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Elemental Fluorine. Part 7.[1,2] New Oxidation Methodology

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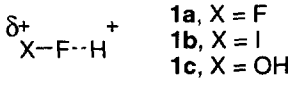
Abstract: Reaction of fluorine with water in the presence of acids provides new oxidants for '*in-situ*' oxidation of ketones. Direct reaction of fluorine with anhydrous alcohols and 1,2-diols provides simple methodology for oxidation to corresponding secondary ketones or α-hydroxy ketones.

INTRODUCTION

In earlier parts of this series, we have described the use of strong acids to promote electrophilic fluorination of aromatic systems by elemental fluorine (**1a**, X = F).[3,4]

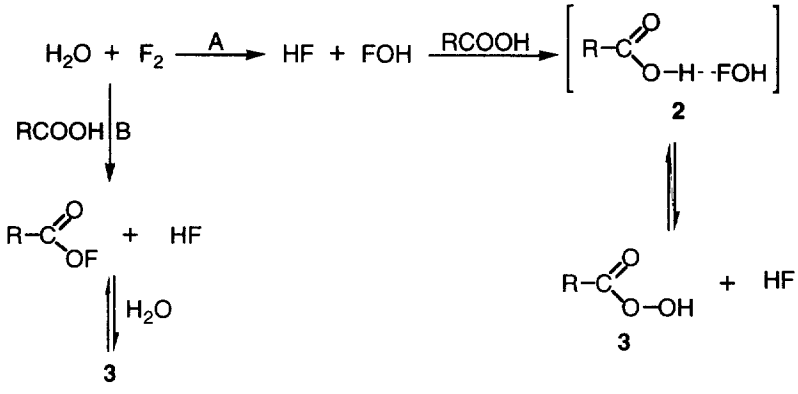


1a, X = F
1b, X = I
1c, X = OH

Then, we extended this approach to iodination of aromatics by the '*in-situ*' formation of 'iodine-fluoride', and the development of a powerful iodinating agent by the interaction of 'iodine-fluoride' with sulphuric acid, **1b**, X = I.[5,6] Here, we extend our investigations to the '*in-situ*' formation of FOH, and the corresponding activation of this species by interaction with acid, **1c**, X = OH.

Rozen and co-workers have pioneered the generation and use of an FOH/CH_3CN complex by reaction of elemental fluorine with water, in acetonitrile, at -10°C and demonstrated that, although the system is unstable (half life *ca.* 3-4 h. at room temperature), it is a very effective oxidising agent.[7-9]

Clearly, there are limitations to *e.g.* the scale of reactions carried out in this way and an '*in-situ*' procedure would be advantageous. Consequently, we have developed an '*in-situ*' procedure for reactions of FOH and established the highly beneficial and sometimes essential use of acid. Reaction of fluorine with water gives FOH and this interacts with acid, *i.e.* **2**, and a question is whether the equilibrium lies significantly in favour of peroxy acid **3**, Scheme 1, or not.



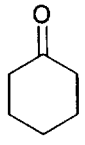
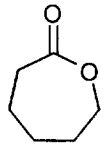
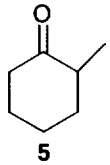
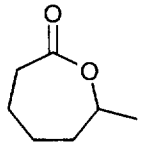
Scheme 1

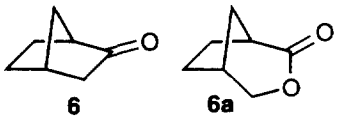
We assume reaction *via* route **A**, rather than **B**, because water is a much more effective nucleophile than a carboxylic acid and, therefore, reaction of fluorine with water will prevail and, in fact, evidence that fluorine is an electrophile in these processes is presented later in this paper.

RESULTS AND DISCUSSION

First, we established that cyclohexanone **4** is, indeed, oxidised directly to the corresponding lactone **4a**, simply by passing fluorine in nitrogen (10% by volume), through a solution of cyclohexanone in aqueous acetonitrile (10% water by volume), at -4°C. The reaction was surprisingly clean but only 40% conversion was observed under these conditions, see Table 1.

Table 1 Effect of Solvent and Temperature on the Baeyer-Villiger Reaction[a]

Ketone	Lactone	Medium (Aqueous)	Temp. (°C)	Conv. (%)	Yield (%)[b]
 **4**	 **4a**	CH_3CN	-4	40	100
		HCOOH	-4	10	100
			3	95	80
 **5**	 **5a**	CH_3CN	-4	0	0
			3	15	90
		HCOOH	-4	10	80
			3	98	90
		CH_3COOH	3	29	100



6 6a

CH_3CN	-4	57	100

a - Reactions were performed using 1.0g of ketone and the mass of isolated material varied between 0.6g and 0.9g

b - Yields are based on GC-MS integration

In contrast, no reaction was observed using 2-methylcyclohexanone **5**.

One of the advantages of an *'in-situ'* procedure is that reaction temperatures can be used at which FOH has a very short lifetime. Consequently, we have used aqueous formic acid (10% water by volume) as solvent, at a reaction temperature of 3°C, and under these conditions a greater than 90% conversion of **5** to **5a** was observed. Other examples are shown in Table 1.

To establish the effect of varying acid strength, we compared oxidations of norcamphor **6** at 3°C, using the acids shown in Table 2, and the effect of strong acid is quite striking. Acetic acid gave a low conversion to

Table 2 Effect of Acid on the Oxidation of Norcamphor

6 6a

i, 10% F_2 (in N_2), H_2O, 3°C

Acid	Acid Strength (pk_a)	Conv.(%) to Lactone
CF_3COOH	0.5	100
HCOOH	3.7	64
CH_3COOH	4.7	29

product whereas the process was quantitative in the case of trifluoroacetic acid. A significant question is whether the system functions *via* **2** or **3**, Scheme 1? Therefore, we carried out a two-step procedure, first passing fluorine through aqueous trifluoroacetic acid at 3°C, and then a subsequent addition, after 15 mins, of norcamphor **6** at the same temperature. However, only a 10% conversion to the corresponding lactone **6a** was obtained and we conclude, therefore, that the peroxy acid **3**, R = CF_3, is unlikely to be the principal oxidant formed because this system is known to be stable at 3°C.[10] Therefore, reactions *via* **2**, Scheme 1, are the most meaningful way to view this oxidation system; like peroxy acids it is a source of electrophilic oxygen.

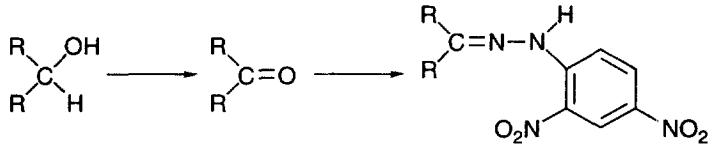
We have established, therefore, that the formation and *'in-situ'* reaction of FOH is a viable process and that the medium may be that of acetonitrile, which has been shown by Rozen[7-9] to stabilise FOH, but strong acid is clearly beneficial, as shown in Table 2. At first sight, the effectiveness of acetonitrile itself is surprising, see Table 1, but it must be emphasised that formation of FOH generates an equivalent amount of hydrogen fluoride which is beneficial to the process, see **1c**.

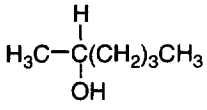
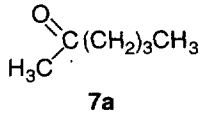
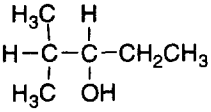
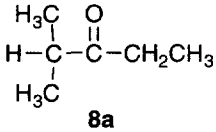
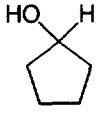
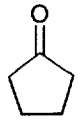
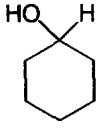
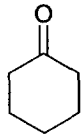
From the studies described above and those by Rozen and co-workers,[7] it is clear that water reacts rapidly with fluorine; alcohols are also known to react with fluorine to give corresponding hypofluorites,[11] but

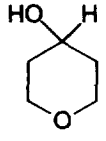
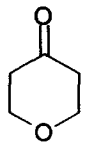
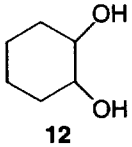
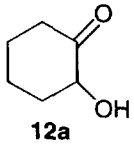
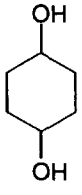
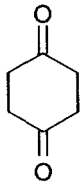
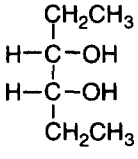
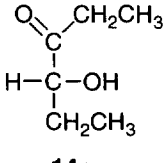
the latter are usually unstable species although the products of decomposition have not been systematically investigated. We have now studied this process because there are potentially significant advantages in using fluorine as an oxidant over *e.g.* the use of heavy-metal salts because the by-product would be hydrogen fluoride (which could be re-cycled to produce fluorine).

Indeed, controlled oxidation of a series of secondary alcohols was possible, giving the corresponding ketones, see Table 3. Generally, characterisation was effected by forming the corresponding 2,4-dinitrophenylhydrazine derivatives, and some of these reactions are highly efficient.

Table 3 Oxidation of Alcohols using *Anhydrous* Acetonitrile and Elemental Fluorine



Mono- or Di-ol	Ketone	Conv. (Yield) (%)	Yield of 2,4-DNP Derivative (%)[a]
 **7**	 **7a**	78 (47)	78
 **8**	 **8a**	100 (72)	61
 **9**	 **9a**	76 (81)	81
 **10**	 **4**	76 (54)	89

 **11**	 **11a**	99 (90)	90
 **12**	 **12a**	91 (79)	-
 **13**	 **13a**	96 (77)	-
 **14**	 **14a**	70 (90)	-

a - Based on the mass of recovered crude products

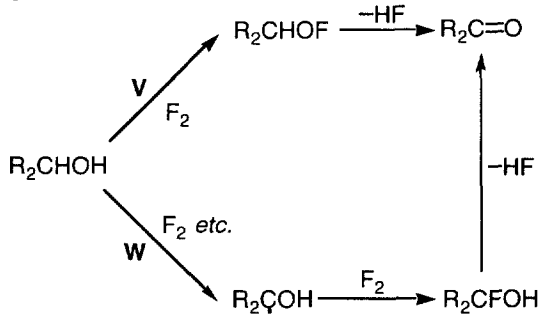
It is important to stress that anhydrous conditions were used and no Baeyer-Villiger products were observed. However, addition of water to the acetonitrile led to ester products as indicated in Table 1 but, in this case, starting with the corresponding alcohol precursor. It is very interesting that 1,2-diols are only oxidised to the α-hydroxy ketones *i.e.* cyclohexane-1,2-diol **12** and hexane-3,4-diol **14** each gave high yields of the corresponding α-hydroxy ketones, **12a** and **14a**, respectively, and this provides a very easy route to α-hydroxy ketones. In contrast, cyclohexane-1,4-diol **13** gave the di-ketone **13a** efficiently. We assume that the α-hydroxy ketone is resistant to further oxidation as a consequence of electron withdrawal by the carbonyl group, since electron withdrawal by perfluoroalkyl had a similar effect. The telomer alcohol **15** was unchanged after passing fluorine through the solution in acetonitrile.

$$H(CF_2CF_2)_3CH_2OH$$

15

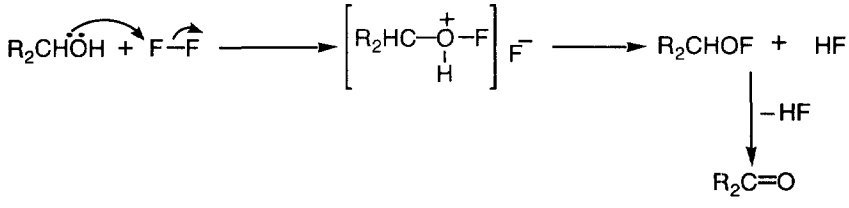
So far, our procedures with other primary alcohols have been discouraging because reaction with fluorine occurred efficiently but complex mixtures containing aldehydes, esters *etc.* were obtained and, consequently, we did not proceed further with these systems.

In principle, reaction of fluorine with an alcohol could proceed by either of two routes **V** and **W**, Scheme 2. A radical process, involving H-atom abstraction at the α-carbon, route **W**, is possible but this reaction appears to be excluded by using the acetate of cyclohexanol, and carried out under conditions identical with those used for the oxidation of cyclohexanol. Only starting acetate was recovered. It seems unlikely that converting from alcohol to acetate would suppress route **W** completely and we would have anticipated formation of fluorinated intermediates or even oxidation to the ketone. Therefore, route **V** is the most likely mechanism for the oxidation process.



Scheme 2

This raises the question of the interesting effect of substituents. Since oxidation of cyclohexane-1,2-diol **12** is halted at the α-hydroxyketone **12a** stage, this indicates that the polar influence is substantial and that the initial reaction of alcohols with fluorine involves fluorine acting as an *electrophile*. Clearly then, the presence of a carbonyl group in a position α- to the hydroxyl would be inhibiting and would rationalise the isolation of α-hydroxy ketones. We would anticipate the electron-withdrawing influence of carbonyl to fall off with



Scheme 3

distance, and it is understandable, therefore, that *both* hydroxyl groups in cyclohexane-1,4-diol **13** are oxidised. In a similar way, we can appreciate that the reactivity of the telomer alcohol **15** would be strongly suppressed.

The reactions described here are further examples of the controlled reaction of fluorine with organic molecules and we could envisage application of some of these procedures on a large scale if required.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13MHz or a Varian VXR400S spectrometer operating at 399.95MHz. ^{13}C NMR spectra were recorded on a Bruker AC250 spectrometer operating at 62.9MHz or a Varian VXR400S spectrometer operating at 100.58MHz. All spectra were recorded with tetramethylsilane as the internal reference. *J* Values are given in Hz. Mass spectra of solid

samples were recorded on a VG 7070E spectrometer. GLC mass spectra were recorded on a VG Trio 1000 spectrometer linked to a Hewlett Packard 5890 series II gas chromatograph, fitted with a 25m cross-linked methyl silicone capillary column. All mass-spectra were generated by electron impact unless stated otherwise.

Baeyer-Villiger Oxidations

General Note.-The following procedures, described for formic acid at 0°C, were performed at several temperatures and in different solvents (*i.e.* CF_3COOH, CH_3COOH, CH_3CN). Where CH_3CN was employed, neutralisation preceded extraction. The results for these reactions are described in Tables 1 and 2.

Oxidation of cyclohexanone **4**-Cyclohexanone **4** (1.00g, 10.2mmol) was added to a mixture of formic acid ($80cm^3$) and distilled water ($8cm^3$). The solution was then cooled to 3°C, using a cryostat, and vigorously stirred. Elemental fluorine (20mmol), as a 10% (v:v) mixture in nitrogen, was then passed at $10cm^3min^{-1}$ for 8.5 h. The resulting solution was then extracted (CH_2Cl_2, $3x30cm^3$), neutralised (saturated $NaHCO_3$, $20cm^3$) and dried ($MgSO_4$). Solvent was removed to give a colourless liquid containing lactone **4a** (0.8g; GC-MS: 95% conversion, 55% yield based on the mass of isolated material). Lactone **4a** was then isolated by preparative scale GLC (column DNP, 110°C) and identified by comparison with literature data;[12] $\delta_H(CDCl_3)$ 2.4 (4H, overlapping m, $2xCH_2$), 1.9 (6H, overlapping m, $3xCH_2$); *m/z* 98 (M^+, 32%), 71 (100).

Oxidation of 2-methylcyclohexanone **5**-Reaction of 2-methylcyclohexanone **5** (1.00g, 8.9mmol), using elemental fluorine (26mmol), afforded a yellow oil containing lactone **5a** (0.8g; GC-MS: 98% conversion, 63% yield based on the mass of isolated material). Lactone **4a** was then isolated by preparative scale GLC (column DNP, 110°C) and identified by comparison with literature data;[13] $\delta_H(CDCl_3)$ 1.15 (3H, d, *J* 6, CH_3), 1.3-2.6 (9H, br m, CH_2); *m/z* 128 (M^+, 20%), 85 (100).

Oxidation of norcamphor **6**-Reaction of norcamphor **6** (1.00g, 8.0mmol), using elemental fluorine (16mmol), afforded a yellow oil containing lactone **6a** (0.85g; GC-MS: 64% conversion, 47% yield based on the mass of isolated material). Lactone **6a** was then isolated by column chromatography (silica; 4:1 CH_2Cl_2:hexane) and identified by comparison with literature data;[14] $\delta_H(CDCl_3)$ (methine-migrated lactone) 4.87 (1H, br s, C*H*-O), 1.7-3.0 (9H, complex m); *m/z* 126 (M^+, 6%), 67 (100).

Oxidation of Alcohols

Oxidation of hexan-2-ol **7**-Hexan-2-ol **7** (1.5g, 15mmol) was dissolved in acetonitrile ($30cm^3$) and placed in a polytetrafluoroethene (PTFE) fluorination apparatus fitted with a drying tube filled with soda-lime. Elemental fluorine (20mmol), as a 10% (v:v) mixture in nitrogen, was passed through the stirred mixture at $10cm^3min^{-1}$ for 8 h. The product mixture was poured into water ($30cm^3$), neutralised (saturated $NaHCO_3$) and extracted (CH_2Cl_2; $3x30cm^3$). The organic extracts were dried ($MgSO_4$) and concentrated (reduced pressure distillation), to give a yellow oil containing ketone **7a** (1.2g; GC-MS: 78% conversion, 47% yield). A solution of acidified 2,4-dinitrophenylhydrazine (3.0g, 15mmol), in methanol (100 ml), was added to crude **7a**. The solution was cooled, to 0°C, until an orange precipitate formed. The precipitate was then filtered off and recrystallised (MeOH), to give the pure 2,4-dinitrophenylhydrazone (1.4 g, 63% yield, based on the mass of isolated material); m.p. 102 °C (lit.[15] 106 °C); (Found: C, 51.1; H, 5.6; N, 20.0. $C_{12}H_{16}N_4O_4$ calculated C, 51.4; H, 5.7;

N, 20.0%); δ_H 11.00 (1H br s, NH), 9.12 (1H, d, *J* 2.4, H-3), 8.29 (1H, dd, *J*9.6 and 3.2, H-5), 7.96 (1H, d, *J*9.6, H-6), 2.44 (2H, t, *J*7.6, CH_2C=N), 2.07 (3H, s, N=CCH_3), 1.62 (2H, m, $CH_2CH_2CH_2$), 1.41 (2H, pseudo-sept, *J*7.6, $CH_3CH_2CH_2$) and 0.97 (3H, t, *J* 6.0, CH_2CH_3); δ_C 158.4 (C=N), 145.02 (C-4), 137.54 (C-1), 129.95 (C-5), 128.90 (C-2), 123.53 (C-6), 116.42 (C-3), 38.75 (CH_2), 28.30 (CH_2), 22.31 (CH_2), 15.86 (CH_3) and 13.87 (CH_3); m/z (CI^+, NH_3) 281 (M^++1, 70%), 124 (40).

Oxidation of 2-methylpentan-3-ol **8**-Reaction of alcohol **8** (2.0g, 20mmol) with fluorine (45mmol), gave a yellow oil containing carbonyl **8a** (1.8g; GC-MS: 100% conversion, 72% yield). Reaction with 2,4-dinitrophenylhydrazine (4.0g, 20mmol) gave the 2,4-dinitrophenylhydrazone as an orange solid (2.2 g, 61% yield, based on the mass of isolated material); m.p. 110 °C (lit.[15] 112 °C); (Found: C, 51.1; H, 5.7; N, 19.7. Calculated for $C_{12}H_{16}N_4O_4$: C, 51.4; H, 5.7; N, 20.0%); δ_H 11.21 (1H, br s, NH), 9.13 (1H, d, *J* 2.8, H-3), 8.30 (1H, dd, *J* 9.8 and 3.2, H-5), 7.97 (1H, d, *J* 9.6, H-6), 2.69 (1H, sept, *J*6.8, $CH(CH_3)_2$), 2.45 (2H, q, *J*8.0, CH_2CH_3), 1.26 (3H, t, *J*8.0,CH_2CH_2) and 1.22 (6H, d, *J*6.4, $CH(CH_3)_2$); δ_C 166.71 (C=N), 145.46 (C-4), 137.49 (C-1), 129.92 (C-5), 123.56 (C-2), 116.45 (C-6), 116.30 (C-3), 36.11 (CH), 21.84 (CH_2), 20.06 (CH_3) and 9.69 (CH_3); m/z (EI^+) 280 (M^+, 100%), 181 (38).

Oxidation of cyclopentanol **9**-Reaction of alcohol **9** (1.7g, 20mmol) with fluorine (30mmol), gave a yellow oil containing carbonyl **9a** (1.5g; GC-MS: 76% conversion, 81% yield). Reaction with 2,4-dinitrophenylhydrazine (4.1g, 21mmol) gave the 2,4-dinitrophenylhydrazone, as an orange solid (2.6 g, 72% yield, based on the mass of isolated material); m.p. 143 °C (lit.[15] 146 °C); (Found: C, 49.7; H, 4.5; N, 21.2. Calculated for $C_{11}H_{12}N_4O_4$: C, 50.0; H, 4.5; N, 21.2%); δ_H 10.81 (1H, br s, NH), 9.12 (1H, d, *J* 2.4, H-3), 8.29 (1H, dd, *J* 9.6 and 3.2, H-5), 7.92 (1H, d, *J* 9.6, H-6), 2.58 (2H, t, *J*7.2, CH_2C=N), 2.48 (2H, t, *J*7.2, CH_2C=N), 2.00 (2H, pseudo-pent, *J*6.8, $CH_2CH_2CH_2$) and 1.88 (2H, pseudo-pent, *J*7.2, $CH_2CH_2CH_2$); δ_C 168.32 (C=N), 145.04 (C-4), 137.51 (C-1), 129.96 (C-5), 128.74 (C-2), 123.60 (C-6), 116.19 (C-3), 33.62 (CH_2), 28.13 (CH_2), 24.90 (CH_2) and 24.81 (CH_2); m / z (EI^+) 264 (M^+, 32%), 149 (97).

Oxidation of cyclohexanol **10**-Reaction of alcohol **10** (3.0g, 30mmol) with fluorine (40mmol), gave a yellow oil containing carbonyl **4** (2.5g; GC-MS: 76% conversion, 54% yield). Reaction with 2,4-dinitrophenylhydrazine (4.6g, 23mmol) gave the 2,4-dinitrophenylhydrazone, as an orange solid (3.1 g, 81% yield, based on the mass of isolated material); m.p. 161 °C (lit.[15] 162 °C); (Found: C, 51.5; H, 5.0; N, 20.0. Calculated for $C_{12}H_{14}N_4O_4$: C, 51.8; H, 5.0; N, 20.1%); δ_H 11.21 (1H, br s, NH), 9.13 (1H, d, *J* 2.4, H-3), 8.29 (1H, dd, *J* 9.6 and 2.8, H-5), 7.97 (1H, d, *J* 9.6, H-6), 2.47 (4H, m, CH_2C=N), 1.80 (4H, m, CH_2CH_2C=N) and 1.73 (2H, m, $CH_2CH_2CH_2$); δ_C 161.39 (C=N), 145.32 (C-4), 137.43 (C-1), 129.94 (C-5), 128.78 (C-2), 123.62 (C-6), 116.22 (C-3), 35.59 (CH_2), 27.21 (CH_2), 27.04 (CH_2), 26.00 (CH_2) and 25.48 (CH_2); m/z (EI^+) 278 (M^+, 41%), 239 (100), 81 (80).

Oxidation of tetrahydro-4H-pyran-4-ol **11**-Reaction of pyranol **11** (2.5g, 25mmol) with fluorine (40mmol), gave a yellow oil containing carbonyl **11a** (1.9g; GC-MS: 99% conversion, 90% yield). Reaction with 2,4-dinitrophenylhydrazine (5g, 25mmol) gave the 2,4-dinitrophenylhydrazone as an orange solid (3.8g, 80% yield based on the mass of isolated material); m.p. 188 °C (lit.[15] 186 °C); (Found: C, 47.0; H, 4.4; N, 25.0. Calculated for $C_{11}H_{12}N_4O_5$: C, 47.1; H, 4.3; N, 25.0%); δ_H 11.21 (1H, br s, NH), 9.13 (1H, d, *J*2.6, H-3), 8.31 (1H, dd, *J*

9.6 and 2.6, H-5), 7.97 (1H, d, *J* 9.6, H-6), 3.91 (4H, m, CH_2OCH_2) and 2.63 (4H, m, $CH_2C{=}N$); δ_C 156.23 (C=N), 145.13 (C-4), 138.54 (C-1), 130.77 (C-5), 129.28 (C-2), 124.21 (C-6), 116.93 (C-3), 69.00 (CH_2O), 66.91 (CH_2O), 36.16 (CH_2) and 29.11 (CH_2); m/z (EI^+) 280 (M^+, 14%), 151 (100%).

Oxidation of trans-cyclohexane-1,2-diol **12**-Reaction of diol **12** (2.0g, 17mmol) with fluorine (34mmol), gave a yellow oil containing α-hydroxyketone **12a** (1.6g; GC-MS: 91% conversion, 79% yield). Reaction with a hot, *neutral*, solution of 2,4-dinitrophenylhydrazine (3.4g, 17mmol), in ethyl acetate, gave the 2,4-dinitrophenylhydrazone as an orange solid (AcOEt) (2.8g, 86% yield, based on the mass of isolated material); m.p. 151 °C (lit.[15] 150 °C); (Found: C, 49.2; H, 4.6; N, 18.9. Calculated for $C_{12}H_{14}N_4O_5$: C, 49.0; H, 4.8; N, 19.05%); δ_H 11.45 (1H, br s, NH), 9.17 (1H, d, *J* 2.6, H-3), 8.37 (1H, dd, *J* 9.6 and 2.7, H-5), 7.97 (1H, d, *J* 9.7, H-6), 3.35 (1H, m, C*H*OH), 2.62-1.51 (8H, m, CH_2) and 1.1 (1H, br s, OH); δ_C 160.21 (C=N), 147.74 (C-4), 140.45 (C-1), 139.67 (C-5), 128.86 (C-2), 123.50 (C-6), 117.38 (C-3), 63.34 (C-OH), 32.55 (CH_2), 27.43 (CH_2), 23.76 (CH_2) and 23.10 (CH_2); m/z (CI^+, NH_3) 295 (M^++1, 32%), 277 (100), 230 (34).

Oxidation of cyclohexane-1,4-diol **13**-Reaction of diol **13** (2.5g, 22mmol) with fluorine (55mmol), gave a yellow oil containing cyclohexane-1,4-dione **13a** (1.9g; GC-MS: 96% conversion, 77% yield). Recrysatallisation (MeOH) afforded pure **13a** (1.2g, 49%) which was identified by comparison with an authentic sample; δ_H 2.73 (s, CH_2); δ_C 37.36 (CH_2), 209.04 (C=O); m/z (EI^+) 112 (M^+, 48%), 56 (35), 28 (100).

Oxidation of hexane-3,4-diol **14**-Reaction of diol **14** (1.0g, 8.5mmol) with fluorine (9.5mmol), gave a yellow oil containing α-hydroxyketone **14a** (0.8g; GC-MS: 70% conversion, 90% yield). Preparative scale GLC (column DNP, 110°C) enabled the isolation of pure **14a**; δ_H 0.94 (3H, t, *J*7.2, CH_3CH_2), 1.00 (3H, t, *J*7.6, CH_3CH_2), 1.44-1.69 (4H, m, CH_3CH_2), 2.50 (1H, t, *J*7.7, CH) and 2.83 (1H, br, COH); δ_C 162.14 (C=O), 42.06 ($CH_2C{=}O$), 26.42 (CH_2CHOH), 16.39 ($CH_3CH_2C{=}O$), 12.92 (CH_3CH_2CHOH); m/z (EI^+) 59 (M^+-57, 100%).

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