118 ( $M - HF$ ), 111 [ $M - (CH=CH_2)$ ], and 91 [ $M - (HF \text{ and } CH=CH_2)$ ] (Found: C, 43.2; H, 3.75; F, 41.0.  $C_8H_5F_3O$  requires C, 43.5; H, 3.65; F, 41.25%).

*Condensation of 2,2,2-Trifluoroethyl Vinyl Ketone with Enamines.*— 4,4-Dimethyl-2-trifluoromethylcyclohex-2-en-1-one (4a). *N*-(2-Methylprop-1-enyl)pyrrolidine (2a) (2.5 g, 0.02 mol) was mixed with 2,2,2-trifluoroethyl vinyl ketone (2.8 g, 0.02 mol) in dry pentane (15 ml) at 20 °C. The mixture was stirred for 18 h and the solvent evaporated under reduced pressure. The residual liquid was shown by  $^1H$  and  $^{19}F$  n.m.r. to consist of 2-pyrrolidino-3,3-dimethyl-6-(2,2,2-trifluoroethyl)-3,4-dihydro-2*H*-pyran (6),  $\delta_H$  ( $CDCl_3$ ) 1.0 (s,  $CH_3$ ), 1.6—2.0 (m), 2.5—3.1 (m), 4.4 (s), and 4.6 (t,  $J_{HH}$  4 Hz,  $CH=C$ );  $\delta_F$  ( $CDCl_3$ ) 68 p.p.m. (t,  $J_{HF}$  11 Hz). The mixture was refluxed with 5*N*-HCl (10 ml) for 20 h, then cooled, and extracted with diethyl ether. The ether layer was dried ( $MgSO_4$ ) and evaporated under reduced pressure. Distillation yielded 4,4-dimethyl-2-trifluoromethylcyclohex-2-en-1-one (2.9 g, 76%), b.p. 55—58 °C at 0.05 Torr;  $\nu_{max}$  ( $CCl_4$ ) 1700—1645  $cm^{-1}$ ;  $\lambda_{max}$  (hexane) 221 nm ( $\epsilon$  6 640);  $\delta_H$  ( $CDCl_3$ ) 1.25 (6 H, s,  $CH_3$ ), 1.8—2.65 (4 H, m,  $CH_2CH_2$ ), and 7.1 (1 H, m,  $CH=C$ );  $\delta_F$  ( $CDCl_3$ ) 66 p.p.m. (d,  $J_{FH}$  1 Hz);  $m/e$  192 ( $M^+$ ), 177 ( $M - CH_3$ ), and 164 ( $M - 60$ ) (Found: C, 56.05; H, 5.85; F, 29.35.  $C_9H_{11}F_3O$  requires C, 56.25; H, 5.75; F, 29.65%).

4-Phenyl-2-trifluoromethylcyclohex-2-en-1-one (4b). *N*-(2-Phenylvinyl)piperidine (2b) (3.7 g, 0.02 mol) was mixed with 2,2,2-trifluoroethyl vinyl ketone (2.8 g, 0.02 mol) in dry pentane (20 ml). The mixture was stirred for 18 h at 20 °C and the solvent then evaporated *in vacuo*. The residual liquid was refluxed with 5*N*-HCl for 0.5 h, cooled, and extracted with diethyl ether. The organic layer was dried ( $MgSO_4$ ). After evaporation under reduced pressure, distillation yielded 3-oxo-6-phenyl-1,1,1-trifluoromethylheptanal (3b) (4.1 g, 80%); b.p. 110—111 °C at 0.08 Torr;  $\nu_{max}$  ( $CHCl_3$ ) 1725  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.8—3.6 (7 H, m and q at  $\delta$  3.15,  $J_{HF}$  10.5 Hz), 7.3 (5 H, m), and 9.6 (1 H, s, CHO);  $\delta_F$  ( $CDCl_3$ ) 63 p.p.m. (t,  $J_{HF}$  10.5 Hz);  $m/e$  258 ( $M^+$ ) (Found: C, 60.7; H, 5.25; F, 21.85.  $C_{13}H_{15}F_3O_2$  requires C, 60.45; H, 5.05; F, 22.05%).

The ketoaldehyde (3b) was refluxed with 5*N*-HCl (15 ml) for 10 h. Then, the mixture was cooled and extracted with diethyl ether. The organic layer was dried ( $MgSO_4$ ) and evaporated under reduced pressure. The residual liquid was a mixture of ketoaldehyde (3b) (30%) and of the two isomers 4-phenyl-2-trifluoromethylcyclohex-2-en-1-one and 4-phenyl-2-trifluoromethylcyclohex-3-en-1-one (70%). The components were separated by column chromatography on silica gel [ $CCl_4$ -ethyl acetate (1:9) as eluant], giving 4-phenyl-2-trifluoromethylcyclohex-2-en-1-one (35%),  $\nu_{max}$  ( $CHCl_3$ ) 1700  $cm^{-1}$ ;  $\delta_F$  ( $CDCl_3$ ) 2.0—2.6 (4 H, m) and 7.0—7.6 (6 H, m);  $\delta_F$  ( $CDCl_3$ ) 66 p.p.m. (s);  $m/e$  240 ( $M^+$ ).

1-Trifluoromethyl- $\Delta^{9,10}$ -octalin-2-one (4c). *N*-Cyclohex-1-enylmorpholine (2c) (3.3 g, 0.02 mol) and 2,2,2-trifluoroethyl vinyl ketone (2.8 g, 0.02 mol) in dry benzene (20 ml) were refluxed for 24 h. Then, the solution was evaporated, giving 2-(3-oxo-1,1,1-trifluoropentyl)cyclohexanone (3c),  $\nu_{max}$  ( $CHCl_3$ ) 1730—1705  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.2—2.8 (m) and 3.2 (q,  $J_{FH}$  10 Hz  $CH_2CF_3$ );  $\delta_F$  ( $CDCl_3$ ) 63 p.p.m. (t,  $J_{FH}$  10 Hz). The diketone (3c) was refluxed with 5*N*-HCl for 50 h. After cooling, the mixture was extracted with diethyl ether; the organic layer was dried ( $MgSO_4$ ), then evaporated *in vacuo*. Distillation yielded 1-trifluoromethyl- $\Delta^{9,10}$ -octalin-2-one (2 g, 46%), b.p. 57—59 °C at 0.05 Torr;  $\nu_{max}$  ( $CHCl_3$ )

1720—1660  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.5—2.9 (12 H, m) and 3.25 (1 H, q,  $J_{HF}$  9 Hz,  $CHCF_3$ );  $\delta_F$  ( $CDCl_3$ ) 68 p.p.m. (d,  $J_{FH}$  9 Hz);  $m/e$  218 ( $M^+$ ), 198 ( $M - HF$ ), and 190 ( $M - CO$ ) (Found: C, 60.36; H, 6.05; F, 25.7.  $C_{11}H_{13}F_3O$  requires C, 60.55; H, 6.0; F, 26.1%).

*Condensation of 2,2,2-Trifluoroethyl Vinyl Ketone with 2-Methylcyclohexanone.*—2-Methylcyclohexanone (2.2 g, 0.02 mol) and 2,2,2-trifluoroethyl vinyl ketone (3 g, 0.022 mol) in dry benzene (40 ml) were refluxed with concentrated sulphuric acid (0.06 ml) for 36 h. The mixture was poured into brine and extracted with diethyl ether. The organic layer was dried ( $MgSO_4$ ), then evaporated under reduced pressure. Distillation yielded 5-methyl-2-(1,1,1-trifluoroethyl)bicyclo[3.3.1]non-2-en-9-one (7) (3.3 g, 71%), b.p. 73—78 °C at 0.1 Torr;  $\nu_{max}$  ( $CHCl_3$ ) 1715  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ; 90 MHz) 1.0 (3 H, s,  $CH_3$ ), 1.45—3.0 (11 H, m and q at  $\delta$  2.7,  $J_{HF}$  10 Hz), and 5.8 (1 H, t,  $CH=C$ );  $\delta_F$  ( $CDCl_3$ ) 68 p.p.m. (t,  $J_{FH}$  10 Hz);  $m/e$  232 ( $M^+$ ) and 217 ( $M - CH_3$ ) (Found: C, 62.15; H, 6.5; F, 24.4.  $C_{12}H_{15}F_3O$  requires C, 62.05; H, 6.5; F, 24.55%).

When the mixture was refluxed for only 7 h and worked up in the way described for compound (7), distillation yielded 2-methyl-2-(3-oxo-1,1,1-trifluoropentyl)cyclohexanone (3d) (2.6 g, 51%), b.p. 100—110 °C at 0.05 Torr;  $\nu_{max}$  ( $CHCl_3$ ) 1710  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.05 (3 H, s,  $CH_3$ ), 1.6—2.6 (12 H, m), and 3.3 (2 H, q,  $J_{FH}$  10 Hz,  $CH_2CF_3$ );  $\delta_F$  ( $CDCl_3$ ) 63 p.p.m. (t,  $J_{FH}$  10 Hz);  $m/e$  250 ( $M^+$ ) and 232 ( $M - H_2O$ ). Diketone (3d) (1.25 g, 5 mmol) and toluene-*p*-sulphonic acid (0.1 g) in benzene (15 ml) were refluxed in a Dean-Stark apparatus for 26 h. The mixture was diluted with water and extracted with diethyl ether. The organic layer was dried ( $MgSO_4$ ), then evaporated under reduced pressure. The residual liquid was shown by  $^{19}F$  n.m.r. to consist of a mixture of diketone (3d), ketone (7), and 10-methyl-1-trifluoromethyl- $\Delta^{1,9}$ -octalin-2-one (4d). Octalone (4d) was purified by preparative g.l.c. on SE 30 (yielded 15%); m.p. 61 °C;  $\nu_{max}$  ( $CDCl_3$ ) 1675—1595  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.3 (3 H, s,  $CH_3$ ) and 1.6—3.0 (12 H, m);  $\delta_F$  ( $CDCl_3$ ) 55 p.p.m. (s);  $m/e$  232 ( $M^+$ ).

*Condensation of 2,2,2-Trifluoroethyl Vinyl Ketone with 2-Methylcyclohexane-1,3-dione.*—2-Methylcyclohexane-1,3-dione (2.5 g, 0.02 mol) and 2,2,2-trifluoroethyl vinyl ketone (3.3 g, 0.024 mol) in dry ethanol (40 ml) were stirred with 5 drops of triethylamine at 20 °C for 16 h. Then, the solvent was evaporated; the residual mixture was diluted with brine and extracted with diethyl ether. The organic layer was dried ( $MgSO_4$ ), then evaporated *in vacuo* giving a viscous oil which crystallized from ethanol-pentane. Recrystallisation in the same mixture gave 2-methyl-2-(3-oxo-1,1,1-trifluoropentyl)cyclohexane-1,3-dione (3e) (4.7 g, 89%), m.p. 50 °C;  $\nu_{max}$  ( $CDCl_3$ ) 1725—1690  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.3 (3 H, s,  $CH_3$ ), 1.8—2.8 (10 H, m), and 3.2 (2 H, q,  $J_{HF}$  11 Hz,  $CH_2CF_3$ );  $\delta_F$  ( $CDCl_3$ ) 64 p.p.m. (t,  $J_{FH}$  11 Hz);  $m/e$  264 ( $M^+$ ), and 246 ( $M - H_2O$ ) (Found: C, 54.5; H, 5.9; F, 20.95.  $C_{12}H_{15}F_3O_3$  requires C, 54.55; H, 5.7; F, 21.55%).

Triketone (3e) (1.3 g, 5 mmol) and 5*N*-HCl (15 ml) were refluxed for 6 h. The mixture was cooled and extracted with diethyl ether. The organic layer was dried ( $MgSO_4$ ), then evaporated under reduced pressure. The residual oil was crystallized in a mixture of benzene and pentane. Recrystallisation in the same solvent gave 3-[6-methyl-1-oxo-3-(2,2,2-trifluoroethyl)cyclohex-2-enyl]propanoic acid (10) (1.1 g, 85%), m.p. 77 °C;  $\nu_{max}$  ( $CCl_4$ ) 1710—1675  $cm^{-1}$ ;  $\lambda_{max}$  ( $CHCl_3$ ) 243 nm ( $\epsilon$  6 570);  $\delta_H$  ( $CDCl_3$ ) 1.1 (3 H, d,  $J_{HH}$

6 Hz, CH<sub>3</sub>), 1.25—2.7 (9 H, m), 3.2 (2 H, q,  $J_{\text{HF}}$  10 Hz, CH<sub>2</sub>CF<sub>3</sub>), and 10.7 (1 H, s, COOH);  $\delta_{\text{F}}$  (CDCl<sub>3</sub>) 62 p.p.m. (t,  $J_{\text{FH}}$  10 Hz);  $m/e$  264 ( $M^+$ ), 246 ( $M - \text{H}_2\text{O}$ ), and 218 ( $M - \text{COOH}$ ) (Found: C, 54.8; H, 5.6; F, 21.75. C<sub>12</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub> requires C, 54.55; H, 5.7; F, 21.55%).

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